Non-collinear Magnetism in $d$- and $f$-electron Systems

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Abstract

In this thesis, non-collinear magnetism has been studied by using density functional theory and the augmented plane wave method with local orbitals (APW+lo). Two conditions for non-collinear instabilities have been identified in this thesis. First, the Fermi energy should cut through both spin up and down states. Secondly, strong nesting between the spin up and spin down Fermi surfaces is needed. The two criteria described here can be fulfilled by tuning the exchange-splitting and/or by modifying the volume. Calculations on several elements; bcc V, bcc and fcc Mn, bcc Fe, bcc and fcc Co, and bcc and fcc Ni show that a non-collinear state can be stabilized provided that the criteria discussed above are met. More complex materials have also been analyzed in terms of these two criteria. The substitutional alloys TiCo,Se,S are found in experiments to possess spin spiral structures for $x = \{0\text{-}1.5\}$ and at a concentration $x = 1.75$ the alloys become ferromagnetic. As S takes the place of Se in the crystal structure the distance between the Co layers is reduced and the turn angle of the spin spiral becomes smaller until it totally vanishes at $x = 1.75$. This thesis show that the evolution of the magnetic structure in these alloys is the consequence of a modification of the distance between Co layers, which induces a change in the interlayer exchange coupling.

Fermi surfaces have been analyzed in TbNi, in order to determine nesting features which would be responsible for the magnetic spin spiral observed in this material. The electronic structure of CeRhIn$_5$ is also reported in this thesis. Furthermore, the 3-k magnetic structure of UO$_2$ was investigated and the crystal field levels were calculated. Transition metal systems such as Fe in the superconducting high-pressure hcp phase and in the fcc crystal structure were also studied. The results obtained for fcc Fe are in accordance with previous reports. However the paramagnetic state in hcp Fe is found to be more stable than the antiferromagnetic configurations discussed earlier in the literature as being favored in the volume range where the hcp phase is stable and superconductivity appears (~ 15 GPa). The complex non-collinear magnetic structure in MnIrSi was calculated and the results are found to be in good agreement with experiments.

Keywords: Non-collinear magnetism, spin spirals, first principles, density functional theory, Fermi surfaces, electronic structure, f-electron systems

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To Bandi
The illustration in the front page is a free interpretation of a non-collinear arrangement of spins, out there, in the free space. It was designed and drawn by Constanza Bertolone Hojas and Ariel Fernández Luna.
List of Publications

This thesis is based on the collection of papers given below. Each article will be referred to by its Roman numeral.

I  Noncollinear magnetization density on VAu$_4$
   R. Lizárraga, L. Nordström, E. Sjöstedt and O. Eriksson

II A crystal and magnetic structure investigation of TbNi$_{5-x}$Cu$_x$ ($x = 0, 0.5, 1.0, 1.5, 2.0$);
    Experiment and Theory
   R. Lizárraga, A. Bergman, T. Björkman, H-P. Liu, Y. Andersson,
   T. Gustafsson, A. G. Kuchin, A. S. Ermolenko, L. Nordström
   and O. Eriksson
   (submitted to Phys. Rev. B)

III Studies of the incommensurate magnetic structure of a heavy
    fermion system: CeRhIn$_5$
   R. Lizárraga, M. Colarieti-Tosti, A. Bergman, T. Björkman, O.
   Eriksson, L. Nordström and J. M. Wills
   (in manuscript)

IV First principles calculations of multiple-k magnetic
    structures, crystal field levels and the oxygen distortion in
    UO$_2$
   R. Lizárraga, M. Colarieti-Tosti, T. Björkman, O. Eriksson, L.
   Nordström and J. M. Wills
   (in manuscript)

V Crystal and magnetic structure of Mn$_3$IrSi
   T. Eriksson, R. Lizárraga, S. Felton, L. Bergqvist, Y. Andersson,
   P. Nordblad, and O. Eriksson
VI  Conditions for noncollinear instabilities of ferromagnetic materials
R. Lizárraga, L. Nordström, L. Bergqvist, A. Bergman, E. Sjöstedt, P. Mohn and O. Eriksson

VII  Noncollinear magnetism in γ-Fe within the local spin density approximation
R. Lizárraga, E. Sjöstedt and L. Nordström.
(in manuscript)

VIII  Theoretical and experimental study of the magnetic structure of TlCo$_2$Se$_2$
R. Lizárraga, S. Ronneteg, R. Berger, A. Bergman, P. Mohn, O. Eriksson and L. Nordström

IX  On the bonding situation in TlCo$_2$Se$_2$

X  On the magnetic structure of TlCo$_2$Se$_2$
R. Lizárraga, S. Ronneteg, R. Berger, P. Mohn, L. Nordström and O. Eriksson,

XI  Non-collinear states in TlCo$_2$Se$_2$$_x$S$_x$ alloys; theory
R. Lizárraga, L. Nordström and O. Eriksson
(in manuscript)

XII  Non-collinear magnetism in the high-pressure phase of iron
R. Lizárraga, L. Nordström, O. Eriksson and J. M. Wills
(in manuscript)

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The following papers are co-authored by me but are not included in this thesis:

- **Electronic structure calculations of electronic and structural properties of plutonium 115 compounds**
  (preprint)

- **Crystal structure and magnetic properties of the new phase Mn₃IrSi**
  T. Eriksson, S. Felton, R. Lizárraga, O. Eriksson, P. Nordblad and Y. Andersson

- **Local and global magnetism in random FeV alloys**
  E. Holmström, R. Lizárraga, S. Shallcross and I. A. Abrikosov
  (in manuscript)

**Comments on my participation**

In the papers where I am the first author I am responsible for the main part of the work, from ideas to the finished papers. Concerning the other papers I have contributed in different ways, such as ideas, various parts of the calculations and the analysis.
Contents

List of publications .................................................. iii
1 Introduction ......................................................... 1
   1.1 Magnetism in condensed matter ......................... 2
2 Density Functional Theory ................................. 5
   2.1 The many-body problem .................................. 5
   2.2 Kohn-Sham equations .................................. 6
   2.3 Exchange-correlation energy functionals .......... 8
   2.4 Spin density functional theory ..................... 9
   2.5 Non-uniformly magnetized systems ................. 10
   2.6 The self-interaction correction .................. 13
3 Computational Methods ................................. 15
   3.1 The secular equation .................................. 15
   3.2 The linear augmented plane wave method .......... 17
   3.3 APW with local orbitals .......................... 19
4 Non-collinear Magnetism ................................. 21
   4.1 Spin spirals ........................................... 21
   4.2 Origin of magnetic ordering ....................... 24
      4.2.1 Itinerant electron theory (Stoner criterion) 24
      4.2.2 The static nonuniform magnetic susceptibility 25
      4.2.3 Fermi surface nesting ........................... 26
      4.2.4 Conditions for non-collinear states ........ 28
      4.2.5 Iron at high pressures .......................... 35
5 Localized States ........................................... 37
   5.1 Hund’s rules ......................................... 37
   5.2 Crystal field ......................................... 38
   5.3 Magnetic structure and distortion in UO$_2$ .... 39
   5.4 Spin spirals in rare earths systems .............. 42
   5.5 TbNi$_5$ and CeRhIn$_5$ ............................... 42
6 Summary and Outlook ........................................ 45
Sammanfattning .............................................. 47
References ..................................................... 51
1. Introduction

The discovery of magnets lies back in ancient times. The legend of a shepherd named Magnes, who found that his iron tipped crook and the nails of his boots were attracted to the ground on the slopes of the mount Ida in Crete, is probably the earliest account we have concerning magnets. The magical powers of magnetite, as the stone Magnes had stepped on was called later, are mentioned in the writings of the Roman encyclopedist Pliny the Elder (23-79 AD). For many years after its discovery, magnetite was surrounded by superstition. The powers of healing the sick, frightening away evil spirits, and attracting and dissolving ships made of iron were some of the prodigies associated with magnetite. As in many other subjects of human knowledge, supernatural influences and divine intervention were left behind when the work of scientists like Oersted (1777-1851), André Marie Ampère (1775-1836), Michael Faraday (1791-1867) and James Clerk Maxwell (1831-1879) cast light on the phenomenon of magnetism and electromagnetism. Since the Chinese compass (3rd BC), which is the first known application of magnetism, technological interest in magnetic materials has grown immensely. Storage media like the hard disks in our computers, floppy disks, tapes and permanent magnets in electric motors are some of the practical uses of magnetism in our everyday lives. This is why magnetism has been of so much interest in the field of condensed matter in recent decades. The manifestation of magnetism in solid state physics is a matter of importance in this thesis.

Magnetic materials are often found to be ferromagnets or antiferromagnets, i.e. magnetic moments pointing parallel or anti-parallel to a certain global quantization axis. However, on some occasions, the moments are orientated in such a manner that there is no global quantization axis. The latter is called non-collinear magnetism. Why the spins choose to order either in a collinear way like in ferromagnets or in a non-collinear way like in spin spirals is a question that has not found a thorough answer yet. In this thesis a serious attempt to find an answer to these questions was made. Before embarking on the discussion of this issue some basis facts of magnetism will be revisited, going all the way from a single electron until it is placed with other electrons in an atom or in a solid.
1.1 Magnetism in condensed matter

The fundamental object in magnetism is the magnetic moment, which in classical electromagnetism is defined as

\[ d\mu = I da \]  

(1.1)

where \( I \) is a current around an elementary oriented loop of area \( |da| \). The direction of the vector \( da \) is normal to the loop and determined by the direction of the current around the elementary loop (the screw rule). A current is produced by the motion of one or more electrical charges which are associated with particles that have mass. Therefore, there is an orbital motion of mass as well as charge in the current loop. The magnetic moment is connected with the angular moment.

When applying a magnetic field \( B \) to a system of interacting electrons, an induced magnetization appears. We could try to calculate the net magnetic moment of this system in a classical manner and then complete the description with the appropriate quantum mechanical corrections. However, as Bohr and Van Leeuwen showed, magnetism can not be understood in the framework of a classical theory based on the magnetism of moving charges. Consequently, a fully quantum mechanical description is necessary in order to give any account of magnetism. This includes the intrinsic angular momentum or spin of the electrons, which is characterized by the spin quantum number \( s \). The spin angular momentum is associated with an intrinsic magnetic moment \( \mu_s = -g\mu_B s \), \( g \) is a constant known as the g-factor and \( \mu_B \) is the Bohr magneton. The total electron magnetic moment contains contributions from the angular and spin magnetic moments.

The Hamiltonian \[1, 2\] that describes an atom with \( Z \) electrons moving in a potential \( V \) due to the nucleus is

\[ H = \sum_{i=1}^{Z} \left( \frac{1}{2m} p_i^2 + V(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \right) \]  

(1.2)

An external magnetic field \( B \) will change the momentum of each electron \( p_i \) to \((p_i + eA/c)\), where \( A \) is the magnetic potential\(^1\). The energy of the magnetic moment in \( B \) is \( -\mu \cdot B \), so the Hamiltonian of the system in the presence of \( B \) can be expressed as

\[ H = \sum_{i=1}^{Z} \left( \frac{1}{2m} \left( p_i + \frac{e}{c} A \right)^2 + V(r_i) + g\mu_B (B \cdot s_i) \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \]  

(1.3)

From quantum mechanics we know that everything we could know about the

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\(^1\)In a purely classical theory this would be the only effect of the field.
system, described by the Hamiltonian in Eqn (1.2), can be found by solving the Schrödinger equation
\[ H \Psi = E \Psi, \]  
where \( \Psi \) is the total wave function of the whole system. This represents a many-body problem. The problem of three bodies is already unsolvable and therefore this approach is intractable for atoms with the exception of the hydrogen atom unless we incorporate some approximations. Hartree introduced an important concept which appeals to the variational principle of quantum mechanics. The principle establishes that the total energy,
\[ E = \langle \Phi | H | \Phi \rangle = \int \Phi^* H \Phi \, dr, \]  
is stationary with respect to variation of \( \Phi \), and that \( E \) is always an upper bound to the ground state energy. In Eqn (1.5) \( \Phi \) is an approximate but normalized wave function that has the appropriate form of the electron system under investigation. Clearly if \( \Phi \) was the exact ground state wave function then \( E \) would be the ground state energy. By writing the wave function \( \Phi \) as a determinant of single-particle wave functions \( \phi_i \), which takes into account the antisymmetry of the wave function, the variation of \( E \) (Eqn (1.5)) with respect to the single-particle wave functions leads to the so-called Hartree-Fock (HF) equations\(^2\),
\[ \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \phi_n(r) + \sum_{j=1}^{N} \int \phi_j^*(r') \phi_j(r') \frac{e^2}{|r - r'|} \, dr' \phi_n(r) \]
\[ - \sum_{j=1}^{N} \int \phi_j^*(r') \phi_n(r') \frac{e^2}{|r - r'|} \, dr' \phi_j(r) \delta_{S_j S_n} = \varepsilon_n \phi_n(r). \]  
In deriving Eqn (1.6) the Hamiltonian in Eqn (1.2) was used. The last term on the left hand side of Eqn (1.6) is called the exchange potential and even though it is Coulombic, its origin is quantum mechanical. If we neglect the last term in Eqn (1.6) which singles out those electrons with spins of state \( j \) parallel to the state \( n \), we obtain the Hartree equations. They represent an electron moving in an effective or averaged potential due to the all other electrons. The HF approximation has turned out to give very accurate agreement with experiments for atoms.

However, in solids, the HF approximation becomes less helpful. The bandwidth obtained by this approach is considerably larger than the experimental values for the simple metals Li, Na, Be, Hg and Al. Moreover the velocity at

\(^2\) The derivation of the Hartree-Fock equations can be found in any solid state book such as Refs. [1, 3, 4].
the Fermi surface diverges, in clear contradiction with experimental observations. The reasons for these failures can be attributed to the unscreened long range Coulomb interactions.

First principles calculations based on density functional theory (DFT) provide an accurate and reliable way to obtain ground state properties of solids. The essential point is to replace the complication of calculating the total wave function of the many-body problem by the problem of finding the ground state density. DFT adds effects of exchange and correlation to the Hartree-type Coulomb terms to describe electron-electron interaction. This theory has been extended to the spin-polarized case which permits us to investigate magnetic systems. This is the avenue we will follow in this thesis in order to investigate magnetism in various systems.

\[A more detailed description of density functional theory will be given in the next chapter.\]
2. Density Functional Theory

DFT is a theory of correlated many-body systems. It provides a way of dealing with the many-body problem by replacing it with an auxiliary independent-particle system in which all the interaction and correlation effects are included in an exchange-correlation functional. As such, DFT has become the primary tool for calculation of electronic structure, magnetism and other properties in condensed matter. The remarkable successes of the local density approximation (LDA) and the generalized gradient approximation (GGA) functionals within the Kohn-Sham scheme have led to widespread interest in DFT as the most promising approach for accurate, practical methods in the study of real materials. In the following sections the basic ideas behind DFT will be outlined.

2.1 The many-body problem

The fundamental equation that governs a non-relativistic, time-independent quantum system is the Schrödinger equation

\[ H \Psi = E \Psi. \]  \hspace{1cm} (2.1)

The total energy of such a system is \( E \), \( \Psi \) is the total wave function which contains information of the whole system and \( H \) is the Hamiltonian, that for an arrangement of electrons and nuclei can be expressed as

\[
H = \sum_{\mu} \left[ -\frac{\hbar^2}{2M_\mu} \nabla_\mu^2 + \sum_{\nu \neq \mu} V_I(X_\mu - X_\nu) \right] + \sum_i \left[ -\frac{\hbar^2}{2m_i} \nabla_i^2 \right. \\
+ \sum_{j > i} \frac{e^2}{|r_i - r_j|} + \sum_{\mu} U_{e-1}(r_i - X_\mu) \Big], \hspace{1cm} (2.2)
\]

where \( X_\mu \) and \( M_\mu \) are the coordinates and masses of the nuclei and \( r_i \) and \( m_i \) are the corresponding quantities for the electrons. The first and the third terms in the Hamiltonian given in Eqn (2.2) are the kinetic energies of the nuclei and the electrons, respectively. The quantity \( V_I(X_\mu - X_\nu) \) is the interaction potential of the nuclei with each other, and \( U_{e-1}(r_i - X_\mu) \) represents
the interaction between the electrons and the nuclei. The simplicity of Eqn (2.1) is deceptive, because it is not possible to solve for solids, in particular metals, whose density of conduction electrons is very high (≈ 10^{23}/cm^3).

The Born-Oppenheimer approximation provides us with a way of simplifying the Hamiltonian of Eqn (2.1), because the electrons are much lighter than the nuclei they move much more rapidly and can follow the slower motions of the nuclei quite accurately. This fact allows us to discuss the motion of the electrons separately from the motion of the nuclei. The Born-Oppenheimer approximation leaves us with an electronic Hamiltonian, in which the nuclear coordinates enter only as parameters. Thus the Hamiltonian becomes less complicated; nevertheless the complexity of the electron-electron term still remains and makes the Schrödinger equation unsolvable. The intricacy of the many-body problem then forces us to find another route towards the understanding of solids.

### 2.2 Kohn-Sham equations

A significant reduction of the complicated many-body problem was supplied by DFT, which was developed by Hohenberg and Kohn [5] and Kohn and Sham [6]. The essential point of DFT is the realization that the ground state density is sufficient to calculate all physical quantities of interest. Therefore, instead of calculating the many-body wave function \( \Psi \), the knowledge of the ground-state density becomes crucial. DFT is based in the following two theorems established by Hohenberg and Kohn:

**Theorem 1** The total ground state energy of a many-electron system is a functional of the density

\[
n(r) = N \int \cdots \int |\Psi(x_1, x_2, \ldots, x_N)|^2 ds_1 dx_2 \ldots dx_N.
\]

(2.3)

where the coordinates \( \{x_i\} = \{r_i, s_i\} \).

**Theorem 2** The functional \( E[n] = \langle \Psi | \hat{H} | \Psi \rangle \) of a many-electron system has a minimum equal to the the ground state energy at the ground state density, \( E_0 \).

The proof of these theorems as well as \( \nu \)-representability issues will not be discussed here but the interested reader can find detailed information in Ref. [7, 8, 9]. Unfortunately these theorems provide no information about the form of the functional \( E[n] \) and therefore the applicability of DFT relies upon our ability to find accurate approximations. Kohn and Sham (1965) used the variational principle implied by the second theorem to derive single-particle Schrödinger
2.2. Kohn-Sham Equations

Following their approach, we proceed by writing the total energy functional \( E[n] \) as

\[
E[n] = T[n] + \int n(r)v_{\text{ext}}(r)\,dr + \int\int \frac{n(r)n(r')}{|r-r'|}\,dr\,dr' + E_{\text{xc}}[n],
\]

which consists of the kinetic energy, the external potential which in the Born-Oppenheimer approximation is the potential due to the ions, the Hartree component of the electron-electron energy, and the exchange-correlation energy. The last term in Eqn (2.4) contains the non-classical contributions to the electron-electron interaction, namely the exchange and Coulomb correlation effects. Since we know the expression for the kinetic energy of non-interacting particles \( T_0[n] \), it is convenient to split up the kinetic energy term in Eqn (2.4) into two terms \( T = T_0 + T_{\text{xc}} \), where \( T_{\text{xc}} \) stands for the exchange-correlation part of the kinetic energy and is simply included in \( E_{\text{xc}} \). Although explicit forms of \( T_{\text{xc}} \) and \( E_{\text{xc}} \) are not known in general, we can use the variational principle on the total energy functional to write

\[
\frac{\delta E[n]}{\delta n(r)} + \mu \frac{\delta (N - \int n(r)\,dr)}{\delta n(r)} = 0,
\]

where \( \mu \) is a Lagrange multiplier which takes care of particle conservation. Finally by using the density

\[
n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2,
\]

where the sum extends over the lowest \( N \) occupied states, we are able to determine the functional derivatives in Eqn (2.5). This procedure leads to effective single-particle equations called the Kohn-Sham (KS) equations

\[
\left[-\nabla^2 + v_{\text{eff}}(r) - \varepsilon_i\right] \psi_i(r) = 0,
\]

which are Schrödinger equations where the external potential has been replaced by an effective potential defined by

\[
v_{\text{eff}}(r) = v_{\text{ext}}(r) + 2 \int \frac{n(r')}{|r-r'|}\,dr' + v_{\text{xc}}(r),
\]
with the exchange-correlation potential

$$v_{xc}(r) = \frac{\delta \{ E_{xc}[n] \}}{\delta n(r)}.$$  \hfill (2.9)

In Eqn (2.9), $E_{xc}$ now contains the exchange-correlation part of the kinetic energy $T_{xc}$. The eigenvalues $\epsilon_i$ obtained above are not in general simply related to measured quantities and their physical meaning is still controversial [4]. It should be noted here that if $E_{xc}$ and $v_{xc}$ were known the KS approach would result in the exact ground state energy.

### 2.3 Exchange-correlation energy functionals

DFT as outlined above supplies a scheme to map the many-body problem into a Schrödinger-like effective single-particle equation provided that we introduce an approximation to the exchange-correlation functional. The local density approximation (LDA) achieves this task by writing the exchange-correlation energy functional as

$$E_{xc}[n(r)] = \int n(r) \epsilon_{xc}(n(r)) \, dr,$$  \hfill (2.10)

where $\epsilon_{xc}(n(r))$ is the exchange-correlation energy per particle of a homogeneous electron gas of density $n(r)$. The performance of LDA can be summarized as follows;

- The equilibrium lattice constants are generally accurate within 0.1 Å, usually predicting too small values.
- The binding energies are often better than 1 eV, although there are cases in which the overbinding is greater.
- There is a 10-20% error in vibrational frequencies.
- Charge densities can be obtained within a 2% error.
- Geometries are frequently correct.
- Physical trends are generally correct [10].

There are attempts to refine LDA, for instance the generalized gradient approximation (GGA) and the weighted density approximation (WDA). An expression similar to that shown in Eqn (2.10) is used in GGA but in this case $\epsilon_{xc}$ is a function of the gradient of the density $|\nabla n(r)|$ as well as the density $n(r)$ [11, 12, 13]. WDA [14, 15, 16] is a more sophisticated approach that incorporates truly non-local information through Coulomb integrals of the density with model exchange correlation holes. Although WDA improves greatly the predicted energies of atoms it is more computationally demanding than LDA or GGA and therefore there are very few reports in the literature of WDA applied to solids. In contrast, GGA has been widely used in first principles.
calculations but despite its success in predicting the bcc ground state of iron, it has not been found to improve significantly LDA calculations in metallic magnets, at least not the ground state magnetic properties.

2.4 Spin density functional theory

So far we have discussed DFT for non-spin-polarized systems and since the work presented in this thesis pertains to magnetic materials we now turn into the description of the spin density functional theory (SDFT). We will emphasize those features that are typical for SDFT, in particular its applications to the study of non-collinear magnets, and omit details since they are similar to what was discussed in earlier sections.

In 1972 von Barth and Hedin extended the DFT to the spin polarized case. They used a $2 \times 2$ matrix formalism to represent the density and the external potential instead of single variables,

$$ n(\mathbf{r}) \quad \Rightarrow \quad \rho(\mathbf{r}) = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} $$ (2.11)

$$ v_{\text{ext}}(\mathbf{r}) \quad \Rightarrow \quad \tilde{v}_{\text{ext}}(\mathbf{r}) = \begin{pmatrix} v_{11} & v_{12} \\ v_{21} & v_{22} \end{pmatrix} $$ (2.12)

We begin our discussion by noticing that the wave functions will take the form of spinors,

$$ \psi_i(\mathbf{r}) = \begin{pmatrix} \phi_{i\alpha}(\mathbf{r}) \\ \phi_{i\beta}(\mathbf{r}) \end{pmatrix} $$ (2.13)

where $\phi_{i\alpha}$ and $\phi_{i\beta}$ are the two spin projections. In the non-spin polarized case we defined the density (see Eqn (2.6)) as the sum of $|\psi_i|^2$ extended over the lowest $N$-occupied states. We now write the density matrix $\rho$ in Eqn (2.11) as

$$ \rho(\mathbf{r}) = \sum_{\varepsilon_{i\alpha}, \varepsilon_{i\beta} \leq E_F}^{N} \begin{pmatrix} |\phi_{i\alpha}(\mathbf{r})|^2 & \phi_{i\alpha}(\mathbf{r})\phi_{i\beta}^*(\mathbf{r}) \\ \phi_{i\alpha}^*(\mathbf{r})\phi_{i\beta}(\mathbf{r}) & |\phi_{i\beta}(\mathbf{r})|^2 \end{pmatrix} $$ (2.14)

which generally can be expanded in terms of the density $n(\mathbf{r})$ and the magne-

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5LDA favors instead a nonmagnetic fcc ground state for Fe in contradiction with experiments.

6Although SDFT was formulated completely general, its earlier implementations were mostly done for the special case of diagonal matrices, i.e. collinear magnetism.
tization density $\mathbf{m}(\mathbf{r})$, that is naturally a vector density

$$\rho(\mathbf{r}) = \frac{1}{2} \left[ n(\mathbf{r}) \mathbb{I} + \mathbf{m}(\mathbf{r}) \cdot \mathbf{\sigma} \right],$$  \hspace{1cm} (2.15)$$

where $\mathbb{I}$ is the $2 \times 2$ unit matrix and $\mathbf{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices.

The next step is to write down the total energy that now is a functional of $\rho$

$$E[\rho] = T_0[\rho] + V_{\text{ext}}[\rho] + \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + E_{\text{xc}}[\rho].$$  \hspace{1cm} (2.16)$$

The external potential $V_{\text{ext}}[\rho]$ in Eqn (2.16) is the potential due to the ions specified by

$$\sum_{\alpha \beta} \int \rho_{\alpha \beta}(\mathbf{r}) v_{\beta \alpha}^{\text{ext}}(\mathbf{r}) \, d\mathbf{r}.$$  \hspace{1cm} (2.17)$$

By applying the variational principle on the total energy functional in Eqn (2.16), and proceeding in the same way as in the non-polarized case we derive the single-particle equations which constitute the KS equations for a spin system,

$$\sum_{\beta} \left( -\delta_{\alpha \beta} \nabla^2 + v_{\alpha \beta}^{\text{eff}}(\mathbf{r}) - \varepsilon_i \delta_{\alpha \beta} \right) \phi_i(\mathbf{r}) = 0,$$  \hspace{1cm} (2.18)$$

where no assumption of collinearity, i.e. all spin being parallel or anti-parallel to a global quantization axis, has been made. The effective potential matrix elements in Eqn (2.18) can be written down as

$$v_{\alpha \beta}^{\text{eff}}(\mathbf{r}) = v_{\alpha \beta}^{\text{ext}}(\mathbf{r}) + 2\delta_{\alpha \beta} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + v_{\alpha \beta}^{\text{xc}}(\mathbf{r}),$$  \hspace{1cm} (2.19)$$

with the exchange-correlation potential matrix elements

$$v_{\alpha \beta}^{\text{xc}}(\mathbf{r}) = \frac{\delta\{E_{\text{xc}}[\rho]\}}{\delta \rho_{\beta \alpha}(\mathbf{r})}.$$  \hspace{1cm} (2.20)$$

### 2.5 Non-uniformly magnetized systems

The application of SDFT as well as its non-spin-polarized partner requires the introduction of an approximation for the exchange-correlation functional. LDA can be readily generalized to the spin-polarized case (LSDA) \[9\] by defining spin-up and spin-down densities. However the aim of this section is to include in our discussion also those cases where there is no global spin quantization axis, i.e. non-collinear magnetization. Hence the discussion presented here will continue in a general way.
In the previous section we learned that SDFT uses a $2 \times 2$ matrix formalism. The density matrix (see Eqn (2.14)) elements were defined as

$$
\rho_{\alpha\beta}(r) = \sum_{i=1}^{N} \phi_{i\alpha}(r) \phi_{i\beta}^*(r).
$$

(2.21)

From the definition in Eqn (2.15) it is clear that the electron and the magnetization density can be expressed as

$$
n(r) = \text{Tr}(\rho(r)) = \sum_{i=1}^{N} |\psi_i|^2 \quad \text{and} \quad m(r) = \sum_{i=1}^{N} \psi_i^\dagger \sigma \psi_i,
$$

(2.22)

where the sums in Eqn (2.22) extend over the lowest occupied states. In the simplest case where the spins are arranged in a collinear way, the density matrix is diagonal and therefore the magnetization becomes,

$$
m_z(r) = \sum_{i=1}^{N} \left[ |\phi_{i\alpha}|^2 - |\phi_{i\beta}|^2 \right] = \sum_{i=1}^{N} [n_\uparrow(r) - n_\downarrow(r)].
$$

(2.23)

In Eqn (2.23) the global magnetization axis was assumed to be in the $z$-direction and the elements of the diagonal density matrix to be $n_\uparrow$ (spin-up density) and $n_\downarrow$ (spin-down density). The exchange-correlation energy in Eqn (2.10) then depends on both spin densities, $\epsilon_{xc}(n_\uparrow, n_\downarrow)$, and corresponds to the exchange-correlation energy density for a spin-polarized homogeneous electron gas. However, in a more general case where non-diagonal matrices are considered the exchange-correlation functional may be given by

$$
E_{xc}[n(r), m(r)] = \int n(r)\epsilon_{xc}(n(r), m(r)) \, dr,
$$

(2.24)

which allows us to determine the exchange-correlation potential (see Eqn (2.20))

$$
\chi_{\alpha\beta}^{xc}(r) = \frac{\delta \{E_{xc}[\rho]\}}{\delta \rho_{\beta\alpha}(r)} = \frac{\delta \{E_{xc}[\rho]\}}{\delta n(r)} \frac{\delta n(r)}{\delta \rho_{\beta\alpha}(r)} + \frac{\delta \{E_{xc}[\rho]\}}{\delta m(r)} \frac{\delta m(r)}{\delta \rho_{\beta\alpha}(r)}.
$$

(2.25)

The first term constitutes a non-magnetic contribution to the exchange-correlation potential whereas the second term is a magnetic potential which adopts the form of a magnetic field,

$$
b(r) = \frac{\delta \{E_{xc}[\rho]\}}{\delta m(r)} = \frac{\delta \{E_{xc}[\rho]\}}{\delta m(r)} \frac{\delta m(r)}{\delta m(r)} = \frac{\delta \{E_{xc}[\rho]\}}{\delta m(r)} \hat{m}.
$$

(2.26)

As follows from Eqn (2.26), in LSDA the magnetic potential is always
allel to the magnetization density everywhere. The effective potential matrix elements (Eqn (2.19)) can now be written as

\[
v_{\alpha\beta}^{\text{eff}}(r) = v_{\alpha\beta}^{\text{ext}}(r) + 2\delta_{\alpha\beta} \int \frac{n(r')}{|r - r'|} \, dr' + \frac{\delta n(r)}{\partial \rho_{\alpha\beta}(r)} \frac{\delta \{E_{\text{xc}}[\rho]\}}{\partial \delta n(r)} + b(r) \frac{\delta m(r)}{\partial \rho_{\alpha\beta}(r)}. \tag{2.27}
\]

By using the fact that \(\delta n(r)/\partial \rho_{\alpha\beta}(r) = 1\) and \(\delta m(r)/\partial \rho_{\alpha\beta}(r) = \sigma\) in Eqn (2.27) we can write the effective potential matrix as the sum of two contributions, a non-magnetic term\(^7\) and the magnetic potential,

\[
v_{\alpha\beta}^{\text{eff}}(r) = v_{\text{nm}}(r)I + b(r) \cdot \sigma. \tag{2.28}
\]

Finally, the KS Hamiltonian matrix in LSDA can be written as

\[
\mathcal{H} = (-\nabla^2 + v_{\text{nm}})I + b(r) \cdot \sigma. \tag{2.29}
\]

The non-magnetic part of the effective potential is diagonal. In the special case of a collinear system with a global magnetization axis chosen along the \(z\)-direction, the magnetic part of the potential becomes

\[
\begin{pmatrix}
    b_z \sigma_z & 0 \\
    0 & -b_z \sigma_z
\end{pmatrix}.
\tag{2.30}
\]

Therefore a collinear system can be treated as two separate electron systems, each moving in an effective potential \(v_{\pm}^{\text{eff}} = v_{\text{nm}} \pm b_z \sigma_z\). An example of a non-collinear magnetization density for VAu\(_4\) is shown in paper I (Fig. 3). VAu\(_4\) is a ferromagnet, therefore the magnetic potential is diagonal as in Eqn (2.30). However the presence of spin-orbit coupling\(^8\) produces a mixing between the different spinor components of the wavefunction in Eqn (2.13) so that an intra-atomic non-collinearity appears, i.e. the direction of the magnetization density varies on the length scale of an atom. The general implementation of SDFT that we have presented here allows us to study magnetism in systems such as VAu\(_4\).

In concluding this section, we point out that the KS equations, in their non-spin and spin-polarized versions, lead to a self-consistent cycle, i.e. a density must be found that produces an effective potential that once inserted in the KS equations yields single-particle wave functions that reproduce the density. This will be discussed to some extent in the next chapter.

\(^7\)This term is equivalent to the effective potential in Eqn (2.8) where magnetism was not considered.

\(^8\)In our discussion we did not introduce the effect of spin-orbit coupling in the Hamiltonian. Details of the implementation of the spin-orbit coupling can be found in Ref. [17].
2.6 The self-interaction correction

So far we have discussed exchange-correlation functionals that are based on the homogeneous electron gas. We could anticipate that such approximations would not do well in materials in which the electrons tend to be localized and strongly interacting, like in transition metal oxides and rare earth elements and compounds. In the Hartree-Fock scheme (Eqn (1.6)), the Hartree energy represents the response of a particular electron to the electron density which is due to all electrons, including the particular electron (the term \( j = i \) is included). This spurious self-interaction energy is exactly canceled out by the self-exchange energy. Unfortunately, LSDA\(^9\) achieves only a partial cancellation. For a metal, this self-interaction is not a terrible disaster since a given electron is only a small part of the vast conduction electron sea. However for a localized state, it can be very harmful. Perdew and Zunger \([18]\) developed the self-interaction correction (SIC). They pointed out that the Hartree energy (see Eqn (2.4))

\[
U[n] = \int \int \frac{n(r)n(r')}{|r-r'|} \, dr \, dr'
\]  

(2.31)

must cancel the exchange-correlation energy of a single, fully occupied orbital \( \psi_\alpha \), i.e.,

\[
U[n_{\alpha\sigma}] + E_{xc}[n_{\alpha\sigma}, 0] = 0.
\]  

(2.32)

We note here that a single orbital is fully spin-polarized e.g., \( n_{\alpha\uparrow} = n \) and \( n_{\alpha\downarrow} = 0 \). In order to satisfy this condition the total energy functional \( E[n] \) (Eqn (2.4)) is corrected for the Hartree and the exchange-correlation energy of each of the occupied electron states,

\[
\tilde{E}_{SIC}\{\psi_\alpha\} = \sum_\alpha \langle \psi_\alpha | -\nabla^2 | \psi_\alpha \rangle + \int n(r) v_{\text{ext}}(r) \, dr + U[n] + E_{LDA}[n_{\alpha\uparrow}, n_{\alpha\downarrow}] - \sum_\alpha \{ U[n_{\alpha\sigma}] + E_{xc}[n_{\alpha\sigma}, 0] \}.
\]  

(2.33)

Here, \( \tilde{E}_{SIC} \) is a functional of a set of \( N \) occupied orthonormal single electron wavefunctions \( \psi_\alpha \). The last term in Eqn (2.33) corresponds to the self-interaction correction, where for each occupied orbital \( \psi_\alpha \), the term \( \{ U[n_{\alpha}] + E_{xc}[n_{\alpha\sigma}, 0] \} \) of the corresponding single-electron spin density \( n_{\alpha\sigma} \) is subtracted. If the orbitals in the kinetic energy term are taken to be KS orbitals and the SIC term is omitted we recover the LSDA total energy functional. In a paper by Lundin and Eriksson \([19]\), it was shown that SIC in Eqn (2.33) removes only partially the self interaction due to the non-linear behavior of the

\(^9\)Here we discuss the collinear case, so that the exchange-correlation functional depends on spin-up and -down densities, \( E_{xc}[n_{\uparrow}, n_{\downarrow}] \).
electron density for the exchange correlation term. SIC-LSDA has been used widely [20] and in this thesis it was used to describe the localized 4f states in TbNi$_5$ in paper II, CeRhIn$_5$ in paper III and the 5f states in UO$_2$ in paper IV.
3. Computational Methods

This chapter is devoted to the application of DFT to real solids. In the previous chapter we found that DFT reduces the complexity of the many-body problem to an effective single-particle theory. In this framework, a set of KS equations are formulated and their solution entails a self-consistent cycle. This means that a density is used to determine an effective potential, which in turn, is inserted into the KS equations, whose solution produces single-particle wave functions $\{\psi_i\}$ called KS orbitals. The new set of $\{\psi_i\}$ yields a new starting density. This process is repeated until the difference between the densities at the beginning and the end of a cycle is substantially small. Then it is said that self-consistency is achieved. The procedure as outlined above normally leads to large oscillations and bad convergence of the self-consistent cycle. Hence the resulting density is always mixed in some way with the initial density to produce a new density to start the process again. The self-consistent cycle is illustrated in Fig. 3.1.

This cycle has been implemented in many codes. Since all calculations in this thesis have been performed using a relatively new linearized form of the augmented planewave (APW) method, the so-called APW with local orbitals (APW+lo) method, we shall describe here both the traditional linear augmented planewave method (LAPW) and APW+lo.

3.1 The secular equation

Although it is not necessary to define a basis to construct the KS orbitals $\{\psi_i\}$ when solving the KS equations\(^1\), it has been customary in DFT-based methods to expand $\{\psi_i\}$ in a certain basis set $\{\chi_j\}$ with coefficients $c_{ij}$,

$$\psi_i(r) = \sum_j c_{ij} \chi_j(r). \quad (3.1)$$

In Eqn (3.1) we have assumed that the KS orbitals can be accurately described by the basis set $\{\chi_j\}$. Unless the chosen basis set is infinitely large, this can never be achieved. Consequently the optimal $c_{ij}$ must be obtained through a variational procedure. Thus, the KS orbitals as defined in Eqn (3.1) are in-

\(^1\) For instance, it is possible to solve the differential equations numerically on grids.
serted in the KS equations (Eqn 2.7) which in turn are multiplied from the left by \( \psi^* \) and integrated. Finally, the resulting expression is varied,

\[
\delta \sum_{jk} c_{ij} c_{ik} \left( \int \chi_j^*(r) H \chi_k(r) \, dr - \varepsilon_i \int \chi_j^*(r) \chi_k(r) \, dr \right) = 0,
\]

(3.2)

which produces

\[
\sum_k \left( \int \chi_j^*(r) H \chi_k(r) \, dr - \varepsilon_i \int \chi_j^*(r) \chi_k(r) \, dr \right) c_{ij} = 0.
\]

(3.3)

Eqn (3.3) is called the secular equation and in a matrix representation it is written as

\[
(\mathcal{H} - \varepsilon \mathcal{O}) c_i = 0,
\]

(3.4)

where \( \mathcal{H} \) and \( \mathcal{O} \) are the Hamiltonian and the overlap matrices respectively and \( c_i \) are vectors containing as many coefficients as the number of basis functions that have been included in Eqn (3.1). This equation has to be solved for each \( k \) point in the irreducible wedge of the Brillouin zone.
3.2 The linear augmented plane wave method

The LAPW method [21] is a slight modification of the APW method of Slater [22]. Consequently, we shall first establish the essence and motivation of the Slater method as follows: The potential and wave functions in the vicinity of a nuclei vary strongly and are nearly spherical. In contrast, they are smoother between the atoms. These observations lead to the division of space into two regions where different kinds of basis functions are used to represent the densities and potentials. Inside the non-overlapping, atom-centered spheres (S) radial solutions of the Schrödinger equation are used to describe the wave functions, whereas planewaves constitute a suitable basis in the remaining interstitial region,

\[ \psi(r) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_K a_K e^{i(K+k)\cdot r} & r \in \text{Interstitial}, \\ \sum_{lm} b_{lm} u_l(r) Y_{lm}(r) & r \in S. \end{cases} \] (3.5)

In Eqn (3.5), \( \Omega \) is the cell volume, \( a_K \) and \( b_{lm} \) are expansion coefficients, \( Y_{lm} \) are spherical harmonics and \( u_l \) is the regular solution of

\[ \left( -\frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right) u_l(r) = 0. \] (3.6)

In Eqn (3.6) \( E_l \) is assumed to be a variable, not an eigenvalue and \( V(r) \) is the spherical component of the potential in the sphere.

In order for the kinetic energy to be well defined the double representation of the basis in Eqn (3.5) must be continuous at the sphere boundary. This is accomplished in the APW method by defining the coefficient \( b_{lm} \) in terms of \( a_K \) and using the spherical harmonic expansion of the plane waves. Subsequently, by matching each coefficient \( b_{lm} \) at the sphere boundary, the coefficients \( b_{lm} \) become

\[ b_{lm} = \frac{4\pi il}{\sqrt{\Omega} u_l(R)} \sum_K a_K j_l(|K + k| R) Y_{lm}^*(K + k), \] (3.7)

where the quantities \( j_l(kr) \) are spherical Bessel functions of order \( l \) and \( R \) is the sphere radius. The coefficients \( b_{lm} \) are completely determined by the planewave coefficients and the energy variables \( E_l \).

The planewaves in the interstitial region that are matched to the radial functions in the spheres constitute what we call the augmented planewaves or APWs. They are the solution of the Schrödinger equation inside the spheres for a given \( E_l \). They do not posses the freedom to allow the wave function to adapt itself as the band energy deviates from the reference \( E_l \). Therefore, the
\( E_l \) must be set equal to the band energy \( \varepsilon \), which makes the APWs energy dependent functions. Thus, the searching for the roots of the non-linear energy dependent secular determinant

\[
\text{det} [\mathcal{H}(E_l) - E_l \mathcal{O}(E_l)] = 0,
\]

must be achieved. This is a much more computationally demanding procedure than the single diagonalization of the secular matrix in Eqn (3.4) as it would be if the \( E_l \) were fixed parameters.

In the LAPW method\(^3\), the exact solutions \( u_l \) for the spherical potential inside the spheres are replaced by linear combinations of \( u_l(r) \) and its energy derivative \( \dot{u}_l(r) \). The wave functions written in terms of this basis are

\[
\psi(r) = \begin{cases} 
\frac{1}{\sqrt{\Omega}} \sum_K a_K e^{i(K+k) \cdot r} & r \in \text{Interstitial}, \\
\sum_{lm} \left[ d_{lm} u_l(r) + g_{lm} \dot{u}_l(r) \right] Y_{lm}(r) & r \in S.
\end{cases}
\]

Here, the \( u_l \) are defined exactly as in APW, i.e. they are the solutions of the radial Schrödinger equation (see Eqn (3.6)), with a fixed \( E_l \), and the energy derivatives \( \dot{u}_l \) satisfy

\[
\left( -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right) r \dot{u}_l(r) = ru_l(r).
\]

As in APW, the wave functions must be continuous at the boundary and therefore the functions \( u_l \) and \( \dot{u} \) are matched to the respective values and derivatives of the planewaves at the boundary.

The inclusion of \( \dot{u}_l \) in the expansion of the wave function inside the sphere supplies more flexibility to the basis set, which enables it to represent all eigenstates in a region around \( E_l \). For instance, if \( E_l \) differs slightly from the band energy \( \varepsilon \), the radial function \( u_l \) at the energy band will be reproduced by a linear combination,

\[
u_l(\varepsilon, r) = u_l(E_l, r) + (\varepsilon - E_l) \dot{u}_l(r) + \mathcal{O} \left( (\varepsilon - E_l)^2 \right).
\]

In this way, all valence bands may be treated with a single set of \( E_l \), leading to an energy independent basis set. Therefore, the secular equation becomes linear in energy and only a single diagonalization is needed to obtain accurate energy bands. The last fact constitutes a great advantage of LAPW compared to APW. However the price that LAPW pays due to its flexible basis is the

\(^2\)The APW basis are energy dependent, so are the \( \mathcal{H} \) and the \( \mathcal{O} \) matrices represented in such basis.

\(^3\)A detailed account of the LAPW method can be found in Ref. [17].
loss of the optimal physical form of \( u_l \) inside the sphere, which implies that a larger number of basis functions is required to achieve convergence.

### 3.3 APW with local orbitals

An alternative linearization of APW was developed by Sjöstedt et al. [23], the so-called APW+lo method. One of the problems of the APW basis set is that it can only describe eigenstates with energies in the immediate vicinity of \( E_l \). The situation improves in LAPW when modifying the augmented planewave inside the sphere, which adds more flexibility to the basis set. However, the wave function inside the sphere is not as well represented as it was in the APW.

APW+lo keeps the original APW basis set (Eqn (3.5)) with the exact radial solutions \( u_l \) of the Schrödinger equation inside the spheres evaluated at \( E_l \) but adds a complementary basis set, namely, a set of local orbitals [17, 24],

\[
\chi_{lo}(r) = \begin{cases} 0 & r \in \text{Interstitial}, \\ (o_{lm} u_l(r) + p_{lm} \dot{u}_l(r)) Y_{lm}(r) & r \in S. \end{cases} \tag{3.12}
\]

This extra basis set introduces the desired variational freedom. Local orbitals were initially brought into the LAPW method to deal with semi-core states. Their local character comes from the fact that they are entirely confined to the spheres. Moreover, they have a specific \( l m \) character and are independent of \( \mathbf{k} \) and \( \mathbf{K} \). As in the former methods, the basis functions must be continuous and consequently local orbitals are matched at the boundary to zero, so we obtain,

\[
p_{lm} = -\frac{o_{lm}}{u_l(R)} \frac{u_l(R)}{\dot{u}_l(R)}, \tag{3.13}
\]

where \( R \) is the sphere radius.

The APW+lo method uses both bases in such a manner that \( u_l \) is included as in APW to describe eigenstates whose eigenenergies are close to \( E_l \) and a linear combination of \( u_l \) and \( \dot{u}_l \) for eigenstates of eigenenergies far away from \( E_l \). Therefore the number of basis functions is considerably smaller than in the LAPW method yielding a faster convergence. Of course, for perfectly converged calculations both methods produce the same result.
4. Non-Collinear Magnetism

Solids may contain magnetic moments that can act cooperatively, leading to a behavior which is quite different from what would be observed if all magnetic moments were isolated from each other. This collective behavior and the diversity of types of magnetic interactions produce a surprisingly rich variety of magnetic properties in real systems. Magnetism is a large field in condensed matter. In this chapter we will concentrate on non-collinear magnetic orderings and its origin within an itinerant picture. We will start by describing spin spirals (see Fig. 4.1) and a way of treating them efficiently within DFT. The origin of magnetism will be considered as a predecessor for a discussion on conditions for non-collinear states to exist. The concepts of a q-dependent susceptibility and Fermi surface nesting will be introduced as indicators of magnetic instabilities.

4.1 Spin spirals

Different types of magnetic ground state order can be found as a direct consequence of the different types of exchange interactions that operate between the magnetic moments in a solid. Some of them are illustrated in Fig. 4.1. The first two spin arrangements are commonly called collinear structures, for there is a global spin quantization axis along which all the spins in the structure are aligned, either parallel or anti-parallel. The last three structures in Fig. 4.1, helical, spin spiral and spin glass, are characterized by the lack of such a global axis and they are called non-collinear structures.

A spin spiral structure as depicted in Fig. 4.1d) can be defined by expressing the Cartesian coordinates of the magnetization density as

$$\mathbf{m}(\mathbf{r}) = m(\mathbf{r}) [\cos(\mathbf{q} \cdot \mathbf{t} + \varphi) \sin \theta, \sin(\mathbf{q} \cdot \mathbf{t} + \varphi) \sin \theta, \cos \theta]$$

(4.1)

where $m$ is the magnitude of the magnetic moment, $\varphi$ and $\theta$ are polar angles, $\mathbf{t}$ is a lattice vector and $\mathbf{q}$ is the wavevector that characterizes the spin spiral. A distinctive property of the spiral structure is the lack of translational symmetry along the direction of the wavevector $\mathbf{q}$ (see Fig. 4.1d)). However, two atoms of the spin spiral, separated by a lattice vector $\mathbf{t}$, become equivalent if a spin rotation about the spiral axis with the proper angle is applied on the magnetic
As was first pointed out by Herring [25] and later by Sandratskii [26, 27], transformations $T_\phi$ combining a translation $T_t$ by a lattice vector $t$ and a spin rotation $R(\phi)$ about the spiral axis $\hat{n}$ (see Fig. 4.1d) by an angle $\phi = q \cdot t$

$$R(\phi) = e^{-i\phi \sigma_z/2}$$

leave the spiral structure invariant,

$$T_\phi \mathbf{m}(\mathbf{r}) = \mathbf{m}(\mathbf{r}).$$

The symmetry operators that describe these transformations belong to a spin-space group (SSG)[28]. Three important properties of these generalized translations can be stated as follows: i) spinors transform according to

$$T_\phi \psi(\mathbf{r}) = \begin{pmatrix} e^{-iq t/2} & 0 \\ 0 & e^{iq t/2} \end{pmatrix} \psi(\mathbf{r} - \mathbf{t}),$$

ii) the generalized translations commute with the Kohn-Sham Hamiltonian (see Eqn (2.29)) of a spin spiral structure, and iii) they form an Abelian group isomorphic to the group of ordinary space translations $T_t$. Therefore, they have the same irreducible representation, which constitutes the Bloch theorem in the case of ordinary space translations. The generalized Bloch theorem is

---

1In writing Eqn (4.2) the spiral axis $\hat{n}$ was taken along the $z$-direction. In the absence of the spin-orbit term, this can be done without any loss of generality.
4.1. SPIN SPIRALS

then established as

\[ T_\phi \psi_k(\mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{t}} \psi_k(\mathbf{r}). \] (4.5)

These properties enable us to express the generalized Bloch spinors [25] that diagonalize the spiral Hamiltonian \( H \) as

\[ \psi_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \begin{pmatrix} e^{-i\mathbf{q} \cdot \mathbf{r}/2 \alpha_k(\mathbf{r})} \\ e^{i\mathbf{q} \cdot \mathbf{r}/2 \beta_k(\mathbf{r})} \end{pmatrix}, \] (4.6)

where \( \alpha_k \) and \( \beta_k \) are the periodic functions for the spin-up and spin-down components respectively. These generalized spinors will produce the same charge density as the ordinary spinors and the magnetization density as defined in Eqn (4.1). The generalized symmetry group permits us to solve the Kohn-Sham equations (Eqn (2.18)) in the presence of spin spirals without using supercells. In this way, we have recovered the symmetry of the chemical unit cell. However, the fast Fourier transforms that full-potential methods based on planewaves use require translationally invariant potentials and densities. Nordström [29] developed a slightly different scheme, which naturally incorporates the spin spiral symmetries. Two new complex quantities are introduced, \( u \) and \( h \), with the spin axis taken in the \( z \)-direction,

\[ u(\mathbf{r}) = e^{-i\mathbf{q} \cdot \mathbf{r}} (m_x(\mathbf{r}) + i m_y(\mathbf{r})) \] (4.7)

\[ h(\mathbf{r}) = e^{-i\mathbf{q} \cdot \mathbf{r}} (b_x(\mathbf{r}) + i b_y(\mathbf{r})), \] (4.8)

where \( m_x \) and \( m_y \) are the perpendicular components of the magnetization density and \( b_x \) and \( b_y \) are the corresponding magnetic field components. The new quantity \( h \) is used now to re-write the Kohn-Sham Hamiltonian matrix (see Eqn (2.29)) as

\[ \mathcal{H} = (-\nabla^2 + v_{nm}) \mathbb{1} + \frac{1}{2} \left( e^{i\mathbf{q} \cdot \mathbf{r}} h(\mathbf{r}) \sigma_- + e^{-i\mathbf{q} \cdot \mathbf{r}} h(\mathbf{r})^\dagger \sigma_-^\dagger \right) + b_z \sigma_z \] (4.9)

with

\[ \sigma_- = \sigma_x - i \sigma_y. \] (4.10)

Finally, we can easily obtain the density \( u \) from the generalized Bloch spinors as defined above,

\[ u(\mathbf{r}) = \sum_{j,k} \psi_{j,k}^\dagger \left( e^{-i\mathbf{q} \cdot \mathbf{r}} \sigma_-^\dagger \right) \psi_{j,k}. \] (4.11)

These quantities are invariant under ordinary space translations by construction, and hence they can be implemented in full-potential methods with normal Fourier transforms.
4.2 Origin of magnetic ordering

The nature of the magnetic ordering in solids is not understood on a microscopic level despite decades of research. In particular it is not known why in Nature one most often observes collinear magnets, non-collinear magnetic ordering appearing less frequently. Before this question is addressed we shall briefly analyze the conditions for magnetism to exist at all. The important role of the magnetic susceptibility as an indicator of magnetic instabilities will be introduced. The concept of Fermi surface nesting will be discussed as a crucial factor in the stabilization of the spin spiral structure.

4.2.1 Itinerant electron theory (Stoner criterion)

In this section, we will derive the Stoner condition in the context of the free-electron model, however this criterion as well as the enhanced magnetic susceptibility can be obtained in a more sophisticated way from DFT. In some cases the magnetic moments in metals are associated with the conduction electrons, i.e. itinerant magnetism. In the Stoner theory of itinerant magnetism \[30, 31\] a molecular field which contains all exchange interactions is introduced. In analogy with the Weiss model\[2\] the molecular magnetic field is written as

\[ H_m = I \zeta, \]

where \( I \) denotes the molecular field constant and \( \zeta \) the magnetization given by the difference of the number of up and down spins that \( H_m \) generates. The total energy \( E(\zeta) \) of electrons moving in the molecular field contains contributions from the kinetic and the field energies \[4, 32\]

\[
E(\zeta) = \int_{\sigma=+}^{\epsilon} \varepsilon \mathcal{N}(\varepsilon) d\varepsilon + \int_{\sigma=-}^{\epsilon} \varepsilon \mathcal{N}(\varepsilon) d\varepsilon - I \int_{0}^{\zeta} \zeta' d\zeta' \\
= \frac{9}{20N_0} \left[ (1 + \zeta)^{5/3} + (1 - \zeta)^{5/3} \right] - \frac{I}{2} \zeta^2, \tag{4.12}
\]

where \( N_0 \) is the density of states at the Fermi energy. A detailed inspection of the total energy (Eqn (4.12)) reveals that as the value of \( N_0 I \) grows larger than one, a minimum in the total energy for a finite value of \( \zeta \) develops, i.e. a spontaneous magnetization appears in the system when

\[ N_0 I > 1. \tag{4.13} \]

\[2\]A complete description of Weiss model can be found in \[32\].
This relation is called the Stoner condition and is fulfilled when the density of states at the Fermi energy is large\(^3\). Therefore the phase transition from the non-magnetic state to the ferromagnetic state is usually caused by a peak in the density of states at the Fermi energy.

The Stoner condition manifests itself also in the enhanced susceptibility, which can be obtained from the total energy in the non-magnetic limit \(\zeta \to 0\) as

\[
\chi = \lim_{\zeta \to 0} \left( \frac{d^2 E}{d\zeta^2} \right)^{-1} = \frac{N_0}{1 - IN_0}.
\] (4.14)

The enhanced susceptibility in Eqn (4.14) can be rewritten as the product of the Pauli susceptibility \(\chi_p\) and an enhancement factor which represents the fact that the susceptibility of an interacting electron system can not be determined merely by the Pauli susceptibility alone. The enhanced susceptibility becomes very large for metals near a magnetic instability. Hence a peak in the susceptibility indicates that the investigated system may be close to a magnetic phase transition. In the framework of DFT, an expression is derived for the Stoner factor \(I\), which is now seen as an exchange-correlation integral, and it is simply called the Stoner exchange constant.\(^4\)

### 4.2.2 The static nonuniform magnetic susceptibility

In the following sections we shall explore the conditions of magnetic instabilities that could lead to spin spiral structures. The magnetic susceptibility is an example of a more general concept, namely, linear response functions. Here we are interested in particular in the magnetic response of an inhomogeneous system to an external static magnetic field that is non-uniform in space. If the magnitude of the field is small, we can assume the response \(\chi\) to be linear. In general, we can write the induced magnetization as

\[
\delta m (\mathbf{r}) = \int \chi (\mathbf{r}, r') \delta B (r') \, dr'.
\] (4.15)

Note that \(\delta m\) responds not just to the field at \(\mathbf{r}\), but to a weighted average over nearby values. The problem can be addressed from DFT [33] by specifying a magnetic field whose spatial variation is characterized by the vector \(\mathbf{q}\),

\[
\Delta B (\mathbf{r}) = \Delta B \sum \left( \cos (\mathbf{q} \cdot \mathbf{R}), \sin (\mathbf{q} \cdot \mathbf{R}), 0 \right) \Theta (|\mathbf{r} - \mathbf{R}|)
\] (4.16)

\(^3\)It has been found that the molecular field constant is an atomic property and of the same order of magnitude for most metals [32].

\(^4\)A detailed derivation of the Stoner exchange constant can be found in Ref. [4, 32].
where $\Theta(r)$ is the unit step function which is 1 for $r$ smaller than the atomic sphere radius and zero otherwise. The magnetic field specified above favors a spiral with $\theta = 90^\circ$ (see Eqn (4.1)). After some calculations, the enhanced susceptibility\(^5\) for static magnetic fields parallel to the magnetization density at each point (see Eqn (2.26)) is found to be

$$\chi = \frac{\chi_0(q)}{1 - I(q)\chi_0(q)}, \quad (4.17)$$

where $\chi_0(q)$ is the susceptibility of a non-interacting uniform electron gas. In Eqn (4.17) we can see that the enhanced $q$-dependent susceptibility will diverge if $I(q)\chi_0(q) > 1$, which means that the non-magnetic state becomes unstable against a magnetic structure characterized by the vector $q$. This is the generalized Stoner condition.

### 4.2.3 Fermi surface nesting

We shall now examine a Fermi surface feature of fundamental interest, nesting. Fermi surface nesting can largely influence the magnetic susceptibility and therefore it constitutes a decisive factor in the study of magnetic instabilities.

Let us start from Eqn (4.17). In order to obtain $\chi_0(q)$, the so-called Lindhard expression in its non-magnetic form is used, which in this case describes

\(^5\)Details of this calculation are given in Ref. [4].
the response function for non-interacting electrons as
\[
\chi^0(r, r') = \sum_{k\mu} \sum_{k'\nu} \Theta(\varepsilon_F - \varepsilon_{k\mu}) - \Theta(\varepsilon_F - \varepsilon_{k'\nu}) \\
\times \psi_{k\mu}(r) \psi_{k\mu}(r') \psi_{k'n}(r') \psi_{k'n}(r).
\]  
(4.18)

Here \(\Theta(x)\) is the unit step function, \(\nu\) and \(\mu\) are band indices, and \(k\) and \(k'\) are wave vectors that label Bloch states. By applying the Fourier transform twice on this equation we obtain (see Ref. [3]),
\[
\chi^0(q, q') = \int \int e^{-iqr} e^{-iqr'} \chi^0(r, r') \, dr \, dr' = \delta_{q,q'} \chi^0(q)
\]  
(4.19)

where
\[
\chi^0(q) = \sum_{k\mu\nu} \frac{[f(\varepsilon_{k\nu}) - f(\varepsilon_{k-q\mu})]}{\varepsilon_{k-q\mu} - \varepsilon_{k\nu} + i\delta} \cdot |\langle k\nu|e^{iqr}|k-q\mu\rangle|^2.
\]  
(4.20)

The expression in Eqn (4.20) was generalized by using the Fermi distribution \(f(\varepsilon)\) instead of the \(\Theta(x)\) function and an infinitesimal \(i\delta\). The denominator in Eqn (4.20) becomes very small if there exist parallel portions of the electron and hole Fermi surfaces that, by a rigid shift defined by a vector \(q\), can be made to coincide (see Fig. 4.2). This feature of the Fermi surfaces is called nesting. It should be noted that in the case of strong nesting and low temperature, \(\chi^0(q)\) becomes very large since the denominator in Eqn (4.20) is almost zero for many values of \(k\) in the sum and the numerator is close to one. Therefore, the susceptibility \(\chi^0(q)\) can become very large for the value of \(q\) that defines the Fermi nesting shift. The generalized Stoner condition
\[
I \chi^0(q) \geq 1,
\]  
(4.21)

is then fulfilled. Fig. 4.2 depicts an illustration of the Fermi surface cross-section, where the \(q\)-vector that separates the portions of electron and hole Fermi surfaces has been identified. It is worth noticing that the magnitude of \(q\) in Fig. 4.2 is less than a reciprocal lattice vector magnitude, which means that the adopted spin spiral structure will not be commensurate with the lattice. Fermi surface nesting has been proved to have a large effect in the susceptibility, which in turn, provides us with an indicator of a magnetic instability.

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6 A derivation of the Lindhard expression can be found in Ref. [3, 4].
Figure 4.3: Schematic energy band structures of a hypothetical element. The blue and red straight lines stand for two orthogonal spin down and up bands respectively in the ferromagnetic state. The presence of a non-collinear coupling allows the hybridization of the two spin channels and the hybridized bands become the color-graded parabolic curves. The horizontal line represents the Fermi energy. Two different possibilities are shown in a) and b).

4.2.4 Conditions for non-collinear states

The most common theoretical explanations for non-collinear magnetic ordering involve either magnetic frustration in materials (see paper V) with crystal structures that have anti-ferromagnetic exchange interactions [4] or nearest neighbor ferromagnetic interactions that are of similar size to next nearest neighbor anti-ferromagnetic interactions [34]. For the late rare earths the RKKY interaction has also been argued to cause non-collinear states [35]. In paper VI of this thesis, two criteria are identified which determine whether a magnetic metal may be stabilized in a collinear or non-collinear arrangement. In the following discussion, only spin spirals will be considered as examples of non-collinear states. Nevertheless the results presented here hold for more general cases as well. To illustrate these ideas, schematic energy bands of a hypothetical element are displayed in Fig. 4.3. In a ferromagnetic state, spin up and spin down bands are orthogonal and therefore they can not hybridize. This is represented by red and blue straight lines in Fig. 4.3. However, as was discussed in chapter 2, in the more general non-collinear formulation the one-electron states do not possess pure spin up or down character and the wave functions are described by two component spinors (see Eqn (2.13)). In the case of spirals, the generalized Bloch spinors that diagonalize the spiral Hamiltonian in Eqn (2.29) were given in Eqn (4.6). Consequently, since the term $\mathbf{b} \cdot \sigma$ in the spiral Hamiltonian is not diagonal, the two spin compo-
nents hybridize. Such hybridization is depicted in Fig. 4.3 as the color-graded parabolic curves. These two bands experience repulsion which opens up an energy gap. If the hybridization gap occurs at the Fermi energy, the band that has been pushed down will lower the total energy whereas the band that has been pushed up will not contribute to the total energy, since it is now empty. Fig. 4.3b presents a similar situation but the mechanism that lowers the total energy is not as efficient as in Fig. 4.3a. Two criteria for the formation of spin spirals can be deduced from the mechanism sketched above. First, the Fermi energy should cut through both spin up and down states. This condition immediately excludes strong ferromagnets such as bcc Fe, hcp Co and fcc Ni, where the spin up band is filled. In contrast, spin spirals are expected to be observed in fcc Fe, bcc Mn and fcc Mn at ambient conditions. Secondly, the mechanism discussed in Fig. 4.3 is extra efficient if there is nesting between spin up and spin down states (see Fig. 4.2 and the discussion around the figure). This guarantees that many $k$-points are involved in the energy lowering process discussed above. It is clear that a larger gap causes a larger effect in lowering the total energy.

To investigate the above suggested scenario we carried out first principles theoretical calculations for several transition metals. In order to meet the demands of our first condition, the exchange splitting was tuned either by modifying the volume or by using the so called fixed spin moment method [36]. All elements that have been investigated, bcc V; bcc and fcc Mn; bcc Fe; bcc and fcc Co; and bcc and fcc Ni, are either non-magnetic or adopt a collinear magnetic structure at normal conditions. We did not include here the most obvious case of spin spiral, fcc Fe, since it has been extensively studied (see Ref. [37] and references therein) and it has also been discussed in paper VII of this thesis. We show our results in Fig. 4.4, where the energy versus the wave vector $q = (0, 0, q)$ that describes the spin spiral structure is plotted for several elements. The ferromagnetic state is represented by $q=0$ and $q=1$ describes an antiferromagnetic ordering; all other $q$ values correspond to different spin spirals. In Fig. 4.4, the equilibrium volumes of bcc V, bcc Mn, bcc Fe, fcc Co, bcc Ni and fcc Ni were modified; whereas in fcc Mn and bcc Co the magnetic moment was fixed to the values shown in the figure. The data in Fig. 4.4 shows that fulfilling the conditions for non-collinear order discussed above is equally well accomplished by changing the lattice constant as by fixing the magnetic moment. In the case of bcc Co, we fixed the moment to be $0.7 \mu_B$ and $0.15 \mu_B$. In the former case a ferromagnetic state has the lowest total energy, while an almost flat curve with several local minima is observed for the latter case. The variations observed in this curve are smaller than the accuracy of the calculations, and it is difficult to conclude if one $q$-vector is more stable than the other. However, one can conclude that there is a competition between non-collinear and collinear interactions that are of almost the same
Figure 4.4: Calculated energies as a function of $q$-value for several elements, Ni, Fe, Co, Mn and V, in the bcc and fcc crystal structures. The wave vector $q$ was considered for simplicity along the (001) except in the case of bcc Fe, where the (110) direction was investigated.
Figure 4.5: Band structures of TlCo$_2$Se$_2$. The upper panel shows the band structures of the ferromagnetic state (solid lines) and a spin spiral with $q = (0, 0, 0.6)2\pi/c$ (dashed line). In the lower panel, the solid line corresponds to the band structure of the ferromagnetic state and the dashed line indicates the band structure of the antiferromagnetic state.

size. In all the cases presented in Fig. 4.4, except for bcc Co, we have found that non-collinear states are favored against collinear magnetism. Hence our first principles results are consistent with the analysis of Fig. 4.3.

In paper VIII, the stability of the non-collinear and the antiferromagnetic states over the ferromagnetic ordering of the TlCo$_2$Se$_2$ compound was analyzed from the electronic structure (the bonding situation of TlCo$_2$Se$_2$ is discussed in paper IX). A powder neutron diffraction study showed that this quasi two-dimensional system has an incommensurate helix running along the c-axis with a turn angle of $\sim 121^\circ$. The magnetic structure can be seen in Fig. 1 of paper VIII. The magnetic moments of the cobalt atoms are ferromagnetically ordered within each layer and perpendicular to the c-axis. The helical wave vector was found to be $(0, 0, q)$ with $q \sim 0.6$ and the moment on Co atoms was $0.46 \mu_B$. However, LSDA first principles calculations showed that the antiferromagnetic configuration was more stable than the helical structure. Here we would like to point out that our linear muffin-tin orbitals with the atomic sphere approximation LMTO-ASA [38] calculations in paper X showed that a spin spiral state was more stable than the antiferromagnetic
configuration in accordance with experiments. However, in paper VII, the discrepancy between the two methods (APW+lo and LMTO-ASA) was ascribed to the less accuracy of the atomic spherical approximation when dealing with open crystal lattices [39], especially considering the very small energies that are involved for resolving the correct magnetic structure. In order to study the magnetic structure the band structure of TlCo$_2$Se$_2$ was investigated. The upper panel of Fig. 4.5 displays the ferromagnetic (dark solid line) and the spin spiral bands with $q = (0, 0, 0.6)2\pi/c$ (dotted-dashed line), while in the lower panel of the figure the ferromagnetic bands (dark solid line) are compared with the bands of the antiferromagnetic configuration (dotted-dashed line). The Fermi level is indicated in both panels by a thin solid line. It is worth noticing that the ferromagnetic bands in the upper and the lower part of the figure do not look the same. This is because of the way we have chosen to represent the spin spiral wavefunction (see Eqn (4.6)) in which the spin up and spin down components are shifted $\pm q/2$, respectively. Therefore in order to represent a ferromagnetic state with this wavefunction, either the wavevector $q = 0$ is used or the polar angles $\theta$ and $\phi$ that describe the direction of the magnetization density (see Eqn (4.1)) are set to zero with an arbitrary $q$. Thus, in the upper panel, the ferromagnetic state was represented by $q = 0.6$ and the polar angles $\theta = \phi = 0$. This was done in order to compare with the band structure of the spin spiral of wavevector $q = 0.6$. In a similar way the ferromagnetic state in the lower panel of the Fig. 4.5 was described by $q = 1$ and $\theta = \phi = 0$ to compare with the band structure of the antiferromagnetic ($q = 1$) configuration. Hence the band structures of the ferromagnetic state in both panels have a different $q$-shift which makes them appear different. In the upper panel of Fig. 4.5, there are two bands of the ferromagnetic system close to the Fermi energy that cross each other twice. In contrast, these two bands in the spin spiral configuration have hybridized and split. In the lower panel of Fig. 4.5, the antiferromagnetic bands resemble the spin spiral bands of the upper panel. According to Fig. 4.5, the lowering energy mechanism described above (see discussion around Fig. 4.3) would be more effective for the antiferromagnetic bands than for the spin spiral configuration, since the band that has been pushed up is completely empty in the former case. This would explain the antiferromagnetic ground state found by our first principles calculations (see paper VIII).

The study of the substitutional alloys TiCo$_2$Se$_2-x$S$_x$ gives us the opportunity to investigate the transition between the ferromagnetic state in TiCo$_2$S$_2$ to the antiferromagnetic state in TiCo$_2$Se$_2$ via a series of non-collinear states. Neutron diffraction experiments on the substitutional alloys TiCo$_2$Se$_2-x$S$_x$ for $x = [0 - 2.0]$ were performed by Ronneteg et al. [40]. The distance between the Co layers (inter-layer distance) and the distance between the Co atoms within a layer (intra-layer distance) were found to decrease almost lin-
4.2. ORIGIN OF MAGNETIC ORDERING

Figure 4.6: The calculated total energy of TlCo$_2$Se$_2$ (open squares), TlCo$_2$S$_2$ (open circles) as a function of $(0, 0, q) 2\pi/c$. The total energies of TlCo$_2$Se$_2$ for different values of the inter-layer distance $c/2 = 6.406$ Å (filled diamonds), $c/2 = 6.567$ Å (filled circles) and $c = 6.489$ Å (filled up triangles) are also displayed. The energy is given with respect to the energy of the ferromagnetic state ($q = 0$) of each curve. The values of the corresponding concentration on the TlCo$_{2-x}$S$_x$ alloys are given in parenthesis.
early with the concentration. Spin spirals are formed in TlCo$_{2-x}$Se$_x$ with different turn angles in the inter-layer distance range of 6.49 $\leq c/2 \leq$ 6.71 Å, which corresponds to the concentration $0 \leq x \leq 1.5$. Finally, at $c/2 = 6.44$ Å ($x = 1.75$), a ferromagnetic phase appears, which persists in TlCo$_2$S$_2$ (see Fig. 1 in paper XI). As S takes the place of Se in the crystal structure the distance between the Co layers is reduced and the turn angle becomes smaller until it totally vanishes at $x = 1.75$. In paper XI we performed total energy calculations using GGA for TlCo$_2$S$_2$ and TlCo$_2$Se$_2$. Our results are plotted in Fig. 4.6. TlCo$_2$Se$_2$ was found to have an energy minimum at $q = (0, 0, 1/2)2\pi/c$ which corresponds to an antiferromagnetic configuration. This result agrees with our previous LSDA findings in paper VIII. We conclude that the small discrepancy between theoretical and experimental values of the magnetic structure of TlCo$_2$Se$_2$ is not resolved by using GGA. The energy curve for TlCo$_2$S$_2$ (open circles) shows a minimum at $q = 0$ which indicates that TlCo$_2$S$_2$ is a ferromagnet in accordance with neutron diffraction experiments [40]. In order to investigate whether or not the transition to a ferromagnetic phase when S replaces Se is an effect caused by the difference in chemistry of these two atomic species, or if it is merely a geometrical effect (the change in the interlayer distance), we have calculated the total energy of TlCo$_2$Se$_2$ for different values of the inter-layer distance. Hence we also present in Fig. 4.6 the calculated total energy of TlCo$_2$Se$_2$ for various values of the inter-layer distance that correspond to different concentrations of the substitutional TlCo$_{2-x}$Se$_x$ alloys. It may be seen that the energy vs. q curve for TlCo$_2$Se$_2$ with a inter-layer distance that has the same length as that of TlCo$_2$S$_2$ (6.406 Å, (filled diamonds)), is very similar to the corresponding curve for TlCo$_2$S$_2$ (open circles). This shows that geometrical effects, i.e. distance between Co planes, is the most important factor for determining the magnetic structure of these material. We note in Fig. 4.6 that for values of the inter-layer distance intermediate between that of TlCo$_2$Se$_2$ and TlCo$_2$S$_2$ we obtain a gradual change in the magnetic structure, from ferromagnetic via non-collinear to anti-ferromagnetic, as a function of increasing c lattice constant.

The band structures of TlCo$_2$Se$_2$ and TlCo$_2$S$_2$ (see Fig. 4 of paper XI) in a ferromagnetic configuration were analyzed in connection with the mechanism that favors non-collinear states. Two almost parallel bands around the Fermi energy were identified in the TlCo$_2$Se$_2$ band structure. In a spin spiral state these two bands can hybridize and repel each other, as discussed earlier in this section. Since the bands lie in the vicinity of the Fermi energy, an energy gap arises, lowering the total energy. If strong nesting exists between spin-up and -down Fermi surfaces there may be an effective energy gain large enough to favor the spin spiral state over the ferromagnetic configuration. These two bands were also observed in the TlCo$_2$S$_2$ band structure, but they were located
4.2. ORIGIN OF MAGNETIC ORDERING

Figure 4.7: The calculated total energy of hcp Fe in the AFM (II) (see text) configuration (open circles), in the paramagnetic state (filled squares) and in the non-symmetrical spin spiral ($\mathbf{q} = (0.56, 0.22, 0)2\pi/a$) (open triangles) are plotted as a function of the volume.

well above the Fermi level. In a spin spiral configuration, the hybridization of these two bands will not lower the total energy for TlCo$_2$S$_2$. As a matter of fact the spin-mixing of the spin spiral state may even increase the energy since the magnetic moments decrease, which increases the intra-atomic exchange energy. Hence, the mechanism discussed above will not favor a spin spiral state in TlCo$_2$S$_2$, which agrees with the experimental findings [40].

4.2.5 Iron at high pressures

Iron is an interesting element in many aspects, being maybe the most remarkable, the richness of its magnetism. At ambient conditions Fe is a ferromagnet in the bcc structure. Non-collinear states are observed in fcc Fe (see paper VII) and fcc Fe$_x$Ni$_{1-x}$ Invar alloys [41, 42]. When applying pressure ($\sim 13$ GPa) Fe undergoes a phase transition by adopting the hexagonal close-packed (hcp) structure which is believed to be a non-magnetic phase [43]. In this high-pressure phase, Shimizu et al. [44] reported the occurrence of superconductivity in a very narrow range of pressure, between 15 and 30 GPa (132 a.u.$^3 < V < 145$ a.u.$^3$). Recently, evidence has been found that suggests that Fe, would develop an antiferromagnetic ground state [45] or a non-collinear magnetic order [46] in the hcp phase under pressure. Spin fluctuations have been discussed to play a role on the appearance of superconductivity in Fe under pressure [47]. Calculations of the static paramagnetic spin susceptibility
under pressure [48] at finite temperatures in the high-pressure phase of iron showed that the dominant magnetic fluctuations are incommensurate AFM, characterized by the wave vector \( \mathbf{q} = (0.56, 0.22, 0)2\pi/a \).

In paper XII, several non-collinear structures such as spin spirals, two types of AFM structures denoted by AFM (I) and (II) (see Fig. 1 in paper XII) and the ferromagnetic configuration were studied. The calculated total energy of hcp Fe in the AFM (II) configuration (open circles) and in the paramagnetic state (filled squares) are plotted as a function of the volume in Fig. 4.7. The paramagnetic curve has a minimum at 70 a.u.\(^3\) and it lies lower in energy (~ 10 mRy) than the AFM (II) configuration whose equilibrium volume is found at 70.7 a.u.\(^3\). This result does not agree with previous first principles calculations (LAPW) [45]. It is worth pointing out here that the magnetic moments calculated in the present investigation (see Fig. 2 in paper XII) are in excellent agreement with those in Ref. [45]. In Fig. 4.7 the energies for the spin spiral with the non-symmetric wave vector \((0.56, 0.22, 0)2\pi/a\) are also displayed. From this figure it is clear that this spin spiral is lowest in energy of all considered magnetic structures. This finding is in accordance with the susceptibility calculations by Thakor et al. [48].
5. Localized Magnetic Moments

In the previous chapter, we discussed the so-called band or itinerant magnetism in metals, where the electrons that are responsible for magnetism form bands and move more or less freely in the solid. Here, we shall consider magnetism in systems that have localized magnetic moments. Such is the case of the rare earth (RE) metals and some actinide compounds where the magnetic electrons are confined to the vicinity of the nucleus. When a large number of RE atoms are brought together to form a solid, the 4f electrons generally remain localized and are shielded by the 5s and 5p states. Instead, the 5d and 6s electrons become delocalized into Bloch states, and compose the conduction band. The case in the actinides is a little more complex because of the greater spatial extension of the atomic wavefunction of the 5f electrons. The phenomena observed in the actinide compounds are related to the peculiarities of the 5f electrons which sometimes behave as localized electrons and sometimes appear to be itinerant. As a starting point we will review Hund’s rules; even though they were established for atoms and ions, they have proven to give a good description of the ground state of a RE ion in a lattice provided that the crystal field effects can be neglected.

5.1 Hund’s rules

In a typical atom, the electrons arrange themselves in filled shells with no net angular moment. However, it could be that some shells are incompletely filled so the electrons in these shells can combine to give a non-zero spin and orbital angular momentum. An atom can thus have a net spin and orbital angular momentum, $S$ and $L$, respectively. The number of ways that the electrons can be combined is given by

\[(2L + 1)(2S + 1)\,.

The configuration that minimizes the total energy can be estimated by using Hund’s rules [1]. They are only applicable to the ground state configuration and assume that there is only one unfilled shell. These three rules state the following:

1. The total spin $S$ should be maximized in order to minimize the Coulomb
energy in accordance with the Pauli exclusion principle, i.e. the exchange energy.

2. The total orbital angular momentum $L$ is maximized according to the value determined for $S$ in the first rule. This can be understood here by imagining that electrons rotating in orbits in the same direction can avoid each other more efficiently and thus reduce the Coulomb repulsion between them.

3. The third rule states that if the shell is less than half full then $J = |L - S|$ and $J = |L + S|$ if it is more than half full. The third rule is caused by the spin-orbit energy.

In condensed matter, Hund’s rules may still be obeyed in systems where the electrons in unfilled shells are confined within the vicinity of the nucleus so, for instance, they do not participate in the bonding. With the exception of Ce and Yb compounds, RE metals can be regarded as such systems.

5.2 Crystal field

The Hamiltonian of a free atom is invariant under all rotations and reflections in space which leave the position of the nucleus unchanged. The degeneracy of its ground state is $2J + 1$. Now, if we imagine placing this free atom at a lattice site the point group of the lattice will determine the symmetry-induced degeneracies of the atomic levels. The electric field that our atom (the central atom) will experience due to the charge distribution of the surrounding atoms is called the crystal field (CF)$^{1}$. The size and nature of CF effects depend crucially on the symmetry of the local environment. The effect of the CF on the 4f electrons in the RE atom is very small since these electrons are confined in the vicinity of the nucleus and are shielded from the rest of the crystal by the 5s and 5p states. The 3d electrons in the transition metals, in the other hand, are more extended and hence the effect of the CF is stronger on them. The situation for 5f electrons is somewhere between that of the 4f and 3d states.

The contribution of the CF to the potential energy is

$$v_{cf}(r) = \int \frac{n(R)}{|r - R|} \, dR,$$

(5.1)

where $n(R)$ is the charge density of the surrounding electrons and nuclei. If this density does not penetrate the charge cloud of the central atom, $v_{cf}$ is a solution of Laplace’s equation, and may be expanded in spherical harmonics$^{2}$

$^{1}$A good account on CF theory can be found in Ref. [34].

$^{2}$Note that the full multipole expansion has not been used since the on-site contribution has been neglected due to the fact that only the charge surrounding the central atom is considered.
as

\[ v_{\text{cf}} = \sum_{lm} A_l^m r^l Y_{lm}(\hat{r}), \]  

(5.2)

with

\[ A_l^m = (-1)^m \frac{4\pi}{2l+1} \int \frac{n(R)}{R^{l+1}} Y_{l-m}(\hat{R}) \, dR. \]  

(5.3)

Stevens [49, 50] pointed out that provided that we remain within a manifold of constant \( J \), in this case the ground state multiplet, the matrix elements of \( v_{\text{cf}}(r) \) are proportional to those of operator equivalents written in terms of the \( \hat{J} \) operators [34]. We may then write the CF Hamiltonian by using the Racah operators \( \tilde{O}_{lm}(\hat{J}) \) as

\[ H_{\text{cf}} = \sum_i \sum_{lm} A_l^m \alpha_i \langle r^l \rangle \left( \frac{2l+1}{4\pi} \right)^{1/2} \tilde{O}_{lm}(\hat{J}_i), \]  

(5.4)

or equivalently, the CF Hamiltonian can be expressed in terms of the Stevens operators \( O_l^m(\hat{J}) \),

\[ H_{\text{cf}} = \sum_i \sum_{lm} B_l^m O_l^m(\hat{J}_i). \]  

(5.5)

The Hamiltonian in Eqn (5.5) lifts the degeneracy of the atomic \(|JM_J\rangle\) states and since it is expressed in terms of the \( \hat{J} \) operators, it may be easily diagonalized to produce the CF energies and eigenfunctions.

In paper IV the effect of the CF on the U ion, due to the surrounding O ions, is very important, even though the 5f electrons in this compound are considered to be well localized. The occurrence of a distortion of the oxygen sublattice at \( T_N \) lifts the degeneracy of the CF, lowering the total energy.

5.3 Magnetic structure and distortion in UO\(_2\)

Complex magnetic structures are common among the actinide compounds. For instance multi-\( k \) arrangements are often observed in these materials [51]. These structures may be found in highly symmetric lattices, such as the fcc lattice, in which the star of the wave vector \( k \) of the magnetic structure contains several members. If three members of the star are needed to describe the magnetic structure, the magnetic ordering is called 3\( k \) and is non-collinear. Such is the case in UO\(_2\), which crystallizes in the fcc CaF\(_2\) type structure (see paper IV).

Unfortunately, neutron diffraction does not distinguish single-\( k \) (collinear)\(^3\)

\(^3\)A simple antiferromagnet is described as a single-\( k \) or 1\( k \) structure.
Figure 5.1: The 3k magnetic structure of UO$_2$ (longitudinal) is shown (for the sake of clarity, only the U ions are depicted). The U magnetic moments are arranged such that they point in the $\langle 111 \rangle$ direction.

From multi-k (non-collinear) structures because they both give the same diffraction pattern. The only way to discriminate between the two structures is by performing neutron diffraction on a single crystal under uniaxial stress or an applied magnetic field.

In paper IV we investigated the magnetic structure of UO$_2$ (see Fig. 5.1), an ionically bonded semiconductor. In this compound the U ions are tetravalent with the 5f$^2$ levels well localized which has been confirmed by optical spectroscopy and photoemission results [52]. There is a first order phase transition at $T_N = 30.8$ K [53] from the paramagnetic phase towards an antiferromagnetic phase with a magnetic moment $\mu = 1.74\mu_B$ [54]. Associated with the magnetic phase transition there is an oxygen distortion that preserves the cubic symmetry [55]. Small volume discontinuities and anomalies in the elastic constants were also found to occur at $T_N$ [56], indicating a coupling between magnetic and lattice degrees of freedom.

First principles calculations of the total energy of the 3k magnetic structures in their transversal and longitudinal forms [57] with and without the associated 3k oxygen distortion proposed in Ref. [57] were performed in paper IV. The 1k oxygen distortion suggested in Ref. [58] was also considered together with a 1k antiferromagnetic structure. The 3k magnetic structures are essentially degenerate within the accuracy of our method, and the 1k is almost always favored against the 3k structure.

In order to analyze further the structural distortion that accompanies the experimental 3k structure, an analysis similar to the one described in Ref. [58] was done. The total energy contains two components, an elastic energy which corresponds to the chemical binding between U and O ions, and a Jahn-Teller (JT) contribution from the CF levels, $E = E_{\text{elast}} + E_{JT}$. Experimentally it is
known that the lowest level, the $\Gamma_5$ triplet, splits up into one singlet and one doublet, which lowers the total energy of the system with an amount $\Delta$ (see Fig. 4 in paper IV). $E_{JT}$ was considered in this thesis to be equal to $\Delta$. The CF energies were evaluated from a method based on DFT described in paper IV. From this calculations the correct ordering of the levels comes out correctly by the theory, with the $\Gamma_5$ triplet being lowest in energy followed by the $\Gamma_3$ doublet, $\Gamma_4$ triplet and $\Gamma_1$ singlet. The energy splittings between the different CF levels are in good agreement with observations. The calculated value of $E_{JT}$ (from the CF level calculations) was added to a calculated elastic energy, to obtain the total energy of UO$_2$ as a function of the oxygen distortion of the 3k structure. The elastic energy follows readily from our total energy calculations, and it is shown in Fig. 5.2 as a function of magnitude of the distortion of the oxygen atoms of the 3k structure. Since two different values of the Jahn-Teller energy were used (one calculated from CF levels and one estimated from experiments), two total energy curves are displayed in Fig. 5.2. Both calculations give a minimum in the total energy for finite values of oxygen distortions and the correct order of magnitude of the distortion is obtained; it is 0.02 Å based on the calculated Jahn-Teller energy and 0.003 Å based on the estimated Jahn-Teller energy, whereas the experimental value is 0.008 Å. The absolute value of the oxygen distortion is not quite reproduced in the calculations, and of the two calculations the one based on an estimated Jahn-Teller energy seems to agree somewhat better with observations.
5.4 Spin spirals in rare earths systems

Two-ion couplings are mainly responsible for cooperative effects and magnetic ordering in the RE. The indirect exchange or RKKY (Ruderman, Kittel, Kasuya and Yosida) interaction, being one of the most important, can be mediated by the conduction electrons. A localized magnetic moment spin-polarizes the conduction electrons and this polarization in turn couples to a neighboring localized magnetic moment. This interaction takes the Heisenberg form [34]

$$H = -\frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

(5.6)

where

$$J_{ij} = \frac{1}{N} \sum_{\mathbf{q}} \mathcal{J}(\mathbf{q}) e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \quad \text{and} \quad \mathcal{J}(\mathbf{q}) = \frac{V}{N\mu_B^2} |I(\mathbf{q})|^2 \chi(\mathbf{q}).$$

(5.7)

In Eqn (5.7), $I(\mathbf{q})$ is the Fourier transform of the exchange integral and $\chi(\mathbf{q})$ is the conduction electron susceptibility. A maximum in $\mathcal{J}(\mathbf{q})$ will favor a $\mathbf{q}$ vector which corresponds to a spin spiral or helical structure.

5.5 TbNi$_5$ and CeRhIn$_5$

In paper II, the magnetic structure of TbNi$_5$ was investigated by first principles theory. This RE-transition metal compound crystallizes in the hexagonal CaCu$_5$-type structure (space group P 6/mmm) [59] with one formula unit per unit cell. There are one Tb (1a) and two non-equivalent Ni sites, Ni1(2c) and
Figure 5.4: The calculated total energy as function of the spin spiral wave vector $q = (0, 0, q)$ in units of $c/2\pi$ (gray dots, the line is just a guide to the eye). In the inset we show a section of the energy curve around the low-q region.

Ni2(3g). The neutron powder diffractogram at 10 K of TbNi$_5$ showed the formation of an incommensurate helimagnetic ordering. The diffraction patterns were fitted with a helimagnetic structure which was resolved into a helix and a ferromagnetic component. The satellite reflections were indexed by a propagation vector $q \sim (0, 0, 0.02)$. The preliminary results indicate that the ferromagnetic component of the magnetic moment was $7.16(1) \mu_B$/Tb atom in the ab-plane and the helical part $4.5(1) \mu_B$/Tb atom. The total magnetic moment, $8.4 \mu_B$/Tb atom, was obtained with the half-cone-angle ($32^\circ$) to the [1 0 0] helical axis, and the spins are rotated $7.0(1)^\circ$ between successive magnetic sheets projected on the ab-plane. The Ni atoms do not carry any significant moment.

In our study, we treated the 4f electrons in Tb as part of the core which reflects their localized nature, while they are still able to produce an exchange field that acts on the valence states by imposing Hund’s first rule (see subsection 5.1). In order to accomplish this, the 4f states have been spin-polarized among the core states [60]. The LSD-SIC approximation was used (see chapter 2). The spin occupation numbers are determined by applying the Russell-Saunders coupling scheme to the 4f shell. The spin spiral symmetry as discussed in chapter 4, was adopted to handle the incommensurate magnetic structure of TbNi$_5$. In Fig. 5.4 the calculated total energy is displayed and a minimum can be seen at $q \sim (0, 0, 0.06)2\pi/c$. Unfortunately, the agreement with the experimental value, $q = 0.02$, is not perfect. The calculated magnetic
moments are observed to be mainly placed on the Tb atoms, $\mu \sim 9 \mu_B$ and antiparallel to those of the Ni atoms, $\mu = 0.04 \mu_B$. To explain the origin of the observed magnetic spin spiral structure we calculated the Fermi surface of TbNi$_5$ (see paper II), in order to analyze possible nesting features of the valence band electronic structure. We found a very small shift between the spin up and down Fermi surface which is expected to result in very strong nesting features in the $z$-axis of reciprocal space. We concluded from this analysis that the strong nesting along the $z$-axis as discussed in chapter 4 may be responsible of the occurrence of a spin spiral in TbNi$_5$.

CeRhIn$_5$ belongs to the family of heavy fermion superconductors in which superconductivity (SC) develops out of a normal state where electronic correlations produce a large enhancement of the effective mass of the conduction electrons. CeRhIn$_5$ is an antiferromagnet [61] at ambient pressure with a Néel temperature of 3.8 K and it becomes a superconductor below $T_c=2.1$ K when pressure is applied (1.65 GPa). This compound crystallizes in the tetragonal HoCoGa$_5$ type of structure which is also common to the ambient-pressure superconductors CeIrIn$_5$ [62], CeCoIn$_5$ [63] and PuCoGa$_5$ [64]. A neutron diffraction study [65] performed on CeRhIn$_5$ revealed an incommensurate magnetic structure with wave vector $q \sim (1/2, 1/2, 0.3)$ and a staggered moment of $0.75(2) \mu_B$ per Ce ion [66] at 1.4 K. The nearest-neighbor moments on the tetragonal basal plane align antiferromagnetically.

A slightly different scheme was used in paper III to treat the 4f electron in CeRhIn$_5$. CF effects seem to play an important role in this material. Hence, in order to evaluate the moment of the Ce ions, the ground state charge and magnetization density were calculated by diagonalizing a CF Hamiltonian as described in paper II and III.

Non-collinear density functional theory was applied on CeRhIn$_5$ as described in chapter 4. The calculated magnetic moment of the Ce ion was found to be $0.7 \mu_B$. The 4f spin density was found to induce a very small valence moment $0.03 \mu_B$ and the total moment in the cell was $0.73 \mu_B$. A Fermi surface cross-section and the band structure were investigated in order to elucidate the origin of the magnetic structure. Unfortunately the very small energy between the different magnetic structures investigated made it impossible to be conclusive.
Density functional theory is a very powerful tool in understanding condensed matter. In this thesis it has been extensively used to investigate non-collinear magnetism, i.e. a spin arrangement in a material where there is no global spin quantization axis for the whole spin system. Two conditions were identified that favor a non-collinear state over the ferromagnetic arrangement of the spins. These conditions involve the presence of spin-up and -down bands at the Fermi energy and strong nesting between spin-up and -down Fermi surfaces. Paramagnetic materials such as bcc V and well-known ferromagnets such as bcc Fe and fcc Ni were studied in order to illustrate the applicability of these criteria. All the investigated materials adopted a spin spiral state after modifying either the volume or fixing the spin moment, which was done in order to meet the conditions described above. The conclusion was that, most likely, any metal could be turned into a non-collinear state provided that the tuning of the exchange-splitting is done properly. Experimentally, this can be observed after applying pressure on materials. It has been widely speculated that this would be the case of Fe in its high-pressure phase (hcp). Although magnetism has not been observed in this material, first principles calculations predict that when Fe is being compressed an antiferromagnetic or a non-collinear state develops. The questions of whether or not Fe is magnetic at all under pressure and if this could be somehow related to the superconducting phase that arises at almost the same volume as the hcp phase appears, are still open.

We investigated more complex materials such as the substitutional TlCo$_2$Se$_{2-x}$S$_x$ alloys. From the theory we concluded that the nature of magnetism in the TlCo$_2$Se$_{2-x}$S$_x$ alloys changes from ferromagnetic for low interlayer distances (distance between Co layers) to anti-ferromagnetic for large distances, via a set of non-collinear structures for intermediate interlayer distances. We also investigated the band structure of TlCo$_2$Se$_2$ and TlCo$_2$S$_2$ and demonstrated that the condition that both spin channels should be present at the Fermi energy was no longer fulfilled in the TlCo$_2$S$_2$ case and therefore a ferromagnetic state becomes more stable. An experimental study for TlCo$_2$Se$_{2-x}$Te$_x$ is proposed to clarify the magnetic ordering in these systems.

The relation between superconductivity and magnetism has also been dis-
cussed in heavy Fermion systems where unconventional superconductivity appears to coexist with non-collinear magnetism. Such is the case on CeRhIn$_5$. A theoretical study of the evolution of the magnetic structure as a function of pressure is still missing.
Sammanfattning på Svenska

Den fasta materien runt omkring oss består som bekant av atomer som ligger tätt ihoppackade. Atomer är också väldigt små och består i sin tur av en positivt laddad kärna som är omgiven av ett negativt laddat "moln" av elektroner. Faktum är att trots att elektronerna är mycket mindre än neutronerna och protonerna i kärnan så är det elektronerna och deras växelverkningar med omgivningen som ger ett material dess flesta egenskaper. Till exempel beror färgen på saker och ting på hur elektronerna reagerar på ljussstrålning eller värme och att metaller känns varmare eller kallare än en träbit vid samma temperatur beror på att elektronerna i en metall leder värme mycket bättre än elektronerna i de kolföreningar som utgör träbiten. För att förstå hur många atomer det finns i ett fast material kan man jämföra med Saharas öken: Om man antar att Sahara är c:a 100 meter djup så finns det uppskattningsvis lika många sandkorn där som det finns atomer i 300 gram järn, d.v.s. 1cm järnväg eller en sjätte dels stekpanna.


Mina undersökningar har varit inriktade på magnetiska egenskaper hos olika material och speciellt på hur magnetismen ser ut inuti materialen. Det

De studier som sammanfattas här i avhandlingen har varit inriktade på att försöka förstå varför dessa spiralstrukturer uppkommer och vilka grundläggande fysikaliska principer som ligger bakom. I figur 6.1 illustreras olika typer av magnetisk ordning. Flera olika material har studerats och det viktigaste resultatet som framkommit är identifieringen av två kriterier som ett material måste uppfylla för att en spiralstruktur ska kunna uppstå. Dessa kriterier är baserade på den exakta fördelningen av elektronhastigheter och elektronernas eget spinn inuti en metall och är beskrivna i detalj i kapitel 4.

Figure 6.1: Olika typer av magnetisk ordning hos ett material: (a) ferromagnetism, (b) antiferromagnetism, (c) helix struktur, (d) spin-spiral struktur och (e) spinglas.
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