The Effects of Anisotropy on the Long-Wavelength Excitations of Itinerant Ferromagnets

by
John A. Godfree

A thesis submitted to the
University of Warwick
for the degree of
Doctor of Philosophy

Department of Physics
University of Warwick
Coventry
CV4 7AL

October 1993

Declaration

This thesis is submitted to the University of Warwick in support of my application for admission to the degree of Doctor of Philosophy. This thesis contains an account of my own independent research carried out in the Department of Physics at the University of Warwick from October 1990 to September 1993 under the supervision of Dr. J. B. Staunton of the University of Warwick. No part of this thesis has been previously submitted for a degree anywhere.

Part of the work has been published in the following paper,

- "*The effects of anisotropy on magnetic interactions -a relativistic electron approach*"
  J. A. Godfree and J. B. Staunton
  Journal of Applied Physics **73** 6557 (1993)

Acknowledgements

I would like to thank Dr Julie Staunton, for her excellent supervision and encouragement during this project. Thanks also go to all the members of the Warwick Theory group, in particular for the many lively lunchtime discussions.

I would also like to thank the Science and Engineering Research Council for funding me during this work. Finally, my thanks go to my Parents and Claire, whose help and support have been vital in the last three years.

Abstract

In this thesis I present a formalism for calculating the effects of magnetic anisotropy on the long wavelength excitations of a magnetically ordered itinerant electron system. It is derived from a relativistic multiple scattering theory treatment of the density functional formalism single electron equations.

Multiple scattering theory is shown to be capable of describing the small anisotropy energies involved via work on the effects of anisotropy on magnetic interactions between magnetic impurities embedded in a non-magnetic metallic host. The addition of a third, heavy non-magnetic impurity is found to enhance the magnetic anisotropy energy of a magnetic pair in the system such that in some cases it becomes comparable in magnitude to the effective exchange energy. The resulting anisotropic magnetic interaction is found to be more complex than that shown by other model calculations.

In attempting an investigation of the magnetic excitations by constructing a relativistic dynamic susceptibility from a two electron Green's function, it is found that solving the Kohn-Sham-Dirac single particle equations together with the Local Density Approximation in this situation leads to an inconsistency. As a result of this, the starting point for the subsequent analysis is the phenomenological equation of motion for a magnetic moment.

It is known that one of the effects of magnetic anisotropy on the excitations is the existence of a gap in the spin-wave dispersion spectrum. The formalism gives the correct result in the non-relativistic limit, an absence of a gap, and is evaluated numerically for bcc iron, fcc nickel and fcc cobalt when relativistic effects are included. The results compare favourably against previous magnetic anisotropy calculations and experimental work.

Contents

List of Figures

List of Tables

Chapter 1

Introduction

The existence of materials with a permanent magnetisation in the absence of a magnetic field has been recognised for a considerable period of time. A reasonable description of the origin and behaviour of the magnetisation in such systems has been one of the hardest problems in solid state physics. Ferromagnetism was known to be a co-operative alignment of permanent magnetic dipoles, in the case of magnetic insulators the magnetisation is due to the intrinsic spin of the unpaired electron, localised on each atom. The origin of the magnetic ordering was shown to be electrostatic in nature, a consequence of the Coulomb and exchange interaction, an effect due to the Pauli exclusion principle, indicating that the origins of magnetism are quantum mechanical.

The above can be seen to hold well in the case of magnetic insulators, but what of metallic systems? It was some time before the idea that the electrons responsible for the magnetic behaviour in itinerant materials were also responsible for the conduction properties [1]. The idea of an exchange coupling between itinerant electrons and its importance in magnetism was put forward by Bloch [2]. In the metallic case it is hard to envisage the magnetic moments, the magnetisation per unit cell, being due to an individual electron's spin, they are not localised long enough to define a spin operator, S_i, as in the case of a local moment-insulator picture [3], [4]. Experimental evidence, such as the non-integral value in Bohr-magnetons of the magnetic moment, points against this concept as well. To produce a theory to explain many of the phenomenon produced by such systems the existence of exchange interactions alone is not sufficient. Exchange deals with the situation where electrons of like spin tend to avoid each other, however electrons of opposite spin will also prefer to stay apart merely from electrostatic repulsion. Hence a full description of magnetic behaviour in itinerant systems will need to deal with an interacting many-body situation.

The first step in producing a theory of such systems started with the free electron gas. In 1929 Bloch [2] suggested that the addition of exchange interactions could lead to the existence of a ferromagnetic ground state. Wigner [5] indicated that when correlations, such as those between unlike spins, were taken into account then ferromagnetism was unlikely. Stoner [6] suggested that the non-integral values of the magnetic moments could be explained if the electrons responsible for the magnetic behaviour were itinerant. Later papers [7] together with work by Wohlfarth [8] and others, used partially filled d-bands as a starting point for a model with adjustable parameters to correlate many physical properties, magnetic moments, electronic specific heats etc., for transition metals and their alloys.

Itinerant magnetism is a competition between the potential energy of the localised coulomb exchange and the kinetic energy of the electrons due to their itinerant nature. One approach to this problem is that due to Hubbard [9]. He put forward a model, equation (1.1), which contains the minimum of features to describe both band-like and localised behaviour in the appropriate limits. However, although it is easy to describe, any solutions require further simplifications.

$$\mathbf{H} = -\sum_{ij,\sigma} t_{ij} c^{\dagger}_{i,\sigma} c_{j,\sigma} + u \sum_{j,\sigma} \hat{n}_{j,\sigma} \hat{n}_{j,-\sigma} \tag{1.1}$$

$c^{\dagger}_{i,\sigma}$, $c_{j,\sigma}$ and $\hat{n}_{j,\sigma}$ are the second quantisation creation, destruction and number operators. The Pauli Principle and Coulomb repulsion are built into the formalism as equation (1.1) does not permit two electrons of the same spin to occupy the same site. The first term models the kinetic energy, it determines the electron hopping from site to site. The second term describes the interactions of the electrons, the competition between the two effects determines the electronic behaviour of the system.

An alternative description of itinerant systems exists in the form of band theories. These, with the addition of exchange and correlation effects have proved very capable in describing a large portion of magnetic behaviour in metallic systems at low temperatures.

Interesting effects can result from the existence of magnetic anisotropy, this is the situation where the magnetic moment is coupled, in some form, to the crystal axes. The origin of magnetic anisotropy is relativistic, mainly due to the existence of a term which couples the electrons intrinsic spin to the orbital angular momentum. In magnetic insulators the origin and behaviour of such terms is quite well known, this leads to phenomenological as well as quantum mechanical descriptions of the behaviour of such systems [10]. From the former comes the concept of anisotropy constants, determined by various symmetry considerations [10], the behaviour of which, as a function of temperature, have provided much discussion.

For itinerant systems the picture is not so clear. A proper relativistic treatment of the many-body problem is required, until this is accomplished then the origins of many of the anisotropic effects will remain uncertain.

The remainder of this chapter deals with descriptions and methods of dealing with interacting electronic systems from a first principles quantum mechanical basis. Details are given on how to tackle the many-body problem, resulting in the production of a set of single particle equations.

1.1 Interacting electronic systems

A first principles description of the behaviour of a material needs to address the fully interacting electron problem. The non-relativistic behaviour of interacting electrons in a solid is determined by the Schrödinger Equation (SE), however even making the approximation that the individual nuclei remain stationary (the Born-Oppenhiemer approximation), then we still have a partial differential equation in $\sim 10^{23} \times 3$ dimensions, which is insolvable.

For a system of M nuclei and N electrons the Schrödinger equation is,

$$\left(\frac{1}{2}\sum_{i}^{N}\nabla_i^2 - \sum_{m}^{M}\sum_{i}^{N}\frac{Z_m}{|\mathbf{R}_m - \mathbf{r}_i|} + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\psi = E\psi \tag{1.2}$$

Naturally attempts have been made to get round this or at least try to solve something similar to equation (1.2). One approach is to try and map equation (1.2) onto a set of equations describing non-interacting electrons moving in effective potentials set up by all the other electrons.

The first attempt towards this single particle approach was to assume that the wavefunction for the full interacting electron system could be approximated by a product of one electron (non-interacting), orthonormal wavefunctions, i.e,

$$|\psi>=|\phi_1(\mathbf{r})\phi_2(\mathbf{r}')\phi_3(\mathbf{r}'')....> \tag{1.3}$$

Therefore the expectation value of **H** becomes,

$$\begin{aligned} <\psi|\mathbf{H}|\psi> \; &= \sum_i \int \phi_i^*(\mathbf{r})\left(-\frac{1}{2}\nabla_i^2 + U_{ion}\right)\phi_i(\mathbf{r})d\mathbf{r} \\ &+\frac{1}{2}\sum_{i\neq j}\int\int \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r})\phi_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \end{aligned} \tag{1.4}$$

For a solution ψ to the wave equation, the variation of the expectation value of **H** with respect to the wavefunction ψ can be shown to be zero,

$$\delta <\psi|\mathbf{H}|\psi>= 0 \tag{1.5}$$

This minimisation condition can be achieved using Lagrange multipliers, λ_i and $\int \delta\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})d\mathbf{r} = 0$ as an orthogonality condition. Hence equation (1.5) becomes,

$$\sum_i \int \delta\phi_i^*(\mathbf{r}) \left((-\frac{1}{2}\nabla_i^2 + U_{ion}) + \frac{1}{2}\sum_{i \neq j} \int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}') d\mathbf{r}' - \lambda_i \right) \phi_i(\mathbf{r}) = 0 \tag{1.6}$$

As $\delta\phi_i^*(\mathbf{r})$ are independent, the above is only satisfied if,

$$\left(\left(-\frac{1}{2}\nabla_i^2 + U_{ion} \right) + \frac{1}{2}\sum_j \int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}') d\mathbf{r}' \right) \phi_i(\mathbf{r}) = \lambda_i \phi_i(\mathbf{r}) \tag{1.7}$$

Therefore in this scheme, known as the Hartree approximation, the electron now moves in an effective potential,

$$V_i^H(\mathbf{r}) = \frac{1}{2}\sum_j \int \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{1.8}$$

By examining the wavefunction produced by the Hartree approximation it can be seen that it is incompatible with the Pauli Principal, e.g. the wavefunction is not anti-symmetric under exchange of electrons. Therefore this indicates that certain important features of the electron-electron interaction, such as exchange, cannot be described by such a simple self-consistent field approach. To remove some of these defects, the many electron wavefunction can be built up from a Slater determinant of one-electron wavefunctions, therefore the Pauli Principal is satisfied from the start. The resulting effective potential produced by such an approximation contains the Hartree term as described above together with an exchange term. However the form of this extra term produces a complication as seen in the resulting single particle equation,

$$\begin{aligned} &\left(\left(-\frac{1}{2}\nabla_i^2 + U_{ion} \right) + V_i^H(\mathbf{r}) \right) \phi_i(\mathbf{r}) \\ +&\frac{1}{2}\sum_j \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}) d\mathbf{r}' = \epsilon_i \phi_i(\mathbf{r}) \end{aligned} \tag{1.9}$$

Its form is such that it is non-local, therefore to make any attempt to solve this type of single particle equation a further approximation has to be made. This leads to the Hartree-Fock method of dealing with the fully interacting problem. The effects of the electron-electron interaction not included in the Hartree-Fock approximation are known as correlations, however it should be noted that these are not really 'missing' from the Hartree-Fock but are the errors that result in making that particular approximation. Both the Hartree and Hartree-Fock approaches need to be solved self consistently in order to generate the correct V^{eff}.

Another method exists which takes account of both exchange and correlation effects, Density Functional Theory.

1.1.1 Density Functional Theory

Density Functional Theory, in principle, includes all the desirable effects of exchange and correlation in a scheme which has the ease of calculation of the Hartree-like single particle equations. For a review of the subject see [11].

It is fundamentally different to the Hartree and Hartree-Fock approaches in that attention is focussed on the density, $n(\mathbf{r})$, of the interacting electron gas rather than the many electron wavefunction. Here we shall outline the basic principles of Density Functional Theory which are formally expressed by the Hohenberg-Kohn Theorem [12], [13].

1 The ground state energy, E_g, is an unique functional of the ground state density.

$$E_g = E_g[n(\mathbf{r})] \tag{1.10}$$

The proof of this consists of showing that there is an unique ground state density for each chosen external potential [12]. Therefore as V^{ext} determines the energy of the state, the energy of the state is determined by the density.

2 The energy functional obtains its minimum value with respect to the density, $n(\mathbf{r})$, at the correct $n(\mathbf{r})$ subject to the condition that the total number of particles remains constant.

This arises from the general Quantum Mechanical variational principle that the ground state energy is a functional of the wavefunction and obtains the correct value when all variations conserve the particle number.

Hence if we could calculate the exact energy functional from a given density then the full interacting problem would be solved, however as it stands this is not possible. A method for calculating the energy functional can be developed by investigating the terms which would contribute to such a functional, hence,

$$E_g[n(\mathbf{r})] = T[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})] \tag{1.11}$$

where $T[n(\mathbf{r})]$ is the kinetic energy of the interacting electron system, $E_H[n(\mathbf{r})]$ is the usual Hartree term and $E_{XC}[n(\mathbf{r})]$ describes all the other electron-electron effects such as exchange and correlation.

By using the variational principal together with the particle conservation condition, a set of Euler Lagrange equations with Lagrange multipliers, μ, are produced,

$$\frac{\delta T[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V^{eff}[n(\mathbf{r})] - \mu = 0 \tag{1.12}$$

where

$$V^{eff}[n(\mathbf{r})] = V^{ext} + e^2 \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{1.13}$$

This is not quite the set of single particle equations we require as not only is $E_{XC}[n(\mathbf{r})]$ unknown but we do not have an exact expression for the kinetic energy of an interacting electron system. The latter point can be remedied by an approach due to Kohn and Sham [13].

The density, $n(\mathbf{r})$, is expanded in terms of single particle states,

$$n(\mathbf{r}) = \sum_i^N |U_i(\mathbf{r})|^2 \tag{1.14}$$

Carrying out the variational principle with this expansion reveals a set of SE-like single particle equations for $U_i(\mathbf{r})$,

$$\left(-\nabla^2 + V^{eff}\right) U_i(\mathbf{r}) = \epsilon_i U_i(\mathbf{r}) \tag{1.15}$$

where $V^{eff}[n(\mathbf{r})]$ is as in equation (1.13). The kinetic energy term is now calculable, this is apparent when the single particle equations, (1.15), are solved self consistently leading to an expression for the ground state energy,

$$E_g = \sum_i^N \epsilon_i - \frac{e^2}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \int \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}n(\mathbf{r})d\mathbf{r} + E_{XC}[n(\mathbf{r})] \quad (1.16)$$

Therefore we have an expression for the ground state energy with the only unknown being $E_{XC}[n(\mathbf{r})]$.

Without a realistic method of dealing with $E_{XC}[n(\mathbf{r})]$ there would be little purpose of taking the DFT route, however there are a number of reasons why such a path can be taken. It is possible to obtain a physical basis for the functional and hence a realistic approximation can be made. The physical origin of $E_{XC}[n(\mathbf{r})]$ can be seen as follows. As the electron moves through the gas the exchange and correlation effects 'dig out' a region of depleted electronic charge or 'hole'. Therefore $E_{XC}[n(\mathbf{r})]$ can be thought of as the interaction of the electron with its exchange correlation 'hole'. Methods exist for calculating $E_{XC}[n(\mathbf{r})]$ for the homogeneous electron gas. In fact, as the density is constant for such a case, the functional becomes just a function of the density, i.e. $E_{XC}[n(\mathbf{r})] = \epsilon_{XC}(n(\mathbf{r}))$. This allows us to make the Local Density Approximation (LDA) to $E_{XC}[n(\mathbf{r})]$, this implies that the exchange-correlation energy at any particular point depends only upon the density at that position and its value is the same as the homogeneous electron gas at that point. Hence,

$$E_{XC}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{XC}(n(\mathbf{r}))d\mathbf{r} \quad (1.17)$$

The LDA has proven to be very successful in a certain number of situations, however its validity in the description of certain electronic behaviour has been questioned for particular systems [14].

For a set of single particle DFT equations describing a system with translational symmetry there exist a number of band structure methods available to produce the required solutions,

1. The single particle wavefunction is expanded via a basis set of orbitals, which are diagonalised to obtain the energy eigenfunctions. Examples of this are the Augmented Plane Wave (APW) and Linear Muffin-Tin Orbital (LMTO) approaches.
2. The single particle Green's function is calculated, from which physical observables can be generated. A typical example of this is the KKR band structure approach, in particular the use of multiple scattering theory.

The solution to the single particle equations by the method described in 2, that of multiple scattering theory, is the subject of Chapter 4.

1.2 Outline of the thesis

Chapter2

Chapter 2 introduces the possible types of magnetic excitations, namely those involving 'single particle' states and those where a collective behaviour of the system is required. Methods are demonstrated for calculating such magnetic responses, both through the construction of a dynamic susceptibility and the solution of an equation of motion for a 'classical' moment.

Chapter 3

The possible mechanisms behind magnetic anisotropy are investigated, in particular the use of a relativistic description for the behaviour of the electron. A phenomenological model, dependent upon the symmetry of the crystal structure is introduced and a review is made of previous magnetic anisotropy calculations in itinerant systems. Although the origins of magnetic anisotropy are relatively well understood in the case of magnetic insulators, which can be described by a localised moment picture, the situation of magnetic conductors is less clear. In particular the necessity to concentrate on a correct description of the interacting many-body effects is evident. The effects of anisotropy in magnetic domains and on the spin-wave excitations is also discussed.

Chapter 4

In chapter 4 the formalism used to solve the single particle equations described in chapter 1, namely multiple scattering theory, is introduced. As an example it is used to calculate the anisotropy energies obtained when magnetic impurities are embedded into a non-magnetic conducting host e.g. Fe in Cu, Mn in Ag. Numerical results are presented including calculations indicating interesting behaviour when additional heavy, non-magnetic, impurities are added to the system. This has implications for the study of materials such as dilute magnetic alloys and spin-glasses.

Chapter 5

Chapter 5 contains the majority of the original work of this thesis. A formalism is developed to investigate the effects of anisotropy on the low-lying magnetic excitations of a metallic system. As a test of the formalism, the limiting non-relativistic case is investigated analytically.

Chapter 6

The results of the numerical calculations for the spin-wave gaps for Fe, Ni and Co are presented. Comparison of the results obtained to previous work on magnetocrystalline anisotropy is made, in particular the justification for a number of approximations made will be discussed.

Chapter 7

Finally, possible future work is proposed and a conclusion made of the contents of the thesis.

Chapter 2

Magnetic excitations

In this chapter the idea of excitations, as applied to magnetically ordered systems, is introduced. The concepts involved for both localised and itinerant systems are discussed, including the construction of phenomenological and first principles approaches.

2.1 Excitations in magnetic systems

In a single domain, ferromagnetic insulator, the ground state consists of all the magnetic moments aligned parallel along a particular spatial direction. At first sight one possible excitation could be the 'flip' of one of the magnetic moments, as shown below. However it can be shown that the energy cost for such an operation is of the order of the exchange energy, $1 \sim 10$ eV. Instead of such a

Figure 2.1: *A possible single 'spin' excitation where one of the spins has been inverted.*

localised excitation, if the ‘flip’ were shared by the system as a whole, say in the form of a wave, then the energy cost would be considerably less. This form of excitation corresponds to the precession of the magnetic moments, the phase of one moment relative to the next is determined by a wave vector **q**. Such a ’spin-wave‘ is illustrated in figure (2.2). Hence for this collective excitation, at

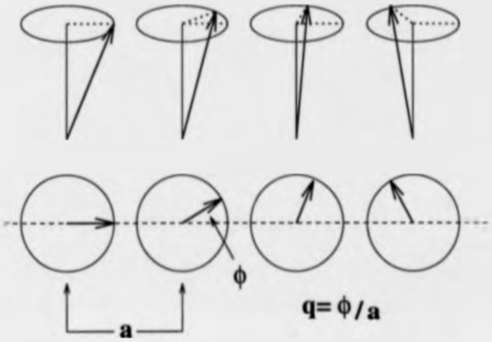

Figure 2.2: *An alternative magnetic excitation is a spin-wave, the relative precession between each spin is determined by the wavevector,* **q**.

least in a classical sense, the excitation energy can vary continuously from zero up to the energy range of the localised, spin ’flip’, excitations. This only really holds in the case where anisotropic effects are ignored.

The concept of spin-waves originated with Bloch [15] who dealt with the problem of a ferromagnetically ordered chain of spins. He calculated the spin-wave dispersion, and used this to evaluate the temperature dependence of the change in magnetic moment and specific heat, leading to the $T^{\frac{3}{2}}$ law. In 1940 Holstein and Primakoff [16] solved the quantum mechanical problem of spin-waves in a Heisenberg ferromagnet. They also showed that by taking magnetic dipole-dipole interactions into account, the spin-wave energy not only had a dependence upon the magnitude of the wave-vector but also on its direction with respect to the direction of ground state magnetisation. This results in the spin-wave dispersion curve becoming a band, and for some orientations the cone of precession of the moment becomes an ellipse.

Physical sample size plays a very important role in the study of spin-wave excitations. For example when $|\mathbf{q}| < \frac{1}{l}$, where l is of the order of the sample size, then the dipole-dipole interaction dominates over any exchange term, this leads to the existence of non-uniform magnetostatic modes whose exact form is highly sample dependent [17]. Also the role of surfaces and thin-films in spin-wave studies has come to the fore, it was shown that surface spin-wave modes, with higher energy than bulk modes, could exist [18], [19]. The reduction in symmetry of such systems allows a variety of anisotropic effects to be measured.

In 1946 Griffiths [20] demonstrated a method by which $\mathbf{q} = 0$ spin-waves could be generated experimentally. Ferromagnetic resonance (FMR) excites these modes via microwave radiation, the theoretical basis for such experiments was provided by Kittel in 1950 [21]. For $\mathbf{q} \neq 0$, microwave excitation of spin-waves runs into a number of difficulties, mainly due the large mis-match of microwave and spin-wave velocities, the microwave field being too uniform, however Kittel pointed out the possibility of exciting surface modes in metallic magnets. This is primarily due to the fact that the microwave field only penetrates as far as the skin-depth, and it was shown that modes of wavelengths up to this length could be induced. Thin-films provide an excellent testing bed for spin-wave theories, due to the sample dimensions a number of modes can be set up. Work on such systems originated in 1958 [18]. A number of solutions to the problem of producing $\mathbf{q} \neq 0$ spin-waves exist, these include applying a non-uniform magnetic field which sets up boundary conditions which make excitations possible, [22], and the use of techniques such as 'parallel pumping', a non-linear process where one photon decays into two spin-waves. Excellent reviews of spin-waves, their history and investigation, include Rado and Suhl [10], the two volume work edited by Borovik-Romanov and Sinha [23] and the work of Akhiezer, Baryakhtar and Peletminskii [24].

2.2 Phenomenological description of magnetic excitations

To illustrate the principles of spin-waves in a localised moment case, we introduce a phenomenological approach, originally due to Landau and Liftschitz [25]. It should be noted that this approach can be made rigorous in the quantum mechanical sense with the appropriate spin operators and equations of motion [16]. In this situation, that of a quantum mechanical Heisenberg ferromagnet, described by the relevant Hamiltonian, **H**, the equation of motion of a spin is given by,

$$i\hbar\frac{\delta \mathbf{S}_i}{\delta t} = [\mathbf{S}_i, \mathbf{H}] \tag{2.1}$$

or, introducing an effective field (with dimensions of energy), $\mathbf{H}_i^{eff}$,

$$i\hbar\frac{\delta \mathbf{S}_i}{\delta t} = i\left(\mathbf{S}_i \times \mathbf{H}_i^{eff}\right) \tag{2.2}$$

It is possible to relate the spin-operator, $\mathbf{S}_i$, to a macroscopic moment, **M**, i.e $\mathbf{M}_i =< \psi|\mathbf{S}_i^z|\psi >$.

The starting point for a phenomenological theory of magnetic excitations is the consideration of a classical continuous magnetic medium, characterized by a definite magnetic moment at each point. As with all the spin-wave theories considered here it is based on the assumption that the deviation of the moment from its equilibrium position is small. Firstly we consider the motion of a rigid magnetic moment, **M**, of unit length in a magnetic field.

$$\frac{\delta \mathbf{M}_i}{\delta t} = -\gamma \mathbf{M}_i \times \mathbf{H}_i^{eff} \tag{2.3}$$

γ is the gyromagnetic ratio and $\mathbf{H}_i^{eff}$ is the magnetic field experienced by the moment at site i. The effective field can be expressed in terms of the functional derivative of the total energy of the magnet [25],

$$\mathbf{H}_i^{eff} = -\frac{\delta E}{\delta \mathbf{M}_i} \tag{2.4}$$

Equations (2.3)-(2.4) are equivalent to the following variational conditions,

$$\delta E_{total} = 0 \tag{2.5}$$

$$\delta \mathbf{M} \cdot \mathbf{M}_0 = 0 \tag{2.6}$$

Hence the equation of motion method will be valid in the region where $|\mathbf{M}|$ remains constant. As long as $\mathbf{H}^{eff}$ changes in direction or magnitude at a rate which is slower than any thermal equilibrium change, then $|\mathbf{M}|$ will stay constant and will be acted upon by a torque proportional to $\mathbf{M}_i \times \mathbf{H}_i^{eff}$. The effective field has a number of contributing terms, for the purpose of this model anisotropic effects will be ignored.

Exchange

The first term to consider in the energy is the exchange interaction. If by assuming a Heisenberg type interaction, i.e,

$$E \propto \sum_{i \neq j} J_{ij} \mathbf{M}_i \cdot \mathbf{M}_j \tag{2.7}$$

and making the approximation that the deviations of the spins from site to site are small,

$$\mathbf{M}_j = \mathbf{M}_i + (\mathbf{r}_j - \mathbf{r}_i) \cdot \nabla_i \mathbf{M}_i + \frac{1}{2}((\mathbf{r}_j - \mathbf{r}_i) \cdot \nabla_i)^2 \mathbf{M}_i + \ldots \tag{2.8}$$

then for a short range interaction, the exchange contribution to the total energy can be expressed as,

$$E_{xc} \propto \mathbf{M}_i \cdot (\mathbf{r}_j - \mathbf{r}_i \cdot \nabla_i)^2 \mathbf{M}_i \tag{2.9}$$

where the inversion symmetry of the crystal lattice has been taken into account. Using the expression for an effective field, (2.4), this exchange energy corresponds to a field, H_{xc},

$$H_{xc} = 2A\nabla^2 \mathbf{M}_i \tag{2.10}$$

where A is known as the exchange stiffness parameter and can be related to the coupling constants, J_{ij}. As can be seen from the form of equation (2.7), the exchange energy is independent of the direction of $\mathbf{M}_i$.

Dipole-dipole interactions

By introducing the dipole-dipole interaction, we now have to consider the energy of the dipole moment interacting with a field set up by all the other moments.

$$E_{dip} = \int \mathbf{M}_i \cdot \mathbf{H}^{dip} d\mathbf{v} \tag{2.11}$$

This magnetostatic energy is hard to evaluate due to its non-local nature and its dependence upon the shape of the sample being investigated [26]. However it can be obtained for situations where the magnetisation is uniform inside the sample (which is what we require for investigations into bulk ferromagnetic excitations). This turns out to be satisfied only for certain sample configurations, for example, an ellipsoid. In this case the magnetostatic, or de-magnetisation energy has the form,

$$E_{dip} = -4\pi \mathbf{N}.\mathbf{M} \tag{2.12}$$

where $\mathbf{N}$ depends upon the sample in question. The above holds for the case of uniform magnetisation, therefore there can be no domain structure.

Equation of motion

The resulting equation of motion for the moment is,

$$\frac{\delta \mathbf{M}_i}{\delta t} = -\gamma \mathbf{M}_i \times \left[2A\nabla^2 \mathbf{M}_i + \mathbf{H}_{demag} + \mathbf{H}_{ext} + \mathbf{H}_{micro} \right] \tag{2.13}$$

$\mathbf{H}_{ext}$ and $\mathbf{H}_{micro}$ are an external static field and an internal microwave field, as required in the case of FMR. The effects of the demagnetisation on this microwave field are taken into account by the appropriate Maxwell equations and boundary conditions. When damping and relaxation terms are introduced then equation (2.13) is known as the Landau-Lifshitz-Gilbert equation [25], [27].

In solving equation (2.13) and looking for plane wave solutions, $\mathbf{M} \propto e^{i(\omega t - \mathbf{q}\cdot\mathbf{r})}$, it is found that the addition of the dipolar interaction couples $\mathbf{q}$ and $-\mathbf{q}$ solutions [23]. This can be shown to indicate that the modes excited are elliptical, the exact modes depend upon the sample shape and the angle of propagation with respect to the equilibrium moment position.

Other non-uniform modes exist in this region where the dipolar energy dominates, particularly where the spatial variation of the spin deviations is of the order of the sample size. These modes depend heavily on the sample shape and the strength of the applied static field. They are really just a consequence of applying a static magnetic field to a dipolar magnetic continuum and are known as magnetostatic modes.

2.2.1 Spin-waves

Fortunately, the density of the usual spin-wave modes is much higher than the magnetostatic modes, therefore in investigating spin-wave effects on magnetisation, specific heats etc, it is not necessary to consider these higher energy static effects.

For our investigation of bulk spin-waves in cubic structures we can ignore the effects of dipolar interactions. Using the exchange field as introduced in equation (2.10) together with a static external magnetic field, $\mathbf{H}^{ext}$, in the $\mathbf{z}$ direction, then the relevant equation of motion of a moment at site i becomes,

$$\frac{\delta \mathbf{M}_i}{\delta t} = \gamma \mathbf{M}_i \times \left(\sum_j J_{ij} \mathbf{M}_j + \mathbf{H}^{ext} \right) \tag{2.14}$$

As we are looking for small deviations about the equilibrium magnetisation, and are required to satisfy the variational condition, equation (2.6), we can rewrite the components of the magnetisation as,

$$\mathbf{M}_i = (\delta M_x^i, \delta M_y^i, M_0) \tag{2.15}$$

Equation(1.24) can then be linearised resulting in two coupled equations for δM^i_x and δM^i_y, which can be solved by forming the linear combinations,

$$\delta M^i_+ = \delta M^i_x + i\delta M^i_y \tag{2.16}$$

$$\delta M^i_- = \delta M^i_x - i\delta M^i_y \tag{2.17}$$

By Fourier transforming, assuming a cubic lattice and using a small $\mathbf{q}$ expansion of the exchange term , then wave-like solutions, $\delta m^i_+ \propto e^{-i\omega t}$ exist for,

$$\omega = \gamma \mathbf{H}^{ext} + Dq^2 + ... \tag{2.18}$$

This form of dispersion relationship is shown in figure (2.3). D is known as the spin-wave stiffness coefficient and can be related to exchange parameter J_{ij}. As can be seen from above, in the absence of any anisotropic effects and zero applied field, $\omega = 0$ as $\mathbf{q} \rightarrow 0$.

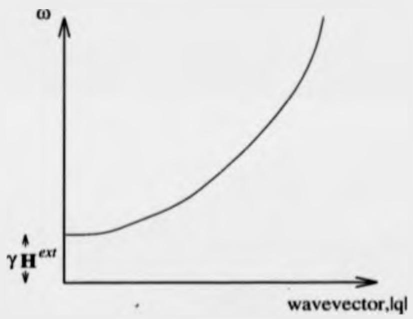

Figure 2.3: *The spin-wave dispersion curve for a ferromagnet, in the absence of an external field* $\omega = 0$ *as* $\mathbf{q} \rightarrow 0$.

2.3 Itinerant systems

As the processes responsible for magnetism in itinerant systems would seem to be considerably different from those where a local moment picture is more applicable, then the corresponding magnetic excitations could be expected to differ also. However, although the possibility of spin-waves in metallic systems had been postulated earlier, some of the first theoretical investigations were undertaken by Herring and Kittel [28]. In an itinerant system the question of timescales is crucial. The magnetic moments are set up by the interacting electronic system, any change in the orientation of the moments is on a much slower timescale than the actual electron motion.

Initial calculations of the dynamic response of itinerant magnetic systems were based on a single conduction band model. They showed the type and energy ranges of the various magnetic excitations, the single spin-wave branch and the broad region of localised, Stoner excitations. It could possibly be thought that such a simple single band picture would not hold for systems such as the transition metals, with their 5 d-bands, however, theories based upon a multiple band approach have shown that such a simple picture is surprisingly good.

The addition of multiple bands was shown to have an effect on the dispersion, including the production of more than one spin-wave branch and a general smearing of spin-wave intensity. Theories based on a random phase approximation of multi-band models (a Hubbard type approach) include work by Lowde and Windsor [29] and Cooke [30]. The calculations of the generalised susceptibility by Cooke [31] reproduce the various dispersion relationships well for Ni and Fe. The free parameters involved in this calculation were chosen to give the correct magnitude of the magnetic moment and its orbital component.

2.3.1 Theoretical approach

To investigate the nature of these magnetic excitations then we should look at the response of the system to a magnetic perturbation. If we assume that the system under investigation responds linearly, to first order, to such a change in magnetic field then we can define a susceptibility, χ,

$$\chi = \frac{\delta \mathbf{M}}{\delta \mathbf{B}} \tag{2.19}$$

A generalised treatment of the magnetic response of a system leads to the idea of longitudinal susceptibility, response parallel to the moment, and transverse susceptibility, response perpendicular to the magnetic moment. Unfortunately, as shown by Rajagopal [32] and Callaway and Chatterjee [33] the longitudinal susceptibility has an additional complication in that the charge and magnetic densities are coupled. However in the region of linear response and hence long-wavelength excitations, the relevant quantity to deal with is the transverse susceptibility. Magnetic excitations will correspond to poles in this susceptibility, i.e. a response in the absence of a perturbing field.

Dynamic susceptibility via the Hubbard Hamiltonian

To introduce the concepts involved, we consider the derivation of the dynamic susceptibility from a single band, many-body Hubbard Hamiltonian, responding to a time and space varying external magnetic field, $\mathbf{H}^{ext}(\mathbf{r}, t)$. The resultant Hamiltonian in second quantised form is [42],

$$\begin{aligned} \mathbf{H} &= \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \frac{1}{2} I \sum_{i,\sigma} \hat{n}_{i,\sigma} \hat{n}_{i,-\sigma} \\ &\quad + \frac{1}{2} \mu_B H^{ext} \sum_{\mathbf{k}} [(c^{\dagger}_{\mathbf{k}+\mathbf{q},\downarrow} c_{\mathbf{k},\uparrow} + c^{\dagger}_{\mathbf{k}-\mathbf{q},\downarrow} c_{\mathbf{k},\uparrow}) e^{i\omega t} \\ &\quad + (c^{\dagger}_{\mathbf{k}+\mathbf{q},\uparrow} c_{\mathbf{k},\downarrow} + c^{\dagger}_{\mathbf{k}-\mathbf{q},\uparrow} c_{\mathbf{k},\downarrow}) e^{-i\omega t}] \end{aligned} \tag{2.20}$$

The components of magnetisation, $M_+(\mathbf{q})$ and $M_-(\mathbf{q})$, introduced earlier, can be defined in terms of creation and annihilation operators, i.e,

$$M_+(\mathbf{q}) = -2\mu_B \sum_{\mathbf{k}} < c^{\dagger}_{\mathbf{k}-\mathbf{q},\uparrow} c_{\mathbf{k},\downarrow} > \tag{2.21}$$

Therefore, to attempt to solve the Hamiltonian above, a reasonable first step would be to construct an equation of motion for this spin-fluctuation, $< c^{\dagger}_{\mathbf{k}-\mathbf{q},\uparrow} c_{\mathbf{k},\downarrow} >$,

$$i\hbar \frac{\delta}{\delta t} < c^{\dagger}_{\mathbf{k}-\mathbf{q},\uparrow} c_{\mathbf{k},\downarrow} > = < [c^{\dagger}_{\mathbf{k}-\mathbf{q},\uparrow} c_{\mathbf{k},\downarrow}, \mathbf{H}] > \tag{2.22}$$

The general form of a number of the terms which result from evaluating the commutator in equation (2.22), is impossible to deal with, hence to proceed further requires the use of an approximation. The random phase or dynamical Hartree-Fock approximation corresponds to retaining only those terms which can be written as a product of a number operator, $\hat{n}_\sigma$, and the spin fluctuation operator, $< c^\dagger_{\mathbf{k-q},\uparrow} c_{\mathbf{k},\downarrow} >$. As a result, the equation of motion becomes,

$$\begin{aligned} i\hbar\frac{\delta}{\delta t} < c^\dagger_{\mathbf{k-q},\uparrow} c_{\mathbf{k},\downarrow} > \;=\; & (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k-q}}) < c^\dagger_{\mathbf{k-q},\uparrow} c_{\mathbf{k},\downarrow} > \\ & + I\sum_{\mathbf{k'}}(\hat{n}_{\mathbf{k'},\uparrow} - \hat{n}_{\mathbf{k'},\downarrow}) < c^\dagger_{\mathbf{k-q},\uparrow} c_{\mathbf{k},\downarrow} > \\ & - I(\hat{n}_{\mathbf{k-q},\uparrow} - \hat{n}_{\mathbf{k},\downarrow})\sum_{\mathbf{q'}} < c^\dagger_{\mathbf{k-q-q'},\uparrow} c_{\mathbf{k-q'},\downarrow} > \\ & + \frac{1}{2}\mu_B H^{ext}(\hat{n}_{\mathbf{k-q},\uparrow} - \hat{n}_{\mathbf{k},\downarrow})e^{i\omega t} \end{aligned} \qquad (2.23)$$

By defining an exchange-corrected electron energy,

$$\hat{\epsilon}_{\mathbf{k}\sigma} = \epsilon_{\mathbf{k}} - I\sum_{\mathbf{k'}}\hat{n}_{\mathbf{k'},\sigma} \qquad (2.24)$$

and assuming that all the spin fluctuations have a time dependence of the form $e^{i\omega t}$, equation (2.23) becomes,

$$\begin{aligned} < c^\dagger_{\mathbf{k-q},\uparrow} c_{\mathbf{k},\downarrow} > \;=\; & \frac{I(\hat{n}_{\mathbf{k-q},\uparrow} - \hat{n}_{\mathbf{k},\downarrow})\sum_{\mathbf{q'}} < c^\dagger_{\mathbf{k-q-q'},\uparrow} c_{\mathbf{k-q'},\downarrow} >}{(\hbar\omega - (\hat{\epsilon}_{\mathbf{k-q},\uparrow} - \hat{n}_{\mathbf{k},\downarrow}))} \\ & + \frac{\frac{1}{2}\mu_B H^{ext}(\hat{n}_{\mathbf{k-q},\uparrow} - \hat{n}_{\mathbf{k},\downarrow})}{(\hbar\omega - (\hat{\epsilon}_{\mathbf{k-q},\uparrow} - \hat{n}_{\mathbf{k},\downarrow}))} \end{aligned} \qquad (2.25)$$

By substituting for the expression for the magnetisation, equation (2.21), and using the definition for the susceptibility, equation (2.19), an expression for the transverse susceptibility can be obtained,

$$\chi_{trans}(\mathbf{q},\omega) = \frac{2\mu_B^2\chi^0(\mathbf{q},\omega)}{(1 - I\chi^0(\mathbf{q},\omega))} \qquad (2.26)$$

$\chi^0(\mathbf{q},\omega)$ is known as the non-interacting susceptibility and is defined as,

$$\chi^0(\mathbf{q},\omega) = \sum_{\mathbf{k}}\frac{\hat{n}_{\mathbf{k-q},\uparrow} - \hat{n}_{\mathbf{k},\downarrow}}{\left(\hbar\omega - (\hat{\epsilon}_{\mathbf{k-q},\uparrow} - \hat{\epsilon}_{\mathbf{k},\downarrow})\right)} \qquad (2.27)$$

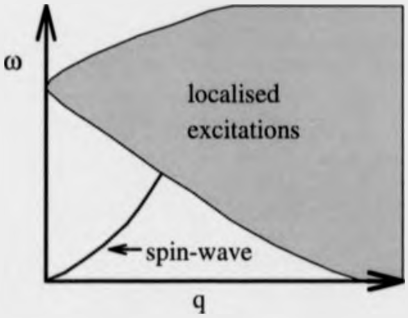

Figure 2.4: *The excitation spectrum of an itinerant electron ferromagnet showing the two types of possible excitations, the spin-wave branch entering a broad region of Stoner excitations.*

The example given above leads to the production of two forms of singularity in the susceptibility, as shown in figure (2.4). One type are singularities in $\chi^0(\mathbf{q},\omega)$ itself, which correspond to localised or Stoner excitations. The second type occur when $1 - I\chi^0(\mathbf{q},\omega) = 0$. These lead to poles at real frequencies dependent on the value of q and are the spin-waves discussed earlier.

The transverse susceptibility, or 2-particle Green's function, also has the added advantage in that it is directly comparable with experiment via inelastic neutron scattering [34]. The inelastic neutron scattering differential cross-section is given by,

$$\frac{\delta^2\sigma}{\delta\Omega\delta\omega} \propto Im\chi_{trans}(\mathbf{q},\omega) \tag{2.28}$$

2.3.2 First principles description

Attempts to produce first principles calculations of spin-wave spectra have centred on the use of Density Functional Theory. Such a theory is valid for a description of the ground state of an interacting electronic system. To extend it into the situation of non-equilibrium systems with time dependent variations in electronic density and exchange correlation potentials is fraught with difficulties. However, as the excitations under investigation here are of long-wavelength and the motion of any moment is slow compared to the electronic motion, then to a reasonable approximation we can take the effective potentials to have their instantaneous equilibrium values. This allows the use of the Density Functional Theory single particle equilibrium state equations.

Callaway [35] used a single band picture together with the Local Density Approximation to calculate the spin-wave spectrum of Ni. The dispersion curve is broader than that produced by Cooke [31] and there is an absence of multiple branches, however this is to be expected, being a single band calculation. Calculations have also been made for iron, Blackman etc. [36], indicated interesting behaviour at higher spin-wave energies including 'optical' modes together with discontinuities in the branches. All these effects are due to the existence of more than one band and indicate that considerable structure exists in the excitation spectra for the itinerant case compared to the localised situation.

Dynamic susceptibility via DFT

One of the earliest attempts to produce a method for the calculation of the transverse susceptibility was that of Callaway and Wang [37]. They used a local exchange approximation together with a perturbation theory approach to demonstrate the existence of collective excitations, spin-waves. To proceed with a first principles calculation requires a modification to Density Functional Theory as presented so far, namely that we are now dealing with a spin-polarised system with the ground state magnetisation aligned along a fixed spatial direction, taken to be the **z** axis. The derivation below follows the route taken by Stenzel and Winter [38] in their derivation of a dynamic susceptibility for paramagnetic metals.

Now the ground state energy is a functional of both charge density, $n(\mathbf{r}, t)$

and magnetisation density, $\mathbf{m}(\mathbf{r},t)$. The Green's function for the time dependent single particle equations becomes,

$$\left(i\delta_t\nabla^2 + V^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)] - \mu_B\sigma\cdot\mathbf{B}^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]\right)\mathbf{G}(\mathbf{r},\mathbf{r}',t,t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \tag{2.29}$$

where the effective fields are given by,

$$V^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)] = V^{ext} + e^2\int\frac{n(\mathbf{r},t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]}{\delta n(\mathbf{r},t)} \tag{2.30}$$

$$\mathbf{B}^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)] = \mathbf{B}^0(\mathbf{r},t) - \frac{\delta E_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]}{\delta\mathbf{m}(\mathbf{r},t)} \tag{2.31}$$

The addition of a magnetic dependence in the energy functional has introduced an effective field, $\mathbf{B}^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]$, which couples to the spin current, $\mathbf{m}(\mathbf{r},t)$, only. This field, or 'moment' is set up by the exchange and correlation effects of the interacting many electron system.

For the calculation of the transverse susceptibility, the time-dependent applied field $\mathbf{B}^0(\mathbf{r},t)$ is perpendicular to the ground state magnetisation, and as we are in the region of linear response the magnetisation, and therefore $\mathbf{B}^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]$, will just rotate, the magnitude remains constant. As stated earlier, these Density Functional Theory equations are only really valid for the description of an equilibrium state. Hence it should be noted that although $V^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]$ and $\mathbf{B}^{eff}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]$ appear to have a time dependence through $n(\mathbf{r},t)$ and $\mathbf{m}(\mathbf{r},t)$, in reality they would be calculated at the equivalent instantaneous equilibrium densities.

As in the previous non-magnetic case, to proceed further we require the use of the Local Density Approximation. As this involves the energy functional due to a homogeneous electron gas, its dependence upon the magnetisation density must only be through the magnitude of the magnetisation, also the densities will lose their time dependence, therefore,

$$E_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)] = E_{XC}[n(\mathbf{r}),|\mathbf{m}(\mathbf{r})|] \tag{2.32}$$

$$= \int n(\mathbf{r})\epsilon_{XC}(n(\mathbf{r}),|\mathbf{m}(\mathbf{r})|)d\mathbf{r} \tag{2.33}$$

The charge and magnetisation densities can be obtained from the single particle Kohn-Sham Greens function, equation (2.29) via,

$$n(\mathbf{r},t) = -iTr\mathbf{G}(\mathbf{r},\mathbf{r},t,t+\epsilon) \tag{2.34}$$

$$\mathbf{m}(\mathbf{r},t) = -iTr\sigma\mathbf{G}(\mathbf{r},\mathbf{r},\mathbf{t},\mathbf{t}+\epsilon) \tag{2.35}$$

Perturbing the system with a time-dependent transverse field, $\delta\mathbf{B}(\mathbf{r},t)$, results in a change in $\mathbf{G}$, to first order, of,

$$\delta\mathbf{G} = -\mathbf{G}_0\delta\mathbf{H}\mathbf{G}_0 \tag{2.36}$$

Using the approximation introduced earlier, that the moment and hence the effective field, $\mathbf{B}^{eff}$, just rotates whilst its magnitude remains constant, gives the following expression for the change in the Hamiltonian, $\delta\mathbf{H}$,

$$\delta\mathbf{H} = -2\int\frac{\delta n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \mu_B\sigma\cdot\delta\mathbf{B}^0(\mathbf{r},t) - \left.\frac{\delta E_{XC}[n(\mathbf{r}),|\mathbf{m}(\mathbf{r})|]}{\delta\mathbf{m}(\mathbf{r},t)}\right|_{\mathbf{m}=\mathbf{m_0}}\sigma\cdot\delta\mathbf{m}(\mathbf{r},t) \tag{2.37}$$

Solving for $\delta n(\mathbf{r},t)$ and the components of $\delta\mathbf{m}(\mathbf{r},t)$ using equations (2.36) and (2.37), gives $\delta n(\mathbf{r},t) = 0$ and $\delta m_z(\mathbf{r},t) = 0$. This confirms that the charge response is decoupled from the magnetic response and that the magnitude of the magnetisation remains constant.

The magnetisation can be calculated via equation (2.36) and using the definition for the susceptibility, equation (2.19) an expression for the transverse susceptibility can be produced. Finally, Fourier transforming, gives,

$$\chi_{trans}(\mathbf{q},\omega) = \frac{\chi^0(\mathbf{q},\omega)}{(1-U^{eff}\chi^0(\mathbf{q},\omega))} \tag{2.38}$$

where,

$$U^{eff} = \left.\frac{\delta E_{XC}[n(\mathbf{r}),|\mathbf{m}(\mathbf{r})|]}{\delta\mathbf{m}(\mathbf{r})}\right|_{\mathbf{m}=\mathbf{m_0},n=n_0} \tag{2.39}$$

As with the Hubbard case, χ^0 is known as the non-interacting susceptibility and is defined for a system where $n(\mathbf{r})$ and $\mathbf{m}(\mathbf{r})$ are fixed at the ground state values, i.e ,

$$\delta\mathbf{H} = \mu_B\sigma\cdot\delta\mathbf{B}^0 \tag{2.40}$$

In agreement with the previous derivation of the dynamic susceptibility via the Hubbard Hamiltonian, the various forms of magnetic excitation which exist, Stoner and spin-waves, are contained in equation (2.38).

Formally it is possible to obtain a dispersion relation for these collective excitations, the form of which will depend upon the energy scale set up by the band splitting, this in turn will determine where the the spin-wave branch will enter the region of single particle excitations. In this region there will be a broadening of the spin-wave modes due to decay into the Stoner excitations as well as possible spin-wave interaction effects. By making a small q expansion of χ^0 it can be shown,

$$h\omega = Dq^2 \tag{2.41}$$

where D is known as the spin-wave stiffness coefficient and is given by,

$$D = |\mathbf{m_0}| \frac{1}{\lim_{q \to 0} \chi^0(q,0)} \tag{2.42}$$

Derivations of D have included simple band models to first principles calculations. Approaches using DFT include work by Edwards and Rahman [39], Liu and Vosko [40] and Callaway et al. [41], where the sign and upper bounds on D have been calculated It should be noted that $\chi^0(q,0)$ and hence D, are ground state properties and therefore can be legitimately calculated via DFT.

The following chapter introduces the concepts of magnetic anisotropy and details methods of how such effects can be dealt with in both localised and itinerant magnetic systems.

Chapter 3

Magnetic anisotropy

In this section another important aspect of magnetically ordered systems is considered, that of magnetic anisotropy. Its origins in a relativistic description of electronic interactions are investigated and a phenomenological model introduced. The difficulties encountered when dealing with an itinerant magnet are discussed and a review made of recent first principles magnetic anisotropy energy calculations. Finally the effects of magnetic anisotropy on the excitations of a magnetic system are investigated.

3.1 Magnetic anisotropy

It is known experimentally that single magnetic crystals are magnetically anisotropic. This describes the situation where the magnetic moment preferentially points along a particular spatial direction, defined by the crystal lattice. Formally this means that there exists a term in the Free energy of the system which couples the magnetisation to the crystallographic axes. The difference in free energies from the lowest energy configuration of the moment to the others is known as the magneto-crystalline anisotropy (MAE). Initial work on magnetic anisotropy concentrated upon ferromagnetic metals, however, as the theory for such systems itself was still open to discussion, theoretical investigations into the origins of anisotropy in such itinerant systems was limited. Progress in the case of magnetic insulators, where the moment is determined by localised electrons, increased at a faster rate. In such systems the origin of anisotropy can be shown to be from the following main sources,

1. effects due to the spin state of a single ion, e.g spin-orbit coupling,
2. the electrostatic coupling between ions, both dipole-dipole and quadrapole-quadrapole as well spin-orbit coupling,
3. magnetic dipolar coupling.

3.1.1 Relativistic treatment

As the electrons are ultimately responsible for most of the magnetic properties we encounter and it is known that they possess an intrinsic magnetic moment or 'spin', we therefore need to consider a relativistic treatment of the motion of an electron about a charged nucleus. Our starting point for the case of a magnetic insulator is the Dirac equation involving an external vector potential, **A** [42]. The resulting Hamiltonian is given by,

$$\mathbf{H} = c\alpha \cdot \left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right) + \beta mc^2 + e\phi \tag{3.1}$$

where α and β are the Dirac matrices. As the energies encountered in magnetic anisotropy calculations and spin-waves are very much smaller than mc^2 we can use a transformation due to Foldy and Wouthuysen to decouple the positive and negative energy solutions to equation (3.1) [43]. The result of such a transformation is,

$$\mathbf{H} = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + e\phi - \frac{e\hbar}{2mc}\sigma \cdot \mathbf{H}^{ext} + \lambda \mathbf{l} \cdot \sigma - \frac{e\hbar^2}{8m^2c^2}\nabla \cdot \mathbf{E} \tag{3.2}$$

This shows the existence of a term which couples the intrinsic spin of the electron to its angular momentum, which itself is directly linked to the atomic arrangement, and hence introduces a coupling between the moment, partly due to the electrons spin, and the crystal structure. This spin-orbit coupling is one of the major contributors to the MAE. If the effects that the electron experiences whilst orbiting the charged nucleus are taken into account, then by making a multipole expansion it can be shown that an electrostatic quadrupole term will enter the Hamiltonian.

Now it is necessary to consider the effects of other electrons and ions. It is relatively easy to picture some of the terms produced in the case of a magnetic insulator, whether they are valid in an itinerant picture will be discussed later. The effects of the other electrons in the system will lead to terms describing screening and exchange. In the insulator example, taking exchange effects into account leads to the concept of the Heisenberg exchange Hamiltonian,

$$\mathbf{H} = -\sum_{i,j}^{N} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \tag{3.3}$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are spin operators acting upon atomic sites i and j, and J_{ij} is a measure of the exchange energy.

Effects from other ions can also contribute to the Hamiltonian, such as the coupling of orbital momenta, both from electrons on the same or different ions. Also electrostatic dipole-dipole and quadrupole-quadrupole coupling between the charge clouds of different atoms, the form of which depends upon the moment through spin-orbit coupling, can contribute to the energy. In a crystalline environment the electrons responsible for the magnetic behaviour experience the inhomogeneous electric fields set up by the surrounding ions. This may mean that the expectation value of the orbital contribution to the magnetic moment vanishes, in which case the orbital angular momentum is said to be quenched [42]. This is an important point, its consequences and validity will be discussed in later chapters. The coupling of magnetic moments between ions leads to the familiar magnetic dipole-dipole interaction.

Not all these terms will contribute to the MAE of a system. The simple exchange interaction depends only upon the relative orientations of the 'spins', and hence no coupling to the lattice vectors. The magnetic dipole-dipole interaction is relatively weak and long ranged. It contributes to a form of anisotropy known as shape anisotropy, for cubic system its effect is minimal, it has zero contribution from a first order perturbation approach. However it does play an important role in macroscopic phenomena such as domain structure and domain size.

The dominant term for anisotropy considerations is spin-orbit coupling.

3.1.2 Phenomenological approach

Many magnetic anisotropy calculations start with a phenomenological approach, particularly in the case of insulators. For low temperatures, the magnitude of the magnetic moment can be thought of as being constant, to lowest order any applied field will just rotate the magnetisation. The anisotropy energy of such a system can then be expanded in powers of the components of the magnetisation, subject to certain symmetry conditions. Invariance under time reversal requires that only even powers can be present and the symmetry of the underlying crystal structure will also impose limits on the form of the anisotropy energy.

For an uniaxial crystal, of ion density N, the anisotropy energy per ion is,

$$E_{aniso} = -\frac{K}{N}(\mathbf{n} \cdot \mathbf{M})^2 \tag{3.4}$$

where the value of the constant K, the anisotropy energy density, will determine the equilibrium orientation of the magnetisation, if $K > 0$ then $\mathbf{M}$ is parallel to $\mathbf{n}$ and if $K < 0$ then $\mathbf{M}$ lies in the plane perpendicular to $\mathbf{n}$.

For a cubic system the first terms which satisfy the symmetry conditions are of fourth order,

$$E_{aniso} = \frac{K_1}{N}(M_x^2 M_y^2 + M_x^2 M_z^2 + M_y^2 M_z^2) + \frac{K_2}{N}(M_x^2 M_y^2 M_z^2) + \dots \tag{3.5}$$

if $K_1 > 0$ then $\mathbf{M}$ is parallel to one of the edges of the cubic structure and if $K_1 < 0$ then $\mathbf{M}$ lies along one of diagonals of the cube.

The anisotropy constants K_1 and K_2 can be experimentally measured using magnetic torque and ferromagnetic-resonance (FMR) techniques [23]. Originally there was some dispute as to whether the anisotropy constants measured from 'static' methods (torque) were comparable to those from 'dynamic' approaches [23].

3.1.3 Itinerant systems

The majority of the above discussion can be seen to be readily applicable to the case of magnetic insulators, the situation of itinerant systems has an equally long history. Work by van Vleck [44] described the origin of MAE as being electrostatic, being dependent upon the orientation of the local spin and orbital magnet moments. His spin Hamiltonian contained a molecular field term as well as dipole-dipole and quadrupole-quadrupole terms, both electrostatic in origin. The MAE was then calculated via a perturbation theory.

Brooks [45] performed the first calculations for an itinerant model of a cubic system. Expressions for the MAE and an explanation for the quenching of the orbital angular momentum were produced. The spin-orbit coupling was treated as a perturbation and terms up to fourth order were required to obtain the anisotropy energy. Brooks noted that the proper treatment of many-body effects was required for a correct description of the MAE. A large part of subsequent MAE calculations have elaborated on this earlier work, many using more realistic band structures for their calculations. Later work by Mori et al. [46] identified areas of the Brillouin zone which provided the dominant contributions to the anisotropy energy, and their calculations were based upon only including these regions.

Other investigations of MAE have looked at systems with reduced symmetry, such as thin films and surface effects. Examples of work on Fe and Ni include papers by Gay and Richter [47], [48].

The most recent attempts at calculating bulk MAEs from first principles have centred on Density Functional Theory as a method for describing the itinerant nature of the system. These include calculations by Daalderop et al. [49] for Fe, Ni and Co and those by Strange et al. [50] for Fe and Ni. Fritsche et al. [51] used a single particle approach, though not based upon the Hohenberg-Kohn-Sham formalism. Guo et al. [52] used a similar method to that of Daalderop in their investigation of Ni and Fe, but as with most of the MAE calculations the values obtained were of the correct magnitude but incorrect easy axes were predicted.

Any first principles calculation will be difficult as it is not clear what are the exact origins of many of the contributions to the anisotropy. The general consensus appears to be that a proper treatment of the many-body effects, exchange and correlation for example, is required.

MAE via Density Functional Theory

In order to perform a first principles anisotropy calculation we require a relativistic formulation of Density Functional Theory. Ramana and Rajagopal [53], [54] and MacDonald and Vosko [55] have shown that the ground state energy of such a system with external fields $(V(\mathbf{r}), \mathbf{A}(\mathbf{r}))$ is a functional of the ground state four-current $(n(\mathbf{r}), \mathbf{J}(\mathbf{r}))$. Rasolt and Vignale [56] have explored the gauge invariance of this approach.). The Hamiltonian describing this situation is,

$$H(\mathbf{r}) =: \psi^{\dagger}(\mathbf{r}) \left[\frac{hc}{i} \alpha \nabla + (\beta - \hat{\mathbf{1}}) mc^2 - e\phi(\mathbf{r}) + e\alpha\mathbf{A}(\mathbf{r}) \right] \psi(\mathbf{r}) : + H_{rad} \qquad (3.6)$$

where $\psi(\mathbf{r})$ are 4-component second quantised Dirac spinors, α and β are the Dirac matrices. H_{rad} denotes the quantised electromagnetic field, $\phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are the scalar and vector potentials arising from such a field. The external fields are treated classically, they only couple to the charge and current densities, which are given, in the notation of [57], by,

$$n = :\psi^\dagger\psi \tag{3.7}$$

$$\mathbf{J} = :\psi^\dagger\alpha\psi \tag{3.8}$$

By using the Gordon decomposition [58] of the current and retaining the 'spin-only' component $\mathbf{m}(\mathbf{r})$, then the Kohn-Sham-Dirac equations reduce to

$$[c\alpha\cdot\mathbf{p}+\beta mc^2+\hat{\mathbf{1}}V^{eff}[n,\mathbf{m}]+\beta\sigma\cdot\mathbf{B}^{eff}[n,\mathbf{m}]]\mathbf{G}(\mathbf{r},\mathbf{r}')=\delta(r-r') \tag{3.9}$$

where the charge and magnetisation densities are given by,

$$n(\mathbf{r}) = Tr\,\mathbf{G}(\mathbf{r},\mathbf{r}) \tag{3.10}$$

$$\mathbf{m}(\mathbf{r}) = Tr\,\beta\sigma\mathbf{G}(\mathbf{r},\mathbf{r}) \tag{3.11}$$

and the effective fields $V^{eff}(\mathbf{r})$ and $\mathbf{B}^{eff}(\mathbf{r})$ are,

$$V^{eff}(\mathbf{r}) = V(\mathbf{r})+\delta E^H/\delta n(\mathbf{r})+\delta E^R_{xc}/\delta n(\mathbf{r}) \tag{3.12}$$

$$\mathbf{B}^{eff}(\mathbf{r}) = -(\mathbf{B}^{ext}(\mathbf{r})+\delta E^R_{xc}/\delta\mathbf{m}(\mathbf{r})) \tag{3.13}$$

Here α,β are the standard Dirac matrices, σ the 4×4 Pauli matrices. E^H is the Hartree energy. $\mathbf{B}^{eff}$ is the effective field which couples to the 'spin-only' current $\mathbf{m}(\mathbf{r})$, and not to the orbital component. If this were the case then a large orbital moment would result, which for transition metals, where the orbital angular momentum is quenched, is not observed. Usually a local approximation is used to evaluate E^R_{xc}, the exchange correlation energy, in terms of the homogeneous spin polarised relativistic electron gas, as in the non-relativistic situation.

Using the relativistic spin density functional formalism together with the local density approximation, the total energy of a system of interacting electrons is given by,

$$\begin{aligned}E[n,\mathbf{m}] &= \int^{\epsilon_F} d\epsilon\epsilon n(\epsilon)-e^2/2\int\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\ &-\int d\mathbf{r}(\frac{\delta E^R_{xc}}{\delta n(\mathbf{r})}n(\mathbf{r})-\frac{\delta E^R_{xc}}{\delta\mathbf{m}(\mathbf{r})}\cdot\mathbf{m}(\mathbf{r}))+E^R_{xc}[n,\mathbf{m}]\end{aligned} \tag{3.14}$$

where $n(\varepsilon)$ is the Kohn-Sham single particle density of states and the magnetisation $\mathbf{m}(\mathbf{r})$, is orientated according to the directions $\{\mathbf{n}_i\}$ associated with the magnetic moments at positions indexed i , ε_F is the Fermi energy.

The majority of the first principles calculations of MAE use the 'force' theorem. This is the assumption that for magnetic anisotropy calculations, if the direction of the magnetisation at the various sites is altered, then due to the stationary nature of the energy functional and the use of the local density approximation, to lowest order the total energy is unaffected by any change in the magnitude of the magnetisation at each site. Also arising from the stationary property, to first order the energy functional is uneffected by a change in charge density. Hence the same charge density, $n(\mathbf{r})$ can be used throughout. This can be seen by examining the expression for the total energy as given by equation (3.14). Hence the magnetic anisotropic contribution to the total energy is contained in the first 'single particle' term. Therefore the MAE can be calculated by looking at the energy difference between two systems of magnetic moments or effective fields, $\mathbf{B}^{eff}$, which differ only by their orientations.

Previous investigations

Jansen [59] started from a relativistic formulation of DFT and attempted to investigate the origin of some of the contributing terms to the MAE. In a relativistic treatment of the many body problem there exist terms which do not appear in the normal DFT equations. For example, the electron-electron interaction is modified, resulting in an additional Breit interaction. Jansen showed that a Hartree treatment of this term leads to the familiar magnetic dipole-dipole (magnetostatic) interaction responsible for the shape anisotropy and domain structure. In subsequent papers [60], [61] he stressed the importance of orbital angular momentum. Angular momentum is created by spin-orbit coupling in the kinetic energy operator of the Dirac equation, however Jansen suggests that it should also originate from many-body correlation terms, perhaps from the introduction of orbital angular momentum in the exchange-correlation functional, although some of its effects may exist in the Hartree treatment of the Breit interaction.

In the calculations of Fritsche et al.[51] instead of the usual Kohn-Sham equations, a set of Dirac-type single particle equations were solved self consistently. By using a non-standard LDA potential they calculated the MAE and easy axes for Fe, Ni and lattice expanded Pd. The correct easy axis for Ni was predicted but not for Fe.

Daalderop et al. [49] calculated the MAE of iron, cobalt and nickel using the Density Functional approach incorporating the LDA. By using the LMTO method [62] to solve the single particle equations, the spin-orbit coupling was added on the last iteration to achieve self consistency. Although the energies calculated were of the correct order of magnitude, the incorrect easy axis was predicted for Ni and Co. They found that the results were highly dependent upon the energy bands near the Fermi surface and they paid particular attention to the convergence of the Brillouin zone integration. They considered the variation of the MAE due to strain, changes in magnitude of the spin-orbit coupling and different choices of the exchange correlation potential and concluded that none of these could be responsible for the errors in the values they obtained. Their suggestion was that the primary source of uncertainty was the use of the force theorem, although they did comment that the addition of an orbital momentum dependence in the exchange correlation potential could remedy some of the deficiencies experienced.

Strange et al. [50] used a relativistic spin-polarised multiple scattering theory to solve the single particle Density Functional equations within the local density approximation. They predicted the correct easy axes for Fe and Ni but with errors in the magnitudes. They also concluded that the main areas of concern were the use of the force theorem and the possibility of needing to include full self-consistency in order to include various many-body effects such as the Breit interaction. In theory this approach should be superior to that of Daalderop et al. as the effects of spin-polarisation and spin-orbit coupling are treated on an equal footing. Work by Ebert [63] compared the two approaches and concluded that the difference was not sufficient to explain the errors in the calculations of anisotropy energies.

The LMTO method undertaken by Guo et al. [52] to solve the single particle DFT equations differs from that of Daalderop in that the energy calculations were fully self consistent, and hence the force theorem was not used. However although the anisotropy energies produced were of the correct magnitude the identification of the easy axes for both Fe and Ni were wrong. The authors suggest the reasons for failure lie in the use of spherical potentials, i.e, the angular momentum plays a small role, and the use of the LDA, possible improvements involve the addition of orbital momentum effects in the exchange-correlation functional.

Further evidence for the need for an adequate treatment of the orbital components of momentum come from work by Eriksson [64]. They were interested in explaining the magnitudes and trends in the orbital contribution to the magnetic moments for Fe, Co and Ni. The local spin density approximation deals with Hund's first rule, maximum spin, in its application to exchange splitting. The third rule, for total angular momentum, is dealt with by taking spin-orbit coupling into account, either self consistently during an iteration as with Daalderop [49], or by solving a spin-polarised Dirac equation, as with Strange [50]. However, only by taking the second rule, maximum orbital momentum, via an orbital polarisation term could they get better agreement with experimental results. When the details of the crystal structure were included, they found they could explain the trends in orbital contributions across the transition metal series.

Table (3.1) gives a comparison between experimental and theoretical values for the MAE for Fe and Ni. A is the experimental value [65], B is from ref. [49], C from ref. [50], D from ref. [51] and E from ref. [52].

In all of the above cases the MAE is obtained as the difference between an energy calculation where the magnetic moments lie along $(0,0,1)$ and one where

$E_{001} - E_{111}$	A	B	C	D	E
Fe	-1.4	-0.5	-9.6	7.4	1.8
Ni	2.7	-0.5	10.5	10.0	-2.7

Table 3.1: The magnetocrystalline anisotropy energy in 10^{-6} eV per atom for Fe and Ni.

the moments lie along $(1, 1, 1)$, i.e.

$$E_{MAE} = E(0, 0, 1) - E(1, 1, 1) \tag{3.15}$$

In view of the fact that the MAE is going to be very small, the chance for numerical inaccuracies with the above approach, the difference between two large numbers, is high, hence we would like to go for a route which would minimise this possibility, by calculating the anisotropy energy directly.

3.1.4 Anisotropy and magnetic domains

By considering the total energy of a ferromagnetic crystal, including the magnetostatic energy, equation (2.11), it is found that a uniform direction of magnetisation throughout the system is not the lowest energy configuration [66]. It is in fact energetically favourable for the system to form domains of uniform magnetisation, as illustrated in figure (3.1), Between each of these magnetic domains

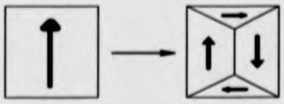

Figure 3.1: *The total energy of the magnetic system is reduced by forming domains, in this case giving no net magnetisation.*

exists a transition region, where the magnetisation rotates from one orientation to another, as demonstrated below in figure (3.2).

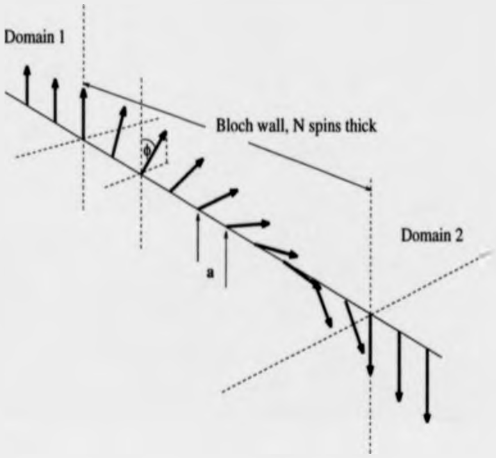

Figure 3.2: *Between the domains of uniform magnetisation exist a region of spin rotation, known as a Bloch wall.*

The exchange energy, equation (2.7), required for this transition is minimised if the rotation occurs over a range of spins, however, if this were the only factor then the domain or 'Bloch' wall would spread throughout the whole system. It is the effects of anisotropy which limit the width of the transition.

If the angle between the rotated spins, ϕ, is small and the total spin rotation after N spins is π, then the exchange energy per pair of spins is given by,

$$\begin{aligned} E_{ex} &= J\cos\frac{\pi}{N} && (3.16)\\ &\simeq J\frac{\pi^2}{N} && (3.17)\end{aligned}$$

If the energy per unit area of the wall is σ, then,

$$\sigma = \sigma_{ex} + \sigma_{aniso} \qquad (3.18)$$

where $\sigma_{ex} = J\pi^2 N a^2$, a is the lattice constant, and the anisotropy energy is approximately the anisotropy energy density, K, multiplied by the wall thickness, Na.

Therefore σ will reach a minimum when,

$$\frac{\delta\sigma}{\delta N} = -\frac{J\pi^2}{N^2 a^2} + Ka = 0 \tag{3.19}$$

i.e,

$$N = \left(\frac{J\pi^2}{Ka^3}\right)^{\frac{1}{2}} \tag{3.20}$$

Hence the study of domain walls can give some insight into the magnitude and effects of magnetic anisotropy.

3.1.5 Anisotropy and dynamics

In addition to calculating the anisotropy energy itself, it is interesting to examine the effect of a preferred spatial direction on the low energy, long-wavelength excitations, namely spin-waves. To give an indication of one of the particular consequences we consider a simple phenomenological model, as introduced earlier.

The addition of anisotropy for a cubic system, the form of which is given by equation (3.5), will result in an additional term to the effective field experienced by the moment. The new effective field, including the exchange and static external field terms is,

$$\mathbf{H}^{eff} = \frac{1}{2}\sum_j J_{ij}\mathbf{M}_j + \mathbf{H}^{ext} + \frac{\delta E_{aniso}}{\delta \mathbf{M}_i} \tag{3.21}$$

If we assume that the equilibrium magnetisation lies along the **z** axis then in the linear regime the moment only deviates slightly from this position, its components given by $(\delta M_x^i, \delta M_y^i, M_0)$. Solving the equation of motion as in equation (1.24) with the new effective field gives,

$$\omega = 2\gamma\frac{K_1}{N} + Dq^2 + \gamma H^{ext} \tag{3.22}$$

As $q \longrightarrow 0$ then $\omega = 2\gamma\frac{K_1}{N}$ for zero external field. The existence of magnetic anisotropy in the system has opened up a gap in the spin-wave spectrum, as demonstrated in figure (3.3). If the equilibrium magnetisation lies along the diagonal of the unit cell, i.e along $\frac{1}{\sqrt{3}}(1,1,1)$, then we can transform to a new coordinate frame, where the new **z** axis is orientated along the direction of equilibrium magnetisation, i.e. $\frac{1}{\sqrt{3}}(1,1,1)$ in the old reference frame. Once the anisotropy energy has been re-written in terms of the new coordinate frame then a similar equation of motion can be solved together with the same linearisation condition, $M_i = (\delta M_x^i, \delta M_y^i, M_0)$. This leads to an expression for ω,

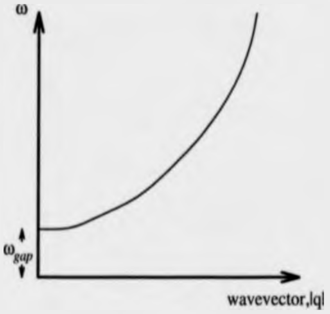

Figure 3.3: *The existence of magnetic anisotropy opens up a gap in the spin-wave spectrum at* $\mathbf{q} = 0$, *even in the absence of an external field.*

$$\omega = \gamma\frac{4K_1}{3N} + Dq^2 + \gamma H^{ext} \tag{3.23}$$

The gap in the spin-wave spectrum can be experimentally determined via FMR and through neutron scattering experiments. However in transition metal systems the value for the anisotropy energy is rather small, making any small **q** neutron experiments particularly hard.

The spin-wave gap and the MAE

In the formulation of the phenomenological model we can relate the expression obtained from the spin-wave gap to the Magnetocrystalline Anisotropy Energy (MAE), as discussed earlier. If we assume that the total energy of the magnetic system can be expressed as an isotropic part plus an anisotropic contribution,

$$E_{tot} = E_{iso} + E_{aniso} \tag{3.24}$$

where, for a cubic system,

$$E_{aniso} = \frac{K_1}{N}(M_x^2 M_y^2 + M_x^2 M_z^2 + M_y^2 M_z^2) \tag{3.25}$$

The MAE, defined as,

$$\begin{aligned} E_{MAE} &= E(0,0,1) - E(1,1,1) && (3.26)\\ &= E_{aniso}(0,0,1) - E_{aniso}(1,1,1) && (3.27)\\ &= 0 - \frac{1}{3}\frac{K_1}{N} && (3.28) \end{aligned}$$

From the derivation of the spin-wave gap,

$$\begin{aligned} \frac{\omega_{gap}}{\gamma} &= 2\frac{K_1}{N} \qquad if \quad \mathbf{M}_0 = (0,0,1) && (3.29)\\ &= \frac{4}{3}\frac{K_1}{N} \qquad if \quad \mathbf{M}_0 = (1,1,1) && (3.30) \end{aligned}$$

Therefore, for a magnetic system which follows the phenomenological description of magnetic anisotropy, i.e. equation (3.5), then,

$$\frac{\omega_{gap}(0,0,1)}{\omega_{gap}(1,1,1)} = \frac{3}{2} \tag{3.31}$$

Using equation (3.28), the magnetic anisotropy energy is given by,

$$\begin{aligned} E_{MAE} &= \frac{1}{6}\frac{\omega_{gap}}{\gamma} \qquad if \quad \mathbf{M}_0 = (0,0,1) && (3.32)\\ &= \frac{1}{4}\frac{\omega_{gap}}{\gamma} \qquad if \quad \mathbf{M}_0 = (1,1,1) && (3.33) \end{aligned}$$

So far we have introduced the concept of dynamic susceptibility and shown that the relevant single particle equations for any magnetic anisotropy calculation are those of Kohn-Sham-Dirac. Hence it would seem logical that in order to obtain a first principles theory of the effects of anisotropy on spin-dynamics, we should combine the two to attempt an approach similar to that described for the non-relativistic case earlier in the chapter. However we shall see that considerable theoretical problems exist in following such a route, this is discussed in Chapter 5.

The following Chapter introduces the multiple scattering solutions to the single particle Kohn-Sham Dirac equations.

Chapter 4

Anisotropy in magnetic interactions

In order to introduce the concepts behind the multiple-scattering solutions to the single particle equations, discussed in Chapter 1, the formalism is used to investigate the magnetic anisotropic effects resulting from the treatment of a number of magnetic impurities embedded in a non-magnetic, metallic host. Also it gives some indication as to whether such a formalism is capable of allowing the calculation of such small energies numerically.

4.1 Magnetic impurities and spin-glass systems

When a magnetic impurity is placed in an insulating host then the impurity moment usually shows behaviour consistent with Hund's rules, with possible modification due to crystal field effects. However when such an impurity is situated in a non-magnetic conducting host, then whether a magnetic moment remains or not is a complex problem. The presence of a conduction band and its interactions with the localised electrons associated with the impurity lead to a wide variety of behaviour [67]. Friedel considered the free electron scattering off a charged impurity potential [68], and found that this resulted in an oscillating charge density surrounding the impurity. It also lead to a self consistency relation for the effective potential. If the impurity potential is strong enough to bind one of the electrons, then by treating the potential plus this bound state as an impurity in the electron gas, then the self-consistency relation indicates that there will be strong, resonance scattering of the electrons by this virtual bound state. This level is termed virtual as it sits in the continuum of the free electron gas and is therefore not localised. Anderson [69] set up a model Hamiltonian where all the levels of a magnetic impurity ion were replaced by one localised level. The coupling between this and the band levels was reduced to a minimum. Even with this massive simplification, solutions to this complex problem of dealing with magnetic impurity potentials in metallic hosts have been hard to find.

Attempts at a first principles approach include the work of Oswald et.al [70]. They used a KKR Greens function method to investigate the magnetic interactions of Cr, Mn and Fe embedded in a metallic host, Cu or Ag. The concentration of impurities plays a crucial role, leading to a range of systems, from dilute magnetic alloys to a spin-glass phase. In the dilute limit, where only a few impurities per million host atoms exist, then the interaction between impurity moments is minimal, the self energy of each moment dominates. An individual moment is effectively screened by a polarised cloud of conduction electrons. In such a limit we see phenomena such as the Kondo effect [71], the existence of a resistance minimum at low temperatures, due to the exchange scattering of the conduction electrons by the magnetic moment. At higher concentrations of impurities the interaction between moments will no longer be negligible. In this case the existence of a localised moment sets up an oscillating polarisation in the surrounding conduction electrons, another moment can then experience this effective interaction which can be ferromagnetic or anti-ferromagnetic depending upon the separation distance.

This form of interaction, as shown in figure (4.1), where $E \propto J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \cos(k_f R_{ij})/R^3$,

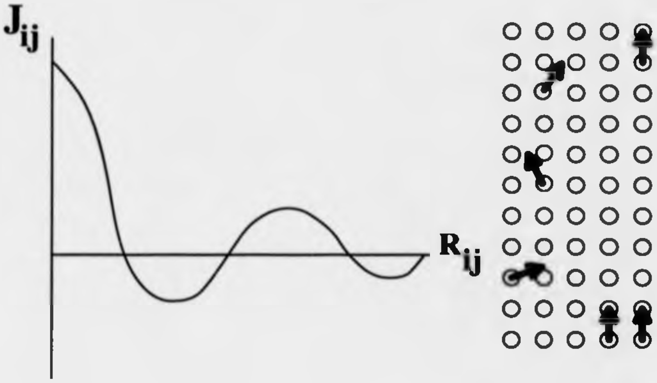

Figure 4.1: *Typical 'classical' spin configuration and corresponding RKKY-type interaction. As the temperature is lowered the spins become 'locked' into certain orientations.*

is known as the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction, it is similar to the Friedel oscillations which exist when an electron gas attempts to screen out a charge impurity [68]. The ground state of such a system, a spin-glass, appears disordered, the moments are locked into certain orientations in order to minimise the total energy. Only above a temperature, T_f, are the moments free to rotate. However the ground state is not unique, there will be many other spin orientations with a similar energy. Also the concept of 'frustration' can be applied, that is there exist situations where no orientation of spins can satisfy all the various interactions. A spin-glass can be defined as having the following properties,

1. The moments appear 'frozen' below a temperature T_f, leading to a peak in the susceptibility.
2. Lack of long range magnetic order.
3. Remanence and magnetic relaxation on a macroscopic timescale at temper-

atures below T_f due to changes in the magnetic field.

Any attempt at a theoretical solution to the problems of spin-glasses requires considerable simplification. Typical approaches include those reviewed in [72] etc.

Magnetic anisotropy plays an important role in such systems, including the possibility of inducing phase changes in the system, responsibility for the long timescales associated with large part of the static and dynamic behaviour and in the existence of hysteresis effects. Considerable attention has been focussed on spin-glasses with single-ion uniaxial anisotropy after it was suggested that two phase transitions are possible on lowering the temperature. For 'easy-axis' anisotropy the longitudinal spin components are frozen before the transverse components. For easy plane anisotropy the reverse holds true. Bray [73] investigated the low energy excitation spectrum within the Sherrington-Kirkpatrick model [72] for spin-glass systems. He found that in the longitudinal phase, a gap was opened up in the spin-wave spectrum which vanished at a non-zero value of the anisotropy strength. This work underlines the difficulties encountered when attempting to relate microscopic interactions, i.e the effects of anisotropy on magnetic interactions, to the magnetic behaviour of such disordered systems. Most approaches assume a simple form for the interactions and then use various theoretical techniques to deal with the large scale behaviour [72].

4.1.1 Anisotropic magnetic impurity interactions

It has been known for some time experimentally [74] that the addition of heavy, non-magnetic impurities, Pt for example, to such dilute magnetic alloy systems, e.g $\underline{\text{Cu}}$Mn, $\underline{\text{Au}}$Fe, can dramatically alter the magnetic anisotropy of the system. Levy and Fert [75], showed that this enhancement of the anisotropy could be accounted for by the existence of Dzyaloshinsky-Moriya (DM) type interactions between the magnetic atoms, mediated by a third non-magnetic impurity. The form of such an interaction is shown below,

$$\mathbf{H}_{DM} \propto (\hat{R}_1 \times \hat{R}_2) \cdot (\hat{s}_1 \times \hat{s}_2) \tag{4.1}$$

They applied perturbation theory to the conduction electrons and kept terms to lowest order in the spin-orbit coupling. Subsequent papers [76] included the possibility of other anisotropic interactions, such as pseudo-dipolar type, equation (4.2), although of much reduced magnitude.

$$E_{dip} \propto (\hat{s}_1 \cdot \hat{R}_{12})(\hat{s}_2 \cdot \hat{R}_{12}) \tag{4.2}$$

A first principles multiple scattering approach to investigate the possible anisotropic interactions in these dilute magnetic systems was carried out by Staunton et al. [77] in 1988. It was based on a relativistic multiple scattering approach formulated from an earlier paper by Strange et al. [78]. A relativistic RKKY interaction was derived between two magnetic impurities leading to the existence of DM interaction terms, the magnitude of this interaction energy between two Fe and two Co impurities was then calculated. Further work in 1989 [79] investigated the situation of three magnetic impurities, where both uniaxial and unidirectional anisotropies were observed and approximate numerical calculations carried out.

The next section describes the formalism used by Staunton et al. in their calculations of the anisotropic interactions between magnetic impurities. It also contains a description of work by [89] on the effects of a third, heavy, non-magnetic atom on the interactions of two magnetic impurities.

4.2 Scattering Theory

4.2.1 Single site scattering

A physical picture for a scattering description of the system is that the electrons, modelled as a plane wave, are scattered by the impurity potentials, which have a magnetic component. To show the consequences of such an event we start by considering single impurity, non-relativistic scattering [80], [81]. The scattering particles involved are spinless, the potential is finite ranged and spherically symmetric and embedded in a non-interacting 'jellium' background. The principles behind the approach can be given as follows,

1. The appropriate wave equation, here the Schrödinger equation, is solved both inside and outside the potential region.
2. The resulting wavefunctions are smoothly matched at the potential boundary.

As the potential is spherically symmetric and the scattering elastic, then angular momentum is conserved. This allows the wavefunction to be written in terms of radial and angular components,

$$\Psi_L(r) = R_L(r) Y_l^m(\theta, \phi) \tag{4.3}$$

$R_L(r)$ satisfies the following differential radial equation,

$$[-\frac{1}{r}\frac{\partial^2}{\partial r^2} - V(r) - \frac{l(l+1)}{r^2} + \varepsilon] R_L(r) = 0 \tag{4.4}$$

and $Y_l^m(\theta, \phi)$ are the spherical harmonics, the eigenfunctions of the angular momentum operator. The radial wavefunction outside the potential region will consist of a linear combination of free-space solutions, such a wavefunction is given below.

$$R_L(r) = A_l(\varepsilon)(\cos\delta_l(\varepsilon))\, j_l(\sqrt{\varepsilon}r) - (\sin\delta_l(\varepsilon))\, n_l(\sqrt{\varepsilon}r) \tag{4.5}$$

where $j_l(\sqrt{\varepsilon}r)$ and $n_l(\sqrt{\varepsilon}r)$ are regular and irregular Bessel functions. For illustration, assuming a square-well potential of depth V_0, then the solution of the radial Schrödinger equation inside the potential region is,

$$R_L(r) \propto j_l(\sqrt{\varepsilon'}r) \tag{4.6}$$

where $\varepsilon' = \varepsilon + V_0$. The second condition must now be satisfied, that is that the two solutions must be smoothly matched at the potential boundary. This defines the constants in the above equation, giving,

$$\tan \delta_l(\varepsilon) = \frac{\sqrt{\varepsilon} j_l'(\sqrt{\varepsilon} a) j_l(\sqrt{\varepsilon'} a) - \sqrt{\varepsilon'} j_l(\sqrt{\varepsilon} a) j_l'(\sqrt{\varepsilon'} a)}{\sqrt{\varepsilon} n_l'(\sqrt{\varepsilon} a) j_l(\sqrt{\varepsilon'} a) - \sqrt{\varepsilon'} n_l(\sqrt{\varepsilon} a) j_l'(\sqrt{\varepsilon'} a)} \tag{4.7}$$

$\delta_l(\varepsilon)$ is known as the 'phase shift'. The reason behind this can be seen if the asymptotic form of the radial wavefunction, equation (4.5), is calculated,

$$\lim_{r \to \infty} R_L(r) = \frac{1}{\sqrt{\varepsilon} r} \sin(\sqrt{\varepsilon} r - \frac{l\pi}{2} + \delta_l(\varepsilon)) \tag{4.8}$$

This form of radial wavefunction differs from the free space case only by a phase factor, $\delta_l(\varepsilon)$, therefore the total effect of the potential on the scattered particle is described by the phase shift. The radial solution can be expressed in a number of ways [81], one such is,

$$R_L(r) = j_l(\sqrt{\varepsilon} r) + i\sqrt{\varepsilon} t_l h_l^+(\sqrt{\varepsilon} r) \tag{4.9}$$

where h_l^+ is a Hankel function,

$$h_l^+(\sqrt{\varepsilon} r) = j_l(\sqrt{\varepsilon} r) + i n_l(\sqrt{\varepsilon} r) \tag{4.10}$$

$t_l(\varepsilon)$ is known as the transition factor, which can be shown to describe the rate of scattering into the l^{th} channel and is function of the phase shift [82]. The transition factor can be related to the scattering amplitude and cross sections [80].

Resonance

Equation (4.7) shows that for certain positive values of E, $\delta_l(\varepsilon)$ will jump by nearly π, this is a form of resonance behavior. The resonance, or meta-stable state can be thought of as arising from the $l(l+1)/r^2$ term in equation (4.4). This is a form of centrifugal barrier to the scattering particle, and hence it can become 'trapped' before tunnelling out.

Green's Function method

For a more general treatment, the integral form of the scattering equations prove to be more convenient than the differential approach. If we consider the relevant wave equation, the Schrödinger equation,

$$(\varepsilon - \mathbf{H}_0)\Psi(r) = f(r) \tag{4.11}$$

where $\mathbf{H}_0$ is the free particle Hamiltonian, then a solution to this has the form,

$$\Psi(r) = \phi(r) + \int dr'\ G_0(r, r'; \varepsilon) f(r') \tag{4.12}$$

where $\phi(r)$ is a solution of the homogeneous equation ($f(r) = 0$) and $G_0(r, r'; \varepsilon)$ is the corresponding Green's function, which is defined in operator form as [80],

$$\mathbf{G}_0(\varepsilon) = \mathbf{P}\frac{\mathbf{1}}{\varepsilon - \mathbf{H}_0} - i\pi\delta(\varepsilon - \mathbf{H}_0) \tag{4.13}$$

where $\mathbf{P}$ is the Principal value. If $f(r')$ is replaced with $f(r') = v(r')\Psi(r')$ then equation (4.12) becomes,

$$\Psi(r) = \phi(r) + \int dr'\ G_0(r, r'; \varepsilon) V(r') \Psi(r') \tag{4.14}$$

or, in operator form,

$$\mid \Psi(r) > = \mid \phi(r) > + \mathbf{G}_0(\varepsilon) V \mid \Psi(r) > \tag{4.15}$$

This is known as the Lippmann-Schwinger equation. It indicates that the scattering wavefunction contains an incident plane wave and a scattered wave, hence the equation contains the outgoing boundary conditions. One of the problems with obtaining a solution to this equation is that the right hand side contains the full wavefunction, $\Psi(r)$. Another operator, $\mathbf{T}(\varepsilon)$ can be defined,

$$\mathbf{T}(\varepsilon) = \mathbf{V} + \mathbf{G}_0(\varepsilon)\mathbf{T}(\varepsilon) \tag{4.16}$$

using this, equation (4.15) can be re-written,

$$\mid \Psi(r) > = \mid \phi(r) > + \mathbf{G}_0(\varepsilon)\mathbf{T}(\varepsilon) \mid \phi > \tag{4.17}$$

The introduction of this T operator does not seem to be particularly useful, its calculation is as hard as solving equation (4.15). However the 'on energy-shell' elements of the T matrix are related to the transition factors in equation (4.9),

$$T(k, k'; \varepsilon) = \sum_{LL'} i^{-l+l'} Y_l^m(\hat{k}) Y_{l'}^{m'}(\hat{k}') t_{ll'}(\varepsilon)(4\pi)^2 \tag{4.18}$$

where $t_{ll'}$ are the angular momentum components of the on energy-shell matrix. In the case of a spherically symmetric potential, $t_{ll'}$ will be diagonal, describing conservation of angular momentum, and will be equal to the transition factors.

The Green's function approach allows a number of important quantities to be expressed in a concise form. From equation (4.13) it can be seen that the number of states per unit energy range, the density of states $n(\varepsilon)$, is given by,

$$\begin{aligned} n(\varepsilon) &= \sum_m \delta(\varepsilon - \varepsilon_m) && (4.19) \\ &= -\frac{1}{\pi} Im\ Tr\ \mathbf{G}(\varepsilon) && (4.20) \end{aligned}$$

where the Trace is carried out after $\mathbf{G}$ has been evaluated in an appropriate basis. Similarly, the integrated density of states, $N(\varepsilon) = \int d\varepsilon n(\varepsilon)$, can be shown to be [81],

$$N(\varepsilon) = -\frac{1}{\pi} Im\ Tr\ \ln \mathbf{G}(\varepsilon) \tag{4.21}$$

The difference between the integrated density of states for a system with an added impurity potential, given by equation (4.21), and a free electron background, $N^{free}(\varepsilon) = -\frac{1}{\pi} Im\ Tr\ \ln \mathbf{G}_0$, is known as the Friedel sum. As discussed earlier, it describes the build up of excess charge around an impurity scattering site.

4.2.2 Relativistic Spin-Polarised Scattering

In treating the scattering electrons relativistically, a number of changes are required, as discussed in Rose [43]. The following explanation follows the work of Strange et al. [78]. Due to the inclusion of spin, the wavefunction is now a

4-component spinor and the Hamiltonian contains a spin-orbit term. The corresponding wave equation for the relativistic situation is the Dirac equation. In polar form,

$$[i\gamma^5\tilde{\sigma}_r(\frac{\partial}{\partial r} + \frac{1}{r} - \frac{\tilde{\beta}}{r}\tilde{\kappa}) + V + \tilde{\beta}]\Psi = \varepsilon\Psi \tag{4.22}$$

where $\hat{\kappa} = \tilde{\beta}(\tilde{\sigma}.\hat{L} + 1)$. Due to the $\hat{\kappa}$ term, $Y_l^m(\hat{r})$ and $X_s^{m_s}$ are no longer eigenfunctions. It can be shown [43], that the correct eigenfunctions are $\chi_\kappa^{m_j}$, defined as,

$$\chi_\kappa^{m_j}(\hat{r}) = \sum_{m_s=\pm\frac{1}{2}} C^{\kappa m_j}_{m_s, m_j - m_s} Y_l^{m_j - m_s}(\hat{r}) X^{m_s}(\hat{r}) \tag{4.23}$$

where $Y_l^m(\hat{r})$ and $X_s^{m_s}$ are the eigenfunctions of the angular momentum and spin operators, and $C^{\kappa m_j}_{m_s, m_j - m_s}$ is a Clebsch-Gordan coefficient. The index κ contains information on the eigenvalues of both $\hat{J}$ and $\hat{L}$,

1. $\kappa = l$ for $j = l - \frac{1}{2}$
2. $\kappa = -l - 1$ for $j = l + \frac{1}{2}$

κ takes all integer values except for zero. The upper and lower components of the wavefunction are proportional to $\chi_\kappa^{m_j}$ and $\chi_{-\kappa}^{m_j}$ respectively, hence the wavefunction can be written, in relativistic units, as,

$$\Psi^{\kappa m_j}(\hat{r}) = \begin{pmatrix} g_\kappa(r)\chi_\kappa^{m_j}(\hat{r}) \\ if_\kappa(r)\chi_{-\kappa}^{m_j}(\hat{r}) \end{pmatrix} \tag{4.24}$$

$g(r)$ and $f(r)$ are radial functions which, in general will have a κ dependence. Using such an expansion in equation (4.24) together with the orthogonality of the spin-angular eigenfunctions, then $g(r)$ and $f(r)$ can be shown to satisfy the following radial equations,

$$\left(\frac{\partial}{\partial r} + \frac{(1-\kappa)}{r}\right) f_\kappa(r) + (\varepsilon - V - 1) g_\kappa(r) = 0 \tag{4.25}$$

$$\left(\frac{\partial}{\partial r} + \frac{(1+\kappa)}{r}\right) g_\kappa(r) - (\varepsilon - V + 1) f_\kappa(r) = 0 \tag{4.26}$$

The appropriate wave equation used for the case of relativistic scattering off a potential with a magnetic (spin-dependent) component, which has been set up by an interacting itinerant electron system, is the Kohn-Sham-Dirac equation. This arises from a relativistic Density Functional treatment of the corresponding many electron system as introduced earlier. In the notation used so far, the Kohn-Sham-Dirac equation with an effective field, $\mathbf{B}(\mathbf{r})$, defining a $\mathbf{z}$ axis, is,

$$[i\gamma^5\tilde{\sigma}_r\left(\frac{\partial}{\partial r}+\frac{1}{r}-\frac{\tilde{\beta}}{r}\tilde{\kappa}\right)+V(r)\hat{\mathbf{1}}+B^{eff}(r)\tilde{\beta}.\tilde{\sigma}_3]\Psi=\varepsilon\psi \qquad (4.27)$$

The integral solution to the above equation is the relativistic Lippmann-Schwinger equation,

$$\Psi^+(r,m_s)=\Psi_0(r,m_s)+\int d\mathbf{r}\,\tilde{G}_0(r,r';\varepsilon)(V(r)\hat{\mathbf{1}}+B^{eff}(r)\tilde{\beta}.\tilde{\sigma}_3)\Psi^+(r',m_s) \quad (4.28)$$

$\tilde{G}_0$ is now a 2×2 matrix and Ψ^+, Ψ_0 are four component spinors. Following the earlier approach, by using the following expansions in the Lippmann-Schwinger equation,

$$\Psi_0(r,m_s) = \sum_{\kappa m}\begin{pmatrix} g_\kappa(r)\chi_\kappa^{m_j}(\hat{r}) \\ if_\kappa(r)\chi_{-\kappa}^{m_j}(\hat{r})\end{pmatrix} \qquad (4.29)$$

$$\Psi^+(r,m_s) = \sum_{\kappa\kappa' m_j m_j'} A(\varepsilon)\begin{pmatrix} g_{\kappa'\kappa}^{m_j m_j'}(r)\chi_{\kappa'}^{m_j'}(\hat{r}) \\ if_{\kappa'\kappa}^{m_j m_j'}(r)\chi_{-\kappa'}^{m_j'}(\hat{r})\end{pmatrix} \qquad (4.30)$$

a set of coupled radial integral equations are produced, the solution to this set satisfy the following radial differential equations,

$$\left(-\frac{\partial}{\partial r}+\frac{\kappa'-1}{r}\right)f_{\kappa'\kappa}^{m_j' m_j}(r)+(V-\varepsilon+1)g_{\kappa'\kappa}^{m_j' m_j}(r)+B^{eff}(r)\sum_{\kappa'' m_j''}G(\kappa'',\kappa';m_j')g_{\kappa''\kappa}^{m_j' m_j}=0 \qquad (4.31)$$

$$\left(\frac{\partial}{\partial r}+\frac{\kappa'+1}{r}\right)g_{\kappa'\kappa}^{m_j' m_j}(r)+(V-\varepsilon-1)f_{\kappa'\kappa}^{m_j' m_j}(r)-B^{eff}(r)\sum_{\kappa'' m_j''}G(-\kappa'',-\kappa';m_j')f_{\kappa''\kappa}^{m_j' m_j}=0 \qquad (4.32)$$

where $G(\kappa'',\kappa';m_j'')=Tr\int d\hat{\mathbf{r}}\,\chi_{\kappa''}^{m_j''}(\hat{r})\tilde{\sigma}_3\chi_{\kappa'}^{m_j''}(\hat{r})$. The above are obtained by acting upon the integral equations with the radial operator equation, (4.22) with $V=0$, and using the definition of the Greens function, $\mathbf{HG}_0(r,r';\varepsilon)=\delta(r-r')$.

The radial functions have two sets of indices, κ and κ'', the first corresponds to the incident electron, the second to the final scattered particle, i.e. all the radial components labelled by κ satisfy the same set of radial equations, equations (4.31)-(4.32), but each individual radial function will satisfy a different boundary condition, depending upon the index κ, describing the incident electron.

The above radial equations form an infinite set, coupled by the non-zero values of $G(\kappa'', \kappa'; m_j'')$. It can be shown [83], that this occurs for each m_j between,

1. $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$
2. l, j and $l \pm 2, j \pm 1$

If 2 is neglected (it can be shown that this is reasonable if B varies slowly in space) then the infinite set reduces to just four coupled equations. As before, the resulting wavefunctions must then be matched to the free space solutions at the potential boundary,

$$\Psi^{\kappa m} = \sum_{\nu(=\kappa_1 \kappa_2)} a_{\kappa\nu}^{m_j} \begin{bmatrix} g_{\kappa_1\nu}^{m_j} \\ i f_{\kappa_1\nu}^{m_j} \\ g_{\kappa_2\nu}^{m_j} \\ i f_{\kappa_2\nu}^{m_j} \end{bmatrix} = \Psi_0^{\kappa m} = \begin{bmatrix} g_{0\kappa_1\kappa}^{m_j} \\ i f_{0\kappa_1\kappa}^{m_j} \\ g_{0\kappa_2\kappa}^{m_j} \\ i f_{0\kappa_2\kappa}^{m_j} \end{bmatrix} \tag{4.33}$$

for each value of κ, i.e κ_1, κ_2. The g_0 and f_0 are the free space radial functions, containing the t matrices between the different κ states, κ_1, κ_2.

Eliminating the coefficients $a_{\kappa\nu}^{m_j}$ produces expressions for the corresponding t matrices, i.e $t_{\kappa_1\kappa_2}$ etc [78] . Unlike the non-relativistic case the t matrices have a m_l dependence (through m_j). It is sometimes easier to visualise the effects of the t matrices in the l, m, m_s representation rather than the κ, m_j representation. The two are linked [78] via Clebsch-Gordan coefficients,

$$t_{l,m_j-m_s,m_s;l',m_j-m_s',m_s'} = \sum_{\kappa\kappa'} C_{\kappa m_j}^{m_s,m_j-m_s} t_{\kappa\kappa'}^{m_j}(\varepsilon) C_{\kappa' m_j}^{m_s',m_j-m_s'} \tag{4.34}$$

If the coupling between l, j is neglected then the t matrix becomes,

$$t_{l,m,m_s;l',m',m_s'} = t_{l,m,m_s;l',m+m_s-m_s',m_s'} \delta_{ll'} \delta_{m,m+m_s'-m_s} \tag{4.35}$$

So far the case has been considered for scattering off a potential with the magnetic component orientated along the axis of quantization, $\hat{\mathbf{z}}$. We now consider the situation where the magnetic component is orientated along an arbitrary direction, $\hat{\mathbf{z}}'$. Therefore we need to relate the t matrix in the local frame (B^{eff} along $\hat{\mathbf{z}}$) to that in the rotated frame (B^{eff} along $\hat{\mathbf{z}}'$). Figure (4.2) demonstrates the relation of the original to the rotated frame. The effect of this rotation on the spin and angular eigenfunctions, Y_l^m and $X_s^{m_s}$, is as in [84],

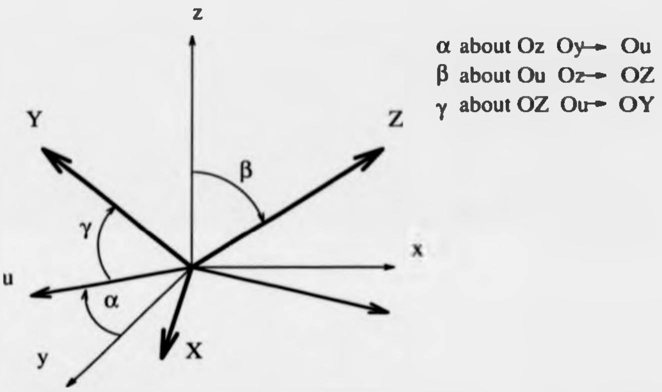

Figure 4.2: *Definition of the Euler angles used in rotating to a new local frame.*

$$Y_l^m(\hat{r}') = \sum_{m'} R^l_{mm'}(\theta) Y_l^{m'}(\hat{r}) \tag{4.36}$$

$$X^{m_s}(\sigma') = \sum_{m_s'=\pm\frac{1}{2}} R^{\frac{1}{2}}_{m_s m_s'}(\theta) X^{m_s'}(\sigma) \tag{4.37}$$

giving

$$\bar{t}_{l,m,m_s;l,m',m_s'} = \sum_{m''m'''m_s''m_s'''} R^l_{mm''}(\theta)[R^{\frac{1}{2}}_{m_s m_s''} t_{l,m'',m_s'';l,m''',m_s'''} R^{\frac{1}{2}}_{m_s''' m_s'}] R^l_{m'''m'}(\theta) \tag{4.38}$$

where θ corresponds to the Euler angles, α, β, γ, and $R^l_{mm'}(\theta)$, $R^{\frac{1}{2}}_{m_s m_s'}$ are the rotation operators, as in Messiah [84] .

4.2.3 Multiple-site scattering

The step now is to use the concepts of the Green's function approach to single site scattering and apply them to the case of many sites. The multiple site configurations used contain no overlap, i.e a cluster of independent potentials. The problem can be approached in a number of ways, either the Green's function can be formulated in terms of the total potential of the system or equivalently, in terms of the total T matrix. The T matrix can be expanded in terms of the individual site t matrices by defining excitation amplitudes [81] or in terms of a Scattering path operator [85]. Here the latter method is used.

The Scattering path operator is defined as,

$$\tau^{ij}(\varepsilon) = \mathbf{t}_i \delta_{ij} + \sum_{k \neq i} \mathbf{t}_i \mathbf{G}_0^{ik}(\varepsilon) \tau^{kj}(\varepsilon) \tag{4.39}$$

where matrix elements of t_i are similar to those of the t matrix defined earlier, except that now the potential is centred at R_i and not at the origin. The Scattering operator approach can be explained as follows, the t_i matrix generates the scattered wave from an incident wave at a particular site i. Therefore τ^{ij} acting on an incident wave at R_i creates all the scattering from that site. This can be seen from equation (4.39). The first term produces the direct scattering, the sum term includes all the effects from all the other sites. Therefore $\sum_{ij} \tau^{ij}$ produces the total scattering from the cluster of potentials, and hence is equivalent to the total T matrix.

This method allows a solution to be found for the multiple site problem in terms of t_i, the solution to the single site case. The information about the potential at each site is contained in the t matrix, the $\mathbf{G}_0^{ij}(\varepsilon)$ are independent of the potential, they describe the spatial arrangement of the scattering sites and are known as the structure factors. As mentioned earlier, the scattering potentials do not overlap, this is reflected in the notation

$$G^{ij}_{L,L'} = \; < i, L \mid \mathbf{G}_0^{ij}(\varepsilon) \mid j, L' > \quad i \neq j \tag{4.40}$$

$$G^{ij}_{L,L'} = \qquad 0 \qquad i = j \tag{4.41}$$

Neglecting the effects of spin, it can be shown [85] that the on energy shell components of equation (4.39) are given by,

$$\tau^{ij}(\varepsilon)_{LL'} = t_l(\varepsilon)^i \delta_{ij}\delta_{ll'} + \sum_{k\neq i}\sum_{L''} t_l^k(\varepsilon) G_{LL''}(R_i - R_k;\varepsilon)\tau^{kj}_{L''L'}(\varepsilon) \tag{4.42}$$

where $G_{LL''}(R_i - R_k;\varepsilon)$ are the structure factors and are related to the Green's functions defined earlier. As with the single site case, it is possible to produce an expression for the integrated density of states. Pre-multiplying equation (4.39) by $\mathbf{t}_i^{-1}$ gives,

$$\sum_k (\mathbf{t}_i^{-1}(\varepsilon)\delta_{ik} - \mathbf{G}_0^{ik}(\varepsilon))\tau^{kj} = \delta_{ij} \tag{4.43}$$

For a regular crystalline array of scatterers, taking the Fourier transform of equation (4.43),

$$\tau_{LL'}(q,\varepsilon) = [(t^{-1}(\varepsilon) - G_0(q;\varepsilon))^{-1}]_{LL'} \tag{4.44}$$

T (and τ) generate the scattered waves from the incident plane waves, so therefore if $\tau(\varepsilon)$ diverges this will correspond to scattered waves existing without incident waves, i.e allowed energy states. Equation (4.44) will diverge if,

$$|t_l^{-1}(\varepsilon) - G_{0LL'}(q;\varepsilon)| = 0 \tag{4.45}$$

where the determinant is over the angular momentum, l. Equation (4.45) arises from the definition of matrix inversion, and is the well known KKR condition for an energy band. It can be shown [85] , that the real space integrated density of states is given by,

$$N(\varepsilon) = -\frac{1}{\pi} Im \ln \| t_{i,l}^{-1}(\varepsilon)\delta_{ij}\delta_{ll'} - G_{LL'}(R_i - R_k;\varepsilon)\| \tag{4.46}$$

where the determinant is over l and the site indices.

4.3 Magnetic impurity calculations

The starting point for the impurity calculations is a relativistic treatment of an inhomogeneous electron gas which can be accomplished using a generalisation of Density Functional theory as introduced in chapter 1.

Using the relativistic, spin density functional formalism together with the local density approximation, the total energy of a system of interacting electrons is given by,

$$\begin{aligned} E[n,\mathbf{m}] &= \int^{\varepsilon_F} d\varepsilon\varepsilon n(\varepsilon) - e^2/2\int\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad - \int d\mathbf{r}(\frac{\delta E^R_{xc}}{\delta n(\mathbf{r})}n(\mathbf{r}) - \frac{\delta E^R_{xc}}{\delta \mathbf{m}(\mathbf{r})}\cdot\mathbf{m}(\mathbf{r})) + E^R_{xc}[n,\mathbf{m}] \end{aligned} \tag{4.47}$$

where $n(\varepsilon)$ is the Kohn-Sham single particle density of states and the magnetisation $\mathbf{m}(\mathbf{r})$ is oriented according to the directions $\{\mathbf{n}_i\}$ associated with the scattering potentials at positions indexed i, ε_F is the Fermi energy.

As stated earlier, the magnetic anisotropy energy can be calculated as just the difference between the single particle energies of two systems, identical except for the orientations of the moments, which are described fully by the t matrices. Therefore, in the notation used so far the anisotropy energy is given by,

$$\Delta E_a \approx E[\mathbf{n}^1_i] - E[\mathbf{n}^2_i] \tag{4.48}$$

$$= \int^{\varepsilon_{F1}} \varepsilon n_1(\varepsilon)d\varepsilon - \int^{\varepsilon_{F2}} \varepsilon n_2(\varepsilon)d\varepsilon \tag{4.49}$$

where $n_1(\varepsilon)$ and $n_2(\varepsilon)$ are the single particle densities of states with potentials whose magnetic components are directed according to the sets of unit vectors $\{\mathbf{n}^1_i\}$ and $\{\mathbf{n}^2_i\}$ respectively. ε_{F1}, ε_{F2} are the corresponding Fermi energies such that $\int^{\varepsilon_{F1}} n_1(\varepsilon)d\varepsilon = \int^{\varepsilon_{F2}} n_2(\varepsilon)d\varepsilon = N$, the total number of electrons in the system. Using $\int^{\varepsilon_F} \varepsilon n(\varepsilon)d\varepsilon = N\varepsilon_F - \int^{\varepsilon_F} N(\varepsilon)d\varepsilon$ it can be seen that

$$\Delta E_a \approx -\int^{\varepsilon_{F1}}(N_1(\varepsilon) - N_2(\varepsilon))d\varepsilon + O(\varepsilon_{F1} - \varepsilon_{F2})^2 \tag{4.50}$$

The Lloyd formula [81] for the integrated density of states $N(\varepsilon)$ can be modified to deal with the case of electrons moving relativistically through a system of potentials, each with their magnetic components orientated along a different set of directions $\{\mathbf{n}_i\}$.

$$N(\varepsilon) = N_0(\varepsilon) - 1/\pi Im \ln \|t^{-1}(\varepsilon) - G^0(\varepsilon)\| \tag{4.51}$$

given in matrix notation (the angular momentum etc. indices have been suppressed). $N_0(\varepsilon)$ describes the free electron density of states. Therefore, the energy difference between two orientations is given by,

$$\Delta E_a \approx (1/\pi) Im \int^{\varepsilon_{F1}} (ln\|1 - t\{\mathbf{n}_i^2\} \cdot G^0\| - ln\|1 - t\{\mathbf{n}_i^1\} \cdot G^0\|) d\varepsilon \tag{4.52}$$

Relativistic multiple scattering puts spin-orbit coupling on a par with spin polarisation unlike many theories of magnetocrystalline anisotropy which treat spin-orbit coupling as a perturbation [86], [87]. Such approaches have been reviewed by [49], [50], [88].

4.3.1 2-site calculation

Staunton et al. [77] applied this formalism to the case of two magnetic impurity potentials embedded in a non-interacting relativistic jellium, used to model a nobel metal host. They showed how magnetic anisotropic effects could arise as a function of both the orientation of the moments together with the relative positions of the impurities.

Examining equation (4.52), we see that the interaction energy for the two site case is given by,

$$\begin{aligned} E_{12} &= (1/\pi) Im \int^{\epsilon_F} d\epsilon \ln \|1 - t_i \cdot G^0\| & (4.53) \\ &= (1/\pi) Im \int^{\epsilon_F} d\epsilon \ln \left\| \begin{array}{cc} 1 & -t_1 G_{12} \\ -t_2 G_{21} & 1 \end{array} \right\| & (4.54) \end{aligned}$$

where the determinant is over site, angular momentum and spin. In the work of Staunton [77] the site determinant was evaluated in the limit of large impurity separation distances, in this region equation (4.53) has the form,

$$E_{imp} = (1/\pi) Im \int^{\epsilon_F} \sum_{\Lambda\Lambda'\Lambda''\Lambda'''} t^{1}_{\Lambda\Lambda'} G^{12}_{\Lambda'\Lambda''} t^{2}_{\Lambda''\Lambda'''} G^{21}_{\Lambda'''\Lambda} \tag{4.55}$$

where $\Lambda = l, m_l, m_s$. This was evaluated numerically for a number of impurity potentials, their magnetic components orientated in various directions. As well as the familiar oscillating RKKY interaction between the impurities they also found that the anisotropy energies, the difference between $E_{\uparrow\uparrow}$ and $E_{\rightarrow\rightarrow}$ for example, also oscillated. However, the magnitude of such anisotropy energies was small, of the order of 10^{-6} Rydbergs. An analytic form for the anisotropy energy was produced,

$$E_{12} = \sum_{n_1,n_2,n_3}^{2l_{max}} b_{n_1,n_2,n_3} \cdot [\hat{R}_{12} \cdot \hat{s}_1 \hat{R}_{12} \cdot \hat{s}_2]^{n_1} [\hat{R}_{12} \cdot (\hat{s}_1 \times \hat{s}_2)]^{2n_2} [(\hat{R}_{12} \cdot \hat{s}_1)^2 - (\hat{R}_{12} \cdot \hat{s}_2)^2]^{n_3} \tag{4.56}$$

where $\hat{s}_1$,$\hat{s}_2$ are unit vectors specifying the orientations of the impurities' magnetic moments and $\mathbf{R}_{12}$ is the vector connecting them. $l_{max} = 2$ for transition metal impurities and $l_{max} = 3$ for rare earth impurities (although the approximation used that only the spin part of the current was retained is no longer really justified). The coefficient b_{n_1,n_2,n_3} depends only on the relative orientation of $\hat{s}_1$ and $\hat{s}_2$ and the distance R_{12} between the two impurities. Both uniaxial and unidirectional magnetic anisotropic effects are contained in equation (4.56), although in the case of two identical impurities only uniaxial terms remain ($n_3 = 0$).

4.3.2 3-site calculation

On adding a third, non-magnetic, impurity these anisotropic effects can be enhanced, as shown by Levy and Fert [75] with their model calculations. In the non-relativistic limit $n_1 = n_2 = n_3 = 0$ and the coefficient b_{000} contains the usual

RKKY term varying as $cos(2k_F R_{12})\hat{s}_1 \cdot \hat{s}_2 / R_{12}^3$ when the impurities are separated by a large distance.

In the work published [89], the formalism developed in the papers of Staunton [77], [79], was generalised for the case of three impurities, two with magnetic components and the third, a heavy strong spin-orbit scatterer. The exact interaction expression was evaluated, valid at all impurity separation distances, unlike the work of Staunton et al [79] where all three impurities were assumed to be far apart. The purpose of this work was to investigate further the form of the anisotropic interactions and obtain a measure their magnitude , in particular the applicability of the DM interaction of [75] was investigated. Numerical calculations were carried out using two magnetic iron impurities together with a non-magnetic platinum atom, embedded in a non-interacting electron gas. This model system was used to extract the qualitative nature of the magnetic anisotropy of noble metals alloyed with small concentrations of magnetic metals. It should be noted that this multiple scattering formalism can be extended to a more accurate description of such impurity systems [90].

4.3.3 Results

By placing the platinum impurity at the origin it is possible to define vectors $\hat{R}_1$ and $\hat{R}_2$ defining the positions of the two iron impurities. This can be seen in figure (4.3). Also vectors $\hat{s}_1$, $\hat{s}_2$ define the orientations of the effective magnetic moments at the two iron sites.

The DM type interaction can then be written as,

$$H_{DM} = A(\hat{s}_1 \cdot \hat{s}_2, \hat{R}_1 \cdot \hat{R}_2)((\hat{R}_1 \times \hat{R}_2) \cdot (\hat{s}_1 \times \hat{s}_2)) \qquad (4.57)$$

as shown in [75]. The coefficient A depends upon the relative orientations of the spins as well as the positions of the three impurities. A range of configurations was examined in order to explore the nature of the interactions including the range

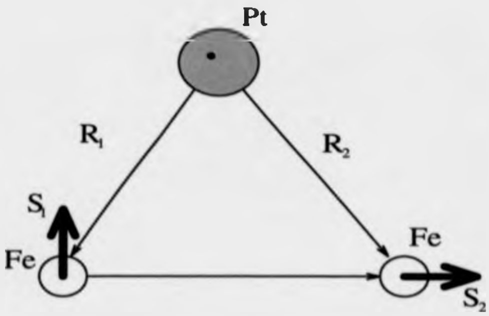

Figure 4.3: *The geometry of the system under investigation.*

of validity of equation (4.57). In order to reduce the possible combinations, two cases were focussed on.

DM-type interaction

Figures (4.5)-(4.6) shows the change in the interaction caused by varying the orientation of the magnetic moments with respect to the plane of the three atoms keeping the relative orientation of the moments fixed, perpendicular to each other. This situation is demonstrated in figure (4.4), the separation distances are in atomic units (a.u). The usual DM interaction should show a simple cosine variation with respect to the moments being rotated. Figure (4.5a) corresponds to the iron impurities being separated by a distance equivalent to two lattice spacings in a FCC crystal and the platinum atom is situated at a nearest neighbour to one of the magnetic impurities. This anisotropic effect is measured on the scale of an effective "exchange" interaction (the difference in energy between the configurations of the two moments being aligned and anti-parallel). Figure (4.5b) describes a similar situation but now the two iron atoms are nearest neighbours. As shown in this example, the anisotropy can in some circumstances be on the same scale as the exchange energy and have a rough DM functional form. In other

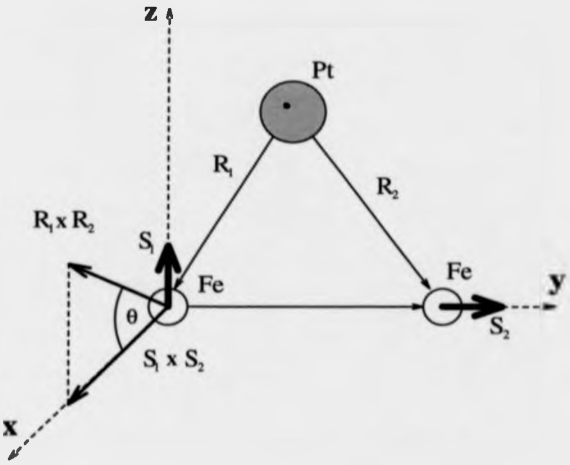

Figure 4.4: *The impurity rotation of angle θ for DM-type interaction.*

cases it can be smaller and deviate significantly from this. Figures (4.6c)-(4.6e) illustrate some of the anisotropy energies obtained for particular configurations, each with various values for $\mathbf{R}_1, \mathbf{R}_2$ and $\mathbf{R}_{12}$. Certain arrangements also show a RKKY like oscillating form for the anisotropy energy as a function of both magnetic and non-magnetic impurity separation distances. It was also noted that the anisotropy can change dramatically when the platinum impurity no longer lies in the plane which bisects and is perpendicular to the vector $\mathbf{R}_{12}$ joining the two iron atoms, this is illustrated by figures (4.6c) and (4.6d).

Non-DM interaction

The figure (4.8) shows an anisotropy not contained in a DM type expression, i.e that $(\hat{R}_1 \times \hat{R}_2) \cdot (\hat{s}_1 \times \hat{s}_2)$ is fixed and the magnetic moments are rotated about the axis $\hat{s}_1 \times \hat{s}_2$. The geometry of such a rotation is shown in figure (4.7). Again the relative orientation of the moments is fixed, and a true DM interaction will be zero for all rotations of the spins about $\hat{s}_1 \times \hat{s}_2$. The form of the anisotropy

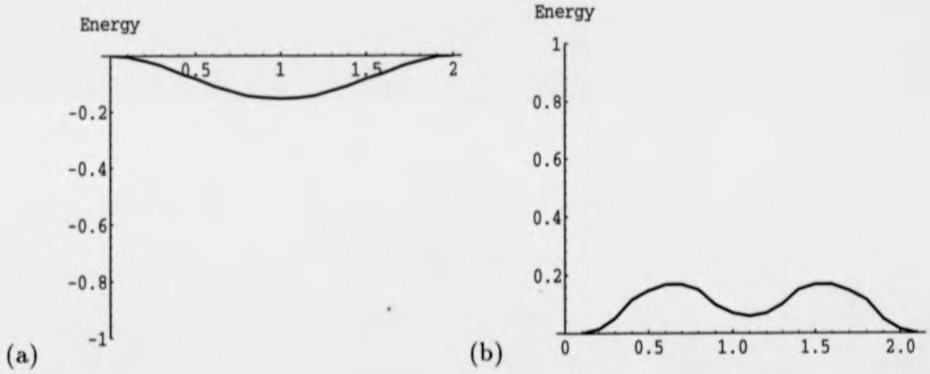

Figure 4.5: *DM type anisotropy energies, measured on the scale of an effective exchange interaction, as θ ranges from 0 to 2π. a) R1=2.8 a.u, R2=2.0 a.u, R12=2.0 a.u, b) R1=1.4 a.u, R2=2.0 a.u, R12=1.4 a.u*

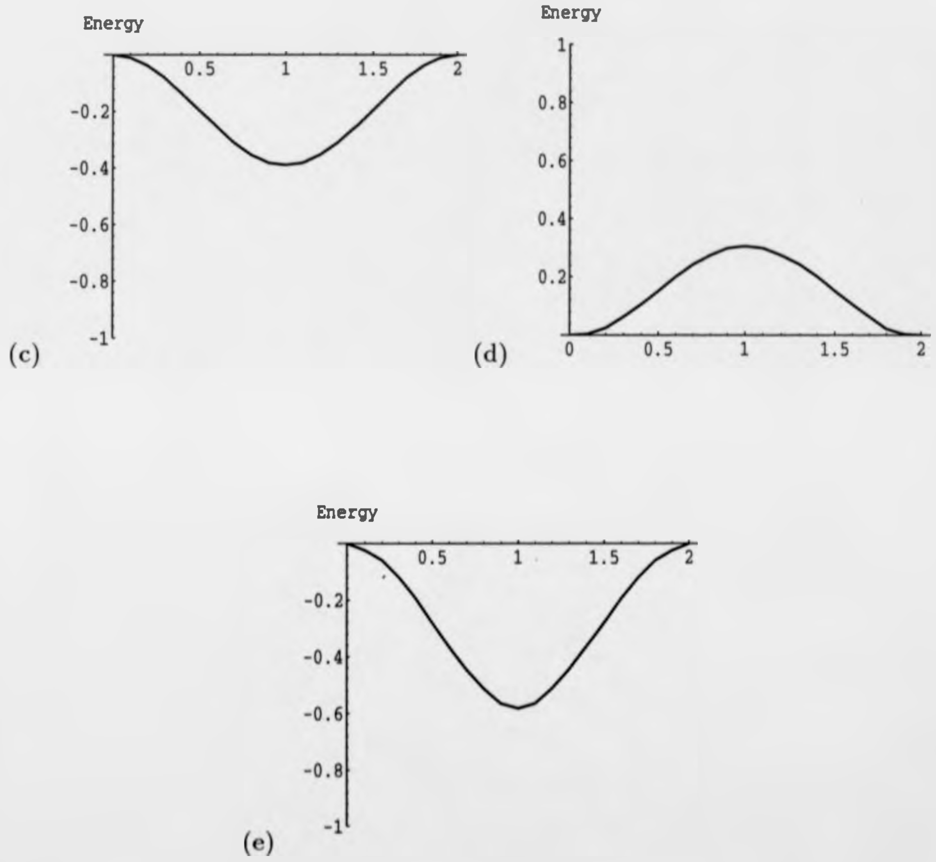

Figure 4.6: *DM type anisotropy energies, measured on a scale of an effective exchange energy, as θ increases from* 0 *to* 2π. *c) R1=2.8* a.u, *R2=1.64* a.u, *R3=2.45* a.u, *d) R1=2.8* a.u, *R2=2.45* a.u, *R12=1.64* a.u, *e) R1=2.8* a.u, *R2=1.4* a.u, *R12=1.4* a.u

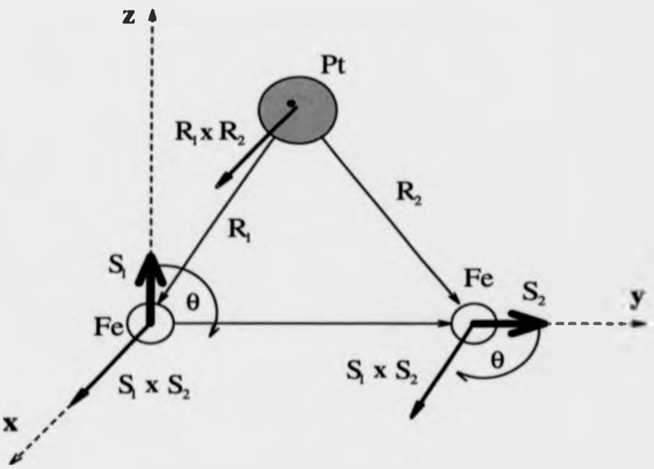

Figure 4.7: *The rotation for non-DM type interaction.*

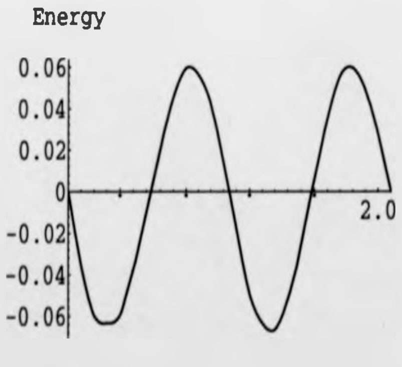

Figure 4.8: *Non-DM type anisotropy energy, measured on a scale of an effective exchange energy, as θ increases from* 0 *to* 2π.

energy suggests a pseudo-dipolar effect, These anisotropy energies are typically an order of magnitude smaller than those exemplified by figures (4.6a)-(4.6e). As with the previous results, the anisotropy energies are measured on a scale of an effective exchange interaction.

4.3.4 Conclusion

A generalisation of the impurity scattering formalism was used to investigate the anisotropic effects of a heavy, non-magnetic atom on the interaction between two magnetic impurities. The formalism allows the calculation of the interaction energy as a function of the relative positions of the impurity scatterers and orientations of their moments. It can also be extended to more realistic calculations. It was found that the anisotropy can be fitted to a DM form in some cases, particularly at large impurity separation distances, however in some configurations where the impurities are fairly close, i.e nearest or second nearest neighbours, then the anisotropy is not purely of this type and contains a pseudo-dipolar component. Remarkably the magnitudes of the anisotropy energies of particular configurations were found to be on the same scale as an appropriate effective exchange energy. In work by Jagannathan [91], he considered the effects of multiple scattering off spin-orbit impurities in a dilute magnetic spin-glass. He found the the anisotropic interactions which were produced were of longer range than usually proposed. A later paper [92], suggested that at certain impurity separation distances then the DM interaction could be of equal strength as a effective exchange interaction.

The evaluation of these anisotropic interactions between magnetic impurities suggests that the multiple scattering approach to the solution of the single particle equations is capable of calculating anisotropy energies accurately and also that, although such energies are very small, numerical investigations are possible. The next chapter takes the relativistic multiple scattering formalism and attempts to investigate the effects of anisotropy on the magnetic excitations of an itinerant system.

Chapter 5

Anisotropy and excitations

In the preceding chapters the ideas leading to a first principles treatment of interacting electrons in an itinerant system were introduced. The concepts behind the excitations of such systems were also examined, leading to an expression for the 'dynamic susceptibility', the poles of which indicated the existence of Stoner excitations and spin waves. The origin and role of magnetic anisotropy in electronic systems was also discussed, in particular, a relativistic treatment of Density Functional Theory was shown to offer a route towards the calculation of magnetic anisotropy energies. The effects of anisotropy on the excitation spectrum of a simple, localised, spin system were demonstrated, namely the creation of a gap at $\mathbf{q} = 0$. Chapter 4 indicated how a multiple-scattering theoretical solution to the single particle equations could be used to calculate anisotropic magnetic interactions in dilute magnetic alloys.

We now wish to turn our attention to the main purpose of the thesis, an investigation into the effects of anisotropy on the long wavelength excitations of an itinerant magnetic system. As stated earlier, the approach needs to be relativistic in nature to capture the full effect of any spin-orbit or other anisotropic interactions.

5.1 Dynamic susceptibility

As introduced in chapter 2, the logical approach would be to set up a relativistic two-particle Greens function, i.e. a dynamic susceptibility. The starting point for such a scheme is a linear response treatment of the Kohn-Sham-Dirac density functional Hamiltonian, as described earlier for the non-relativistic case.

The aim of this work is to investigate the long wavelength excitations via some form of local density approximation, therefore we consider the perturbation of the time-independent density functional equations, which describe the equilibrium state, by a time-dependent transverse external magnetic field, $\delta\mathbf{B}(\mathbf{r},t)$. The Hamiltonian, in relativistic units, together with the self consistent expressions for the charge and magnetic densities in a Greens function approach, are given by,

$$[c\alpha\cdot\mathbf{p}+\beta mc^2+\hat{\mathbf{1}}V^{eff}[n,\mathbf{m}]+\beta\sigma\cdot\mathbf{B}^{eff}[n,\mathbf{m}]-i\hbar\frac{\delta}{\delta t}]\mathbf{G}(\mathbf{r},\mathbf{r}':t,t')=\delta(r-\mathbf{r}')\delta(t-t') \tag{5.1}$$

$$\begin{aligned}
n(\mathbf{r},t) &= Tr\;\mathbf{G}(\mathbf{r},\mathbf{r}':t,t+\epsilon)_{\epsilon\to 0} && (5.2)\\
\mathbf{m}(\mathbf{r},t) &= Tr\;\beta\sigma\mathbf{G}(\mathbf{r},\mathbf{r}':t,t+\epsilon)_{\epsilon\to 0} && (5.3)\\
V^{eff}(\mathbf{r},t) &= V(\mathbf{r},t)+\delta E^{H}/\delta n(\mathbf{r},t)+\delta E^{R}_{xc}/\delta n(\mathbf{r},t) && (5.4)\\
\mathbf{B}^{eff}(\mathbf{r},t) &= -(\mathbf{B}^{ext}(\mathbf{r},t)+\delta E^{R}_{xc}/\delta\mathbf{m}(\mathbf{r},t)) && (5.5)
\end{aligned}$$

where α and β are the Dirac matrices, σ is the corresponding 4×4 Pauli spin matrices vector and the effective field, $\mathbf{B}^{eff}(\mathbf{r},t)$, couples to the spin current only, as described earlier in Chapter 2. E^{R}_{xc} is the relativistic form of the exchange and correlation functional. The trace is carried out once $\mathbf{G}$ has been evaluated in an appropriate basis.

The Greens function, $\mathbf{G}(\mathbf{r},\mathbf{r}':t,t')$ is now given by,

$$\mathbf{G}=\begin{pmatrix} G_{11} & G_{12}\\ G_{21} & G_{22}\end{pmatrix} \tag{5.6}$$

and each component is a 2×2 matrix in spin-space. Following the same route as in the non-relativistic case, the starting point is the operator definition of the ground state Greens function,

$$\mathbf{H_0 G}_{gs} = \hat{\mathbf{1}} \tag{5.7}$$

and the change, to first order, in the Greens function due to a perturbing transverse magnetic field is,

$$\delta\mathbf{G} = -\mathbf{G}_{gs}\delta\mathbf{H}\mathbf{G}_{gs} \tag{5.8}$$

where $\delta\mathbf{H}$ includes changes to the effective potential, V^{eff}, and magnetic field, $\mathbf{B}^{eff}$. The resultant change in charge and magnetic densities due to the perturbation are given by,

$$\begin{aligned}
\delta n(\mathbf{r},t) &= Tr\ \delta\mathbf{G}(\mathbf{r},\mathbf{r}' : t, t+\epsilon) && (5.9)\\
&= Tr\ (-\mathbf{G}_{gs}\left[1\Delta V^{eff} + \beta\sigma\cdot(\delta\mathbf{B}^{ext} + \Delta\mathbf{B}^{eff})\right]\mathbf{G}_{gs}) && (5.10)\\
\delta\mathbf{m}_i(\mathbf{r},t) &= Tr\ \beta\sigma_i\delta\mathbf{G}(\mathbf{r},\mathbf{r}' : t, t+\epsilon) && (5.11)\\
&= Tr\ \beta\sigma_i(-\mathbf{G}_{gs}\left[\hat{\mathbf{1}}\Delta V^{eff} + \beta\sigma\cdot(\delta\mathbf{B}^{ext} + \Delta\mathbf{B}^{eff})\right]\mathbf{G}_{gs}) && (5.12)
\end{aligned}$$

where,

$$\begin{aligned}
\Delta V^{eff} &= -\left[\int \frac{\delta n(r',t)}{|r-r'|}dr' + \frac{\delta V_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]}{\delta n(\mathbf{r},t)}\delta n(\mathbf{r},t)\right.\\
&\qquad \left. + \frac{\delta V_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]}{\delta\mathbf{m}(\mathbf{r},t)}\cdot\delta\mathbf{m}_i(\mathbf{r},t)\right] && (5.13)
\end{aligned}$$

$$\Delta\mathbf{B}^{eff} = \delta n(\mathbf{r},t)\frac{\delta\mathbf{V}^{s}_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]}{\delta n(\mathbf{r},t)} + \sum_i \delta m_i \frac{\delta\mathbf{V}^{s}_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)]}{\delta\mathbf{m}(\mathbf{r},t)} \tag{5.14}$$

and,

$$\begin{aligned}
V_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)] &= \delta E^{R}_{xc}/\delta n(\mathbf{r},t) && (5.15)\\
\mathbf{V}^{s}_{XC}[n(\mathbf{r},t),\mathbf{m}(\mathbf{r},t)] &= \delta E^{R}_{xc}/\delta\mathbf{m}(\mathbf{r},t) && (5.16)
\end{aligned}$$

Our approach is based upon a perturbation of the equilibrium state, in using the Local Density Approximation we use the time independent exchange correlation energy, E^{r}_{xc}, calculated from a homogeneous electron gas at the equilibrium ground state charge density, $n_0(r)$. Also E^r_{xc} will only depend upon the magnitude of the ground state magnetisation, which is taken to define a $\mathbf{z}$ axis. As a result of introducing the LDA, the effective field, $\mathbf{B}^{eff}$, will just rotate, its magnitude remains constant. Therefore ΔV^{eff} and $\Delta\mathbf{B}^{eff}$ become,

$$\begin{aligned}\Delta V^{eff} &= -\left[\int \frac{\delta n(r',t)}{|r-r'|}dr' + \left.\frac{\delta V_{XC}[n(\mathbf{r}),|\mathbf{m}(\mathbf{r})|]}{\delta n(\mathbf{r})}\right|_{n=n_0,\mathbf{m}=\mathbf{z}} \delta n(\mathbf{r},t)\right. \\ &\quad \left. + \left.\frac{\delta V_{XC}[n(\mathbf{r}),|\mathbf{m}(\mathbf{r})|]}{\delta|\mathbf{m}(\mathbf{r})|}\right|_{n=n_0,\mathbf{m}=\mathbf{z}} \delta m_z(\mathbf{r},t)\right] \qquad (5.17) \\ \Delta\mathbf{B}^{eff} &= -\delta n(\mathbf{r},t)\frac{\delta\mathbf{V}^{s}_{XC}[n(\mathbf{r}),|\mathbf{m}(\mathbf{r})|]}{\delta n(\mathbf{r},t)} + \left.\frac{\delta E^R_{xc}}{\delta|\mathbf{m}(\mathbf{r})|}\right|_{\mathbf{m}=\mathbf{z}} \delta\mathbf{m}(\mathbf{r}) \qquad (5.18)\end{aligned}$$

By writing the spin components of G_{11}, G_{12} etc. explicitly as,

$$G_{11} = \begin{pmatrix} G^{11}_{\uparrow\uparrow} & G^{11}_{\uparrow\downarrow} \\ G^{11}_{\downarrow\uparrow} & G^{11}_{\downarrow\downarrow} \end{pmatrix} \qquad (5.19)$$

and evaluating the spin algebra contained in equations (5.10)-(5.12) then a set of coupled equations involving δn, δm_x, δm_y and δm_z are produced. These are simplified by forming the linear combinations, $\delta m_+ = \delta m_x + i\delta m_y$ and $\delta m_- = \delta m_x - i\delta m_y$ leading to the following equations for each of the components of $\mathbf{G}$, i.e. G_{11}, G_{12} etc,

$$\begin{aligned}\delta n &= -\Big[G_{\uparrow\uparrow}(\Delta V^{eff} + B^{eff}_z)G_{\uparrow\uparrow} + G_{\downarrow\uparrow}(\Delta V^{eff} + B^{eff}_z)G_{\uparrow\downarrow} \\ &\quad + G_{\downarrow\downarrow}(\Delta V^{eff} - B^{eff}_z)G_{\downarrow\downarrow} + G_{\uparrow\downarrow}(\Delta V^{eff} - B^{eff}_z)G_{\downarrow\uparrow} \\ &\quad + G_{\uparrow\downarrow}(\Delta B^{eff}_x + i\Delta B^{eff}_y)G_{\uparrow\uparrow} + G_{\downarrow\downarrow}(\Delta B^{eff}_x + i\Delta B^{eff}_y)G_{\uparrow\downarrow} \\ &\quad + G_{\uparrow\uparrow}(\Delta B^{eff}_x - i\Delta B^{eff}_y)G_{\downarrow\uparrow} + G_{\downarrow\uparrow}(\Delta B^{eff}_x - i\Delta B^{eff}_y)G_{\downarrow\downarrow}\Big] \qquad (5.20)\end{aligned}$$

$$\begin{aligned}\delta m_z &= -\Big[G_{\uparrow\uparrow}(\Delta V^{eff} + B^{eff}_z)G_{\uparrow\uparrow} - G_{\downarrow\uparrow}(\Delta V^{eff} + B^{eff}_z)G_{\uparrow\downarrow} \\ &\quad - G_{\downarrow\downarrow}(\Delta V^{eff} - B^{eff}_z)G_{\downarrow\downarrow} + G_{\uparrow\downarrow}(\Delta V^{eff} - B^{eff}_z)G_{\downarrow\uparrow} \\ &\quad + G_{\uparrow\downarrow}(\Delta B^{eff}_x + i\Delta B^{eff}_y)G_{\uparrow\uparrow} - G_{\downarrow\downarrow}(\Delta B^{eff}_x + i\Delta B^{eff}_y)G_{\uparrow\downarrow} \\ &\quad + G_{\downarrow\downarrow}(\Delta B^{eff}_x + i\Delta B^{eff}_y)G_{\uparrow\downarrow} - G_{\downarrow\uparrow}(\Delta B^{eff}_x - i\Delta B^{eff}_y)G_{\downarrow\downarrow}\Big] \qquad (5.21)\end{aligned}$$

$$\begin{aligned}\delta m_{+} &= -2\Big[G_{\downarrow\uparrow}(\Delta V^{eff}+\Delta B_z^{eff})G_{\uparrow\uparrow}+G_{\downarrow\downarrow}(\Delta V^{eff}-\Delta B_z^{eff})G_{\downarrow\uparrow} \\ &\quad +G_{\downarrow\downarrow}(\Delta B_x^{eff}+i\Delta B_y^{eff})G_{\uparrow\uparrow}+G_{\downarrow\uparrow}(\Delta B_x^{eff}-i\Delta B_y^{eff})G_{\downarrow\uparrow}\Big] \quad (5.22)\end{aligned}$$

$$\begin{aligned}\delta m_{-} &= -2\Big[G_{\uparrow\uparrow}(\Delta V^{eff}+\Delta B_z^{eff})G_{\uparrow\downarrow}+G_{\uparrow\downarrow}(\Delta V^{eff}-\Delta B_z^{eff})G_{\downarrow\downarrow} \\ &\quad +G_{\uparrow\downarrow}(\Delta B_x^{eff}+i\Delta B_y^{eff})G_{\uparrow\downarrow}+G_{\uparrow\uparrow}(\Delta B_x^{eff}-i\Delta B_y^{eff})G_{\downarrow\downarrow}\Big] \quad (5.23)\end{aligned}$$

where $\delta n(\mathbf{r},t) =< \mathbf{r},t|\delta n|\mathbf{r},t >, \delta m_{+}(\mathbf{r},t) =< \mathbf{r},t|\delta m_{+}|\mathbf{r},t >$ etc.

These constitute a full set of coupled equations, and therefore we would try to make a suitable approximation to proceed further. In the non-relativistic case it was possible to show that the charge and magnetic densities could be decoupled and that the Local Density Approximation was consistent with the solution of the appropriate wave equation, however if we attempt to do this here we then encounter a number of difficulties. If the ground state magnetisation is calculated using equation (5.12) then it can be seen that it possesses δm_x and δm_y components. But in the derivation of the response equations, and in particular in the use of the local density approximation, we have assumed that the ground state magnetisation lies along the **z** axis. It would appear that the local density approximation is not consistent with solving the Kohn-Sham-Dirac equation. Possible solutions to this problem involve going further than the usual LDA, such as some form of gradient expansion, or introducing an explicit dependence of the energy functional on the orbital current, as suggested by Jansen [61].

In the light of this, it would seem reasonable that we should use a method which builds upon the advances made in the recent calculations of magnetocrystalline anisotropy energies, i.e. the anisotropy energy is obtained by allowing the magnetic moment to just rotate, its magnitude remaining constant. This, hopefully, would remove any inconsistencies arising from the coupling of charge and magnetic densities.

5.2 Landau equations

Due to the problems outlined in the previous section we now attempt an approach which arises from ideas originating in phenomenological models of magnetic anisotropy and current 'state of the art' first principles calculations. At this stage we say nothing about the type of magnetic ordering in this magnetic itinerant system, merely that a set of 'spins' or moments exist, and are orientated along a set of directions denoted by $\{\mathbf{n}_i\}$.

As introduced in the second chapter, the motion of an individual moment, experiencing a magnetic field $\mathbf{H}_i^{eff}$, is given by,

$$\frac{\delta \mathbf{n}_i}{\delta t} = \gamma \mathbf{n}_i \times \mathbf{H}_i^{eff} \tag{5.24}$$

The effective field at a site i can be expressed as the functional derivative of the total energy of the magnetic system with respect to the moment at that site,

$$\mathbf{H}_i^{eff} = -\frac{\delta \Omega}{\delta \hat{\mathbf{n}}_i} \tag{5.25}$$

where Ω is the total energy of the magnetic system and $\hat{\mathbf{n}}_i$ denotes the orientation of the moment at site i. Our aim is to use Ω calculated via a relativistic density functional theory.

Although this approach was originally used in a phenomenological sense the justification for its use in this situation, namely that of an itinerant magnet, is as follows. As we are interested in the long-wavelength, $\mathbf{q} \rightarrow 0$, region of the spin-wave spectrum, then the interacting conduction electrons which set up the effective magnetic moment at an atomic site, move between sites on a timescale much shorter than that in which the moments are rotated by any effective field due to exchange or anisotropic interactions. As the basis for the formalism is a linear response approach and therefore a small deviation and low energy situation, then the use of an equation of motion for the magnetic moment, equation (2.3), seems reasonable. We now look at how such an effective field experienced by the magnetic moment can be derived from a first principles scheme.

The energy of such a system of spins can be expressed in a scattering formalism, as shown in Chapter 4, and hence the change in the energy of the system due to a rotation of one of the 'spins', the effective field, can be produced. With the use of the 'force' theorem we can express $\delta\Omega$ as the difference between single particle energy states of a system with its 'spins' orientated along a set of directions and a system with one of the spins, at site i, rotated such that the change in its orientation is given by $\delta\hat{\mathbf{n}}_i$. Hence,

$$\delta\Omega = -\frac{1}{\pi}\int d\varepsilon\ Im\left(\ln\|\hat{t}^{-1}(\varepsilon) - G(\varepsilon)\| - \ln\|t^{-1}(\varepsilon) - G(\varepsilon)\|\right) \tag{5.26}$$

where $\hat{t}^{-1}$ corresponds to the system where the spin at site i has been rotated. In the scattering formalism the rotation of the moment or 'spin' at a site i corresponds to rotating only the t-matrix at that site, in operator form, $\hat{t}^{-1}(\varepsilon) = R\, t^{-1}(\varepsilon)\, R^{\dagger}$. This is due to that fact that all the information about the electrons interaction with the potential at the particular site is contained in the t-matrix, the physical positions of the scattering potentials are described by the structure factors.

Therefore under a local rotation at site i the change in energy becomes,

$$\begin{aligned}\delta\Omega &= -\frac{1}{\pi}\int d\varepsilon\ Im \\ &\quad \left(\ln\|(t^{-1}(\varepsilon) - G(\varepsilon))(\mathbf{1} + (t^{-1}(\varepsilon) - G(\varepsilon))^{-1}(R_i t^{-1}(\varepsilon) R_i^{\dagger} - t^{-1}(\varepsilon)))\|\right. \\ &\quad \left. - \ln\|t^{-1}(\varepsilon) - G(\varepsilon)\|\right)\end{aligned} \tag{5.27}$$

where the rotation $R_i t^{-1}(\varepsilon) R_i^{\dagger}$ acts only upon site i. Using the definition of the $\tau(\varepsilon)$ operator, equation (4.39) in site notation, reduces to,

$$\delta\Omega = -\frac{1}{\pi}\int d\varepsilon\ Im\left(\ln\|\hat{\mathbf{1}} + \tau_{ii}(\varepsilon)(R_i t_i^{-1}(\varepsilon) R_i^{\dagger} - t_i^{-1}(\varepsilon))\|\right) \tag{5.28}$$

Here, and in the following formalism, the angular momentum and spin indices have been suppressed. This expression can be simplified further using the matrix relationship,

$$Im \ln\|\mathbf{M}\| = Im Tr\ \ln \mathbf{M} \tag{5.29}$$

and a Taylor expansion of ln, as the second term in equation (5.28) will be small compared to unity, due to the fact that the deviations from the ground state orientations have been assumed to be small. This allows the change in energy to be expressed as

$$\delta\Omega = -\frac{1}{\pi}\int d\varepsilon \; ImTr \; \left(\tau_{ii}(R_i t_i^{-1} R_i^{\dagger} - t_i^{-1})\right) \tag{5.30}$$

It can be shown [84] that the operator R_i, corresponding to a rotation β about an axis $\hat{\mathbf{m}}_i$, can be expressed in terms of infinitesimal rotations,

$$R_i \simeq \hat{\mathbf{1}} - i\beta\hat{\mathbf{m}}_i \cdot \hat{\mathbf{J}} \tag{5.31}$$

where $\hat{\mathbf{J}}$ is the total angular momentum operator. If, after rotation, the original orientation $\mathbf{n}_i^0$ becomes $\mathbf{n}_i$ then an axis $\hat{\mathbf{m}}_i$ can be defined as,

$$\hat{\mathbf{m}}_i = \frac{\mathbf{n}_i^0 \times \mathbf{n}_i}{|\mathbf{n}_i^0 \times \mathbf{n}_i|} \tag{5.32}$$

with $|\mathbf{n}_i^0| = 1$. For rigid, infinitesimal rotations, $\mathbf{n}_i = \mathbf{n}_i^0 + \delta\mathbf{n}_i$, and $\beta \simeq |\delta\mathbf{n}_i|$ therefore,

$$\beta\hat{\mathbf{m}}_i \simeq \frac{\mathbf{n}_i^0 \times \delta\mathbf{n}_i}{|\mathbf{n}_i^0|} \tag{5.33}$$

The geometry of the rotation is shown in figure (5.1). The effects of the rotation operators can now be expressed,

$$R_i t_i^{-1}(\mathbf{n}^0) R_i^{\dagger} - t_i^{-1}(\mathbf{n}^0) = (\mathbf{1} - i\beta\hat{\mathbf{m}}_i \cdot \hat{\mathbf{J}}) t_i^{-1}(\mathbf{n}^0)(\mathbf{1} + i\beta\hat{\mathbf{m}}_i \cdot \hat{\mathbf{J}}) - t_i^{-1}(\mathbf{n}^0) \tag{5.34}$$

or keeping to first order,

$$\begin{aligned} R_i \; t_i^{-1}(\mathbf{n}^0) \; R_i^{\dagger} - t_i^{-1}(\mathbf{n}^0) &= -i(\beta\hat{\mathbf{m}}_i \cdot \hat{\mathbf{J}} t_i^{-1}(\mathbf{n}^0) - t_i^{-1}(\mathbf{n}^0)\beta\hat{\mathbf{m}}_i \cdot \hat{\mathbf{J}}) && (5.35) \\ &= -i[\beta\hat{\mathbf{m}}_{\mathbf{i}} \cdot \hat{\mathbf{J}}, t_i^{-1}(\mathbf{n}^0)] && (5.36) \\ &= -i[(\mathbf{n}_i^0 \times \mathbf{n}_i) \cdot \hat{\mathbf{J}}, t_i^{-1}(\mathbf{n}^0)] && (5.37) \end{aligned}$$

This allows the change in energy of the system to be written in terms of the relevant direction-vectors,

$$\delta\Omega = -\frac{1}{\pi}\int d\varepsilon \; ImTr \; \left(-i\tau_{ii}[(\mathbf{n}_i^0 \times \delta\mathbf{n}_i) \cdot \hat{\mathbf{J}}, t_i^{-1}(\mathbf{n}^0)]\right) \tag{5.38}$$

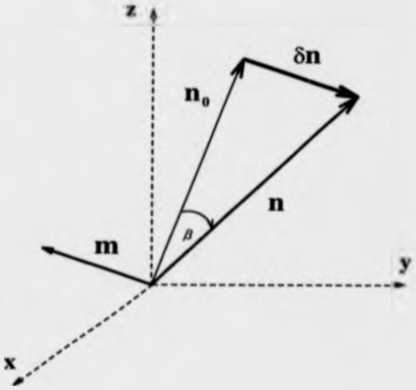

Figure 5.1: *The geometry of the rotation.*

Using the vector identity,

$$(\mathbf{a}\times\mathbf{b})\cdot\mathbf{c} = \mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) \tag{5.39}$$

then the effective field at site i experienced by a moment orientated along a direction $\mathbf{n}_i$, is given by,

$$\mathbf{H}_i^{eff} = -\frac{\delta\Omega}{\delta\hat{\mathbf{n}}_i} \tag{5.40}$$

$$= \frac{1}{\pi}\int d\varepsilon\ ImTr\left(i\tau_{ii}[(\mathbf{n}_i\times\hat{\mathbf{J}}, t_i^{-1}(\mathbf{n}_i)]\right) \tag{5.41}$$

It should be noted that the above is valid for any spin configuration $\{\mathbf{n}_i\}$, the electronic structure corresponding to such a 'spin' state is described by τ_{ii}.

5.2.1 Expansion of Ground State

So far nothing has been said about the state of the spin system described by τ_{ii}, only that a set of moments exist and their orientation is described by the set of unit vectors $\{\mathbf{n}_i\}$. As a spin-wave excitation is a collective event we should allow all of the spins of the system to respond, i.e. we need to make some form of expansion about a fixed state. In the spirit of linear response we should look for small deviations about the chosen ground state, i.e. expand the τ_{ii} thus,

$$\tau_{ii}(\mathbf{n}_1, \mathbf{n}_2, ...) \simeq \tau_{ii}(\mathbf{n}_1^0 + \delta\mathbf{n}_1, \mathbf{n}_2^0 + \delta\mathbf{n}_2, ...) \tag{5.42}$$

The type of spin system indicated by this expansion of τ_{ii} is shown in figure (5.2). Using the definition of the multiple scattering operator, τ_{ii}, an expansion can be made about a particular ground state, described by $\tau^0 = \tau(\mathbf{n}_1^0, \mathbf{n}_2^0, ...)$,

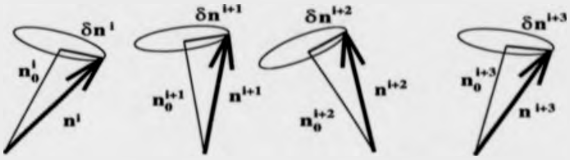

Figure 5.2: *The expansion of the original spin system.*

$$\begin{aligned}
\hat{\mathbf{1}} &\simeq \tau^{-1}(\mathbf{n}_1^0 + \delta\mathbf{n}_1, \mathbf{n}_2^0 + \delta\mathbf{n}_2, ...)\tau && (5.43)\\
&\simeq (\hat{t}^{-1} - G)\tau && (5.44)\\
&\simeq (t_0^{-1} + \Delta t^{-1} - G)(\tau^0 + \Delta\tau) && (5.45)
\end{aligned}$$

Keeping to first order, the change in τ becomes,

$$\Delta\tau = -\tau^0 \Delta t^{-1} \tau^0 \tag{5.46}$$

rewriting in terms of site indices,

$$\Delta\tau_{ii} = -\sum_j \tau^{ij}(\mathbf{n}_1^0, \mathbf{n}_2^0, ...)\Delta t_j^{-1} \tau^{ji}(\mathbf{n}_1^0, \mathbf{n}_2^0, ...) \tag{5.47}$$

where,

$$\begin{aligned}
\Delta t_j^{-1} &= t_j^{-1}(\mathbf{n}_j^0 + \delta\mathbf{n}_j) - t_j^{-1}(\mathbf{n}_j^0) && (5.48)\\
&= -i(\mathbf{n}_j^0 \times \delta\mathbf{n}_j) \cdot [\hat{\mathbf{J}}, t_j^{-1}(\mathbf{n}_j^0)] && (5.49)
\end{aligned}$$

Therefore, this allows the original τ_{ii} to be expressed,

$$\tau_{ii}(\mathbf{n}_1, \mathbf{n}_2, ...) \simeq \tau(\mathbf{n}_1^0, \mathbf{n}_2^0, ...) - \sum_j \tau^{ij}(\mathbf{n}_1^0, \mathbf{n}_2^0, ...)\Delta t_j^{-1} \tau^{ji}(\mathbf{n}_1^0, \mathbf{n}_2^0, ...) \tag{5.50}$$

This gives an expansion of the τ operator which describes a system of spins aligned along a set of directions, $\{\mathbf{n}_i\}$, in terms of small deviations, $\delta\mathbf{n}$ about the ground state directions, $\mathbf{n}_1^0, \mathbf{n}_2^0$ etc.

5.2.2 Spin-wave equations

The expansion about a particular ground state, equation (5.50), can be introduced into the vector equation for the effective field, equation (5.41). Using this expression in the Landau equation gives an equation of motion describing the behaviour of a magnetic moment at site i, orientated along a direction, $\mathbf{n}_i$,

$$\begin{aligned} \frac{\delta \mathbf{n}_i}{\delta t} &= \gamma \mathbf{n}_i \times \mathbf{H}_i^{eff} \\ &= \gamma \mathbf{n}_i \times \frac{1}{\pi} \int d\varepsilon \; ImTr \left(i\tau_{ii}[(\mathbf{n}_i \times \hat{\mathbf{J}}, t_i^{-1}(\mathbf{n}_i)] \right) \end{aligned} \tag{5.51}$$

where the τ_{ii} is replaced by the expansion given in equation (5.50). The trace in the above equation is evaluated once the operators have been expressed in an appropriate basis set, i.e the spin-angular eigenfunctions introduced in Chapter 4. In the linear regime, $\mathbf{n}_i = \mathbf{n}_i^0 + \delta\mathbf{n}_i$, then evaluating equation (5.51), keeping everything to first order in $\delta\mathbf{n}_i$ and using the linear response condition, $\mathbf{n}^0 \cdot \delta\mathbf{n} = 0$, as introduced in Chapter 2, gives,

$$\begin{aligned} \frac{\delta \mathbf{n}_i}{\delta t} &= \gamma \mathbf{n}_i \times \mathbf{H}_i^{eff} \\ &= \gamma \frac{1}{\pi} \int d\varepsilon \; ImTr \Big(i\tau_{ii}(\mathbf{n}_1^0, \mathbf{n}_2^0, ...)\mathbf{A}\,) \\ &\quad - (i \sum_j \tau^{ij}(\mathbf{n}_1^0, ...)(\delta\mathbf{n}_j \times \mathbf{n}_j^0) \cdot [\hat{\mathbf{J}}, t_j^{-1}(\mathbf{n}_j^0)] \tau^{ji}(\mathbf{n}_1^0, ...) \Big) \mathbf{B} \end{aligned} \tag{5.52}$$

where **A** and **B** are given by,

$$\begin{aligned} \mathbf{A} &= \left[(\mathbf{n}_i \cdot \mathbf{J})\mathbf{n}_i^0 + (\mathbf{n}_i^0 \cdot \mathbf{J})\delta\mathbf{n}_i - \mathbf{J}, t_i^{-1}(\mathbf{n}^0) - i[(\mathbf{n}_i^0 \times \delta\mathbf{n}_i) \cdot \mathbf{J}, t_i^{-1}(\mathbf{n}^0)] \right] \\ \mathbf{B} &= \left[(\mathbf{n}_i^0 \cdot \mathbf{J})\mathbf{n}_i^0 - \mathbf{J}, t_i^{-1}(\mathbf{n}^0) \right] \end{aligned} \tag{5.53}$$

This set of equations describes the spin-wave excitations as set up in a global frame, where the ground state magnetic moments lie along the directions $\{\mathbf{n}_i^0\}$. However it is possible to write a set of equations where each of the magnetic moments lie along a local $\mathbf{z}$ axis. This simplifies matters to a large extent, as in this situation, due to the requirement that the response is linear, the change in the orientation of the moment can be expressed as $\delta\mathbf{n} = (\delta n_x, \delta n_y, 0)$, i.e. the magnitude of the moment remains constant. The geometry of this situation is illustrated in figure (5.3).

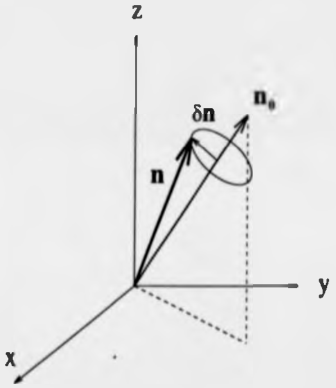

Figure 5.3: *Motion of a 'classical' spin about ground state position.*

The relationship of various quantities between the two frames is given in the table below,

$$\begin{array}{ccl}
\text{local} & & \text{global} \\
\hline\hline
\mathbf{z} & \rightarrow & \mathbf{n}^0 = R\;\mathbf{z}R^\dagger \\
(\delta n_x, \delta n_y, 0) & \rightarrow & (\delta n'_x, \delta n'_y, \delta n'_z) = R\;(\delta n_x, \delta n_y, 0)\;R^\dagger \\
\mathbf{J} & \rightarrow & \mathbf{J}' = R\;\mathbf{J}\;R^\dagger \\
t_i^{-1}(\mathbf{z}) & \rightarrow & t_i^{-1}(\mathbf{n}_i^0) = R\;t_i^{-1}(\mathbf{z})\;R^\dagger
\end{array} \qquad (5.54)$$

where the rotation operators, R and $R^\dagger$, describe the rotation from the local frame to the global frame. They have the same form as the rotation operators introduced earlier to deal with the case of scattering of a potential with a magnetic component not aligned along the **z** axis.

The purpose of this work is to investigate the effects of anisotropy on the low-lying excitations of a ferromagnet therefore we should choose the ground state to be the system in which the moments on all the sites are aligned, defining a local $\hat{\mathbf{z}}$ axis. All the vectors, t-matrices and angular momentum operators in the following equations correspond to the local frame, to evaluate them with respect to the global frame requires the use of the rotation operators, as in equations (5.54). This would occur in order to evaluate the spin-wave spectrum for a system where the ground state magnetisation lay along the diagonal of the unit cell, i.e. $\mathbf{M}_0 = (1,1,1)$.

The vector equation, equation (5.52), can be resolved into its components, δn_x, δn_y and δn_z. The condition for linear response is that the magnitude of the moment remains constant, i.e. $\delta n_z = 0$. The **z** component of equation (5.52) is,

$$\begin{aligned} \delta n_z &= \frac{1}{\pi}\int d\varepsilon \; ImTri(\tau_{ii}(\hat{\mathbf{z}}) \\ &\quad \Big([J_x, t_i^{-1}(\hat{\mathbf{z}})]\delta n_x + [J_y, t_i^{-1}(\hat{\mathbf{z}})]\delta n_y + 2[J_z, t_i^{-1}(\hat{\mathbf{z}})]\delta n_z\Big) \end{aligned} \tag{5.55}$$

Therefore $\delta n_z = 0$ is a solution to the above, if both,

$$Tri\left(\tau_{ii}(\hat{\mathbf{z}})[J_x, t_i^{-1}(\hat{\mathbf{z}})]\right) = 0 \tag{5.56}$$

$$Tri\left(\tau_{ii}(\hat{\mathbf{z}})[J_y, t_i^{-1}(\hat{\mathbf{z}})]\right) = 0 \tag{5.57}$$

This can be shown analytically in the non-relativistic case and can shown to be true by numerical means in the relativistic extension.

The formalism can be used for any type of magnetic ordering, however we shall now concentrate of the ferromagnetic case, $t_j^{-1} = t_i^{-1}$. Using the definition of a spin-wave, i.e. it is a collective excitation such that the precession of the moments on each site is related by a phase factor, i.e.

$$\delta n_{jx} = \delta n_x e^{i\mathbf{q}\cdot\mathbf{R}_j} \tag{5.58}$$

then this allows the components of the vector equation to be written as,

$$\frac{1}{\gamma}\frac{\delta\delta n_x}{\delta t} = A_1\delta n_x + B_1\delta n_y \tag{5.59}$$

$$\frac{1}{\gamma}\frac{\delta\delta n_y}{\delta t} = A_2\delta n_x + B_2\delta n_y \tag{5.60}$$

The component δn_z can be shown to be zero, as expected, due to the requirement that the rotation of the moment is rigid. The coefficients A_1 etc. are given below,

$$A_1 = \frac{1}{\pi}\int d\varepsilon\ ImTri(A_{11} + A_{12}) \tag{5.61}$$

$$A_2 = \frac{1}{\pi}\int d\varepsilon\ ImTri(A_{21} + A_{22}) \tag{5.62}$$

$$B_1 = \frac{1}{\pi}\int d\varepsilon\ ImTri(B_{11} + B_{12}) \tag{5.63}$$

$$B_2 = \frac{1}{\pi}\int d\varepsilon\ ImTri(B_{21} + B_{22}) \tag{5.64}$$

where,

$$A_{11} = \tau_{00}(\hat{\mathbf{z}})\left([J_z, t^{-1}(\hat{\mathbf{z}})] + i[J_x, [J_y, t^{-1}(\hat{\mathbf{z}})]]\right) \tag{5.65}$$

$$A_{12} = -\left(\sum_{\mathbf{R}_j}\tau^{0j}(\hat{\mathbf{z}})(i[J_y, t^{-1}(\hat{\mathbf{z}})]e^{i\mathbf{q}\cdot\mathbf{R}_j})\tau^{j0}(\hat{\mathbf{z}})\right)[J_x, t^{-1}(\hat{\mathbf{z}})] \tag{5.66}$$

$$A_{21} = \tau_{00}(\hat{\mathbf{z}})\left([J_y, [J_y, t^{-1}(\hat{\mathbf{z}})]]\right) \tag{5.67}$$

$$A_{22} = -\left(\sum_{\mathbf{R}_j}\tau^{0j}(\hat{\mathbf{z}})(i[J_y, t^{-1}(\hat{\mathbf{z}})]e^{i\mathbf{q}\cdot\mathbf{R}_j})\tau^{j0}(\hat{\mathbf{z}})\right)[J_y, t^{-1}(\hat{\mathbf{z}})] \tag{5.68}$$

$$B_{11} = -\tau_{00}(\hat{\mathbf{z}})\left([J_x, [J_x, t^{-1}(\hat{\mathbf{z}})]]\right) \tag{5.69}$$

$$B_{12} = \left(\sum_{\mathbf{R}_j}\tau^{0j}(\hat{\mathbf{z}})(i[J_x, t^{-1}(\hat{\mathbf{z}})]e^{i\mathbf{q}\cdot\mathbf{R}_j})\tau^{j0}(\hat{\mathbf{z}})\right)[J_x, t^{-1}(\hat{\mathbf{z}})] \tag{5.70}$$

$$B_{21} = \tau_{00}(\hat{\mathbf{z}})\left([J_z, t^{-1}(\hat{\mathbf{z}})] - i[J_y, [J_x, t^{-1}(\hat{\mathbf{z}})]]\right) \tag{5.71}$$

$$B_{22} = \left(\sum_{\mathbf{R}_j}\tau^{0j}(\hat{\mathbf{z}})(i[J_x, t^{-1}(\hat{\mathbf{z}})]e^{i\mathbf{q}\cdot\mathbf{R}_j})\tau^{j0}(\hat{\mathbf{z}})\right)[J_y, t^{-1}(\hat{\mathbf{z}})] \tag{5.72}$$

Rewriting equations (5.59) and (5.60) in matrix form,

$$\frac{1}{\gamma}\frac{\delta}{\delta t}\begin{pmatrix}\delta n_x \\ \delta n_y\end{pmatrix} = \begin{pmatrix}A_1 & B_1 \\ A_2 & B_2\end{pmatrix}\begin{pmatrix}\delta n_x \\ \delta n_y\end{pmatrix} \tag{5.73}$$

By making the assumption that the time-dependence of the spin deviation can be described by $\delta n_{+} \propto e^{-i\omega t}$ then,

$$\left(\begin{pmatrix} A_1 & B_1 \\ A_2 & B_2 \end{pmatrix} - (-i\frac{\omega}{\gamma})\hat{\mathbf{1}} \right) \begin{pmatrix} \delta n_x \\ \delta n_y \end{pmatrix} = 0 \tag{5.74}$$

which has a non-trivial solution when,

$$\left\| \begin{pmatrix} A_1 & B_1 \\ A_2 & B_2 \end{pmatrix} - (-i\frac{\omega}{\gamma})\hat{\mathbf{1}} \right\| = 0 \tag{5.75}$$

leading to,

$$-i\frac{\omega}{\gamma} = \frac{A_1 + B_2}{2} \pm \frac{\sqrt{(A_1 + B_2)^2 - 4(A_1 B_2 - B_1 A_2)}}{2} \tag{5.76}$$

The introduction of the Fourier transforms,

$$\begin{aligned} \tau^{00} &= \int_{BZ} \mathbf{dq}' \tau(\mathbf{q}') && (5.77) \\ \tau^{0j} &= \int_{BZ} \mathbf{dq}' \tau(\mathbf{q}') e^{i\mathbf{q}' \cdot \mathbf{R}_j} && (5.78) \\ \tau^{j0} &= \int_{BZ} \mathbf{dq}'' \tau(\mathbf{q}'') e^{i\mathbf{q}'' \cdot \mathbf{R}_j} && (5.79) \end{aligned}$$

allows the coefficients A_1, A_2 etc to be rewritten in terms of an integration over the whole Brillouin zone, i.e. in the case of A_2,

$$\begin{aligned} A_2 &= \frac{1}{\pi} \int d\varepsilon \; ImTri \int_{BZ} \mathbf{dq}'\mathbf{dq} \left(\tau(\mathbf{q}', \hat{\mathbf{z}}) \left([J_y, [J_y, t^{-1}(\hat{\mathbf{z}})]] \right) \right) \\ & -\tau(\mathbf{q}', \hat{\mathbf{z}})(i[J_y, t^{-1}(\hat{\mathbf{z}})])\tau(\mathbf{q}' + \mathbf{q}, \hat{\mathbf{z}})[J_y, t^{-1}(\hat{\mathbf{z}})] && (5.80) \end{aligned}$$

Evaluation of equation (5.76) together with equation (5.80) etc. will produce the spin-wave dispersion curve. In order to calculate the gap in the spectrum due to the effects of anisotropy then equation (5.80) etc. are evaluated with $\mathbf{q} = 0$. The results of this will be presented in Chapter 6.

5.2.3 Non-relativistic limit

One rigorous test of the formalism is to evaluate the spin-wave gap non relativistically, as this implies an absence of anisotropy then the gap should disappear. This can be demonstrated formally and numerically.

In this situation the t-matrix, t^{-1}, no longer has any magnetic quantum number dependence and therefore it can be expressed in terms of spin basis functions. Also now it only contains diagonal spin elements, i.e,

$$t^{-1}_{l,m,m_s;m',m'_s} = t^{-1}_{l,m_s;m'_s}\delta_{m_s,m'_s} \tag{5.81}$$

This also means that the rotation operators in equations (5.54) act only upon the spin blocks and allow the effects of rotating from a local **z** axis to a new direction $\hat{\mathbf{n}}$ to be written as,

$$R\, t^{-1} R^{\dagger} = t_{+}^{-1}\hat{\mathbf{1}} + t_{-}^{-1}\sigma\cdot\hat{\mathbf{n}} \tag{5.82}$$

where,

$$t_{+}^{-1} = \frac{1}{2}(t_{\uparrow}^{-1} + t_{\downarrow}^{-1}) \tag{5.83}$$

$$t_{-}^{-1} = \frac{1}{2}(t_{\uparrow}^{-1} - t_{\downarrow}^{-1}) \tag{5.84}$$

As the structure constants, G_{ij}, are independent of spin and the t-matrices are now diagonal in spin, then the τ_{ij} have the following form in the spin representation,

$$\tau_{ij} = \begin{pmatrix} \tau_{\uparrow}^{ij} & 0 \\ 0 & \tau_{\downarrow}^{ij} \end{pmatrix} \tag{5.85}$$

Evaluating the commutators in equations (5.65)-(5.72), noting that now the total angular momentum operator, J, is replaced by the spin operator, σ, and that for $\mathbf{q} = 0$ then $\delta\mathbf{n}_j = \delta\mathbf{n}$, gives,

$$A_{11} = 0 \tag{5.86}$$

$$A_{12} = -\left(\sum_{\mathbf{R}_j}\tau^{0j}(\hat{\mathbf{z}})(-t_{-}^{-1}\sigma_x)\tau^{j0}(\hat{\mathbf{z}})\right)(-t_{-}^{-1}\sigma_y) \tag{5.87}$$

$$A_{21} = \tau_{00}(\hat{\mathbf{z}})(t_{-}^{-1}\sigma_z) \tag{5.88}$$

$$A_{22} = -\left(\sum_{\mathbf{R}_j}\tau^{0j}(\hat{\mathbf{z}})(-t_{-}^{-1}\sigma_x)\tau^{j0}(\hat{\mathbf{z}})\right)(-t_{-}^{-1}\sigma_x) \tag{5.89}$$

$$B_{11} = -\tau_{00}(\hat{\mathbf{z}})(t_{-}^{-1}\sigma_z) \tag{5.90}$$

$$B_{12} = \left(\sum_{\mathbf{R}_j} \tau^{0j}(\hat{\mathbf{z}})(-t_-^{-1}\sigma_y)\tau^{j0}(\hat{\mathbf{z}})\right)(-t_-^{-1}\sigma_y) \tag{5.91}$$

$$B_{21} = 0 \tag{5.92}$$

$$B_{22} = -\left(\sum_{\mathbf{R}_j} \tau^{0j}(\hat{\mathbf{z}})(-t_-^{-1}\sigma_y)\tau^{j0}(\hat{\mathbf{z}})\right)(-t_-^{-1}\sigma_x) \tag{5.93}$$

Evaluating the spin algebra gives,

$$A_{12} = \sum_{\mathbf{R}_j} \left(\tau_\uparrow^{0j}(\hat{\mathbf{z}})\tau_\downarrow^{j0}(\hat{\mathbf{z}}) - \tau_\downarrow^{0j}(\hat{\mathbf{z}})\tau_\uparrow^{j0}(\hat{\mathbf{z}})\right) t_{j-}^{-1}t_{i-}^{-1} \tag{5.94}$$

$$A_{21} = \left(\tau_\uparrow^{00}(\hat{\mathbf{z}}) - \tau_\downarrow^{00}(\hat{\mathbf{z}})\right) t_{i-}^{-1} \tag{5.95}$$

$$A_{22} = \sum_{\mathbf{R}_j} \left(\tau_\uparrow^{0j}(\hat{\mathbf{z}})\tau_\downarrow^{j0}(\hat{\mathbf{z}}) + \tau_\downarrow^{0j}(\hat{\mathbf{z}})\tau_\uparrow^{j0}(\hat{\mathbf{z}})\right) t_{j-}^{-1}t_{i-}^{-1} \tag{5.96}$$

$$B_{11} = -\left(\tau_\uparrow^{00}(\hat{\mathbf{z}}) - \tau_\downarrow^{00}(\hat{\mathbf{z}})\right) t_{i-}^{-1} \tag{5.97}$$

$$B_{12} = -\sum_{\mathbf{R}_j} \left(\tau_\uparrow^{0j}(\hat{\mathbf{z}})\tau_\downarrow^{j0}(\hat{\mathbf{z}}) + \tau_\downarrow^{0j}(\hat{\mathbf{z}})\tau_\uparrow^{j0}(\hat{\mathbf{z}})\right) t_{j-}^{-1}t_{i-}^{-1} \tag{5.98}$$

$$B_{22} = \sum_{\mathbf{R}_j} \left(\tau_\uparrow^{0j}(\hat{\mathbf{z}})\tau_\downarrow^{j0}(\hat{\mathbf{z}}) - \tau_\downarrow^{0j}(\hat{\mathbf{z}})\tau_\uparrow^{j0}(\hat{\mathbf{z}})\right) t_{j-}^{-1}t_{i-}^{-1} \tag{5.99}$$

Using a similar expansion of τ_{00} as in equation (5.50) but also in terms of spin blocks,

$$\begin{aligned}
\tau_{00\uparrow}(\hat{\mathbf{z}}) - \tau_{00\downarrow}(\hat{\mathbf{z}}) &= -\sum_{\mathbf{R}_j} \tau_\downarrow^{0j}(\hat{\mathbf{z}})(t_{j\uparrow}^{-1} - t_{j\downarrow}^{-1})\tau_\uparrow^{j0}(\hat{\mathbf{z}}) && (5.100)\\
&= -\sum_{\mathbf{R}_j} \tau_\downarrow^{0j}(\hat{\mathbf{z}})(t_{j\uparrow}^{-1} - t_{j\downarrow}^{-1})\tau_\uparrow^{j0}(\hat{\mathbf{z}}) && (5.101)\\
&= -\sum_{\mathbf{R}_j} \tau_\uparrow^{0j}(\hat{\mathbf{z}})(t_{j\uparrow}^{-1} - t_{j\downarrow}^{-1})\tau_\downarrow^{j0}(\hat{\mathbf{z}}) && (5.102)
\end{aligned}$$

This, together with the ferromagnetic condition, i.e $t_j^{-1} = t_i^{-1}$ gives,

$$A_{12} = 0 \tag{5.103}$$

$$A_2 = A_{21} + A_{22} = 0 \tag{5.104}$$

$$B_1 = B_{11} + B_{12} = 0 \tag{5.105}$$

$$B_{22} = 0 \tag{5.106}$$

and therefore gives the non-relativistic result,

$$\omega(q = 0) = 0 \tag{5.107}$$

i.e. there is no longer a gap in the spin-wave spectrum.

5.2.4 Stiffness coefficient

It is possible to show that in the low energy limit the q dependence of the dispersion relationship will go as q^2. This can be shown with formalism as developed here and is mainly a consequence of the symmetry properties of the underlying cubic lattice and the ferromagnetic ground state. If equation (5.52) is Fourier transformed and the magnetic ordering is assumed to be ferromagnetic, i.e. $\mathbf{n}_j = \mathbf{n}_i$, then,

$$\begin{aligned} \frac{1}{\gamma}\frac{\delta \mathbf{n}}{\delta t} &= \frac{1}{\pi}\int d\varepsilon \; ImTri \int_{BZ} \mathbf{dq}'\mathbf{dq} \Big(\tau(\mathbf{q}', \hat{\mathbf{z}}) \; \mathbf{A} \\ &\quad - \tau(\mathbf{q}', \hat{\mathbf{z}}) i[(\delta \mathbf{n} \times \mathbf{n}_0) \cdot \mathbf{J}, t^{-1}(\hat{\mathbf{z}})] \tau(\mathbf{q}' + \mathbf{q}, \hat{\mathbf{z}}) \; \mathbf{B}\Big) \end{aligned} \tag{5.108}$$

A and **B** are given in equation (5.53) and (5.53). By making a small q Taylor expansion of $\tau(\mathbf{q}' + \mathbf{q}, \hat{\mathbf{z}})$,

$$\tau(\mathbf{q}' + \mathbf{q}, \hat{\mathbf{z}}) = \tau(\mathbf{q}', \hat{\mathbf{z}}) + q_i \frac{\delta}{\delta x_i} \tau(\mathbf{q}', \hat{\mathbf{z}}) + \frac{1}{2} q_i q_j \frac{\delta}{\delta x_i}\frac{\delta}{\delta x_j} \tau(\mathbf{q}', \hat{\mathbf{z}}) + \ldots \tag{5.109}$$

From the definition of the multiple scattering operator τ, it can be seen that the q dependence is contained in the structure factors. As these remain invariant under inversion of the crystal lattice it can be shown that the first non-zero q dependent term is q^2. Hence the dispersion relation can be written as,

$$\begin{aligned} \omega &= \omega_{gap} + \frac{\gamma}{\pi}\int d\varepsilon \; ImTri \\ &\quad \int_{BZ} \mathbf{dq}' \tau(\mathbf{q}', \hat{\mathbf{z}}) i[(\delta \mathbf{n} \times \mathbf{n}_0) \cdot \mathbf{J}, t^{-1}(\hat{\mathbf{z}})] \frac{\delta^2 \tau(\mathbf{q}, \hat{\mathbf{z}})}{\delta q^2}) \; \mathbf{B} \; q^2 \end{aligned} \tag{5.110}$$

An advantage of this method of dealing with the effects of anisotropy on spin-wave excitations is that the formalism is independent of the way the t-matrix, and hence the description of the effects of scattering off the potential, are derived. Hence it should be possible to see the effects of different methods of calculating t on the spin-wave spectrum, such as a more refined treatment of the relativistic interactions.

Chapter 6

Results and discussion

6.1 Results

The purpose of the formalism is to investigate the effects of anisotropy on the long-wavelength excitations of itinerant electron ferromagnets, in particular the existence of a gap in the spin-wave spectrum at $\mathbf{q} = 0$.

Spin-wave gap

Non-relativistically (i.e. no anisotropy) the absence of a gap was found analytically, for the relativistic situation the values obtained for the spin-wave gap for bcc iron, fcc nickel and fcc cobalt about the equilibrium moment directions $(0,0,1)$ and $(1,1,1)$ are summarised in table (6.1). They were obtained by evaluating equation (5.76) together with the Fourier Transformed coefficients, e.g. equation (5.80) etc.

Spin-wave gap ratio

Table (6.2) contains the ratios of the spin-wave gaps evaluated for the moment orientated along $(0,0,1)$ and $(1,1,1)$. The phenomenological theory as described in Chapter 3, indicates that this ratio should have the value $3/2$ if the magne-

system	$\omega_{gap}/\gamma \times 10^{-6}$ eV Equilibrium direction	
	(0, 0, 1)	(1, 1, 1)
iron (b.c.c)	-0.89	-0.60
nickel (f.c.c)	6.98	5.10
cobalt (f.c.c)	11.7	6.86

Table 6.1: The spin-wave gap due to magnetic anisotropy for bcc iron, fcc nickel and fcc cobalt, evaluated for the moment equilibrium directions $(0,0,1)$ and $(1,1,1)$.

tocrystalline anisotropy energy follows the form given in equation (3.5).

system	$\omega_{gap}(0,0,1)/\omega_{gap}(1,1,1)$
iron	1.48
nickel	1.37
cobalt	1.70
theory	1.50

Table 6.2: The ratio of the spin-wave gaps for moment equilibrium directions (0, 0, 1) and (1, 1, 1) for bcc iron. The result for the theory corresponds to the phenomenological model discussed in Chapter 3.

Magnetocrystalline Anisotropy Energy

By using the approach demonstrated in Chapter 3, a value for the magnetocrystalline anisotropy energy (MAE) can be calculated from the expressions for the spin-wave gap. The relevant equations are,

$$\begin{aligned} E_{MAE} &= \frac{1}{6}\frac{\omega_{gap}}{\gamma} \qquad if \quad \mathbf{M}_0 = (0,0,1) \qquad (6.1) \\ &= \frac{1}{4}\frac{\omega_{gap}}{\gamma} \qquad if \quad \mathbf{M}_0 = (1,1,1) \qquad (6.2) \end{aligned}$$

The calculated MAEs for the three systems under investigation is contained in table (6.3) below. There is no experimental value for cobalt as it only exists in a hexagonal structure at low temperature.

system	$\lvert MAE \rvert$ in 10^{-6} eV per atom	
iron	0.15	1.40
nickel	1.28	2.7
cobalt	1.72	

Table 6.3: The MAE for bcc iron, fcc nickel and fcc cobalt

6.2 Discussion

Table (6.4) gives a comparison between experimental and theoretical values for the MAE for Fe and Ni. A is the experimental value [65], B is from ref. [49], C from ref. [50], D from ref. [51], E from ref. [52] and the final column are the results of this thesis. The values obtained for the gap in the spin-wave spectrum and hence the magnetocrystalline anisotropy energies are of the correct order of magnitude compared with previous experimental work [65].

We now go on to compare with previous theoretical investigations and to discuss possible explanations for the discrepancies between the calculated values and those obtained from experimental data.

$\lvert E_{001} - E_{111} \rvert$	A	B	C	D	E	F
Fe	1.4	0.5	9.6	7.4	1.8	0.15
Ni	2.7	0.5	10.5	10.0	2.7	1.28

Table 6.4: The magnetocrystalline anisotropy energy in 10^{-6} eV per atom for Fe and Ni, A is the experimental result and F is the work of this thesis.

This work

A particular advantage of the approach taken by the formalism presented in this thesis in the calculation of magnetic anisotropy energies is that the anisotropy is calculated directly. This compares with previous theoretical approaches where the anisotropy energy is obtained as the difference between two single particle energies, i.e. the total energy of the system is calculated for the case where the magnetic moment lies along one particular crystallographic direction and then for the situation where the moment is aligned along another axis, the anisotropy energy is the difference between the two. In attempting to evaluate the anisotropy directly the formalism should reduce the possibility of numerical inaccuracies.

Table (6.2) gives the ratio of the MAE calculated for magnetisations lying along the $(0,0,1)$ and $(1,1,1)$ directions. In Chapter 3 it was noted that for the phenomenological approach this ratio should be 3/2, the result for iron is very close to this. This would seem to indicate that the phenomenological expression for the anisotropy energy,

$$E_{aniso} = \frac{K_1}{N}(M_x^2 M_y^2 + M_x^2 M_z^2 + M_y^2 M_z^2) \qquad (6.3)$$

holds well for iron but not for nickel and cobalt. Previous work [93], [94] and [95] have indicated that indeed this is the case, it is possible to fit the anisotropy energy of iron to a simple functional form, but for nickel this is not seem reasonable.

Energy and Brillouin zone integration

The energy integral in equation (5.80) is replaced by a Matsubara sum over a discrete set of complex energy points off the real axis [96], with a cut-off at a suitable value.

Numerical accuracy is particularly important in the case of evaluating the integration of equation (5.80) etc. Concerns over convergence in the necessary Brillouin zone integrations have been expressed in other work on MAEs. Extensive numerical calculations by Daalderop et.al. [49] show that these are not likely to be responsible for the variation of results between the different approaches to calculating the MAE.

At each energy point the Brillouin zone integration, of equation (5.80) for example, was carried out by dividing the Brillouin Zone into 48 tetrahedra. The integration of each of these tetrahedra was approximated by performing an integration along a number of weighted rays. The integrand, equation (5.80), was evaluated at a number of points along each ray before being fitted to a cubic function. This was then integrated analytically, the total BZ integration being the sum of the rays and 48 tetrahedra.

The Brillouin zone integration required for the results presented here was performed with 36 rays and 50 points per ray for each energy point. The tables below give the imaginary part of the integration for the case of bcc iron, firstly as the number of points on each ray is increased, and then the total integration as the number of rays used is varied. Each is carried out for one energy point.

Previous theoretical investigations of magnetic anisotropy in itinerant electron systems have focussed on a number of possible causes of the differences between theory and experimental data, in particular, the approximations contained in the use of the 'force theorem' and the Local Density Approximation.

Number of points along one ray	Integrand
50	3.623×10^{-6}
75	3.600×10^{-6}
100	3.600×10^{-6}
125	3.600×10^{-6}

Table 6.5: The value of the integration of equation (5.80) depending upon the number of points along a ray

Number of rays	Value of integration
1	3.623×10^{-6}
3	3.366×10^{-7}
10	7.760×10^{-6}
15	1.216×10^{-5}
36	1.111×10^{-5}
45	1.200×10^{-5}

Table 6.6: The value of the BZ integration of equation (5.80) depending upon the number of rays, each ray evaluated at 50 points.

Force theorem

Although in a numerical sense the force theorem is not used, it is implicit in our construction of the effective field, equation (5.41). Previous theoretical investigations of magnetic anisotropy energies have questioned the use of such an approximation. These include calculations via the LMTO method of solution to the single particle density functional equations by Daalderop et. al. [49] and those using a multiple scattering approach, such as Strange et al. [50]. However, a self consistent LMTO approach by Guo [52] does not use this approximation and the differences in the values for the MAE remain.

The local density approximation

The majority of opinion on the discrepancy between theoretical calculations and experimental results seems to lie in questioning the form of the local density approximation. Jansen [59], [61] believes the lack of an orbital current dependence in the exchange correlation functional is crucial, other investigations have indicated that this, together with other many-body effects, could play a leading role in the origin of the discrepancies. The experience reported here in the attempt to calculate a relativistic dynamic susceptibility would seem to indicate that there is a problem with consistency. Whether or not this could be resolved with the addition of approximate orbital current effects remains to be seen.

In summary, the results obtained here for the MAEs are of the correct order of magnitude. The analysis of the ratio of the spin-wave gaps indicate that the phenomenological description of the magnetic anisotropy is quite successful for iron, however, for nickel and cobalt this appears not to be the case.

Chapter 7

Conclusion

The main purpose of this thesis is the presentation of a formalism for calculating the effects of magnetic anisotropy on the long-wavelength excitations of a magnetically ordered itinerant system. It is based upon a relativistic multiple scattering theory solution of the Kohn-Sham-Dirac density functional equations. Numerical calculations for bcc iron, fcc nickel and fcc cobalt have been presented and compare favourably to experimental results.

The multiple scattering formalism has been shown to be capable of producing the small anisotropy energies involved via work on the effects of anisotropy on magnetic interactions in dilute magnetic alloys. The theory was used to evaluate the consequences of the addition of a heavy, non-magnetic, strong spin-orbit scatterer to a system consisting of two magnetic transition metal impurities embedded in a relativistic jellium. It was found that the magnetic anisotropy of the system was significantly enhanced, as predicted in papers by Fert and Levy [75]. However the form of the anisotropic interaction was not as simple as that suggested earlier, and in certain configurations the anisotropy energy was on the same scale as an effective exchange interaction.

The low lying excitations of an ordered magnetic system are known as spin-waves. They are collective excitations and correspond to a precession of each moment about its ground state position, the relative phase between successive moments is determined by a wave-vector, $\mathbf{q}$. In the absence of any magnetic anisotropy the energy of these modes goes to 0 as $\mathbf{q} \rightarrow 0$. However the addition of anisotropy, via spin-orbit coupling for example, opens up a gap in the spin-wave spectrum at $\mathbf{q} = 0$.

Our initial investigation into these effects followed the example set in the non-relativistic case, the construction of a dynamic susceptibility from the two particle Green's function, the poles of which determine the excitation spectrum. However it was soon found that problems arose in attempting a first principles investigation, namely the use of the local density approximation in solving the Kohn-Sham-Dirac equations consistently. As a result a new approach was tried, avoiding the previous difficulties.

The theory is based upon a linear response framework, it builds on advances made in recent magnetic anisotropy calculations, i.e. the anisotropy is calculated by just rotating the magnetic moment, keeping its magnitude constant. The question of timescales is an important one in discussing the validity of any approach. As the excitations under investigation are of long-wavelength($\mathbf{q} \rightarrow 0$) then the movement of the magnetic moments under the influence of any effective field is slow compared to the electronic motion which is responsible for generating the moments. This allows the use of the Landau, or phenomenological equation as a starting point for our equation of motion of the magnetic moment. A result of this approach is that the effective field which the moment experiences can be formulated in terms of the total energy of the spin system, which, for a itinerant magnetic system, is achieved via a multiple scattering theory solution to the relativistic Kohn-Sham-Dirac density functional equations together with a local density approximation. The result of this is a set of expressions describing the motion of a magnetic excitation, a spin-wave, in a general reference frame. These can be solved analytically in the non-relativistic case to show the absence of a gap in the spin-wave spectrum, and numerically for the relativistic situation leading to values for the energy gap. In particular these have been evaluated for bcc iron, fcc nickel and fcc cobalt.

The numerical values obtained for these itinerant ferromagnets are of the correct order of magnitude compared with experimental evidence, the deviations could be due to a number of factors. These include the use of the force theorem, the convergence of the Brillouin zone integrations and the validity of the local density approximation. This formalism has an advantage over previous investigations into magnetic anisotropy energies in that the anisotropy is calculated directly rather than the difference between two configurations. It is hoped that this has considerably reduced any problems regarding numerical accuracy, in particular the calculation of the Brillouin zone integration.

An interesting point regarding this formalism is that if the magnetic systems follow the much used phenomenological description of magnetic anisotropy, i.e. equation (3.5), then the ratio of the spin-wave gaps calculated for moment orientations $(0,0,1)$ and $(1,1,1)$ should be $3/2$. Our calculations indicate that this is the case for iron but not so for nickel and cobalt. Whether this indicates that such a description for these systems is no longer valid remains to be seen, previous work, [93], [94] and [95], indicate that this is the case.

In the light of previous work together with our experience in attempting to calculate a relativistic dynamic susceptibility, attention is focussed on the use of the local density approximation. Other authors [49], [50], have indicated that possible many body effects, described by the exchange-correlation functional, could have a role to play in anisotropy calculations, in particular the possibility of an orbital current dependence as described by Jansen [61].

The formalism, as shown here, is not only valid for ferromagnetic ordering and is not just restricted to calculating the spin-wave gap, but also the excitation spectrum for small $\mathbf{q}$. Finally it should be noted that the spin-wave equations are independent of the method used to obtain the t matrix. This means that the addition of other relativistic effects as well as improvements in the treatment of many-body interactions can be incorporated easily into calculations of magnetic anisotropy energies.

Bibliography

[1] Herring C 1966 *Magnetism Volume IV* Ed. Rado G T and Suhl H (New York: Academic Press)

[2] Bloch F 1929 *Z. Phys* **57** 545

[3] Heisenberg W 1928 *Z. Phys* **49** 619

[4] Dirac P A M 1958 *Principles of Quantum Mechanics* (Oxford: OUP)

[5] Wigner E P 1938 *Trans. Faraday Soc.* **34** 678

[6] Stoner E C 1933 *Phil. Mag.* **15** 1018

[7] Stoner E C 1947 *Rep. Prog. Phys* **11** 43

[8] Wohlfarth E P 1953 *Rev. Mod. Phys* **25** 211

[9] Hubbard J 1963 *Proc. Roy. Soc.* **276A** 238

[10] Rado G T and Suhl H 1963 *Magnetism Volume I* (New York: Academic Press)

[11] Callaway J and March N H 1984 *Solid State Physics* **38** 135

[12] Hohenberg P and Kohn W 1964 *Phys. Rev* **136** 864

[13] Kohn W and Sham L J 1964 *Phys. Rev* **140** A1133

[14] Gunnarsson O and Lundqvist B I 1976 *Phys. Rev B.* **13** 4274

[15] Bloch F 1930 *Z. Phys* **61** 206

[16] Holstein T and Primakoff H 1940 *Phys. Rev.* **56** 1098

[17] Walker L 1957 *Phys. Rev.* **105** 310

[18] Kittel C and Herring C 1950 *Phys. Rev.* **77** 725

[19] Damon R W and Eshbach J R 1961 *J. Phys. Chem. Solids* **19** 308

[20] Griffiths J H E 1946 *Nature* **158** 670

[21] Kittel C *Phys. Rev.* **110** 1295

[22] Eshbach J R 1963 *J.Appl. Phys.* **34** 1298

[23] Borovik-Romanov A S and Sinha S K 1988 *Spin Waves and Magnetic Excitations* (Amsterdam: North-Holland)

[24] Akhiezer A I, Baryakhtar V G and Peletminskii S V 1968 *Spin waves* (Amsterdam: North-Holland)

[25] Landau L D and Lifshitz E M 1935 *Phys. Z. Sowjetunion* **8** 153

[26] Landau L D and Lifshitz E M 1960 *Electrodynamics of continuous media* (Pergamon Press)

[27] MacDonald J R 1956 *Phys. Rev.* **103** 280

[28] Kittel C and Herring C 1951 *Phys. Rev.* **81** 869

[29] Lowde R D and Windsor C G 1970 *Adv. Phys* **19** 813

[30] Cooke J F, Lynn J W and Davis H L 1980 *Phys. Rev. B* **21** 4118

[31] Cooke J F, Blackman J A and Morgan T 1985 *Phys. Rev. B* **54** 718

[32] Rajagopal A K 1978 *Phys. Rev. B.* **17** 2980

[33] Callaway J and Chatterjee A K 1978 *J. Phys. F* **8** 2569

[34] Marshall W and Lovesey S W 1971 *Theory of Thermal Neutron Scattering* (London: Oxford University Press)

[35] Callaway J, Arum K, Chatterjee Singhal S P and Zeigler A 1983 *Phys. Rev. B* **28** 3818

[36] J A, Morgan T and Cooke J F 1985 *Phys. Rev. Lett* **55** 2814

[37] Callaway J and Wang C S 1975 *J. Phys. F* **5** 2119

[38] Stenzel E and Winter H 1985 *J. Phys. F: Met. Phys.* **15** 1571

[39] Edwards D M and Rahman M A 1978 *J. Phys. F* **8** 1501

[40] Liu K L and Vosko S H 1978 *J. Phys. F* **8** 1539

[41] Callaway J Wang C S and Laurent D G 1981 *Phys. Rev. B.* **24** 6491

[42] White R M 1970 *Quantum Theory of Magnetism* (New York: McGraw-Hill)

[43] Rose M E 1961 *Relativistic Electron Theory* (New York: Wiley)

[44] van Vleck J H 1937 *Phys. Rev.* **52** 1178

[45] Brooks H 1940 *Phys. Rev.* **58** 909

[46] Mori N, Fukuda Y and Ukai T 1973 *J. Phys. Soc. Jpn.* **37** 1263

[47] Gay J G Richter R 1986 *Phys. Rev. Lett* **56** 2728

[48] Gay J G Richter R 1987 *J. Appl. Phys.* **61** 3362

[49] Daalderop G H O, Kelly P J and Schuurmans M F H 1990 *Phys. Rev. B* **41** 11919

[50] Strange P, Staunton J B, Gyorffy B L and Ebert H 1991 *Physica B* **172** 51

[51] Fritsche L, Noffke J and Eckardt H 1987 *J. Phys. F* **17** 943

[52] Guo G Y, Temmerman W M and Ebert H 1991 *Physica B* **172** 61

[53] Ramana M V and Rajagopal A K 1983 *Adv. Chem. Phys.* **54** 231

[54] Rajagopal A K 1978 *J. Phys. C* **11** L943

[55] MacDonald A H and Vosko S 1979 *J. Phys. C* **12** 2977

[56] Vignale G and Rasolt M 1988 *Phys. Rev. B* **37** 10685

[57] Bjorken J D and Drell S D 1965 *Relativistic Quantum Fields* (New York: McGraw-Hill)

[58] Baym G 1974 *Lectures on Quantum Mechanics* (New York: Benjamin)

[59] Jansen H J F 1988 *Phys. Rev. B.* **38** 8022

[60] Jansen H J F 1990 *J. Appl. Phys.* **67** 4555

[61] Jansen H J F 1991 *Phys. Rev. B.* **43** 12025

[62] Skriver H L 1984 *The LMTO Method* (New York: Springer Verlag)

[63] Ebert H 1988 *Phys. Rev. B.* **38** 9390

[64] Eriksson O, Johansson B, Albers R C and Boring A M 1990 *Phys. Rev. B.* **42** 2707

[65] Escudier P 1975 *Ann. Phys.* **9** 142

[66] Rado G T and Suhl H 1963 *Magnetism Volume III* (New York: Academic Press)

[67] Rado G T and Suhl H 1963 *Magnetism Volume V* (New York: Academic Press)

[68] Friedel J 1958 *Nuovo Cimento Suppl.* **7** 287

[69] Anderson P W 1964 *Concepts in Solids* (Benjamin)

[70] Oswald A, Zeller R, Braspenning P J and Derderichs P H 1984 *J. Phys. F: Met. Phys.* **15** 193

[71] Kondo J 1964 *Prog. Theoret. Phys.* **32** 37

[72] Binder K and Young A P 1986 *Reviews of Modern Physics* **58** 801

[73] Bray A J 1987 *Phys. Rev. B.* **35** 4850

[74] Prejean J J, Joliclerc M and Monod P 1980 *J. Phys. (Paris)* **41** 427

[75] Levy P M, Fert A 1981 *Phys. Rev. B.* **23** 4667

[76] Levy P M, Morgan-Pond C and Fert A 1982 *J. Appl. Phys.* **53** 2168

[77] Staunton J B, Gyorffy B L, Poulter J and Strange P 1988 *J. Phys. C* **21** 1595

[78] Strange P, Staunton J B and Gyorffy B L 1984 *J. Phys. C* **17** 3355

[79] Staunton J B, Gyorffy B L, Poulter J and Strange P 1988 *J. Phys. Condens. Matter* **1** 5157

[80] Newton R G 1966 *Scattering Theory of Waves and Particles* (New York: McGraw-Hill)

[81] Lloyd P and Smith P V 1972 *Adv. Phys.* **21** 69

[82] Rodberg L S and Thaler R M 1967 *Introduction to the Quantum Theory of Scattering* (New York: Wiley)

[83] Feder R, Rosicky F and Ackermann B 1983 *Z. Phys.* B **52** 31

[84] Messiah A 1965 *Quantum Mechanics* (Amsterdam: North-Holland)

[85] Gyorffy B L and Stocks G M *Band Theory of Random Metallic Alloys*

[86] Mori N, Ukai T and Ohtsuka S 1983 *J. Mag. Magn. Mat.* **31** 43

[87] Kondorskii E I and Straube E 1973 Sov. Phys. JETP **36** 188

[88] Eckardt H, Fritsche L and Noffke J N 1987 *J. Phys. F.* **17** 943

[89] Godfree J A and Staunton J B 1993 *J. Appl. Phys.* **73** 6557

[90] Dederichs P H, Zeller R, Akai H and Ebert H 1991 *J. Mag. Magn. Mat.* **100** 241

[91] Jagannathan A 1991 *Europhys. Lett.* **16** 217

[92] Jagannathan A 1992 *J. Mag. Magn. Mat.* **104-107** 1673

[93] Aubert G 1976 *Phys. Rev. B.* **14** 5314

[94] Gersdorf R 1978 *Phys. Rev. Lett.* **40** 344

[95] Gersdorf R and Aubert G 1978 *Physica B* **95** 135

[96] Negele J W and Orland H 1988 *Quantum Many-Particle Systems* (Addison Wesley)