Statistical mechanics of itinerant-electron magnets

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K S Chana.

May 1993.

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Abstract.

The transition metal iron is the archetypal magnetic material. However some aspects of its magnetic behaviour are still not fully understood. The conceptual difficulty is that, while unpaired electrons responsible for magnetism in an insulator are localised on the atomic sites, in a metal they have extended states. In iron these *itinerant 3d* electrons may conspire to form well-defined local magnetic moments. In this limit one can treat metals such as iron in a similar fashion to insulators in the framework of the Heisenberg model. The local moments align at low temperatures giving rise to ferromagnetic behaviour and above the Curie temperature, $T_C$, misalign to destroy long range order. The correlation between the directions of the neighbouring moments in the paramagnetic phase remains a subject of controversy. Neutron scattering data would indicate that the magnetic moments are more correlated than would be expected in an insulator. This is generally referred to as *magnetic short range order*.

One of the aims of this work is to address the fundamental issue of magnetic short range order in iron. This is accomplished through an investigation of the statistical mechanics of an effective spin Hamiltonian derived from electronic structure calculations. The unique feature of the model is that the nearest- and next-nearest-neighbour exchange interactions are of a *non-pairwise* nature; that is these interactions depend on the *local* magnetic environment of the interacting magnetic moments. The larger nearest-neighbour interaction increases with increasing disorder (or as the temperature of the system is raised). This means that at higher temperatures an increasingly large amount of effort is required for the system to disorder. It is this behaviour that leads one to speculate that as the system goes through the phase transition from the ferromagnetic to paramagnetic phase any short range order found at $T_C$ should remain in the paramagnetic phase. Further this short range order should be greater than that found in the nearest-neighbour Heisenberg model.
The statistical mechanics of the model are investigated using the Monte Carlo method. The short range order in the model of iron and the Heisenberg model is compared by comparing the values of the nearest-neighbour real space correlation function at $T_C$. The results from Monte Carlo simulations suggest that the degree of short range order in iron is in fact not substantially greater than in the Heisenberg model. In order to investigate the nature of the non-pairwise exchange interactions, an extreme limit of the nearest-neighbour interaction is also considered. In this case there is a zero next-nearest-neighbour interaction and the nearest-neighbour interaction vanishes in the ferromagnetic state. This means that the ground state will no longer be ferromagnetic and may possibly break up into clusters of reversed magnetisation. If these clusters were large and persisted up to $T_C$ then large short range order (of the order of the size of the clusters) would be found in the paramagnetic state of iron. The Monte Carlo results however indicate that even in this extreme case the degree of short range order is not much greater than in the nearest-neighbour Heisenberg model. Clusters of reversed magnetisation in the ground state of the model of iron are however observed when the extreme non-pairwise nearest-neighbour interaction is used in a two dimensional Ising model.

The model of iron is rather interesting and further investigations have been made. Early neutron scattering data indicated that the spin wave energies in iron are only weakly temperature dependent, even at temperatures above $T_C$. To make a comparison of the model of iron and real iron the spin wave dispersion at temperatures up to $T_C$ has been calculated. The expected decrease in magnon energies with temperature is compensated for by the increase in the average exchange interaction with increasing temperature (or decreasing order); this in fact results in a slight increase in the magnon energies with temperature in the model of iron.

The conclusion that one must draw from these results is that iron does not behave in a substantially different way from an insulator. Although this is a negative result it does highlight the fact that the calculation of the electronic structure is at fault. The main approximation made in the calculation is the static approximation. Here the quantum electron
hopping process is considered to be much faster than the classical precession of the magnetisation, thus quantum effects are not suitably taken into account. To go beyond the static approximation a more direct numerical calculation of the statistical mechanics from a microscopic viewpoint is needed.

The microscopic description of itinerant-electron magnets is provided by the Hubbard Hamiltonian and its statistical mechanics can be investigated by a quantum Monte Carlo evaluation of the partition function in a functional integral formalism. Calculations made in static approximation indicate that the statistical mechanics are substantially different from those obtained from a calculation with quantum effects included. The conclusion therefore is that if the statistical mechanics of itinerant-electron systems are to be calculated in a framework that one can believe in, then these need to be performed from a microscopic viewpoint using a quantum Monte Carlo scheme.
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"...one can philosophize indefinitely about matters of this kind but in practice one is limited by circumstance..."

Aristotle - "Politics"
Chapter One.

Introduction - Magnetic properties of matter.

1.1 Background.

Magnetic phenomena in materials are wide ranging from the well known ferromagnetism (anti-ferromagnetism)/paramagnetism to the more exotic helimagnetism and metamagnetism. The mechanism responsible for magnetism is the magnetic moment of the atoms that constitute a material. The most basic questions that must be addressed by any theory that tries to explain magnetic phenomena are firstly how do these magnetic moments arise and secondly how do they interact to produce the different magnetic structures. Quantum mechanics addresses the former attributing the magnetic moment of an ion to unfilled atomic shells. The theories that address the latter are now well established and interpret the experimental measurements made on a range of materials fairly well. For example the Heisenberg theory of magnetism successfully describes the behaviour of insulators.

In an insulator the electrons responsible for magnetism have localised states and the magnetic moments have a localised character. However the electrons responsible for the magnetic moment of a transition metal atom are itinerant; that is, there is considerable overlap of the electron wave functions of the atoms. The question then is how is it possible for a local magnetic moment to form in these materials. The early band theory description of itinerant-electron magnets developed by Stoner (1938) interprets the formation of a magnetic moment as the splitting of the majority and minority electron sub-bands. The magnitude of the moment is the difference between the number of majority and minority electrons. The ground state of itinerant-electron magnets is successfully described by Stoner theory; however, there is no adequate interpretation or prediction of the magnetic behaviour at finite temperatures in the theory. If we can envisage the itinerant-electrons conspiring somehow to produce local moments then a Heisenberg-like model can be applied to describe the thermodynamics of these materials. The phase transition from the magnetically ordered to the
magnetically disordered (paramagnetic) state in metallic magnets can then be viewed as the disordering of the magnetic moments.

The paramagnetic state of 3d transition metal magnets such as iron and nickel has been the subject of much controversy in recent years. An unresolved issue is that of the existence and extent of magnetic short range order (SRO) above the Curie temperature $T_c$, in excess of that normally expected as critical fluctuations in a short range Heisenberg model. The controversy was started by the inelastic neutron scattering data of Mook et al (1973), on nickel, and Lynn (1975), on iron. Their observations indicated the persistence of spin waves well above $T_c$. Two schools of thought have emerged from these observations. On the one hand the fluctuating local band theory (FLBT) of Korenman et al (1977) assumes SRO to exist from the outset; above $T_c$ the spin direction varies sufficiently smoothly for a local band structure and broadened spin waves to be supported. On the other hand Edwards (1980, 1983a) argues that this interpretation is incompatible with thermal and susceptibility data which shows a normal magnetic phase transition, and that SRO is not needed to explain the neutron data. The disordered local moment (DLM) picture of Hubbard (1979a), Hasegawa (1980) and others, in which the nearest-neighbour correlation is zero in the paramagnetic state, is compatible with the susceptibility and thermal data. Lowde et al (1983) have described a further model of an itinerant magnet with coarse-grained disorder. In this model large blocks of reversed magnetisation develop at temperatures just below $T_c$. These are larger than those normally expected from critical fluctuations. This is an alternative picture to the smooth magnetisation of FLBT. They interpret their neutron data on an impure sample of nickel in terms of such a block model. Angle-resolved photoemission studies of the band splitting in the electronic structure of paramagnetic iron also suggest the existence of SRO (Haines et al 1985, Kischer et al 1985).

1.2 Aims and plan of thesis.

The aim of the work in this thesis is firstly to try and resolve the issue of the existence and extent of magnetic short range order in the 3d transition metal iron. Previous work (Lin-Chung and Holden, Heine et al 1981, You and Heine, Holden and You 1982,
Samson 1983, Small and Heine 1984, Luchini and Heine 1989,1991) has produced considerable information on the energetics of configurations of the magnetisation in iron rather than the statistical mechanics. I therefore investigate the statistical mechanics of iron in the ferromagnetic and paramagnetic phase. In Chapter two I present a review of the scheme used to calculate the electronic structure and the approximations made in these calculations. The energetics of the magnetic configurations has yielded a model of iron, which is also developed and discussed in Chapter two. In order to investigate the statistical mechanics of this model of iron the Monte Carlo method has been used and in Chapter three I give a review of the techniques used. The results of Monte Carlo simulations of the nearest-neighbour Heisenberg model and the model of iron are presented in Chapter four. To address the question of the formation of blocks of reversed magnetisation in the ground state of iron, simulations of a 2D Ising model at $T = 0$ have been performed. The standard Monte Carlo method is not applicable at $T = 0$ therefore a modified calculation scheme has been used, which is presented in Chapter five. A calculation of the spin wave energies provides a useful comparison with the experimentally measured spin wave dispersions in iron. Monte Carlo simulations do not provide information on spin wave energies, however the spin wave dispersion of the model of iron can be calculated using non-interacting and interacting spin wave theory. The details and results of such a calculation are presented in Chapter six. The insights that have been gained from the Monte Carlo simulations and calculation of the spin wave dispersions are discussed in Chapter seven. Essentially the results show that the magnetic behaviour of iron is not substantially different from the nearest neighbour Heisenberg model. The main approximation made in the calculation of the energetics of iron is the so-called static approximation; here the energies are calculated for frozen configurations of the magnetisation. Electrons hopping between atomic sites therefore "see" a static configuration of magnetisation. Clearly this is not very representative of the magnetisation in real materials, where the magnetic moment on an atomic site may change in direction as an electron hops from atom to atom. To go beyond the static approximation we must calculate the statistical mechanics of a system from the microscopic viewpoint using an appropriate many-body Hamiltonian and evaluating its partition function.

This is the second aim of this work. The Hubbard model is simplest model that describes
itinerant-electron magnetism and the partition function for the model can be calculated using a functional integral scheme. I review the Hubbard model and derive the functional integral in Chapter eight. The details of the quantum Monte Carlo method which is used to evaluate the functional integral are also presented in Chapter eight. The main point of these calculations was to gain some insight into the effects of making the static approximation. The results of a quantum Monte Carlo calculation of the 1D and 3D Hubbard model are presented in Chapter nine. The work is concluded and some directions for further work are presented in Chapter ten.

In this introductory chapter the basis of magnetism in materials and a brief review of the early theories of magnetic behaviour are given in sections (1.3-6). Throughout most of this work it is assumed that local magnetic moments exist in itinerant magnets. The validity of making this assumption is discussed in section (1.7). Section (1.8) is concerned with a more detailed review of the experimental results that have been obtained for 3d transition metal magnets in order to clarify the problems faced when trying to derive a theory of magnetism for these materials. The more recent theories to interpret the experimental observations, the fluctuating local band theory and the disordered local moment theory are reviewed in section (1.10).

1.3 The magnetic moment of an ion.

The magnetic moment of an atom or ion must be due to partially filled atomic shells since in a filled shell there are equal contributions from electron spins in opposite spin directions. The electrons thus contributing to the atomic moment usually belong to partially filled d or f shells of magnetic materials.

The ith electron in partially filled shell of a free atom will have an orbital quantum number \( l_i \) and a spin quantum number \( s_i \). The total orbital and spin angular momenta \( L \) and \( S \) are vector sums of the individual electron orbital and spin angular momenta \( hl_i \) and \( hs_i \) respectively. The two momenta are maximized by Hund's rules and coupled by Russell-Saunders coupling. The total angular momentum \( J \) is then given by the vector sum \( L+S \).
The magnetic moment \( m \) of the atom with the total angular momentum \( J \) is given by

\[
m = -g\mu_B (J(J+1))^{1/2},
\]

where \( g \) is the Landé splitting factor

\[
g = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)},
\]

and \( \mu_B \) is the Bohr magneton.

The formulation above does not include thermal effects nor does it say anything about the various magnetic phenomena. Assuming we have a magnetic moment then we must develop a theory to describe how the magnetic moments cooperate and the thermodynamics of the collective system of magnetic moments.

1.4 A simple model - Mean field theory.

Weiss proposed a theory to describe the cooperative behaviour of ferromagnetic materials, which is generally called the mean or molecular field theory. As the name implies the basis of the theory is that any ion is subject to the mean molecular magnetic field due to the other ions. The theory describes the thermodynamics of ferromagnets above and below the Curie temperature.

Consider the ferromagnetic phase. We want to find the value of the saturated magnetisation at very low temperatures in the absence of any external magnetic fields. Van Vleck used quantum mechanics to derive an expression for the average magnetisation of the material

\[
M = \frac{N}{V} g \mu_B J B_f(x),
\]

where \( N \) is the number of atoms in a volume \( V \), and \( B_f(x) \) is the Brillouin function, this is related to the Langevin function \( L(x) = \coth(x) - 1/x \). The parameter \( x \) is

\[
x = \frac{g \mu_B J H}{k_B T},
\]
where \( k_B \) is the Boltzmann constant. The internal molecular field \( H_{\text{int}} \) can be written as \( \alpha M \), where \( \alpha \) is called the Weiss constant. By replacing \( H \) with \( H_{\text{int}} \), we have the following expression for the saturated magnetisation

\[
M_S = \frac{N g \mu_B J_B}{k_B T} \left( \frac{g \mu_B \alpha M}{k_B T} \right) \tag{1.4}
\]

This equation has to be solved graphically by plotting \( M \) against \( x \). The intersection of this curve and that of \( M = k_B T/(g \mu_B J \alpha M) x \) for low temperatures \( (T < T_C) \) will give the value of the saturated magnetism.

The **paramagnetic phase** - above the critical temperature there is no net magnetisation due to the ions. If however an external magnetic field, \( H_{\text{ext}} \), is applied to the material the magnetic moments will align to produce a net magnetisation \( M \) in the direction of the external field. The paramagnetic response or susceptibility \( \chi_0 \) of the material subject to the external field is given by

\[
\chi_0 = \frac{M}{H_{\text{ext}}}. \tag{1.5}
\]

At high temperatures \( g \mu_B J H \ll k_B T \), by expanding \( \coth(x) \) and taking the leading term we can write

\[
\chi_0 = \frac{\mu_B^2 N}{3 k_B T} = \frac{C}{T}. \tag{1.6}
\]

This result is called the Curie Law and \( C \) is called the Curie constant. Let us now correct this result for the effect of the internal molecular field by writing

\[
\chi_0 = \frac{M}{H_{\text{ext}} + H_{\text{int}}}. \tag{1.7}
\]

The internal field can be written as \( \alpha M \) and \( \chi_0 \) has a Curie susceptibility \( C/T \) so the normal susceptibility \( \chi \) can be written as

\[
\chi = \frac{M}{H_{\text{ext}}} = \frac{\chi_0}{1 - \alpha \chi_0} = \frac{C}{T - \alpha C} = \frac{C}{T - T_C}. \tag{1.8}
\]
This is known as the Curie-Weiss law and compares very well with experimental results. Near the critical temperature $T_C$ there is a difference between experiment and theory and this is due to critical behaviour the simple theory ignores. This law is a useful test of the predictions of any theory that claims to describe magnetic behaviour.

1.5 The Heisenberg model.

Heisenberg (1928) attributed the origin of the molecular field to the quantum-mechanical exchange interaction between neighbouring atoms. The Hamiltonian of the model is

$$H = - \sum_{i,j} J_{ij} S_i S_j,$$  \hspace{1cm} (1.9)

where $i$ and $j$ are site indices, $S_i$ is the spin at site $i$ and $J_{ij}$ is the exchange interaction between the sites $i$ and $j$. In general terms the exchange interaction is due to the Coulomb electron repulsion and the Pauli exclusion principle, this often referred to as direct exchange. If the magnetic atoms in a material are separated by non-magnetic atoms (one with closed electronic shells) it is possible for the magnetic moments to interact via the overlap of the magnetic atoms with non-magnetic atoms. This type of interaction is called the super exchange interaction. Yet another type of interaction is possible, the indirect exchange interaction. In this case the magnetic atoms are quite far apart so that there is no overlap of the orbitals; this is true of the rare earths. The exchange interaction between the magnetic 4f electrons in these materials is mediated by the $sp$ conduction electrons. This is also called the RKKY interaction. The exchange interaction is discussed in detail by Mattis (1981).

The exchange interaction for iron will be discussed in Chapter two.

The origin of the molecular field can be described with the use of the exchange interaction. The exchange energy of atom $i$ is given by

$$-(\sum_j J_{ij} S_j) S_i,$$  \hspace{1cm} (1.10)
where the summation is over the neighbours of atom \( i \). The magnetic moment at site \( i \) is given by

\[
m_i = -g\mu_B S_i,
\]

(1.11)

assuming that the orbital contribution is quenched. Orbital quenching is due to the Stark splitting effect which lifts the \((2L + 1)\) degeneracy of the orbitals in the presence of crystal fields, for any given \( L \). This will then reduce the contribution of the orbital motion to the magnetic moment. The exchange energy can be written as

\[
\frac{1}{g\mu_B} \sum_j J_{ij} S_j \cdot m_i.
\]

(1.12)

The exchange interaction can be replaced by the interaction between a spin moment and an effective induction field given by

\[
\frac{1}{g\mu_B} \sum_j J_{ij} S_j.
\]

(1.13)

Consider the case where there is only a nearest-neighbour interaction \( J \). The local field at the site of atom \( i \) due is therefore

\[
H_{\text{int}} = \frac{1}{g\mu_B} \sum_j J_{ij} S_j = \frac{2JS}{g\mu_B},
\]

(1.14)

where the \( z \) nearest-neighbours of \( i \) have the spin \( S \).

In the ground state all the spins will have an average magnitude of \( \langle S \rangle \) and so the magnetisation in the nearest-neighbour Heisenberg model can be written as

\[
M = g\mu_B \langle S \rangle.
\]

(1.15)

In the mean field approximation the Curie temperature is given by

\[
T_C = \frac{2JS(S+1)}{3k_B}.
\]

(1.16)
The model will describe ferro- and anti-ferromagnetism if the sign of the exchange interaction is positive or negative respectively. Parallel magnetic moments will lower the overall energy of the system if the exchange interaction has a positive sign. If the exchange interaction has a negative sign then anti-parallel spins will lower the energy. The spins will order in one of the states (or some other state) at low temperatures and will disorder above the transition temperature. A good review of the model and its basis has been given by Mattis (1981) and the statistical mechanics of the model have been studied by Rushbrooke et al (1974) amongst others. The results from the model compare well with experimental results particularly for magnetic insulators. The spin in these systems is formed by strongly correlated electrons localised on atomic sites. In the transition metals, or itinerant-electron systems the magnetic properties are due to the conduction electrons and the occupation at an atomic site can fluctuate so the Heisenberg model cannot be applied directly to transition metals. Some assumptions about the magnetic moments in transition metals have to be made before a Heisenberg-like model can be used to study the statistical mechanics of such materials. This will be discussed in section (1.8).

The Heisenberg model and the mean field approximation is very useful for the study of magnetic properties of materials. In Chapter two the Heisenberg Hamiltonian will be used as a basis for the development of a model of iron using results from electronic structure calculations. The statistical mechanics of the nearest-neighbour Heisenberg model and the model of iron will be studied using Monte Carlo methods in Chapter four. The model is also used to study the low-temperature magnetic excitations (spin waves) in the model of iron and in the nearest-neighbour Heisenberg model. The spin wave theory introduced in Chapter six is a mean field approach.

1.6 The Stoner itinerant-electron model.

The Heisenberg model is only directly applicable to systems with localised electron states such as insulators. In metals the conduction electrons form electron bands and Stoner (1938) gave the first band theory of itinerant-electron magnetism. This treats uncorrelated itinerant-electrons in a mean field approximation. The electrons are allowed to interact
through the internal molecular field which causes a splitting of the majority (↑) and minority (↓) spin sub-bands. The separation of the bands is called the exchange-splitting $\Delta$, and the shifted density of states (Figure 1.1) of the sub-bands are

$$n_{\uparrow}(E) = n_0(E + \frac{1}{2}\Delta),$$

$$n_{\downarrow}(E) = n_0(E - \frac{1}{2}\Delta),$$

where $n_0$ is the density of states of the electrons in the non-magnetic phase (or equivalently the Pauli spin susceptibility). In the Hartree-Fock approximation the exchange field is given by

$$\Delta = mI,$$

where $I$ is called the Stoner parameter and $m$ is the magnetic moment per atom. The magnetic moment is defined as the difference between the number of majority and minority electrons on the site

$$m = \int_{-\infty}^{\infty} dE f(E,T) (n_{\uparrow}(E) - n_{\downarrow}(E)),$$

$$= \int_{E_F}^{\infty} dE (n_{\uparrow}(E) - n_{\downarrow}(E)), \quad \text{as } T \to 0$$

$$= n(E_F)\Delta,$$

where $f(E,T)$ is the Fermi function and $E_F$ is the Fermi energy. The self-consistent solution of equation (1.18) and (1.19) gives the magnetic moment as a function of temperature $T$. For a ferromagnetic ground state there must exist a non-zero solution of equation (1.19) and this is found when

$$\ln n_0(E_F) \geq 1.$$  

This is called the Stoner criterion. The origin of $I$ is in fact due to the exchange and correlation arising from many body electron interactions (e.g. Wohlfarth, 1980) and is related to the $I$ in the Hubbard model used in Chapter two to calculate the electronic structure of transition metals.
Figure 1.1. Splitting of minority and majority spin sub-bands in the Stoner model. Thin line: density of states in the non-magnetic state. Thick line: density of states in the ferromagnetic state.

As the temperature is increased thermal excitations of the electrons between the sub-bands will lead to a continual decrease in $\Delta$ and thus the magnetic moment. At the transition temperature the magnetic moment falls to zero, above the transition temperature no moment exists. Further the transition temperature calculated using the theory is too high, Gunnarsson (1976) has calculated $T_C = 4400-6200, 3300-4800$ and 2900K for Fe, Co, Ni, while the experimental values are 1043, 1388, and 628K respectively. The theory fails to predict a correct transition temperature because the energy required to make the exchange splitting vanish is much greater than the typical thermal energies $k_B T_C$(theory) of the electrons at the transition temperature. The theory also neglects the interactions between the magnetic moments, these spin wave excitations have lower energies than thermal excitations and are found to dominate the low temperature behaviour of real systems, this gives a $T^{3/2}$ low temperature dependence of magnetisation while Stoner theory predicts a $T^2$ dependence. Finally above the transition temperature neutron scattering experiments performed on
transition metals reveal the existence of well defined magnetic moments. The theory therefore fails in describing the paramagnetic state of metallic magnets. Also there is no adequate account for the Curie-Weiss behaviour of the susceptibility found in many metallic magnets.

There are several corrections that have been made to the theory. Herring and Kittel (1951) have included the effect of spin waves on a phenomenological basis by treating these as long wavelength fluctuations in the direction of the magnetisation. Herring (1952) used the dynamical Hartree-Fock or random phase approximation (RPA) to provide a microscopic basis for spin waves. Izuyama et al (1963) used RPA theory of general spin fluctuations to study paramagnetic spin fluctuations and also fluctuations near the critical point. The inclusion of spin waves gives a correction to the low temperature predictions, Thompson et al (1964) derived an expression for the magnetisation of the form

\[
M(T) = M(0)[1 - A(k_B T/D)^{3/2} - B(k_B T)^2 - O(T^{5/2})].
\]  

(1.21)

where \(A\) is a parameter of the order 1, \(B\) is a functional of the density of states, and \(D\) is the spin wave stiffness constant.

1.7 The phase transition in itinerant-electron magnets.

We have considered above two models of magnetic behaviour which are mutually opposite to each other. In the Heisenberg model, the electrons are well localised on the atomic sites, whereas in the Stoner model the electrons are itinerant and localised in reciprocal space. We have also considered how the two theories predict the phase transition from the ordered to the paramagnetic state; in the Heisenberg model the transition is described simply by considering the magnetic degrees of freedom; it is the misalignment of the spins that causes the phase transition. For transition metals the magnetic degrees of freedom cannot be separated from the translational degrees of freedom (the magnetic carriers are itinerant) and so a Heisenberg-like description cannot be employed directly, unless some kind of localised moment is assumed to exist (see section 1.8). Turning to an electron band
description, the Stoner model, we find that the reduction of the magnitude of the magnetic moment to zero above the transition temperature is too simple a description of the phase transition.

The question then is what mechanism is responsible for the phase transition in itinerant-electron magnets. Other than the temperature dependence of the exchange splitting, in the past two possible explanations have been offered. Both are based on fluctuations of the magnetic moments. Firstly we can consider amplitude (longitudinal) fluctuations (Moriya, 1979). In this description magnetic moments persist above $T_C$ however the amplitude of the magnetic moments fluctuates strongly in both space and time. Long range order is therefore destroyed by these strong amplitude fluctuations. Although this mechanism may explain the behaviour of weak itinerant ferromagnets it is not adequate for transition metals since the energies required for large amplitude fluctuations are of the order of the exchange splitting which is not available at $T_C$ for transition metals.

Secondly we may consider transverse fluctuations of the magnetic moment. We assume that the magnetic moments have a fixed magnitude (we ignore longitudinal fluctuations) but above the transition temperature they fluctuate in direction as in the Heisenberg model. Transverse fluctuations in the ground state and at temperatures below $T_C$ are spin-waves and the energy cost associated with a transverse fluctuation is small (of the order $0.05eV$). The phase transition may then be due to the population of these spin wave states leading to the destruction of long range order. In the paramagnetic phase spin waves may persist leading to short range order. The modern theories of metallic magnetism discussed in section (1.10) are based on transverse fluctuations however these offer different perspectives on short range order above $T_C$.

In Chapter eight, the correspondence of transverse and longitudinal fluctuations to spin and charge fluctuations respectively will be considered in the framework of the Hubbard-Stratonovich transformation and the functional integral and how the two can be coupled to give a more complete description of itinerant-electron ferromagnets.
1.8 Local moments in itinerant-electron magnets.

The modern theories of itinerant-electron magnets assume that local moments exist in transition metals, but how confident can one be in making this assumption? The measurements of the Fermi surface for materials like nickel and iron prove that the magnetic d electrons in these materials are itinerant. Fermi surface studies on iron and nickel have been reviewed by Lonzarich (1980). The choice of either an itinerant-electron or localised electron description can be made on the basis of different classification schemes. These will be discussed briefly in this section.

A local moment $m_{\text{eff}}$ can be obtained from the Curie-Weiss susceptibility above $T_C$ as

$$m_{\text{eff}} = \sqrt{\frac{3k_B C}{(N/V)\mu_B^2}}, \quad (1.22)$$

From which the number of magnetic carriers $n_c$ per atom, can be determined,

$$m_{\text{eff}}^2 = n_c(n_c + 2). \quad (1.23)$$

A similar number, $n_8$, can be found from the saturated ordered moment for low temperatures. The ratio of $n_c/n_8$ (called the Rhodes-Wohlfarth ratio) has been considered by Wohlfarth (1980) for a range of materials. It would appear that, if $T_C$ is not too high, this ratio gives a reliable measure of the itinerancy of the magnetic electrons. The ratio is unity for the insulator EuO, as one would expect since this material has well localised magnetic electrons. The ratio is expected to be higher for itinerant-electron systems and is about 8 for Ni$_3$Al and 6 for ZrZn$_2$.

Another classification is given by examining the magnetic excitations of the material. The relationship between the spin wave energies in comparison with $T_C$ and the localised or itinerant nature of electrons was first discussed by Mook (1983). Measurements of the magnetic excitation spectrum in Gd (Mook, 1983) show that $T_C$ is higher in energy than the spin wave energies and at the zone boundary spin wave energies reach a value just equal to $k_BT_C$. For EuO no distinct spin waves are found at or above $T_C$, except near the zone boundary. Two important classification schemes can be derived from these observations.
Firstly it is suggested that the ratio of the spin wave stiffness $D$ and $T_C$ (in units meVÅ²/K) relates to the itinerancy of the electrons, and that a smaller ratio suggests a more localised electron system. This ratio is 0.17 and 0.16 for EuO and EuS, respectively, while for the itinerant system Ni₃Al it is near 2.0. The ratio is 0.87 for nickel, suggesting a partly itinerant-electron character. However it is smaller (0.28) for iron, nearer the value for more localised electron systems. A similar result is found in the Rhodes-Wohlfarth ratio (it is 1.05 for iron) which would also suggest that a localised picture is more appropriate for iron.

The ratio of the maximum spin wave energy to $k_BT_C$ is also an important number and may provide a better classification for itinerant-electron magnetism (Mook, 1988). The maximum spin wave energy is at the zone boundary for insulators and at the value of $q$ at which the spin wave mode enters the Stoner continuum for itinerant magnets (see section 1.9). This ratio is known accurately for EuO and EuS, 1.0 and 1.8, respectively. Higher numbers would suggest more itinerant-electron behaviour and the values for nickel and iron are estimated to be in the range 6-10 from band structure calculations and the extrapolation of neutron scattering data. Table 1.1 summarises the magnetic properties and classification parameters for some common materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_C$(K)</th>
<th>$m_{sat}$(μB)</th>
<th>$D$(meVÅ²)</th>
<th>$n_d/n_s$</th>
<th>$D/T_C$(meVÅ²/T)</th>
<th>$Z_B/k_BT_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>628</td>
<td>0.615</td>
<td>550</td>
<td>1.46</td>
<td>0.87</td>
<td>6.5</td>
</tr>
<tr>
<td>Fe</td>
<td>1043</td>
<td>2.217</td>
<td>281</td>
<td>1.03</td>
<td>0.28</td>
<td>9.0</td>
</tr>
<tr>
<td>Co</td>
<td>1388</td>
<td>1.753</td>
<td>510</td>
<td>1.34</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>Cr(a)</td>
<td>300</td>
<td>-</td>
<td>500</td>
<td>-</td>
<td>16.7</td>
<td>1.6</td>
</tr>
<tr>
<td>EuO</td>
<td>69</td>
<td>6.8</td>
<td>12</td>
<td>-</td>
<td>0.17</td>
<td>1.0</td>
</tr>
<tr>
<td>EuS</td>
<td>16.9</td>
<td>-</td>
<td>2.6</td>
<td>-</td>
<td>0.15</td>
<td>1.8</td>
</tr>
<tr>
<td>Ni₃Al</td>
<td>41</td>
<td>-</td>
<td>85</td>
<td>-</td>
<td>2.07</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 1.1. Magnetic properties and classification parameters of magnetic materials: $T_C$ is the Curie temperature, $m_{sat}$ is the saturated magnetic moment, $D$ is the spin wave stiffness (at room temperature), $n_d/n_s$ is ratio of magnetic carriers in the paramagnetic state and at $T = 0$, $Z_B/k_BT_C$ is the maximum spin wave energy divided by $k_BT_C$. The data are from [1]: Mook (1988 and references therein) and [2]: Wohlfarth (1980). (a)Cr is an anti-ferromagnet so its Néel temperature is given.
So which model best applies to the archetypal magnet iron? Experimental results and different classification schemes would suggest that a localised electron picture is more appropriate to more or less the same degree. Band structure calculations and measurements of the Fermi surface however would suggest that the magnetic electrons in iron are more itinerant. We find that neither the localised nor the itinerant-electron theory provides a complete description of magnetic behaviour in itinerant systems but instead metallic magnets fall between the two extremes of a Stoner model and an itinerant Heisenberg-like model, Figure 1.2. The possibility of local moments in metals has been investigated, van Vleck (1953) discussed the local moment in terms of the electron correlation in the narrow $d$ bands in metals. The theories that have had the most impact however are due to Friedel (1956) and Anderson (1961). These discuss the formation of local moments on transition metal impurities in alloys. In these it is assumed that the electrons form a virtual bound state around a metal atom to give a localised magnetic moment.

The formation of a local moment in itinerant-electron magnets described by a Hubbard model will be demonstrated in Chapter nine using quantum Monte Carlo simulations.

\[ T = 0 \quad 0 < T < T \quad T > T \]

(i) The Stoner model.

(ii) The Heisenberg model.

(iii) Spin fluctuation theories.

**Figure 1.2.** Models of magnetism.
1.9 A review of experimental results.

Before discussing the modern theories of metallic magnetism a review of the experimental results obtained for metallic magnets such as iron and nickel and the controversy surrounding these materials shall be given. The expressions for the susceptibilities are included for sake of completeness and to give an idea of how the magnetic excitations can be measured by experiment.

The main experimental method for studying the magnetic properties of materials is neutron scattering. The neutron can interact with matter through a nuclear interaction and its spin can interact with the magnetic moments through a magnetic dipole-dipole interaction. These two interactions can be separated in an experiment and it is the interaction of the neutron spin with the magnetic spin of the atoms that is important for the measurement of magnetic excitations.

The interaction of a monochromatic beam of neutrons (a beam in which all the neutrons have the same wavelength or energy) with a target may be defined by the partial differential cross-section (Marshall and Lovesey, 1971)

\[
\frac{d^2\sigma}{d\Omega dE'} = \gamma_0 \left[ \frac{1}{2} g F(K) \right]^2 \sum_{i,j} \frac{k'}{k} \left( \delta_{ij} - \vec{K}_i \vec{K}_j \right) d\Omega' \frac{1}{2\pi \hbar} \int dr \exp(i\omega t) \langle S_i(K,0) S_j(-K,t) \rangle.
\] (1.24)

This represents the fraction of neutrons scattered into an element of solid angle \(d\Omega\) with an energy between \(E'\) and \(E' + dE'\) (\(E'\) is the final energy of the neutron), the cross-section has units of area/energy. In equation (1.24) \(\gamma_0\) is a constant related to the nuclear magneton, \(k'\) and \(k\) are the wave vector of the incident and scattered neutron, \(K = k - k'\) and \(\vec{K}\) is a unit vector. The function \(F(K)\) is called the magnetic form factor, which is the Fourier transform of the magnetic electron spin density and can be determined using elastic polarized neutron scattering. The quantity of interest when discussing short range order is the thermal averaged spin-spin correlation function, \(\langle S_i(K,0) S_j(-K,t) \rangle\), between the spin at coordinate \(i\)
at time 0 and the spin with coordinate \( j \) at time \( t \). This quantity can also be calculated through Monte Carlo simulation (for equal time) and in Chapter four it will be used to compare short range order in the nearest neighbour Heisenberg model and iron. The correlation function can also be extracted from imaginary time data obtained from quantum Monte Carlo simulations. The correlation function therefore provides a useful parameter for comparison of experimental and theoretical results.

When investigating itinerant-electron systems it is usual to express the neutron cross-section in terms of the generalised susceptibility \( \chi^{\pm}(k, \omega) \) (Mook, 1988; Lynn, 1975). This contains a complete description of the magnetic energy spectrum of the system; therefore the linear response of the system to any magnetic perturbation (e.g. spin wave) can be found. The generalised susceptibility is related to the spin correlation function by (Mook, 1988)

\[
\frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle S_i(k,0)S_j(k,t) \rangle
\]

\[
= \frac{\hbar \omega}{\exp(\hbar \omega/k_BT) - 1} \frac{N}{2\pi i \omega (g\mu_B)^2} [\chi_{ij}(k,\omega) + \chi_{ji}(k,\omega)^*],
\]  

(1.25)

where \( N \) is the number of atoms, \( T \) is the temperature, \( g \) is the Landé splitting factor, \( k_B \) is the Boltzmann factor and \( \mu_B \) is the Bohr magneton. The cross-section can then be written as (Mook, 1988)

\[
\frac{d^2\sigma}{d\Omega dE'} = \gamma_0 \frac{1}{2} g F(K)^2 \frac{k'}{k} \\
\times \left\{ (1 - \tilde{K}^2) \frac{N}{\pi (g\mu_B)^2} \frac{\exp(\hbar \omega/k_BT)}{\exp(\hbar \omega/k_BT) - 1} \text{Im}\chi^{zz}(\omega) \\
+ (1 + \tilde{K}^2) \frac{N}{4\pi (g\mu_B)^2} \frac{\exp(\hbar \omega/k_BT)}{1 - \exp(\hbar \omega/k_BT)} \\
\times \text{Im}[\chi^+(K,\omega) + \chi^-(\mathbf{-K},\omega)] \right\}.
\]  

(1.26)

The imaginary part of the susceptibility is given by
Chapter One: Introduction

where $I$ is the Coulomb repulsion between electrons on an atomic site and $\chi^0_0(k, \omega)$ is called the non-interacting susceptibility the imaginary part of which is related to the single particle (Stoner) excitations (Mook, 1988)

$$\chi^0_0(k, \omega) = -\frac{(g\mu_B)^2}{N} \sum_q \frac{f_{k+q} - f_{k\uparrow}}{E_{k+q} - E_k + \Delta + \hbar \omega + i\epsilon}.$$ (1.28)

where $\Delta$ is exchange splitting at the $N$ atomic sites, $f_{k\uparrow}$ is the Fermi-Dirac distribution for the state $k$, $E$ are the band energies and $\epsilon$ is a small constant. The density of Stoner excitations is proportional to the imaginary part of $\chi^0_0(k, \omega)$ (Lynn, 1975). The Stoner excitation energies are given by

$$\hbar \omega_{\text{Stoner}} = E_{k+q} - E_k + \Delta.$$ (1.29)

These energies dominate the energy spectrum at high $q$ values. Using equation (1.26) the cross-section for small $q$ values can be expressed as (Mook, 1988)

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{1}{4} \frac{[F(K)]^2}{k^2} (1 + k^2/2\mu_B^2 \frac{N\Delta}{I})$$

$$\times \sum_{q,R} n_q(\omega') \delta(\hbar \omega + \hbar \omega') \delta(K + q - R)$$

$$+ \left[ 1 + n_q(\omega') \right] \delta(\hbar \omega - \hbar \omega') \delta(K - q - R),$$ (1.30)

where $n_q$ is the Fermi occupation function, $R$ is the reciprocal lattice vector.

This expression gives the complete description of the excitations that a neutron scattering experiment will measure. The susceptibilities can also be calculated and so provide a comparison of theory and experiment. Figure (1.3) shows the energy spectrum for a single band itinerant-electron system. Excitations due to spin waves start at $\hbar \omega = 0$ and $q = 0$. As $q$ increases from zero there is an increase in the number of energies that satisfy
equation (1.29) and so the single particle excitations fan out from $\Delta$. At some value of $q$ the spin wave mode is damped out by the Stoner excitations.

![Spinwave mode](image)

**Figure 1.3.** Energy spectrum of magnetic excitations in a single band itinerant magnet.

The neutron scattering experiments of Lynn for iron (1975) and Mook *et al* for nickel (1973) were performed using a constant energy transfer and varying the momentum transfer. In the ferromagnetic region below $T_C$ the results indicated a spin wave peak in the region of $(q,\omega)$ space where no Stoner excitations occur. When the Stoner continuum is reached the spin wave peak is reduced. This is the expected behaviour of itinerant magnets. The controversy surrounds the higher temperatures. The constant energy scans at large energy transfer show that the spin wave peak drifts to a larger $q$ as $T_C$ is encroached, the width of the peak also increases with temperature. Above $T_C$ no further shift to larger $q$ or increase in the peak width is observed as the temperature is increased. Further if the spin wave dispersion is plotted for different temperatures a weak renormalisation of the magnon energies is observed (refer also to Chapter six of this thesis). More recently Wicksted *et al* (1984), Shirane (1984) and Shirane *et al* (1986) have conducted a polarized-neutron-beam scattering study of iron. Their results would indicate that spin wave modes are *not* present.
above $T_C$. Their constant q scans consist of broad energy distributions centred at zero energy. In contrast to the results of Lynn (1975) they find no peaks at finite energy transfers. Further they interpret the constant energy peaks in iron as slices of a simple paramagnetic scattering function and not as spin wave modes.

A more direct measurement is reported by Brown et al (1982,1983) and Johnson et al (1987). This is a measurement of the scattering function $S(q)$ above $T_C$. This function is related to the spin density - spin density correlation function by

$$S_{ij}(q,\omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} e^{i\omega t} g^2 \mu_B^2 \langle S_i(q,\omega) S_j(q,t) \rangle \, dt,$$

where $S_{ij}(q,t)$ represents the qth component of the Fourier expansion of the spin density function, it is related to the real space spin correlation function $S_{ij}(r,t)$ by

$$S_{ij}(q,t) = \sum_r e^{iqr} S_{ij}(r,t).$$

The measured scattering can be expressed in terms of an "effective moment" $M(q)$, which is the energy integral of $S(q)$. If $q^2 M(q)$ is plotted against q for iron the correlation function does not follow a Ornstein-Zernike form (see Chapter four). The plot is a direct indication of the values of q that contribute significantly to the Fourier spectrum of the spin density function and therefore the real space spin correlation. A peak in the function is observed at around $q = 0.4\text{Å}^{-1}$, which gives a typical wave length $\lambda = 2\pi/q$ in the Fourier spectrum which is of the order of 16Å. This peak is also found to be weakly dependent on temperature. The value of q at which this peak occurs therefore establishes a scale at which disorder occurs.

Edwards (1983a,b) has challenged the interpretation of this result. Experimentally the energy integral of $S(q)$ cannot be performed between infinite limits, instead there is an energy window. Edwards argues that the experiment may miss a substantial weight in the integral, especially at high q, and therefore the interpretation of the results overestimates the
short range order. The Monte Carlo analysis by Shastry (1984) of the dynamics of a nearest neighbour Heisenberg model also finds a large amount of missing weight at high \( q \).

An alternative experimental method to neutron scattering is angle resolved photoemission (Haines et al 1985, Kisker et al 1985). This allows a probe of the electronic states of materials. The method determines the one-electron states due to scattering from magnetic excitations. Now if short range order occurs on a large scale then within this region the magnetisation would be fairly constant and therefore the electronic structure would resemble that of the ground state or low temperatures. This essentially is the viewpoint of the fluctuating local band theory, therefore photoemission experiments allow the theory to be tested. The measurements on nickel do not conclusively prove the fluctuating local band theories correct, the measurements on iron however do appear to demonstrate the correctness of the theories. At the symmetry point \( \Gamma \) there appear polarized, exchange split states (Kisker et al 1985). As the temperature is raised the states essentially remain fixed, but their polarisation changes indicating that the local exchange field has changed its direction but not its magnitude. This verifies that the phase transition in metallic magnets is driven by transverse fluctuations and not by longitudinal fluctuations. The degree of short range order can be determined by an analysis of the electronic structure measured by the method at different \( k \) points. Haines et al (1985) predict that the disordered local moment picture is incorrect and short range order of about 4Å. The analysis is based on the spin-spiral model and the random cluster approach (random exchange field distributions).

1.10 Modern theories of magnetism.

In the preceding section the controversy surrounding metallic magnets in particular the issue of magnetic short range order in the paramagnetic state was discussed briefly. We saw how neutron scattering and measurements apparently indicate short range order. The angle-resolved photoemission experiments support transverse fluctuations as the major mechanism that drives the phase transition. Two theoretical models have been developed in the past in an attempt to explain the magnetic behaviour of metallic magnets. Most other
theories are essentially based on these. The fluctuating local band theory supports short range order whereas the disordered local moment theory does not. The experimental results, in particular those from photoemission experiments tend to favour the fluctuating local band theory. The main points of these theories are now discussed.

1.10.1 Fluctuating local band picture.

The fluctuating local band theory has been developed by Korenman, Murray and Prange (1977) in order to explain the apparently large magnetic short range order observed in metallic magnets. The theory uses an effective Hubbard Hamiltonian and its partition function is calculated using the functional integral method (see Chapter eight of this thesis for a review of the Hubbard model and derivation of the functional integral). The integral is performed as a sum over selected important configurations. The large SRO is introduced at this point as the smooth variation in the direction of magnetisation from atom to atom, the pitch angle between neighbouring spins having a value of the order of 36°. The direction of spin quantisation is redefined with respect to the direction of the local magnetisation and the band structure is recovered. This leads to a Heisenberg type behaviour for the energy of the configuration. The theory thus supports SRO above $T_c$, since it is argued that exchange-split local band structure is needed to support the spin wave behaviour observed in experiment.

1.10.2 Disordered local moment picture.

Hubbard (1979) has developed a theory based on the Stoner model but with a more general behaviour of the exchange field. Firstly since the exchange field on an atom depends on the spin of the atom, which is a vector quantity, then it is reasoned that the exchange field is also a vector quantity. The unified model allows the exchange field to fluctuate in both amplitude and direction. The exchange field does not necessarily vanish above the transition temperature. The model does not support SRO above $T_c$ since it is based on the coherent potential approximation (CPA). This treats the configuration of the local exchange fields in a mean field type of approximation. The basic assumption of the theory is that at any time the magnetic configuration is described by some specific distribution of the spin up and spin
down electrons. The electrons are itinerant and so hop from atom to atom, within some time period which is much shorter than the spin wave lifetimes. This is the static approximation. In the framework of the theory the electron hopping is a process in which the spin up electrons visit sites with a predominant number of spin up electrons and the spin down electrons visit sites with a predominant number of spin down electrons; thus establishing local moments. The magnetic configuration is characterised by the exchange field vectors. The phase transition is due to randomisation of the directions of the exchange fields, i.e. transverse fluctuations. There is no correlation of the exchange fields at neighbouring sites above the Curie temperature.

1.10.3 Spin polarised band theory.

The spin polarised band theory at finite temperatures (Gyorffy et al, 1983) is based on first principles band structure calculations. This is a parameter free method for investigating the properties of materials, both electronic and magnetic, and so is more accurate than the semi-empirical FLBT and DLM methods. The theory incorporates features of both the FLBT and DLM viewpoints. The direction of the magnetic moment is characterised by a unit vector and the static approximation is made, and so "binary alloy" type of configurations of DLM or spin wave type of configurations of FLBT can be set up. The essence of the theory is that the statistical mechanics of spin configurations can be derived from the grand potential function which is given by the energy of a given configuration of the magnetic moments. The energy is calculated using spin density functional theory in the KKR-CPA, which is a self-consistent version of the CPA. The theory leads to the formation of a local moment and a Curie-Weiss behaviour above the transition temperature. The main point is that the theory is entirely parameter free and so calculates the electronic structure to a greater accuracy than the theory outlined in Chapter two of this thesis which is parameterised by band structure calculations. This fact leads one to speculate on the form of the exchange interactions calculated by Luchini and Heine (1991) and a possible improvement in our understanding of the nature of non-pairwise exchange interactions in itinerant magnets might be gained in calculating the electronic structure using spin density functional theory.
Chapter Two.

Electronic structure calculations - a model of iron.

2.1 Many-atom exchange interactions.

In the introduction we looked at the Heisenberg model which describes the interaction of localised magnetic moments through an exchange interaction, $J_{ij}$. Due to the itinerant nature of the magnetic electrons in iron a memory of the magnetic environment is retained by the electrons as they hop from atom to atom. This implies that if iron is to be described as a system of localised moments (formed somehow by the itinerant-electrons) the possibility that the exchange interaction between the moments may be affected by the magnetic environment around a pair of moments must be taken into consideration.

If one can obtain the energetics of configurations of the magnetic moments in iron then the statistical mechanics of iron can be investigated fairly easily. The topic of the present chapter is to review a scheme for studying the electronic properties of itinerant-electron systems such as iron. The results of such calculations have yielded much important information on iron and have implications for short range order in iron above $T_C$. The energetics for configurations of magnetisation in iron can be used to derive a Heisenberg-like model of iron, the statistical mechanics of which can be investigated using Monte Carlo simulation.

2.2 Electronic structure in a local atomic environment.

The microscopic description of iron is based on the Hubbard model. This is a simple model that interpolates between the localised and itinerant extremes of magnetism. The procedure of how one can set up calculations for the electronic structure of the Hubbard model is discussed here as some of the principles will also be relevant when the Hubbard model is solved using a functional integral scheme and the quantum Monte Carlo method (Chapter eight). The parameterisation of the Hamiltonian for iron or any other material it
Chapter Two: A model of iron.

describes is the same for both schemes. The Hubbard model will be discussed further in Chapter eight.

The method used to calculate the electronic structure is the self-consistent solution of a one-electron Hamiltonian (Lin-Chung and Holden, Heine et al 1981, You and Heine, Holden and You 1982, Samson 1983, Small and Heine 1984, Luchini and Heine 1989, 1991). The Hamiltonian for these calculations can be written as

\[
H = H_{\text{band}} + H_{\text{int}}
\]

\[
H_{\text{band}} = \sum_{i,j,\alpha,\beta,\sigma} t_{ij\alpha\beta\sigma} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + (\text{h.c})
\]

\[
H_{\text{int}} = I_{\alpha\beta} \sum_{i\alpha\beta} n_{i\alpha\uparrow} n_{i\beta\downarrow}.
\]

The first term is the one-electron nonmagnetic Hamiltonian in the tight-binding approximation with \( t_{ij\alpha\beta\sigma} \) the hopping integral between the orbitals \( \alpha \) and \( \beta \) on sites \( i \) and \( j \), \( \sigma \) labels the spin state, \( c_{i\alpha\sigma}^\dagger \) and \( c_{j\beta\sigma} \) are the creation and annihilation operators respectively and \( n_{i\alpha\sigma} = c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma} \) is the number operator. The second term describes the electron-electron interaction \( I_{\alpha\beta} \) at a site. This term is not rotationally invariant and needs to be transformed from a many-body term to many one-body terms in order to solve the electronic structure. We shall see later how this is achieved by a Hartree-Fock approximation. The two-centre hopping integral between the \( d \) orbitals of iron can be expressed in terms of hopping matrix elements (Slater and Koster, 1954): \( d d \sigma \) (when the orbitals have \( s \) symmetry about the axis joining the atomic sites), \( d d \pi \) (for \( p \) symmetry about the axis) and \( d d \delta \) (for \( d \) symmetry about the axis). In Pettifor's (1977) scheme for Andersen's (1973) parameters these are

\[
\begin{align*}
dd \sigma &= -60 \\
\frac{dd \pi}{40} &= \left( \frac{S}{R} \right)^{15} \frac{W_d}{25} \\
\frac{dd \delta}{-10} &= -10
\end{align*}
\]

where \( S \) is the radius of the Wigner-Seitz atomic sphere, \( R \) is the interatomic distance and \( W_d \) is the band width resulting from these matrix elements. The tight-binding parameters to
represent the \(sp\) band and its hybridisation with the \(d\) band have to be obtained by empirical fitting to band structure calculations. In this model the electron-electron interaction in the second term is purely intra-atomic and is described by the parameter \(I_{\alpha\beta}\). This parameter may be different between the electrons in the same \(d\) orbital and between electrons on different \(d\) orbitals (Holden and You, 1982). For the five \(d\) orbitals in iron \(I_{\alpha\beta}\) will be a \(5 \times 5\) matrix for each site or a \(9 \times 9\) matrix if \(s\) and \(p\) bands are included. To keep the computations simple all the terms in the \(5 \times 5\) matrix have the same averaged \(I\) value. Luchini and Heine (1989) have extended this model for the full \(spd\) bands in iron.

The model is solved using a self-consistent solution based on the Hartree-Fock approximation. In this approximation the interaction term is written as

\[
-\frac{1}{2} \Delta_i \hat{\sigma}_i
\]

where \(\hat{\sigma}_i\) is the Pauli spin operator and \(\Delta_i\) is the exchange splitting on site \(i\). We have also moved from a many-body operator to many one-body-operators. Different forms of representing the interaction term will also be described in Chapter eight. In equation (2.1) \(H_{\text{band}}\) is defined in terms of global spin axes whereas \(H_{\text{int}}\) is defined with respect to local spin quantisation axes, therefore a transformation is required such that both \(H_{\text{band}}\) and \(H_{\text{int}}\) are defined for the same quantisation axes. To make the computations easier to set up a rotation matrix to transform \(H_{\text{int}}\) to the global spin axes is defined. The exchange splitting now depends on the angle between the electron spin and the global \(z\)-axis and so

\[
H_{\text{int}} = \frac{\Delta_i}{2} \begin{pmatrix} \cos \theta_i & \sin \theta_i e^{i\phi_i} \\ \sin \theta_i e^{i\phi_i} & -\cos \theta_i \end{pmatrix}
\]

(2.4)

Here \(\Delta_i\) is the magnitude of the exchange splitting, \(\theta_i\) and \(\phi_i\) are the azimuthal and polar angles of the spins on site \(i\). A similar rotation matrix will also be used in Chapter eight.

The electrons polarise in the direction of the exchange splitting and give rise to magnetic moments. The magnetic moment on site \(i\) can be found as the difference between the numbers \(N\) of up and down spin electrons.
where \( n_{i\alpha\sigma}(E) \) is the local density of states projected on atom \( i \), orbital \( \alpha \) and spin state \( \sigma \) and \( E_F \) is the Fermi energy. For a given configuration of the exchange splitting there will exist a set of self-consistent moments \( \{ m_i \} \). The self-consistency condition is then

\[
\Delta_i = \mathbf{m}_i. \tag{2.6}
\]

This term is generalised to

\[
\Delta_{i\alpha} = \sum_{\beta} I_{\alpha\beta} m_{i\beta}, \tag{2.7}
\]

if the exchange splitting and interaction are not the same for different orbitals and \( m_{i\alpha} = N_{i\alpha\uparrow} - N_{i\alpha\downarrow} \). This is a Stoner-like ansatz. In general \( m_i \) will not be quite parallel to \( \Delta_i \) due to induced moments in the orthogonal directions caused by the polarisation of the electron cloud with the environment (Small and Heine, 1985). Therefore for a general configuration full self-consistency defined in equation (2.6) is not obtained. The self-consistency condition is achieved by adjusting the magnitude of the exchange splitting so that self-consistency parallel to the field direction is obtained (Luchini and Heine, 1989). The induced moments play a central role in the calculation of the non-pairwise exchange interactions that define the present model of iron and will be described further in section (2.4).

The procedure for calculating the energies of the model is to set up configurations of the exchange field by setting the values of the angles \( \theta_i \) and \( \phi_i \). The magnitude of the exchange fields are then varied as described until self-consistency is reached. This is roughly the magnetic equivalent of the Born-Oppenheimer approximation (You and Heine, 1982). The magnetisation is taken as a classical field precessing slowly in comparison to electron hopping, and the energy calculated is that of electrons moving on this frozen configuration. This is the main approximation made in the calculation and it is generally called the static
approximation. There are justifications for making this approximation; one has to consider time scales. A typical magnetic excitation, a spin wave will have a lifetime of about $10^{-13}s$, whereas electron hopping occurs on the time scale of about $10^{-15}s$ so an electron hopping from an atomic site to another site and then back will "see" the same magnetic configuration during this process.

The quantities of central importance are the density of states. The local density of states $n_{\alpha}(E)$ (we will ignore the spin index for now) is related to the imaginary part of a Green function $G_{i\alpha i\alpha}(E)$ by the relation

$$n_{\alpha}(E) = -\pi^{-1} \text{Im} G_{i\alpha i\alpha}(E), \quad (2.8)$$

where

$$G_{i\alpha i\alpha}(E) = \langle i\psi_i \mid (E + i\Omega - H)^{-1} \mid i\psi_i \rangle, \quad (2.9)$$

here $|i\psi_i\rangle$ is defined in terms of a local basis set $\psi_{i\alpha}$, where $i$ is the site label and $\alpha$ indicates the type of atomic orbital (e.g., $3s$, $3p_x$, $3p_y$). This basis set is appropriate for the approximation of iron atoms since the atomic orbitals are localised at the atomic sites. The recursion method (e.g. see Haydock 1980) provides an efficient method of calculating any quantity that can be written as a diagonal element of the Green function. In the recursion method this is given by a continued fraction

$$G_{i\alpha i\alpha} = \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{E - a_2 - \cdots}}}, \quad (2.10)$$

Truncating at level $N$ simplifies equation (2.10) to a sum of rational fractions

$$\sum_s \frac{w_s}{E - E_s},$$

$w_s$ is the weight that eigenstates (labelled by $s$) of $H$ have on a particular atomic orbital and $E_s$ are the eigenvalues of $H$. If $E$ is interpreted as a complex number $E + i\Omega$ then the local density of states is given as a sum of delta functions.
The parameters that define the continued fraction are generated iteratively by the recurrence relation

\[ b_{n+1} = H|a_n\rangle - a_n|b_n\rangle - b_n|a_{n-1}\rangle , \]

where \( u_n \) is a new orthonormal basis set. If we let \( |u_0\rangle \) be \( |\alpha\rangle \) and assume it is localised on a central atom, then the Hamiltonian \( H \) in equation (2.12) is a matrix connecting \( |u_0\rangle \equiv |\alpha\rangle \) with \( |\nu \alpha\rangle \) on nearby atoms. Graphically this is depicted below.

Therefore the recurrence relation in equation (2.12) will transform the original system into a linear chain with the set of coefficients \( \{a_0, a_1, \ldots\} \) defining the energies of the states \( \{u_1, u_2, \ldots\} \) and \( \{b_1, b_2, \ldots\} \) defining the interaction between nearest neighbours of the chain. The recursion method then provides a method for calculating the local electronic structure properties of an ordered or disordered system (since the atomic orbitals \( |\alpha\rangle \) are defined in real space and not in \( k \)-space).

Let us now turn our attention to the data that can be obtained from the electronic structure calculations before looking at how this data can actually be used to investigate the statistical mechanics of iron. The total energy \( U \) of the system for any configuration of the exchange fields \( \Delta_i \) and self-consistent moments \( \mathbf{m}_i \) can be written as (Luchini and Heine, 1989)

\[ U = \sum_i \left\{ \int_{-\infty}^{E_F} E n_i(E) dE \cdot \frac{1}{4} \text{Im}_i^2 + \frac{1}{2} \Delta_i \cdot \mathbf{m}_i \right\} , \]
the first term in equation (2.13) is the sum of the one-electron energies. The second term corrects for double counting of exchange in the first term. The last term represents the interaction energy of the magnetic moment $m_i$ on each site with the exchange splitting on the site. The total energy for an arbitrary configuration relative to the ferromagnetic ground state could be represented as a sum of pairwise terms:

$$\Delta U = \frac{1}{2} \sum_{ij} J_{ij} (1 - \cos \theta_{ij}),$$

(2.14)

where $\theta_{ij}$ is the angle between moment at atom $i$ and atom $j$ and $J_{ij}$ is the exchange interaction between $i$ and $j$. This fitting is questionable as we shall see later on. By restricting the summation over the $z$ nearest neighbours of $i$ then the energy can obtained as a function of

$$\langle 1 - \cos \theta_{ij} \rangle = \frac{1}{2} \sum_{j=1}^{2} (1 - \cos \theta_{ij}).$$

(2.15)

In the next section use of the energetics to investigate short range order in iron is discussed.

2.3 Short range order.

There are various ways in which the resulting data on the energetics can be used. One can attempt to fit the data to a classical Heisenberg Hamiltonian of the form

$$H = - \sum_{i,j} J_{ij} \hat{e}_i \cdot \hat{e}_j,$$

(2.16)

where $\hat{e}_i$ is the direction of the magnetic moment on atom $i$. The magnetic moment on atom $i$ is $m \hat{e}_i$ and the exchange splitting is $\Delta \hat{e}_i$; we have absorbed the spin into the $J_{ij}$. This assumes pairwise exchange interactions $J_{ij}$ (which could be of fairly long range). This has been used in the past (Holden and You, 1982) to calculate the exchange interaction $J_{ij}$ up to the fifth neighbour. The configurations used in these calculations are the spin spirals and alternating tilts (which correspond to zone boundary spin waves). The spin spiral consists of planes of neighbouring spins. The spins in each plane are rotated at an angle with respect to the global axis. The difference in angle between neighbouring spins is fixed and this pitch
angle is used to characterise the spin spiral, this is equivalent to the configurations in the fluctuating local band theory. The spin spiral can be considered as an excited state of the Hamiltonian in equation (2.1) and is stable with respect to changes in the magnitude of $\Delta$. The alternating tilt again consists of planes of spins, however the spins are tilted at $\pm \frac{1}{2} \theta$ to the global axis. This is equivalent to the "binary alloy" limit in the disordered local moment picture. The exchange interactions obtained from these calculations were used by Holden and You (1982) to calculate the spin wave dispersion, the Curie temperature and the stiffness constant $D$ for iron. Luchini and Heine (1989) extended these calculations by using a full $spd$ tight-binding Hamiltonian finding $D = 313$ meVÅ$^2$. This is fairly close to the experimentally measured result of 281 meVÅ$^2$.

If an entropy can be attached to the various configurations used in the calculation of the energetics then the energies can be used in an alternative to fitting them to an effective Heisenberg Hamiltonian. This assumes less about the form of the effective Hamiltonian however it can be approximated by an arbitrary function $U = V_T(\Delta, \Delta \cos \theta, q)$ of three parameters: the amplitude $\Delta$ of the exchange field, the order parameter or reduced magnetisation (cos$\theta$) and a short range order parameter, the spin wave vector $q$. The entropy corresponds to the number of configurations in phase space which are "similar to" the chosen configuration, for example by finding the equivalent frozen spin wave

$$\Delta_i = \Delta (\sin \theta \cos q \cdot r_i, \sin \theta \sin q \cdot r_i, \cos \theta).$$  \hspace{1cm} (2.17)

By minimising the free energy

$$F = \min_{\Delta, \theta, q} \left[ U(\Delta, \theta, q) - TS(\Delta, \theta, q) \right]$$  \hspace{1cm} (2.18)

with respect to the three parameters the order parameter and short range order can be found.

The entropy may be calculated in closed form in terms of lattice Green functions. Such an idea was proposed by Heine and Joynt (1988) and developed by Samson (1989). This reduces to mean field theory (MFT) if the energy is independent of the short range order parameter, and to the spherical model of Berlin and Kac (1952) if the energy is linear.
in the order parameter and the short range order parameter. Samson (1989) has defined this as the extended spherical model (ESM). This analytical approach has been used to study the model of iron elsewhere (Chana et al 1991).

Let us consider now what insights have been gained on short range order in iron from the electronic structure calculations. We have come across two theories that address this issue; the fluctuating local band theory and the disordered local moment theory. These offer a differing perspective on short range order. The former claims short range order as a smooth variation in the spin direction, supporting spin waves. The later claims there is zero short range order above \( T_c \) in iron. Heine and Joynt (1988) offer a picture which is intermediate between these two extremes.

If we assume that the phase transition is driven purely by the population of spin-wave modes, then the wave vector at which disorder occurs should be related to the maximum wave vector \( q_e \) of the spin waves (Heine and Joynt, 1988). For insulators this will be the zone boundary and for itinerant magnets it is the point at which the spin-waves enter the Stoner continuum. The crux of the model proposed by Heine and Joynt is the plot of the energy of configurations as a function of order. In this plot a pronounced "kink" occurs at \( q_e \) (or the corresponding \( \theta_c \) value) and it is argued that this leads to short range order on the length scale of \( 2\pi/q_e \). The paramagnetic state of iron in this model would be broken up into domains of this size. Heine and Joynt also argue that this kink corresponds to the cross over from the "acoustic" to the "optical" mode in the spin spiral energies. Such a kink in the total energy is found in the initial \( d \)-band calculations of spin spirals (You and Heine, 1982; Holden and You, 1982). The extended calculations using a full \( spd \) band by Luchini and Heine (1989) reveal only a small kink at \( q_e \), however they do find that \( \theta_c \approx 60^\circ \) as predicted by Heine and Joynt. The ESM calculations by Samson (1989) based on the results of Luchini and Heine (1989) show only a small degree of short range order, comparable with the nearest neighbour Heisenberg model.

At the outset of this chapter the effect of the local environment of magnetic moments on the exchange interactions was commented on. Lin-Chung and Holden (1981) did indeed
find substantial multi-atom interactions by a calculation of the change in total energy due to a local perturbation. The nearest and next-nearest neighbour exchange interactions, $J_1$ and $J_2$ are found to be ferromagnetic whereas the more distant interactions are anti-ferromagnetic. However these are not likely to be accurate as the magnetic moments are not brought to self-consistency with the exchange fields on the perturbed or surrounding atoms. The change in sign of the more distant exchange interactions would support significant short range order.

The significance of their results however was that the exchange interactions change as a function of angle, calling into question the $\cos \theta$ dependence assumed in the Heisenberg model and any fitting of energies to this model.

An alternative to fitting the energies to pairwise Heisenberg exchange interactions is that one can calculate the total energies $U$ of a number of configurations and define the exchange interactions as

$$J_{ij}^{\nu\nu'} = -\frac{1}{2} \left( \frac{\partial^2 U}{\partial \nu \partial \nu'} \right)$$

where $\nu, \nu' = x, y$ or $z$. (2.19)

These are in general functions of the exchange field and they correspond to the $J_{ij}$ of equation (2.16) only if they are constant and isotropic in spin space. Essentially this exchange interaction is the second derivative of the total energy of the system with respect to the local magnetisation, characterised by the directions of the unit vectors $\hat{e}_i$ and $\hat{e}_j$ on sites $i$ and $j$. Small and Heine (1984) developed a method for calculating the exchange interactions in terms of the "couple" exerted by one spin on a neighbour, or the transferred moment at one site due to an exchange splitting on another - in effect the first derivative of the Hamiltonian. Luchini and Heine (1991) have shown that the non-pairwise exchange interactions as defined as in equation (2.19) are strongly affected by the amount of order in the surrounding shells. Since it is these results that form the basis of the statistical mechanics calculations, they are discussed in more detail here.
2.4 The magnetic couple.

The magnetic couple as derived by Small and Heine (1984) provides a method of investigating the behaviour of magnetic moments. The influence of the local environment on a moment or two neighbouring moments can also be investigated. The expression for the couple is given by

\[ G_i = \frac{1}{2} \Delta_i \times m_i \]  \hspace{2cm} (2.20)

To investigate the influence from a particular atom \( j \), the moment at that site is rotated and \( G_i \) is examined. Since the magnetic electrons in iron are itinerant, they carry a memory of the directions of the exchange fields on neighbouring sites, thus the atom \( j \) "induces" a very small moment \( \delta m_i^{(j)} \) on atom \( i \). This is more or less parallel to \( m_j \) and nearly independent of the direction of the exchange field on atom \( i \). This is defined as the transferred moment (Small and Heine, 1984) and has a magnitude of about \( 0.1 \mu_B \) from a nearest neighbour in iron in a ferromagnetic environment. These small moments are part of the spin-polarised electron cloud of site \( j \) and represent the Friedel oscillations in the electron gas due to the exchange field at site \( j \) (Luchini, 1989). The effect of transferred moments is the reason full self-consistency is never achieved in the calculation of the electronic structure. The self-consistency condition is achieved by adjusting the magnitude of the exchange splitting so that self-consistency parallel to the field direction is obtained (Luchini and Heine, 1989). The initial directions and magnitudes of the exchange fields for clusters of about 1000 atoms are read into the computer at the start of the calculation.

A value for the exchange interaction can be derived from the transferred moments (Luchini, 1989; Luchini and Heine 1991). They set up configurations of moments (shown schematically in Figure (2.1)) with a given average magnetisation

\[ \langle \vec{e}_j \rangle = (0, 0, \cos \theta_j). \] \hspace{2cm} (2.21)

The couple is calculated using the components \( m_{ix} \) and \( m_{iy} \) of the transferred moment,

\[ G_i = \frac{1}{2} \Delta m_{ix}. \] \hspace{2cm} (2.22)
Figure 2.1. Schematic diagram of configurations used to calculate the exchange interaction $J_{ij}$ in the ferromagnetic state representing (i) smallest and (ii) largest perturbation from ground state.

The various components $m_\chi$ of $\mathbf{m}_i$ in directions $\chi$ parallel and perpendicular to $\Delta_i$ are calculated using

$$m_\chi = \sum_l \langle (n_{il\uparrow\chi} - n_{il\downarrow\chi}) \rangle.$$  

where $l$ labels the atomic orbitals. The local density of states in equation (2.23) is calculated using a Green function and the recursion method. Fitting the transferred moment to

$$m_{ix} = s_i^{(j)} \sin \theta_{ij}$$  

(2.24)

gives the couple

$$G_i = \frac{1}{2} \Delta_i s_i^{(j)} \sin \theta_{ij}$$  

(2.25)

where $s_i^{(j)}$ is the slope of the graph of $m_{ix}$ against $\sin \theta_{ij}$. If the interaction between a pair of atoms $i$ and $j$ has the Heisenberg form

$$-J_{ij} S_i S_j \cos \theta_{ij}$$  

(2.26)
differentiation gives the expression of the couple as
\[ G_i = -J_{ij} \left( \frac{m_i}{2} \right) \left( \frac{m_j}{2} \right) \sin \theta_{ij}, \] \hspace{1cm} (2.27)

Let us now define the exchange interaction from
\[ G_i^{(j)} = J_{ij} \left( \frac{\Delta_i}{2I} \right) \left( \frac{\Delta_j}{2I} \right) \sin \theta_{ij}, \] \hspace{1cm} (2.28)

with \( \theta_{ij} \) the angle between \( \Delta_i \) and \( \Delta_j \) (Luchini, 1989). Using equation (2.25) and comparing with equation (2.27) gives
\[ J_{ij} = s_{ij} \frac{2I^2}{\Delta_j}, \] \hspace{1cm} (2.29)

where \( \Delta_j \) is kept fixed to the ferromagnetic value throughout the rotation. The exchange interactions calculated and shown in Figure (2.2) are actually the second derivatives of the energy with respect to the vectors \( \hat{e}_i \) and \( \hat{e}_j \) in the direction of the local moment on sites \( i \) and \( j \) (equation (2.19)). The exchange interaction has been calculated for the first five neighbours (Luchini and Heine 1991); however, the magnitude of \( J_{ij} \) beyond the next-nearest neighbour is found to be small and can be neglected from further calculations.

In the ferromagnetic state \( (\sigma^2 = 1) \) the nearest neighbour interaction \( J_1 \) is slightly greater than the next-nearest neighbour interaction \( J_2 \). As the system disorders with increasing temperature, \( J_1 \) increases and \( J_2 \) decreases (Figure (2.2)), so that at the DLM \( (\sigma^2 = 0) \) end the interaction is almost entirely between nearest neighbours. Longer range interactions are smaller in magnitude and fall off rapidly with increasing disorder. An independent check (Luchini, private communication) has been made of the sum \( \sum J \) of the \( J_{ij} \); this agrees with the values used for \( J_1 \) and \( J_2 \), so that longer range interactions are unimportant. The interactions are assumed to be isotropic. For symmetry considerations, \( J_{ij} \) must be an even function of magnetisation and one can therefore fit them to the form
\[ J_{ij} = A_{ij} + B_{ij} [\sigma(i,j)]^2. \] \hspace{1cm} (2.30)
Here \( \sigma \) is the average magnetisation on shells of atoms "near" \( i \) and \( j \) (The meaning of "near" is discussed in section (2.5)).

The values of \( A \) and \( B \) for nearest and next-nearest neighbours are

\[
\begin{align*}
A_1 &= 2.5 \text{ mRyd} & B_1 &= -1.5 \text{ mRyd} \\
A_2 &= 0.2 \text{ mRyd} & B_2 &= 0.6 \text{ mRyd}. 
\end{align*}
\]

Figure (2.2) shows the dependence of the \( J_{ij} \) with these parameters on the order in the surrounding shell of neighbours.

The variation is due in some way to the change in the band structure on disordering. Luchini and Heine (1991) argue that the range of exchange interactions is reduced in the disordered state as a result of the reduction in electron mean free path through disorder scattering. Heine et al (1990) show how the behaviour of the couplings may also be understood through perturbation theory. Hubbard (1979) had also observed the effective exchange interaction to increase with disorder. The tendency for the interactions to be of short range in the DLM state was also noted by Oguchi et al (1983), whose CPA calculations show that the nearest neighbour interaction dominates. The CPA calculations of Lipiński (1989) do however find large second- and third-neighbour interactions in the DLM state. The Hamiltonian is in any case rather unusual and an investigation of its properties form the framework of the present work. The behaviour of the exchange interactions effectively means that magnetic excitations in the FM state have low energy. As the disorder increases, the system becomes stiffer towards further disorder, leading Luchini and Heine (1991) to speculate that substantial SRO remains in the paramagnetic state. This then is our hypothesis leading to short range order in iron above \( T_C \).
2.5 A Hamiltonian for iron.

The investigation will consider several Hamiltonians, taking as a reference the classical nearest-neighbour Heisenberg model in equation (2.16). The effective spin Hamiltonian relevant for iron is an immensely complicated functional of the magnetisation, even in the static approximation. To study its statistical mechanics, whether analytically or by Monte Carlo simulation, requires extrapolation from the small subset of phase space for which the energies have been calculated, which inevitably leads to some ambiguities.

The basic idea is that the exchange interactions in iron are stronger in the DLM state than in the FM state, as defined by equation (2.30) and equations (2.31a,b). The $J_i$ depend on the band structure and therefore on the order in the surrounding shell through the parameter
where $S(i,j)$ is the shell of neighbours of atoms $i$ and $j$, and $z(i,j)$ is the number of atoms in that shell. The question now arises of the degree of locality: how large a shell $S(i,j)$ is needed to define the interactions. One limit is for $S(i,j)$ to be the entire solid. This then gives a type of mean field theory, where the (short range) interactions depend on the (long range) order parameter. Let us consider a nearest-neighbour interaction $J$. Suppose the zero-field magnetisation in the nearest neighbour Heisenberg model to be a function $M_H(ksT/J)$; the magnetisation in the non-pairwise model will then be 

$$M(T) = M_H\left(\frac{k_B T}{(A + BM^2)}\right),$$

(2.33)

to be solved self-consistently. If $J$ increases with decreasing order, the magnetisation will initially fall more rapidly with reduced temperature $T/T_C$ than in a Heisenberg model. The magnetisation curves will be distorted below $T_C$. All zero-field quantities above $T_C$ will be identical to those in the Heisenberg model. If the shell $S(i,j)$ is fairly large, equation (2.33) still provides a good "mean field" solution of the problem that reduces to the Heisenberg model in the case $B = 0$. The other limit is for $S(i,j)$ to consist of only the atoms $i$ and $j$ themselves. This leads to a Hamiltonian with biquadratic pair interactions, as studied by Brown (1971) and others (Samson, private communication). The larger the shell, the smaller the fluctuations in $J$ and the smaller the deviation from the Heisenberg model. Luchini and Heine (1991) find that the interactions depend principally on the nearest-neighbour shell. On that basis, the shell is considered to consist of the nearest neighbours of $i$ and $j$. For $J_1$, this consists of 16 sites (including $i$ and $j$); for $J_2$, this consists of 12 sites.

It must be stressed that the exchange parameters calculated by Luchini and Heine (1991) are the second derivative of the Hamiltonian with respect to the directions of the magnetisation, as in equation (2.19), and not the coefficients in a Hamiltonian of the form
(2.16). To demonstrate the importance of this distinction (Samson private communication), consider the extreme case $B_1 = -A_1$ or

$$J_1 = J \sin^2 \theta,$$

(2.34)

in which the exchange interaction vanishes in the FM state. Suppose that this is the coefficient in a Hamiltonian of the form (2.15). The energy of the ferromagnetically ordered state is zero, as $J_1 = 0$; however, it is unstable towards the reversal of a spin. Reversing a spin turns on ferromagnetic interactions in the neighbourhood of the spin, the number of bonds depending on the degree of locality of the Hamiltonian. Since the majority of these bonds will be formed between ferromagnetically aligned spins, the total energy will be reduced, and the ferromagnetic state will be unstable. Similarly, the energy of a domain wall will be negative. Now if $J_1(\theta = 0)/J_1(\theta = \pi/2)$ is just large enough to stabilise the FM state, one could imagine that the domain wall energies will be small and the reversed-spin clusters described by Lowde et al (1983) would be observed at finite temperatures. The present Hamiltonian however is not of this form. The calculations of Luchini and Heine (1991) give the second derivative of the Hamiltonian; any instability of the FM state would show up in these energies.

There is no simple expression for the Hamiltonian itself, only its second derivative $J_{ij}$. Samson (private communication) has attempted to integrate this twice to obtain the Hamiltonian: the quadratic form of the $J_{ij}$ in equation (2.30) suggests a quartic Hamiltonian with an inconveniently large number of four-spin terms. He also tried to fit the exchange interactions to four-site coefficients arising from a fourth order perturbation expansion of the electronic energy in powers of the exchange field, but no reasonable fit was obtained, in the sense that the coefficients did not fall off in the expected way with the size of the four-site loops. This may be due to the existence of higher order terms, or to the localisation effect mentioned above.

Although the derivation of a complete Hamiltonian has not been achieved, one can still use the exchange interactions, $J_{ij}$. Luchini and Heine (1991) found that the couple
acting on atom $i$ as it is rotated in a random environment is nearly proportional to $\sin \theta_i$ over the full range of $\theta_i$ from $0$ to $\pi$, where $\theta_i$ is the angle with respect to the direction of magnetisation. One can then use the parameters in equations (2.31a,b) to give the change in the energy on rotating a single spin in an arbitrary environment. This is precisely the information required for a Monte Carlo simulation. The difficulty of not having an explicit Hamiltonian does not therefore vitiate a Monte Carlo calculation. The work in the next chapter is concerned with how one can set up such a calculation for the Heisenberg model and the model of iron with non-pairwise exchange interactions. Chapter four gives the results of the Monte Carlo simulations.
Methods of Monte Carlo simulation of classical systems.

3.1 Introduction.

Consider a classical system of \( N \) particles, with each particle having a site label \( i \) and at least one dynamic variable \( \alpha_i \) (e.g. the position of the particles or spin orientations). The set \( \{ \alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_N \} \) then describes a configuration \( x \) of the system. The particle interactions are described by a Hamiltonian \( H(x) \). The expectation value of any observable \( O \) can be calculated from the canonical ensemble

\[
\langle O \rangle = \frac{\int dx \: O(x) \exp[-H(x)/k_B T]}{\int dx \: \exp[-H(x)/k_B T]},
\]

(3.1)

when the dynamic variables have continuous values. For the case where the dynamic variables take on discrete values (labelled \( k \)) then the expectation value of \( O \) is given by

\[
\langle O \rangle = \frac{\sum_k O(x_k) \exp[-H(x_k)/k_B T]}{\sum_k \exp[-H(x_k)/k_B T]},
\]

(3.2)

If there are a small number of particles in the system, one could evaluate the integrals in equations (3.1 and 3.2) using standard numerical integration methods, where the integrals are approximated by a sum of a finite number of terms. However as the system size increases (usually one has several hundred particles in the system) standard numerical integration becomes increasingly less feasible. The points in the phase space (configurations) of the system could be chosen at random, rather than making use of a regular set of points in the integration. If a sufficient number of points is taken then the integrals could be evaluated to an acceptable accuracy. However the integrand \( \exp[-H(x_k)/k_B T] \) can have a variation
over many orders of magnitude for a many-body system at some temperatures (Binder and Heermann 1988). This means that simple random sampling of the points could again render evaluation of the integral impractical.

The idea behind the Monte Carlo method in statistical mechanics is to construct a sample of configurations which is representative of the canonical ensemble at a given temperature \( T \). One could use a simple sampling technique, that is to choose configurations at random, however this method is similar to standard integration and consequently the method suffers from the same problems. The Monte Carlo method introduced by Metropolis \textit{et al} (1953) is based on the idea of "importance sampling". In this method rather than choosing points in the phase space of the system at random, points are chosen from the region of phase space where the dominant contributions to the integrals in equations (3.1 and 3.2) come from. The points are chosen according to the probability distribution

\[
P(x_v) \, dx = \frac{\exp[-H(x_v)/k_BT] \, dx}{\int dx \, \exp[-H(x_v)/k_BT]} \tag{3.3}
\]

The Monte Carlo estimate for the average \( \langle O \rangle \) then reduces to a simple arithmetical average

\[
\overline{O} = \frac{1}{M} \sum_{\nu=1}^{M} O(x_v), \tag{3.4}
\]

where \( M \) is the total number of configurations generated in the Monte Carlo sequence. The distribution in equation (3.3) is generally not known; however, one can perform a random walk of points \( x_v \) through the phase space by constructing a Markov process consisting of \( M \) configurations generated according to a transition probability \( W(x_v \rightarrow x'_v) \) which gives the probability of the system making the transition from a configuration \( x_v \) to a configuration \( x'_v \). The process is constructed such that in the limit \( M \rightarrow \infty \) the probability that a configuration occurs in the process is given by the distribution in equation (3.3).
The choice of a transition probability must satisfy certain conditions:

(i) Normalisation condition

\[ \sum_{v'} W(x_v \rightarrow x_{v'}) = 1 \quad \text{for all } v \]

(ii) Ergodicity condition: If \( P(x_v) > 0 \) and \( P(x_{v'}) > 0 \), it is required that

\[ W(x_v \rightarrow x_{v'}) > 0 \]

(iii) Homogeneous state condition

\[ \sum_{v} P(x_v) W(x_v \rightarrow x_{v'}) = P(x_{v'}), \quad \text{for all } v' \]

The sums over \( v \) and \( v' \) run over all possible states of the system. A simple choice which satisfies condition (i) is provided by the detailed balance condition

\[ P(x_v) W(x_v \rightarrow x_{v'}) = P(x_{v'}) W(x_{v'} \rightarrow x_v). \quad (3.5) \]

This does not define \( W \) uniquely and one usually takes the transition probability in the Metropolis algorithm as

\[
W(x_v \rightarrow x_{v'}) = \begin{cases} 
\exp \left[ \frac{E(x_{v'}) - E(x_v)}{k_BT} \right] & \text{if } E(x_{v'}) > E(x_v) \\
1 & \text{otherwise,} 
\end{cases} \quad (3.6)
\]

where \( E(x_v) \) and \( E(x_{v'}) \) are the energies of configuration \( x_v \) and \( x_{v'} \) respectively. This is not normalised; however this is not important for practical purposes. A simple argument is reproduced here to justify this (Metropolis et al 1953). Consider a large number of Markov processes together. At the \( v \)th step of the processes suppose we have \( N_r \) systems in the \( x_r \) state with energy \( E(x_r) \) and \( N_s \) systems in the state \( x_s \) with energy \( E(x_s) \); also let \( E(x_r) < E(x_s) \). Using random numbers, one may construct moves \( x_r > x_s \), with \textit{a priori} probability for this change \( W_{rs} = W_{sr} \) (i.e without conditions (i) and equation (3.6) satisfied). Therefore we find the transition probabilities satisfying equation (3.5) by taking
W(x_r \rightarrow x_s) = W_{rs} \exp\left\{\frac{E(x_s) - E(x_r)}{k_B T}\right\} \quad (3.7)

and

W(x_s \rightarrow x_r) = W_{sr} = W_{rs} \quad (3.8)

The total number of transitions from $x_r$ to $x_s$ is then

$$N_{r \rightarrow s} = N_r W(x_r \rightarrow x_s) = W_{rs} \exp\left\{\frac{E(x_r) - E(x_s)}{k_B T}\right\} N_r,$$  \quad (3.9)

and for the reverse process

$$N_{s \rightarrow r} = N_s W(x_s \rightarrow x_r) = W_{sr} N_s; \quad (3.10)$$

thus the total number of transitions $N_t$ is

$$N_t = N_r W_{rs} \left\{\frac{\exp\left[-E(x_s)/k_B T\right]}{\exp\left[-E(x_r)/k_B T\right]} \cdot \frac{N_s}{N_r}\right\} \quad (3.11)$$

If $N_s/N_r$ is smaller than the canonical value, then $N_t > 0$, i.e. $N_s/N_r$ increases. If $N_s/N_r$ is larger than the canonical value, $N_t < 0$, and $N_s/N_r$ is decreased. A steady state is reached when $N_s/N_r$ has precisely the canonical value.

3.2 Practical considerations.

In order to calculate averages correctly using a Monte Carlo simulation it is important that when changes are made no quantities are conserved. Some of the practicalities of performing Monte Carlo simulations and the basis for the implementation of the Monte Carlo simulations of Chapter four are now discussed.

3.2.1 Variables.

The variable $\alpha_i$ attributed to a particle $i$ will obviously depend on the system to be modelled. For the case of magnetic systems one has in general two possible choices:
(i) **Ising spin variables** - simply \( \alpha_i = -\alpha_i \) (usually \( \alpha_i = \pm 1 \)). Although very different from real physical variables, Ising variables can be useful for modelling very large systems where computer time and memory are restrictive. The collective model of Ising variables is called the Ising model and is useful for describing much of the magnetic phenomena found in real magnetic systems. The Ising model is discussed in more detail in Chapter Six, where the ground state of the model of iron is investigated.

(ii) **Vector spin variables** - For vector spins \( \alpha_i \) is a unit vector \( S_i \)

\[
(\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i),
\]

where \( 0 \leq \theta_i \leq \pi \) and \( 0 \leq \phi_i \leq 2\pi \). The change in the variable is made when one of the angles is changed. These are usually chosen at random from a uniform distribution. A more efficient method is used in the Monte Carlo simulations of Chapter Four. This involves changing \( \cos \theta_i \) (with \(-1 \leq \cos \theta_i \leq 1\)); then

\[
\sin \theta_i = \sqrt{1 - \cos^2 \theta_i}.
\]

The angle \( \phi_i \) is also changed in order to have a spherically symmetrical spin direction. The choice of a vector spin variable is much more representative of real spin variables. The systems under investigation are assumed to have spin \( S \rightarrow \infty \); that is classical behaviour and so the Hamiltonian reduces to the internal energy of the system.

Often it is useful if the new state is rather close to the old one (Metropolis et al., 1953) so an alternative representation is to introduce a parameter \( \delta \) and use Cartesian coordinates

\[
S_i^x' = \frac{S_i^x + \xi^x \cdot \delta}{Z}, \quad S_i^y' = \frac{S_i^y + \xi^y \cdot \delta}{Z}, \quad S_i^z' = \frac{S_i^z + \xi^z \cdot \delta}{Z},
\]

(3.13a)

where

\[
Z = \sqrt{\left[(S_i^x + \xi^x \cdot \delta)^2 + (S_i^y + \xi^y \cdot \delta)^2 + (S_i^z + \xi^z \cdot \delta)^2\right]},
\]

(3.13b)

where \( \xi^x, \xi^y, \text{ and } \xi^z \) are random numbers satisfying \(-1 \leq \xi^x, \xi^y, \text{ and } \xi^z \leq 1 \). The phase space of this representation can be viewed as a cube of sides \( S^x, S^y, S^z \) and there is a
possibility that the spin can be "trapped" in one corner of the cube due to sequential correlations between the random numbers. The main advantage of using this representation is that the difference between states can be controlled through the parameter $\delta$. This method was tested in the development stage of the Monte Carlo simulations described in Chapter four, however it was found that using a unit vector to represent the spin was a more suitable approach for $S \rightarrow \infty$. Further using the unit vector, equation (3.12), the phase space can be viewed as a sphere of unit radius; this has the advantage that the magnitude of the spin is fixed and is spherically symmetric.

3.2.2 Correlations between random numbers.

The effects of correlations between random numbers has not been studied as it is assumed that the sequences generated from the random number generator used are relatively uncorrelated. It was found that the random number generators built into the computer system used suffered from sequential correlations and therefore to obtain accurate results a more complex random number generator was used (Appendix A and Press et al (1985)).

Since the systems under investigation all have a three dimensional lattice, it is desirable not to use random numbers in the same sequence to select the coordinates of a lattice site $i$. Instead a separate random number sequence is used to select each coordinate. The same random number generator can be used but with different starting numbers. This is to ensure that each site in the lattice is sampled with equal probability during the simulation, otherwise regions sampled infrequently will lead to the formation of domains of magnetisation.

Separate random number sequences are also used to select trial values of $\cos \theta_i$ and $\phi_i$, to avoid any possible correlations between $\theta_i$ and $\phi_i$.

3.2.3 Influence of the starting configuration.

The starting configuration can either be random or ordered, in the case of spin systems the spins are either randomly orientated or ordered in the ferromagnetic state for
example. The starting configuration and some of the subsequent configurations do not satisfy equation (3.3) and so need to be excluded from the averages, equation (3.4); since the system has not reached thermal equilibrium. In practice it is difficult to decide exactly how many early configurations to exclude, since relaxation to thermal equilibrium may be slow. The error due to slow equilibrium may be minimised by taking a large number of Monte Carlo steps (MCS). There is no a priori information of how many MCS should be taken in a practical calculation however. In practice one may carry out several Monte Carlo simulations with the same parameters, but using different starting configurations (Binder 1972). If the results of these simulations agree to within the estimated statistical error, it can be concluded that the influence of the starting configuration has been eliminated. Statistical analysis of the data provides an alternative to this method (Wood, 1968). One estimates the statistical error from the last $M/2$ configurations and excludes at the beginning of the simulation just those configurations which exceed this error significantly.

For the calculations in Chapter four a ferromagnetically aligned starting configuration is used. Since we are not specifically interested in the critical region, the number of early configurations excluded from the averages is not expected to be a serious problem. In practice 1000 MCS per spin are generated after allowing 200 MCS per spin for the relaxation of the lattice, and the required thermodynamic quantities are calculated every 10 MCS per spin.

The magnetisation for a Heisenberg ferromagnet on a BCC lattice with 250 lattice sites is plotted against Monte Carlo steps for various temperatures in Figure 3.1. In this case there is a total of 50000 warm-up steps and 250000 further steps during which the measurements are made. The magnetisation was recorded at every 500 MCS in the warm up period and then after 2500 MCS during the rest of the simulation. The reason for the sharp drop in the magnetisation around the 50000 MCS mark is because data is recorded less frequently after warm up (the next output is at the 52500 mark). The straight horizontal lines are the averaged magnetisation at the respective temperatures. One can observe from this plot that as the temperature is increased the oscillations in the magnetisation increase and
around the critical temperature these are slow and wide, this is more apparent at \( T = 7.0 \). A simulation with a longer period of 400 MCS was also performed; however since a large number of averages of the magnetisation are taken during the simulation the final results were exact. The time period for 200 MCS per spin warm up period can therefore be assumed to be sufficiently long for the system to reach equilibrium.

![Magnetisation against time (Monte Carlo steps) in the Heisenberg model for a BCC lattice with 250 sites at various temperatures. Solid horizontal lines indicate the thermal averages taken after warm-up period.](image)

**Figure 3.1.** Magnetisation against time (Monte Carlo steps) in the Heisenberg model for a BCC lattice with 250 sites at various temperatures. Solid horizontal lines indicate the thermal averages taken after warm-up period.

An interesting point (Heine, private communication) is included here, although has not been fully investigated. The choice of using a randomly or ferromagnetically aligned starting configuration should be determined by the thermal approach to the critical point. A ferromagnetic configuration should be used when heating the system up and a random configuration should be used when cooling the system. This prevents the formation of
domains of reversed magnetisation which will give incorrect results. This is the approach adopted in the present calculations although the critical point is never approached from above.

3.2.4 **Statistical inaccuracy.**

The Monte Carlo average will deviate from the expectation value \( \langle O \rangle \) since a finite number of MCS will be performed. There is no *a priori* information of the degree of deviation, however standard methods of statistical data analysis may be applied to determine the statistical error.

One method of estimating statistical error (Wood, 1968) is presented here. Subtracting an appropriate number \( \delta M \) of initial configurations there are \( M' \) configurations for further analysis which are subdivided chain into \( n' \) pieces. The number \( n' \) should be as large as possible and the sub-chains should be statistically uncorrelated. Denoting the partial average of \( O \) in the \( m' \)th subdivision as \( \bar{O}_{m'} \), the statistical error \( \Delta O^{\text{exp}} \) of \( O \) is estimated from

\[
\Delta O^{\text{exp}} \equiv \sqrt{\frac{\sum_{m' = 1}^{n'} (\bar{O}_{m'} - \bar{O})^2}{n' (n' - 1)}}. \tag{3.14}
\]

An analysis of a Monte Carlo simulation of a BCC lattice with 1024 sites showed that the error in the magnetisation at low temperatures was of the order of 1% and at temperatures near the phase transition of the order of 3-5%. This was calculated by letting \( \delta M = 200 \) MCS per spin (204800 MCS) and \( n' = 100 \) giving the sub-chains a length of 102400 MCS. One method of reducing this error further is to allow a larger number of warm-up steps and Monte Carlo steps per spin. However the statistical error in the present calculations is small and the increase in computation time resulting from a larger number of Monte Carlo steps per spin was not thought to be justified.
3.2.5 Boundary conditions.

The issue of boundary conditions arises due to the finite size of the systems under study, particularly if bulk properties are to be studied. The simplest boundary condition one can use is provided by free surfaces, which is useful if small particles or surfaces are being studied. However in order to approximate an infinite system one usually takes periodic boundary conditions. For the spin systems under study, interactions of spins at the surfaces are linked to the corresponding spins at the opposite surface of the system. Let $\lambda$ and $\lambda'$ represent the two sublattices of a BCC lattice and let a site $i$ at the surface of a lattice have the coordinates $(x, y, z)$. The new coordinates $x', y', z', x'', y''$ and $z''$ are used to locate the nearest- and next-nearest neighbours of the site $i$. These (with periodic conditions applied) for the nearest-neighbours are found as

$$
x' = \begin{cases} 
1 & \text{if } x + 1 > N_x \\
x + 1 & \text{otherwise},
\end{cases}
$$

for lattice $\lambda$, $y'(z') = \begin{cases} 
N_y (N_z) & \text{if } y - 1 (z - 1) < 1 \\
y - 1 (z - 1) & \text{otherwise},
\end{cases}$

for lattice $\lambda'$, $y'(z') = \begin{cases} 
1 & \text{if } y + 1 (z + 1) > N_y (N_z) \\
y + 1 (z + 1) & \text{otherwise}.
\end{cases}$

and for next nearest neighbours

$$
x' (y') (z') = \begin{cases} 
N_x (N_y) (N_z) & \text{if } x - 1 (y - 1) (z - 1) < 1 \\
x - 1 (y - 1) (z - 1) & \text{otherwise},
\end{cases}
$$

$$
x'' (y'') (z'') = \begin{cases} 
1 & \text{if } x + 1 (y + 1) (z + 1) > N_x (N_y) (N_z) \\
x + 1 (y + 1) (z + 1) & \text{otherwise}.
\end{cases}
$$

where $N_x, N_y, N_z$ are lattice sizes in the $x, y, z$ axes. These coordinates are used in "look-up" tables to locate the nearest- and next-nearest-neighbours of site $i$ (see section 3.3.2).
Periodic boundary conditions model the bulk behaviour fairly well for large systems (Binder and Heermann, 1988) and surface effects are eliminated. Finite size effects cannot be eliminated and are only minimised by using large systems; close to the phase transition they are important and a distinct phase transition is therefore not observed. The effect is clearly observed in Figure 3.2, where the root mean square magnetisation (an order parameter) is plotted as a function of temperature for a nearest-neighbour Heisenberg model on a BCC lattice for various system sizes. In this model the exchange interaction is unity for nearest-neighbours and zero for all other pairs of spins. The calculation of the magnetisation is reported in more detail in section (4.3.1) of Chapter four. The phase transition is not very distinct for the smallest system size (54 spins) however at larger system sizes the magnetisation is close to zero near $T_C$. The magnetisation for the $N = \infty$ case has been determined by extrapolation from a plot of magnetisation as a function of $N^{-1/2}$; this is discussed in more detail in section (4.3.1) of Chapter four. There is still some magnetisation above $T_C$ since the magnetisation is actually calculated as the root mean square magnetisation and is not the component of the spins in the ferromagnetic direction. Or rather the direction in which all the spins are aligned at the start of the simulation (in this case the global z-axis). The magnetisation is averaged over the components of the spins in the three global axis, leading to some root mean square magnetisation at temperatures greater than $T_C$. Finite size effects also contribute to give a non-zero magnetisation above the phase transition.

3.3 Setting up a Monte Carlo simulation on the computer.

In the previous section some of the practicalities of performing a Monte Carlo simulation were considered. This is now expanded by considering how one actually sets up a Monte Carlo simulation on a computer system. The two points discussed are how one can setup a crystal lattice on the computer and how the interactions between the neighbouring sites on this lattice can be determined.
3.3.1 Representation of lattices.

The systems under investigation in Chapter four have body centred cubic (BCC) lattices. A BCC lattice can be constructed using two interlocked simple cubic sublattices which ultimately in the computer memory are defined as two multi-dimensional arrays. The corner spin of one sublattice forms the centre spin of the other sublattice. This also makes it simple to determine the locations of the neighbours of any site. A further simplification is made when one makes use of lookup tables of the neighbours of a site.

3.3.2 Lookup tables.

The coordinates of the nearest and next-nearest neighbours are stored in a lookup table. The coordinates of the nearest neighbours of a lattice site \( i \) with coordinates \( x, y, z \) are
The coordinates $x', y', z'$, $x'', y''$ and $z''$ are found by applying the boundary conditions described above. These lookup tables provide the information needed to calculate the change in energy associated with a change in the spin vector at site $i$, and for the calculation of the correlation functions. Similar tables for the third, fourth and fifth neighbours have also been used.

The Monte Carlo simulation methods described in this chapter have been used to perform the simulations of the nearest-neighbour Heisenberg model and the model of iron with non-pairwise interactions. These form the topic of discussion in the next chapter.
Chapter Four.

Magnetic short range order in iron above $T_C$.

A Monte Carlo investigation.

4.1 Introduction.

In the previous chapter the Monte Carlo method and how one can set up simulations to investigate the statistical mechanics of classical systems using the method were discussed. The topic of this chapter is the investigation of magnetic short range order (SRO) in iron above the Curie temperature $T_C$ by Monte Carlo simulations. The model of iron is that presented in Chapter two and the nearest-neighbour Heisenberg model is used for comparison. The property one uses as a handle on degree of SRO in both models is the real space spin correlation function; if the correlation function for the nearest- and next-nearest neighbours in iron is greater than in the corresponding Heisenberg model, one can conclude that substantial SRO exists above $T_C$ in iron.

4.2 Description of systems investigated.

For both the Heisenberg model and the model of iron the Hamiltonian is

$$ H = -\sum_{i,j} J_{ij} \hat{e}_i \cdot \hat{e}_j, \quad (4.1) $$

where $J_{ij}$ is the exchange interaction between atoms $i$ and $j$, and $\hat{e}_i$ is the spin on atom $i$. For the Heisenberg model (System I) the exchange interaction is

$$ J_{ij} = \begin{cases} 1 & \text{if } i \text{ and } j \text{ nearest-neighbours} \\ 0 & \text{otherwise}, \end{cases} \quad (4.2) $$

and for the model of iron with non-pairwise exchange interactions

$$ J_{ij} = A_{ij} + B_{ij} [\sigma(i,j)]^2, \quad (4.3) $$
here \( \sigma(i,j) \) is the average magnetisation on shells of atoms near \( i \) and \( j \). The values of the parameters \( A_{ij} \) and \( B_{ij} \) for nearest- and next-nearest neighbours are

\[
\text{System II} \quad \begin{cases} 
A_1 = 2.5 \text{ mRyd} & \quad B_1 = -1.5 \text{ mRyd} \\
A_2 = 0.2 \text{ mRyd} & \quad B_2 = 0.6 \text{ mRyd}.
\end{cases}
\] (4.4)

These exchange interactions are shown in Figure 2.2 as a function of the mean-square magnetisation \( \sigma^2 \) in the surrounding shell of neighbours of sites \( i \) and \( j \). Hereafter the notation \( J_1 \) and \( J_2 \) refers to these non-pairwise exchange interactions (which are not the coefficients of \( H \) in equation (4.1) but the second derivatives of the electronic energy (refer to Chapter two)). To further investigate the effect of non-pairwise exchange interactions on the magnetisation and the correlation functions two extreme cases of equation (4.3) are also considered. The parameters for the models of iron with extreme nearest-neighbour exchange interaction are

\[
\text{System III} \quad \begin{cases} 
A_1 = 2.5 \text{ mRyd} \\
B_1 = -1.5 \text{ mRyd},
\end{cases}
\] (4.5)

\[
\text{System IV} \quad \begin{cases} 
A_1 = 2.5 \text{ mRyd} \\
B_1 = -2.5 \text{ mRyd}.
\end{cases}
\] (4.6)

In systems III and IV there is zero next-nearest-neighbour interaction \( J_2 \). In system IV the nearest-neighbour exchange interaction vanishes in the ferromagnetic state. Simulations have also been carried out for systems between these cases; Figure 4.1 shows how \( J_1 \) varies with local order. The effect of the next-nearest neighbour interaction \( J_2 \) can be examined with the choice of parameters of system III since this system is just system II with \( J_2 = 0 \). Also with the parameters of system IV the ferromagnetic ground state may break up into clusters of reversed magnetisation (no interaction exists), which may or may not have a direct effect on the SRO above \( T_C \) in this model of iron. The exchange interaction in all cases is considered to be isotropic in space.
4.3 Details of Monte Carlo simulation.

The Hamiltonians are those of classical systems therefore the change in energy associated with a change in spin configuration at site $i$ is

$$\Delta E = -2\sum_j [ (J_{ij}\hat{e}_i)_{\text{new}} - (J_{ij}\hat{e}_i)_{\text{old}} ] \cdot \hat{e}_j .$$  \hspace{1cm} (4.7)

A Monte Carlo simulation requires knowledge of the change in energy on rotating a single moment. This could be obtained fairly directly from recursion method calculations of the moment on a rotated exchange splitting in a random medium, in the spirit of CPA calculations of Hubbard (1979a,b). A check at a few energies (Luchini, private communication) shows that such energies are consistent with the exchange interactions already calculated; the
exchange interactions in equation (4.3) can therefore be used to represent the change in energy.

The change in spin configuration is accepted with the transition probability

\[
W(\Delta E) = \begin{cases} 
1 & \text{if } \Delta E \leq 0 \\
\exp(-\Delta E/k_B T) & \text{if } \Delta E > 0.
\end{cases}
\]

This is used in the simulations of all the models. The system is allowed to relax to equilibrium (see section 3.2.3) before averages for the required thermodynamic quantities are taken at each temperature.

4.4 Thermodynamic quantities.

The thermodynamic quantities that are important for this investigation are the magnetisation and the real space correlation function. In the simulation the magnetisation and correlation function to the fifth neighbour is calculated at every 10 Monte Carlo steps per spin. This allows 100 lattice averages to be taken at each temperature. A greater number of lattice averages could have been taken however it was found that the increase in accuracy was not substantially higher (a fraction of 1%) to merit the increase in computation time this would require. The susceptibility above the Curie temperature has also been calculated for systems I and II. The evaluation of the averages of the thermodynamic quantities are outlined in sections (4.3.1, 4.3.2 and 4.3.3) and the results are discussed in sections (4.4, 4.5 and 4.6).

4.4.1 Magnetisation.

In a ferromagnetic system the two phases on either side of the Curie temperature have different spatial symmetries. Above \( T_C \), there is no bulk magnetisation and the system is rotationally invariant. Below \( T_C \) a spontaneous magnetisation forms and the magnetisation vector defines the preferred spin direction in space, thus destroying rotational symmetry. The reduction of symmetry requires the definition of a parameter to define the
phase transition from one phase to the other. A useful order parameter one can use to define the phase transition is the root mean square magnetisation.

The reduced magnetisation is defined as the lattice sum

$$M_v = \frac{1}{N} \sum_{i=1}^{N} \hat{e}_i,$$

which has a value of 1 at temperature $T = 0$. This quantity is evaluated at every 10 Monte Carlo steps per spin. The mean magnetisation can now be defined as

$$\langle M \rangle = \frac{1}{R} \sum_{v=1}^{R} |M_v|,$$

and the root mean square magnetisation as

$$M_{rms} = \sqrt{\langle M^2 \rangle} = \sqrt{\frac{1}{R} \sum_{v=1}^{R} (M_v \cdot M_v)},$$

where $R$ is the number of lattice sums taken during the Monte Carlo process.

In order to estimate the magnetisation per atom of an infinite system $M_\infty$, the root mean square magnetisation $M_{rms}$ is calculated for a number of system sizes $N$ from 54 (3 x 3 x 3 BCC unit cells) to 2000 (10 x 10 x 10 BCC unit cells). A plot of $M_{rms}$ as a function of $N^{-1/2}$ for the nearest neighbour Heisenberg model is shown in Figure 4.2. It is observed that except for temperatures in the critical region the points lie on a straight line. A similar set of results is found in the other systems under investigation. Making use of the asymptotic form (Paauw et al, 1975)

$$M_{rms}(N) = M_\infty + KN^{-1/2},$$

where $K$ is a constant, one can then extrapolate to find $M_\infty$. 

Chapter Four: SRO above $T_C$ in iron.  

Figure 4.2. Magnetisation as a function of $N^{-1/2}$ for increasing temperature in a Heisenberg model on a BCC lattice. Top line: $T = 1.0 \ (k_B / J)$ and bottom line: $T = 8 \ (k_B / J)$. The other lines are for temperatures between $T = 1.0 \ (k_B / J)$ and $T = 8 \ (k_B / J)$ in steps of 0.5.  

4.4.2 Real space correlation function.  

The real space correlation function $c(n)$ provides useful information about the phase transition. With the definitions above for the reduced magnetisation $M_v$ the $n$th neighbour correlation can be defined as the lattice sum  

$$c_v(n) = \left( \frac{1}{z(n)N} \right) \sum_{i; \text{nth neighbours}} \hat{e}_i \cdot \hat{e}_j \cdot (M_{v'}M_{v'}) \quad 1 \leq n \leq 5. \quad (4.13)$$  

The Monte Carlo average of the correlation function for the first five shells of neighbours is then defined as  

$$c(n) = \frac{1}{R} \sum_{v=1}^{R} c_v(n). \quad (4.14)$$
The correlation function measures the "persistence of memory" of spatial fluctuations in the order parameter. We can relate this directly to magnetic short range order, since SRO is exactly this; spatial fluctuations in magnetisation (order) in the lattice. We have already seen in Chapter one how the spin-spin correlation function can be obtained from data of neutron scattering experiments. Brown et al (1982 and 1983) relate the spin-spin correlation to an "effective moment" which is an energy integral of the magnetic scattering function \( S(q) \). The correlation function defined above can be related to the experimentally determined correlation function as \( q \to 0 \), therefore providing a useful comparison of experimental and theoretical results. The correlation function in the limit \( q \to 0 \) corresponds to the nearest neighbour correlation function calculated in the present Monte Carlo calculations.

Correlation functions are usually described in the general framework of the Ornstein-Zernike equation (e.g any text on statistical mechanics). In this theory a correlation function \( \Gamma(r) \) takes the form

\[
\Gamma(r) = \frac{e^{-r/\xi}}{r},
\]

where \( \xi \) is called the correlation length which diverges at the critical point. The degree of SRO in the Heisenberg model and the model of iron with non-pairwise exchange interactions can therefore be compared directly by comparing the values of the nearest neighbour correlation function at \( T_C \).

### 4.4.3 Susceptibility above \( T_C \)

The susceptibility for the nearest-neighbour Heisenberg model and the model of iron has been calculated for temperatures above the Curie temperature. The usual definition for susceptibility (e.g Landau and Lifshitz, 1958) is

\[
\chi_N = T^{-1} N (\langle M \cdot M \rangle - \langle M \rangle \cdot \langle M \rangle),
\]

where \( M \) is the magnetisation and \( N \) is the system size. This is a special case of the general relation known as the fluctuation-dissipation theorem. Now for temperature \( T > T_C \) the expectation value of the magnetisation is zero and so the susceptibility can be defined as
\[
\chi_N^{(T>T_c)} = \frac{1}{3} T^{-1} N \langle M^2 \rangle.
\] (4.17)

This definition arises since the components of the average squared magnetisation in each of the three global magnetisation axes for \( T > T_C \) is equal.

In order to estimate the susceptibility \( \chi_{\infty}^{(T>T_c)} \) of an infinite system, \( \chi_N^{(T>T_c)} \) is calculated for a number of system sizes \( N \) from \( 54(3 \times 3 \times 3 \text{ BCC unit cells}) \) to 2000 \( (10 \times 10 \times 10 \text{ BCC unit cells}) \). Using the asymptotic form (Paauw et al 1975)

\[
\chi_N^{(T>T_c)} = \chi_{\infty}^{(T>T_c)} + CN^{-1/3}
\] (4.18)

one can extrapolate for \( \chi_{\infty}^{(T>T_c)} \). This definition assumes that the susceptibility of the finite system contains a surface contribution and \( C \) is a constant related to the surface susceptibility.

### 4.5 Magnetisation and Correlation.

The magnetisation and correlation to the fifth neighbour have been calculated for the nearest-neighbour Heisenberg model and the model of iron as outlined above. Table 4.1 gives the results for the Curie temperature of the different systems, evaluated by mean field theory and Monte Carlo simulations. The extreme cases will be discussed later. The Curie temperature is estimated "by eye" from the magnetisation curves. For the nearest neighbour Heisenberg model it is found to be

\[ T_C = (3.95 \pm 0.05) J/k_B. \]

This is to be compared with \( (4.11 \pm 0.015) J/k_B \) found by Rushbrooke et al (1974) by series expansion, \( 3.83 J/k_B \) from the extended spherical model (Chana et al 1991) and \( 5.33 J/k_B \) from mean field theory. This result also agrees with the Monte Carlo data for a BCC Heisenberg ferromagnet of Binder et al (1970). This data provides a useful test for the computer program. If the parameters in equation (4.3) are assigned the following values
the model of iron is equivalent to a nearest neighbour Heisenberg model. The results of this simulation (not shown) agree with the result of Binder et al. (1970) within statistical error. The Curie temperature in this case is the same as in the Heisenberg model.

With the parameters of system II, $T_C = 1600\text{K}$ for iron, compared with an experimental value of $1040\text{K}$. The reason that the calculated $T_C$ is larger than the experimental value is that the nearest-neighbour interaction is large at the DLM ($\sigma^2 = 0$) end, and it is this interaction that largely determines $T_C$. The effect of $J_2$ will be discussed in section (4.5). The table also confirms that mean field theory overestimates $T_C$. The Curie temperature in a mean field approximation for a Heisenberg model with nearest- and next-nearest-neighbour interactions is given by

$$T_C = \frac{(8J_1 + 6J_2)S(S + 1)}{3k_B} \quad (4.20)$$

The magnitude of the spins in the present calculations in unity. The units of temperature in the simulation and from the mean field result are $J/k_B$ and the units of the exchange interaction are mRyd, and a conversion to degree K has been made.

<table>
<thead>
<tr>
<th>System</th>
<th>Mean field</th>
<th>Monte Carlo</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5.33 $J/k_B$</td>
<td>3.95 $J/k_B$</td>
</tr>
<tr>
<td>II</td>
<td>2230 K</td>
<td>1600 K</td>
</tr>
<tr>
<td>III</td>
<td>2106 K</td>
<td>1450 K</td>
</tr>
<tr>
<td>IV</td>
<td>2106 K</td>
<td>1300 K</td>
</tr>
</tbody>
</table>

Table 4.1. Calculated Curie temperatures for the systems described in §4.2.
The magnetisation against reduced temperature for the Heisenberg model, the model of iron and the extreme case is plotted in Figure 4.3. The magnetisation in the model of iron falls slightly more rapidly near \( T = 0 \) and less rapidly as \( T \to T_c \) compared with the magnetisation in the Heisenberg model. This is because the model of iron disorders more rapidly than the Heisenberg model at lower temperatures, however as the surrounding shell of neighbours (the local magnetisation) disorders, the system becomes more stiff to disorder and so the bulk magnetisation decreases less rapidly than in the Heisenberg model. It is this behaviour that leads one to suspect that SRO greater than that in the Heisenberg model should be present above \( T_c \). All the magnetisation curves deviate considerably from the experimental data; this is inevitable in a classical spin system.

**Figure 4.3.** Magnetisation in principal systems. Thin line: System I (Heisenberg model); bold line: System II (iron); dotted line: System IV (extreme case); crosses: experimental data for iron (Landolt-Börnstein, 1962).
The principal aim of this investigation is to investigate the possibility of large SRO above $T_C$ in iron. This can be achieved by calculating the real space correlation function $c(n)$, as defined in equations (4.13) and (4.14). The temperature dependence of the correlation functions for the the first five shells of neighbours in the nearest neighbour Heisenberg model, the model of iron and the extreme case of exchange interactions, is shown in Figure 4.4 and their values at $T_C$ are listed in Table 4.2. It is immediately apparent that the real space correlation function in the model of iron is almost indistinguishable from that for the nearest-neighbour Heisenberg model. The correlation function $c(n)$ is plotted against $n$ in Figure 4.5 at $T = 0.5T_C$, $T = T_C$ and $T = 1.5T_C$. At $T = T_C$ one can clearly see that the correlation of the spins in the model of iron is similar to that in the nearest neighbour
Heisenberg model. In both cases the nearest-neighbour correlation, $c(1)$, is small (0.16) at $T_C$.

The conclusion therefore is that the degree of SRO in iron is not greater than that in the nearest-neighbour Heisenberg model. The next-nearest neighbour correlation, $c(2)$, is slightly large in the model of iron, however this can be attributed to the next-nearest neighbour interactions rather than to non-pairwise interactions.

The correlation curves have also been calculated in the ferromagnetic state in an attempt to investigate the possibility of formation of substantial clusters of reversed spin. The results, when compared with the Heisenberg model, do not appear to support this claim. The difference between the model of iron and the Heisenberg model reflect the effective stretching of the temperature scale and the change in the range of interactions with temperature. If substantial clusters of reversed spin did form then the nearest- and next-nearest neighbour correlation functions in the ferromagnetic state would be much larger than found. These would also imply a higher degree of SRO in iron. The next-nearest neighbour correlation $c(2)$ in the model of iron is larger than $c(2)$ in the Heisenberg model, but this can again be attributed to the next-nearest neighbour interactions. The correlation in the more distant shells is very similar in the model of iron and the Heisenberg model indicating that the effects of the interactions are concentrated within the nearest- and next-nearest shells.

<table>
<thead>
<tr>
<th>System</th>
<th>$c(1)$</th>
<th>$c(2)$</th>
<th>$c(3)$</th>
<th>$c(4)$</th>
<th>$c(5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.163</td>
<td>0.110</td>
<td>0.078</td>
<td>0.057</td>
<td>0.039</td>
</tr>
<tr>
<td>II</td>
<td>0.156</td>
<td>0.115</td>
<td>0.074</td>
<td>0.058</td>
<td>0.040</td>
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<tr>
<td>III</td>
<td>0.172</td>
<td>0.118</td>
<td>0.084</td>
<td>0.064</td>
<td>0.044</td>
</tr>
</tbody>
</table>

Table 4.1. Correlation function at $T_C$ calculated by Monte Carlo simulation. I: nearest-neighbour Heisenberg model, II: iron with non-pairwise exchange interactions, III extreme case of non-pairwise exchange interactions.
Correlation between first five neighbours of a lattice site. Top: $T = 0.5T_C$; middle: $T = T_C$; bottom: $T = 1.5T_C$. Thin line: Heisenberg model (System I); bold line: iron (System II).

4.6 The effect of non-pairwise interactions.

The results so far indicate that even with the order dependent interactions of the model of iron, the SRO is not much greater than that found in the Heisenberg model. The only difference between the two models is the effective stretching of the temperature scale. This is because of the non-pairwise exchange interactions in the model of iron. It can be observed from Figure 2.2 that the nearest-neighbour interaction is the more dominant and more order dependent. To investigate the effect of this interaction on the statistical mechanics of the model of iron various different systems were modelled by changing the parameters in equation (4.3). The next-nearest neighbour interaction was eliminated. In
iron with the extreme non-pairwise exchange interactions (system IV) the nearest neighbour exchange interaction vanishes in the ferromagnetic state. Figure 4.1 shows the order dependence of the nearest-neighbour interaction for the different models.

The Curie temperatures for System III and IV calculated in mean field theory and from Monte Carlo simulation are listed in Table 4.1. The Curie temperature obtained from Monte Carlo simulation is much lower in these systems because of the absence of the $J_2$ term. The $J_2$ term reduces the average exchange interaction and its absence means that the system disorders more rapidly (thus the lower $T_C$). This is because of the nature of $J_1$ (Figure 4.1). The table also confirms that in the mean field approximation the effect the $J_2$ interaction is largely neglected as its absence only reduces $T_C$ slightly.

The magnetisation curves for the models are shown in Figure 4.6. The main effect on the magnetisation is the stretching of the temperature scale. The magnetisation of the extreme case (system IV) is compared with the original model of iron (system II) and the Heisenberg model (system I) in Figure 4.3. The exchange interaction in the extreme case is more strongly order dependent than in the model of iron. The effect of this is that the bulk magnetisation in the extreme case decreases much more rapidly than in the model of iron. In the extreme case $J_1$ is zero at $T = 0$, therefore the ground state in this case is not likely to be ferromagnetic. This leads one to believe that clusters of reverse spins are more likely to form in the extreme case. This can be investigated by a calculation of the real space correlation function. The real space correlation function for the Heisenberg model (system II), the model of iron, and the extreme case is plotted in Figure 4.4. Iron with the extreme case of non-pairwise interactions does show correlations increasing with temperature rather more rapidly than in the Heisenberg model. However at $T_C$ the values of the correlation functions are similar; this again is due to the rate of increase of the exchange interaction with disorder. The conclusion that can be drawn from this therefore is that even in the extreme case the behaviour of the correlations is due to the rate increase of the exchange interactions with disorder and not as a result of the formation of clusters of reversed spin. If such clusters did form the values of the correlation functions would be higher in the extreme case than in
the Heisenberg model and a larger degree of SRO above $T_C$ would result. It must be pointed out that the Monte Carlo method does not allow one to perform simulations of the ground state of these systems, and consequently the concluding remarks do not apply to the ground state. It is entirely possible that the ground state could break up into clusters of reversed magnetisation. This claim will be investigated further in Chapter five using a two dimensional Ising model at temperature $T = 0$.

Figure 4.6. Magnetisation as a function of temperature on an arbitrary scale for different extreme cases of the exchange interaction in iron. Top and bottom bold lines are the results for systems III and IV and the other lines are for systems intermediate between systems III and IV.
4.7 Susceptibility above $T_C$.

The reciprocal susceptibility for both the systems is plotted in Figure 4.7. The curves are found to be very similar, and the gradients are nearly equal (11.54 for the Heisenberg model and 10.00 for iron). The Curie constant for the model of iron derived from the calculated susceptibility is $0.55 \times 10^{-4}$. The reciprocal susceptibility calculated from the Monte Carlo simulations also shows that the behaviour of the nearest-neighbour Heisenberg model and the model of iron above the Curie temperature is very similar. The reciprocal susceptibility for the model of iron and a linear extrapolation of the susceptibility from high temperatures is also plotted in Figure 4.7. A slight deviation is observed in these two curves as $T$ approaches $T_C$, however a conclusion that this result is similar to the experimental result cannot be formed, as this may just be an artifact of the Monte Carlo simulation.

![Figure 4.7](image-url)  
*Figure 4.7.* Reciprocal susceptibility for the Heisenberg model (thin line) and iron (bold line). The high temperature extrapolation for the susceptibility is also shown for iron (dotted line).
In conclusion, one finds that the model of iron with non-pairwise order dependent exchange interactions determined by equation (4.3) does not behave in a substantially different way form the nearest-neighbour Heisenberg model. In order to investigate the effect of non-pairwise interactions some extreme cases of the exchange interactions have been examined and it is found that even in these cases the correlation of the spins is similar to that found in the nearest-neighbour Heisenberg model. The ground state of the systems cannot be investigated using the standard Monte Carlo method (because of the inverse temperature in the Boltzmann weights), also it is not possible to directly observe clusters of reversed magnetisation in these three dimensional lattices. However one can use the same Hamiltonians and parameters in a two dimensional Ising model and a modified Monte Carlo scheme which would allow the direct observation of the dynamics of the spins. This is the subject of the next chapter.
Chapter Five.

An investigation of the ground state of iron.

5.1 Clusters of reversed magnetisation.

The three dimensional Monte Carlo simulations in Chapter four showed that the model of iron with non-pairwise exchange interactions behaves in a similar way to the nearest-neighbour Heisenberg model, even in an extreme case. The main difference is in the magnetisation curves and a stretching of the temperature scale. There is a possibility of the formation of clusters of reversed spin in the ground state of iron (Heine, private communication) and the effect of this on the magnetic short range order above the Curie temperature, was commented on. The physical property investigated was the real space spin correlation function. Although this provided information on the phase transition and the short range order above the Curie temperature it did not reveal any information about the ground state. This is due to the fact that using the standard Monte Carlo simulation it is not possible to reduce the temperature to zero (because of the inverse temperature in the Boltzmann weighting of configurations). One can however use a modified simulation and in order to directly observe the spin dynamics, a two-dimensional Ising model. This is the subject of investigation in this chapter.

5.2 Definition of the model.

The Ising model is a system of \( N \) fixed points. Associated with each point is a spin variable, \( S_i \), which can only have a value of +1 or -1, this corresponds to spin-up and spin-down respectively. The Hamiltonian of the system is that of the Heisenberg model

\[
H = -\sum_{i,j} J_{ij} S_i S_j. \tag{5.1}
\]
In the standard model the exchange interaction $J_{ij}$ is a constant. In two dimensions spontaneous magnetisation does exist below a certain temperature. A simple proof of which is presented in Appendix B. The non-pairwise exchange interactions described in Chapter two can be incorporated in the model by defining the exchange interactions as

$$J_{ij} = A_{ij} + B_{ij} [\sigma(i,j)]^2. \quad (5.2)$$

The exchange interactions are taken to be the second derivatives of the Hamiltonian as in the previous Monte Carlo simulations. The average magnetisation surrounding sites $i$ and $j$ is given by

$$\sigma(i,j) = \frac{\sum_{k \in S(i,j)} S_k}{z(i,j)}, \quad (5.3)$$

where $S(i,j)$ is the shell of neighbours of sites $i$ and $j$, and $z(i,j)$ is the number of sites in the shell. The magnetisation in this case will be two-dimensional. The shell for both $J_1$ and $J_2$ in this case consists of 8 sites (including $i$ and $j$). The exchange interactions in the systems are determined by the parameters:

**System I:** nearest neighbour Heisenberg model with

$$J_{ij} = \begin{cases} 
1 & \text{if } i \text{ and } j \text{ nearest-neighbours} \\
0 & \text{otherwise.} 
\end{cases} \quad (5.4)$$

**System II:** iron with non-pairwise exchange interactions $J_1$ and $J_2$, with the following parameters,

$$\begin{align*}
A_1 &= 2.5 \text{ mRyd} \\
B_1 &= -1.5 \text{ mRyd} \\
A_2 &= 0.2 \text{ mRyd} \\
B_2 &= 0.6 \text{ mRyd.}
\end{align*} \quad (5.5)$$

**System III:** iron with non-pairwise exchange interaction $J_1$ and $J_2 = 0$,

$$\begin{align*}
A_1 &= 2.5 \text{ mRyd} \\
B_1 &= -1.5 \text{ mRyd.}
\end{align*} \quad (5.6)$$
System IV: iron with extreme non-pairwise exchange interaction \( J_1 \) and \( J_2 = 0 \),

\[
\begin{aligned}
A_1 &= 2.5 \text{ mRyd} \\
B_1 &= -2.5 \text{ mRyd}.
\end{aligned}
\]  

(5.7)

In systems III and IV there is zero next-nearest-neighbour interaction \( J_2 \). In system IV the nearest-neighbour exchange interaction vanishes in the ferromagnetic state. These are the same parameters for the systems investigated in Chapter four. Systems III and IV allow the effect of next-nearest-neighbour interaction \( J_2 \) on the ground state to be investigated.

5.3 Monte Carlo simulation.

Since one is interested in the ground state, the standard transition probability for the Metropolis algorithm

\[
W(\Delta E) = \begin{cases}
1 & \text{If } \Delta E \leq 0 \\
\exp(-\Delta E/k_B T) & \text{If } \Delta E > 0,
\end{cases}
\]  

(5.8)

cannot be used in the present simulations as this probability involves the inverse temperature \( 1/k_B T \). \( \Delta E \) is the change in energy associated with a change in spin configuration. One can however, set \( T = 0 \) and use the transition probability

\[
W(\Delta E_T) = \begin{cases}
1 & \text{If } \Delta E_T < 0 \\
0 & \text{If } \Delta E_T \geq 0.
\end{cases}
\]  

(5.9)

Therefore all spin flips that lower the total energy \( E_T \) of the system are accepted. After a sufficient number of Monte Carlo steps have been performed the system should therefore have reached its ground state. Random spin flips after this can occur due to numerical inaccuracy, however it was found that these do not occur very frequently and so one can be confident that the ground state is reached after a large number of Monte Carlo steps have been performed.
Periodic boundary conditions have also been applied in order to approximate a larger lattice. These simply link the spins along an edge of the lattice with the spins on the opposite edge.

5.4 Dynamics of spins.

In this simulation one is specifically interested in the "dynamics" of the spins in the ground state. The results are obtained by allowing the simulation to progress and generating "snapshots" of the lattice after every 200 Monte Carlo steps (MCS). The process is allowed to continue for several thousand MCS until the energy has been minimised, that is spin flips do not occur frequently or at all and one is certain that the ground state has been reached.

In order to check that the algorithm is actually correct, a simulation of the nearest-neighbour Heisenberg model was carried out. The 2D Ising model has a ferromagnetic ground state. One can observe from Figure 5.1 that this is in fact the case when the above Monte Carlo algorithm is used. The system has a random starting state and eventually the system reaches a ferromagnetic ground state. After 4400 MCS further spin flips do not occur. Figures 5.5a and 5.5b show the behaviour with a ferromagnetic starting state. After 1000 MCS have been performed in this case the system remains in a ferromagnetic state. One can therefore be confident that the algorithm with the modified transition probability does give the correct results.

Let us now turn our attention to the model of iron with non-pairwise exchange interactions. In system II where both the nearest and next-nearest-neighbour interactions have positive values dependent on the local magnetisation, one observes from Figure 5.2 that a ferromagnetic ground state is reached after several thousand MCS. This is encouraging since it indicates that even with non-pairwise exchange interactions the ground state of iron is ferromagnetic. There is no evidence of clusters of reversed spin forming. Figures 5.5c and 5.5d show the state of the lattice after 1000 MCS with a ferromagnetic starting state. It is found that for systems III and IV starting with a ferromagnetic state, the results after 1000 MCS are the same as in system II.
Chapter five: Ground state of iron.

The effect of next-nearest-neighbour interaction $J_2$ is found to be important. Figure 5.3 shows the spin dynamics of system III. This is the same as system II, but there is a zero next-nearest-neighbour interaction $J_2$. It is immediately apparent what the effect of $J_2$ is; one observes that after about 600 MCS well defined clusters of reversed magnetisation do indeed begin to form in this system and after about 4400 MCS these become stabilised. Figures 5.5c and 5.5d show the behaviour with a ferromagnetic starting state. One observes in this case that the lattice does not break up into clusters of reversed spin; this is because the ferromagnetic starting state is in fact a special case of a very large cluster, one that expands over the entire lattice.

Clusters of reversed spin are also found in system IV, iron with extreme non-pairwise exchange interaction $J_1$. The main effect here is that clusters form much more quickly, this is to be expected since $J_1$ changes much more rapidly with local order in this system. The ferromagnetic starting state again is a special case of a cluster in this system, Figures 5.5c and 5.5d.

Simulations with an anti-ferromagnetic starting state were also carried out, although the results are not reported here. The same behaviour as with a random starting state was found in the respective systems. This is as one would expect since the nearest-neighbour Heisenberg model and iron with non-pairwise $J_1$ and $J_2$ will form a ferromagnetic state and the other models of iron will form clusters in the ground state. Although this is an over simplified approximation to the three dimensional BCC systems used in Chapter four, one can gain some insight into how blocks of reversed magnetisation form. The effect of next-nearest-neighbour interaction $J_2$ is found to be important. It would appear that $J_2$ stabilises the ferromagnetic ground state of iron; without $J_2$ the ground state breaks up into clusters of reversed magnetisation. Consider now the configuration
Chapter five: Ground state of iron.

If there is a $J_2$ interaction then the spin at site $i$ will favour the state $-1$ as most of the second neighbours are in this state and the total energy of the system will be lowered. Therefore the spins in this cluster will flip to the ferromagnetic direction. If now there is a zero $J_2$ interaction then the spin at site $i$ will be neutral since the two $+1$ neighbouring spins are cancelled by the other two $-1$ neighbouring spins and there is no effect from the next-nearest-neighbours. This cluster then will be stable to spin flips. Notice also along the same arguments most of the smallest clusters will be of a $2 \times 2$ size. This is observed for the extreme case (system IV) in Figure 5.4.

Whether these clusters would persist as the temperature is raised is not conclusive yet. The three dimensional BCC Monte Carlo results would indicate that clusters do not persist as the Curie temperature is approached.
Figure 5.1 Spin dynamics of nearest neighbour Heisenberg model (System I). Random starting state.
Figure 5.1 Spin dynamics of nearest neighbour Heisenberg model (System I). Random starting state.
**Figure 5.1** Spin dynamics of nearest neighbour Heisenberg model (System I). Random starting state.
Chapter five: Ground state of iron.

Figure 5.2 Spin dynamics of iron with non-pairwise exchange interactions (System II).
Random starting state.
Figure 5.2 Spin dynamics of iron with non-pairwise exchange interactions (System II). Random starting state.
Figure 5.2 Spin dynamics of iron with non-pairwise exchange interactions (System II). Random starting state.
Figure 5.3 Spin dynamics of iron with non-pairwise exchange interactions ($J_2 = 0$; System III). Random starting state.
Figure 5.3 Spin dynamics of iron with non-pairwise exchange interactions ($J_2 = 0$; System III). Random starting state.
### Figure 5.3 Spin dynamics of iron with non-pairwise exchange interactions ($J_2 = 0$; System III). Random starting state.

<table>
<thead>
<tr>
<th>(i) MCS = 2400</th>
<th>(j) MCS = 3000</th>
</tr>
</thead>
<tbody>
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<td>- + + + + + + + - - - + + - - + + + + + + + + - - + + - - + + + + + + + + - - + - - - + + + + + + + + - + + - - - - - - - + + + + - - - + + + + + + + + - - + + - - - - - - - - - - - - + + - + - - - + + + + + + + + - + + - - - - - - - - - - - - + + - + - - - + + + + + + + + - + + - - - - - - - - - - - - + + - + - - - + + + + + + + + - + + - - - - - - - - - - - - + + - + - - - + + + + + + + + - + + - - - - - - - - - - - - + + - + - - - + + + + + + + + - + + - - - - - - - - - - - - + + - + - - - + + + + + + + +</td>
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<table>
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<th>(k) MCS = 3600</th>
<th>(l) MCS = 4200</th>
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<td></td>
</tr>
</tbody>
</table>
Figure 5.4 Spin dynamics of iron with extreme non-pairwise exchange interactions ($J_2 = 0$; System IV). Random starting state.
Figure 5.4 Spin dynamics of iron with extreme non-pairwise exchange interactions

\((J_2 = 0; \text{System IV})\). Random starting state.
Figure 5.4 Spin dynamics of iron with extreme non-pairwise exchange interactions ($J_2 = 0$; System IV). Random starting state.
Figure 5.5  Spin dynamics of (a - b): nearest neighbour Heisenberg model (System I) and (c - d) iron with non-pairwise exchange interactions (Systems II-IV). Ferromagnetic starting states.
Chapter Six.

Spin waves in the Heisenberg model and Iron.

6.1 Introduction.

In Chapter four the effect of non-pairwise interactions was examined, using a classical Monte Carlo method, and comparing with the nearest-neighbour Heisenberg model. Through a calculation of the real space correlation function it was concluded that non-pairwise interactions do not lead to substantial short range magnetic order above \( T_C \) in iron. Lynn (1975) measured the spin wave dispersion for iron at temperatures below and above \( T_C \). In this paper he reported that the spin wave dispersion is only slightly renormalised with increasing temperature and above \( T_C \) there is no further renormalisation. This has the obvious implication of some sort of short range order supporting spin waves above \( T_C \). Therefore a calculation of the spin wave dispersion of the model of iron described in Chapter two would allow a direct comparison with experimental results to be made and also provide an alternative investigation to Monte Carlo simulation. The spin wave dispersion at \( T = 0 \) and \( T > 0 \) can be calculated using non-interacting and interacting spin wave theory, respectively. The topic of the present chapter is such a calculation for iron and the nearest neighbour Heisenberg model. To check the theory a calculation of the dispersion in EuO is also reported. The derivation and formalisation throughout this chapter follows Lovesey (1984). The theory is presented here to make the work complete.

6.2 The ground state - non-interacting spin waves.

The spin wave can be thought of as one spin reversal spread coherently over the entire lattice of a system. The concept of spin waves as non-interacting quasiparticles is valid at very low temperatures (i.e well below \( T_C \)) as the number of spin waves excited is much less than the total number of spins therefore we can treat one spin wave excitation independently from other spin wave excitations. We start with the Heisenberg Hamiltonian
Chapter Six: Spin waves in iron.

\[ H = -\sum_{i,j} J_{ij} S_i S_j \quad (6.1) \]

Here \( S_i \) is the spin operator and \( J_{ij} \) is the exchange interaction between spins at sites \( i \) and \( j \).

Let us now introduce the following operators

\[ S_i^+ = S_i^x + iS_i^y \quad ; \quad S_i^- = S_i^x - iS_i^y \quad (6.2a,b) \]

These are the spin raising and lowering operators; \( S_i^+ \) raises the spin by 1, and \( S_i^- \) lowers the spin by 1. So \( S_i^+ \) acting on an electron in a down spin state will flip it to an up spin state. This can be easily verified. Assume we have spin 1/2 particles. If the state \( |\uparrow\rangle \) is an eigenstate of \( S_i^z \) and has an eigenvalue of \( 1/2h \), then \( S_i^- |\uparrow\rangle \) is the eigenstate \( |\downarrow\rangle \) of \( S_i^z \) having an eigenvalue \(-1/2h\):

\[
S_i^- (S_i^z |\uparrow\rangle) = (S_i^+ S_i^- - h S_i^-) |\uparrow\rangle
= (\frac{1}{2}h S_i^z - h S_i^-) |\uparrow\rangle
= \frac{1}{2}h (S_i^z) |\downarrow\rangle.
\]

These operators satisfy the following commutation relations

\[
[S_i^+, S_j^-] = 2\delta_{ij} S_i^z \quad (6.3a)
\]

\[
[S_i^+, S_j^+] = \delta_{ij} S_i^z \quad (6.3b)
\]

\[
[S_i^-, S_j^-] = -\delta_{ij} S_i^z \quad (6.3c)
\]

Consider now the following

\[
S_i^+ S_j^- = (S_i^x + iS_i^y) (S_j^x - iS_j^y) \quad (6.4a)
\]

\[
S_i^- S_j^+ = (S_i^x - iS_i^y) (S_j^x + iS_j^y) \quad (6.4b)
\]

we can therefore write

\[
S_i^- S_j^- + \frac{1}{2} [S_i^+ S_j^+ + S_i^- S_j^-] + S_i^z S_j^z. \quad (6.5)
\]
We can rewrite the Hamiltonian in equation (6.1) as

\[ H = -\sum_{i,j} J_{ij} \left\{ \frac{1}{2} [S_i^+ S_j^- + S_i^- S_j^+] + S_i^z S_j^z \right\} \]  

(6.6)

Now the exchange interaction \( J_{ij} \) must be translationally invariant, i.e. \( J_{ij} = J_{ji} \), so we can simplify equation (6.6) to

\[ H = -\sum_{i,j} J_{ij} (S_i^+ S_j^- + S_i^z S_j^z) \]  

(6.7)

The first term in equation (6.7) describes the interaction of magnetic moments at site \( i \) and \( j \). The second term describes the propagation of a spin flip through the system. \( S_i^+ \) will flip a reversed spin to the direction of magnetisation and \( S_j^- \) will reverse a spin at a neighbouring site.

The equation of motion of this spin flip is given by

\[ i\hbar \partial_t S_i^+ = [S_i^+, H] = [S_i^+, \sum_{i,j} J_{ij} (S_i^+ S_j^- + S_i^z S_j^z)] \]  

(6.8)

Using the commutator relation

\[ [\hat{A}, \hat{B} \hat{C}] = [\hat{A}, \hat{B}] \hat{C} + \hat{B} [\hat{A}, \hat{C}] \]  

(6.9)

we can write the commutation

\[ [S_i^+, S_j^z S_j^-] = [S_i^+, S_j^z] S_j^- + S_j^- [S_i^+, S_j^z] \]  

(6.10)

using the relation

\[ [S_i^+, S_j^-] = -[S_j^-, S_i^+] = -\delta_{ij} S_i^+ \]  

(6.11)

then we can write

\[ [S_i^+, S_j^z S_j^-] = -\delta_{ki} S_k^+ S_j^- - \delta_{kj} S_k^+ S_i^- \]  

(6.12)
Similarly
\[ [S_k^+, S_i^+ S_j^-] = [S_k^+, S_i^-] S_j^- + S_i^+ [S_k^+, S_j^-] \] (6.13)
we have
\[ [S_k^+, S_i^-] = 0 \] (6.14)
therefore
\[ [S_k^+, S_i^+ S_j^-] = 2 \delta_{ki} S_k^+ S_i^+ \] (6.15)

Substituting equation (6.12) and equation (6.15) into equation (6.7), we get
\[ [S_k^+, H] = - \sum_{i,j} J_{ij} \{2 \delta_{ij} S_k^+ S_i^+ - \delta_{ki} S_k^+ S_j^- - \delta_{kj} S_k^- S_i^+ \} \] (6.16)

Again making use of the symmetry of \( J_{ij} \), we can write
\[ [S_i^+, H] = \sum_{i,j} J_{ij} \{ S_j^- S_i^+ - S_i^+ S_j^- \} \] (6.17)

Now at very low temperatures \( (T \to 0) \), there are a few spin waves excited therefore \( S_i^+ \) will be very nearly the saturation value \( S \), and so we can write equation (6.17) as
\[ [S_i^+, H] = 2S \sum_j J_{ij} (S_i^+ - S_j^-) \] (6.18)

We now make a transformation from real space to reciprocal space through
\[ S_i^+ = \frac{1}{N} \sum_q \exp(\pm iq \cdot l_i) S_q^+ \] (6.19)
where \( N \) is the number of unit cells, and \( l_i \) is the lattice vector of site \( i \). So
\[
\begin{align*}
\text{i} \hbar \partial_t S_i^+ &= 2S \sum_j J_{ij} \left\{ \sum_q \exp(iq \cdot 0) S_q^+ + \sum_q \exp(iq \cdot l_j) S_q^+ \right\} \\
&= 2S \sum_j J_{ij} \left\{ \sum_q 1 - \exp(iq \cdot l_j) S_q^+ \right\} \\
&= 2S \sum_j \left\{ \sum_q J_{ij} - J_{ij} \exp(iq \cdot l_j) S_q^+ \right\} \\
&= 2S \sum_j \left( \sum_q J_{ij} - J_{ij} \exp(iq \cdot l_j) S_q^+ \right)
\end{align*}
\] (6.20)
Let us now define

\[ \vec{J}_q = \sum_j J_{ij} \exp(iq \cdot \mathbf{l}_j) \]  

so we can write

\[ i\hbar \partial_t S_i^+ = 2S(\vec{J}_0 - \vec{J}_q) S_q^+ \]  

we can solve this time-dependent function by setting

\[ S_q^+(t) = \exp\left(\frac{itH}{\hbar}\right) S_q^+ \exp\left(\frac{-itH}{\hbar}\right) = \exp(-i\omega_q t) S_q^+ \]  

so

\[ \hbar \omega_q = 2S (\vec{J}_0 - \vec{J}_q) \]  

This is the spin wave dispersion for spin waves of wave vector \( q \) for a system that is described by a Heisenberg Hamiltonian. The \( q = 0 \) term corresponds to ferromagnetic resonance.

Let us consider the nearest neighbour Heisenberg Hamiltonian which has a constant exchange interaction between nearest neighbour spins of magnitude \( J \). The spin wave dispersion is given by equation (6.24). Now

\[ \vec{J}_q = \sum_j J_{ij} \exp(iq \cdot \mathbf{l}_j) = zJ \gamma_q \]  

for \( z \) nearest neighbours and

\[ \gamma_q = \frac{1}{z} \sum_j \exp(iq \cdot \mathbf{l}_j) \]  

so

\[ \hbar \omega_q = 2S (zJ - zJ \gamma_q) \]

\[ = 2S J z (1 - \gamma_q) \]
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For small values of \( q \), we can write

\[
\gamma_q = \frac{1}{z} \sum_{\rho} \exp(iq \cdot \rho) = \frac{1}{z} \sum_{\rho} \left[ 1 + iq \cdot \rho + \frac{1}{2} (iq \cdot \rho)^2 + \ldots \right] \tag{6.28}
\]

where \( \rho \) is the lattice vector joining nearest neighbours. Let us truncate this series, so

\[
\gamma_q = \frac{1}{z} \sum_{\rho} \left( 1 - \frac{1}{2} \frac{q^2 \rho^2}{z} \right) = 1 - \frac{1}{6} q^2 \rho^2 \tag{6.29}
\]

Now

\[
\rho^2 = \begin{cases} 
  a^2 & \text{simple cubic (} z = 6 \text{)} \\
  3a^2/4 & \text{body centred cubic (} z = 8 \text{)} \\
  a^2/2 & \text{face centred cubic (} z = 12 \text{)}
\end{cases} \tag{6.30}
\]

so

\[
z \frac{1}{6} \rho^2 = a^2 \tag{6.31}
\]

for all three cubic lattices. Therefore

\[
\hbar \omega_q = 2Ja^2 q^2 = Dq^2 \tag{6.32}
\]

\( D \) is called the stiffness constant.

We can also calculate the average of the magnetisation using spin wave theory. For the moment we have ignored the interaction between two or more spin waves, however we will take these into account later and make the corrections to the dispersion relation and the magnetisation. Magnons populate states according to Bose-Einstein statistics, that is

\[
n_q = \frac{1}{\exp(\hbar \omega_q/k_BT) - 1} \tag{6.33}
\]

where \( k_B \) is the Boltzmann constant. Each magnon excited will reduce the total spin by 1 unit, so the average \( z \)-component of the spin, the magnetisation at a given temperature \( T \) is...
given by

\[
(S^2)_T = S - \frac{1}{N} \sum_q n_q
\]

\[
= S - \frac{1}{N} \sum_q \left[ \exp \left( \frac{\hbar \omega_q}{k_B T} \right) - 1 \right]^{-1}
\]

\[
= S - \frac{1}{N} \sum_q \left[ \exp \left( Dq^2 / k_B T \right) - 1 \right]^{-1}
\]

(6.34)

let us now change the summation to an integral by making use of the identity

\[
\sum_q \rightarrow \frac{V}{(2\pi)^2} \int_0^{2\pi/a_0} dq
\]

so

\[
\frac{1}{N} \sum_q \left[ \exp \left( Dq^2 / k_B T \right) - 1 \right]^{-1} = \frac{1}{N} \frac{V}{(2\pi)^3} \int dq \left[ \exp \left( Dq^2 / k_B T \right) - 1 \right]^{-1}
\]

\[
= \frac{V_0}{(2\pi)^3} \int dq \left[ \exp \left( Dq^2 / k_B T \right) - 1 \right]^{-1}
\]

(6.36)

where \( V \) is the volume of the system, \( a_0 \) is the distance between neighbours and \( v_0 \) is the volume of a unit cell. If we now make the substitution

\[
\frac{Dq^2}{k_B T} \rightarrow x
\]

then

\[
S - (S^2)_T = \frac{V_0}{4\pi^2} \left( \frac{k_B T}{D} \right)^{3/2} \int_0^{\infty} dx \frac{x^{1/2}}{\exp(x) - 1}
\]

This integral can be evaluated using the Riemann zeta function

\[
\zeta(n) = \frac{1}{\Gamma(n)} \int_0^{\infty} dx \frac{x^{n-1}}{\exp(x) - 1}
\]

(6.39)

where \( \Gamma(n) \) is the gamma function. This function has common values

\[
\zeta(\frac{3}{2}) = 2.612, \quad \zeta(\frac{5}{2}) = 1.341 \quad \text{and} \quad \zeta(\frac{7}{2}) = 1.127.
\]

also

\[
\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}
\]
We thus obtain the result

\[ \langle S^2 \rangle_T = S - v_0 \left( \frac{k_B T}{4 \pi D} \right)^{3/2} \zeta \left( \frac{3}{2} \right) \]  

(6.40)

This is the $T^{3/2}$ law for magnetisation (for low temperatures) and has been verified experimentally, e.g. Gossard et al. (1961).

### 6.3 Magnon-magnon interactions.

The theory outlined above does not take into account the interactions between two or more spin waves, i.e. it is a linear theory. The interaction between spin waves becomes more important at elevated temperatures as an increasingly greater number of magnon states become occupied. Clearly if spin waves interact the dispersion relation will be modified. The interaction between spin waves arises in two parts, called the kinematic and dynamic interactions. This terminology was introduced by Dyson (Mattis, 1981) in his treatment of two magnon interactions in the Heisenberg ferromagnet. The kinematic interaction is a consequence of spin statics, that is the maximum number of spin excitations that can occur at any site with a spin $S$ is $2S$ or alternatively that the total number of independent states should not exceed $(2S + 1)^N$. The kinematic interaction is therefore a repulsive one. At low temperatures a small number of spin waves will be excited so the kinematic interaction will be small and can be neglected. The dynamic interaction arises because it costs less energy for a spin to deviate from its fully aligned state if the neighbouring spins with which it interacts through $J_{ij}$ have also deviated from their fully aligned states.

We now introduce the Bose operator representation of the spin operators

\[ S_i^z = S - a_i^+ a_i \]  

(6.41a)

\[ S_i^\pm = (2S)^{1/2} a_i \]  

(6.41b)

\[ S_i^z = (2S)^{1/2} a_i \left( 1 - \frac{a_i^+ a_i}{2S} \right) \]  

(6.41c)
where
\[ a_i a_j - a_j a_i = [a_i, a_j] = [a_i^+, a_j^+] = 0 \] (6.42a)
and
\[ [a_i^+, a_j] = \delta_{ij} \] (6.42b)

Bose operators have an infinite spin spectrum and so the kinematic interaction is effectively neglected by making use of the above transformations. Using these transformations we can re-write the Heisenberg Hamiltonian, equation (6.1), as

\[ H = \sum_q 2S \left[ \vec{J}_0 - \vec{J}_q \right] a_q^+ a_q - \frac{1}{N} \sum_{q_1 q_2 q_3 q_4} a_{q_1}^+ a_{q_2} a_{q_3} a_{q_4} \left[ \vec{J}_{q_1 - q_2} - \vec{J}_{q_3 - q_4} \right] \] (6.43)

where
\[ a_q = \frac{1}{\sqrt{N}} \sum_q \exp(iq \cdot \xi) a_q, \text{ etc.} \] (6.44)
and
\[ [a_{q}, a_{q'}] = \delta_{q,q'} \] (6.45)

The first term in equation (6.43) represents the non-interacting spin waves and the second term is the interaction between them. We now make the Hartree-Fock approximation and replace the product of four operators with the products of two operators times a thermal average. We can write the four operator product

\[ a_{q_1}^+ a_{q_2}^+ a_{q_3} a_{q_4} \]
as the sum of all non-zero pairings of two operators,

\[ a_{q_1}^+ a_{q_2}^+ a_{q_3} a_{q_4} \rightarrow \langle a_{q_1}^+ a_{q_4} \rangle a_{q_2}^+ a_{q_3} + \langle a_{q_3}^+ a_{q_4} \rangle a_{q_1}^+ a_{q_2} \]

\[ + \langle a_{q_2}^+ a_{q_3} \rangle a_{q_1}^+ a_{q_4} + \langle a_{q_4}^+ a_{q_3} \rangle a_{q_2}^+ a_{q_1} \]

\[ - \langle a_{q_3}^+ a_{q_1} \rangle \langle a_{q_2}^+ a_{q_4} \rangle - \langle a_{q_1}^+ a_{q_4} \rangle \langle a_{q_2}^+ a_{q_3} \rangle. \] (6.46)

We also have the result

\[ \langle a_{q}^+ a_{q} \rangle = \delta_{q,q'} \langle a_{q}^+ a_{q} \rangle \] (6.47)
and so equation (6.46) reduces to

\[
\begin{align*}
  n_q & \left( \delta_{q,q'}a_q^\dagger a_q + \delta_{q_0,q}a_{q_0}^\dagger a_{q_0} \right) + n_{q_0} \left( \delta_{q_0,q}a_{q_0}^\dagger a_{q_0} + \delta_{q,q_0}a_{q_0}^\dagger a_{q_0} \right) \\
  -n_q, n_q & \left( \delta_{q,q_0}a_{q_0}^\dagger a_{q_0} + \delta_{q_0,q} \right)
\end{align*}
\]

(6.48)

where

\[
\begin{align*}
  n_q = \langle a_q^\dagger a_q \rangle = \langle n_q \rangle
\end{align*}
\]

(6.49)

We can now write equation (6.43) as

\[
H = \sum_q 2S \left( \langle J_0 - \tilde{J}_q \rangle \right) n_q - \frac{2}{N} \sum_{q,q'} \left( \langle J_0 + \tilde{J}_{q,q'} \rangle - \langle \tilde{J}_q \rangle \right) n_q n_{q'}
\]

\[
+ \frac{1}{N} \sum_{q,q'} \left( \langle J_0 + \tilde{J}_{q,q'} \rangle - \langle \tilde{J}_q \rangle \right) n_q n_{q'}.
\]

(6.50)

We can use this Hartree-Fock approximated Hamiltonian to obtain the equation-of-motion for \( a_q \), and obtain the result

\[
i\hbar \partial_t \langle a_q \rangle = [a_q, H] = 2S \left( \langle J_0 - \tilde{J}_q \rangle \right) a_q - \frac{2}{N} \sum_{q'} \left( \langle J_0 + \tilde{J}_{q,q'} \rangle - \langle \tilde{J}_q \rangle \right) n_{q'} a_q.
\]

(6.51)

The spin wave spectrum in the theory of interacting spin waves is therefore

\[
h \omega_q = 2S \left( \langle J_0 - \tilde{J}_q \rangle \right) - \frac{2}{N} \sum_{q'} \left( \langle J_0 + \tilde{J}_{q,q'} \rangle - \langle \tilde{J}_q \rangle \right) n_{q'}.
\]

(6.52)

This equation represents a shift in energy from its ground state value equation (6.24) due to the interaction of two spin waves, one with wave vector \( q \) and one with wave vector \( q' \). Since the temperature of the system has been raised, then the magnons will populate states according to equation (6.33) and so we include this term to represent a temperature dependent shift in the magnon energies.
The exchange interaction in the Heisenberg model (and in the model of iron) is isotropic, and we can introduce a simplification to equation (6.52). We know from equation (6.21) that

\[ \tilde{J}_q = \sum J_{ij} \exp(iq \cdot \mathbf{l}_j) \]

\[ = z_1 J_1 \gamma_1^q + z_2 J_2 \gamma_2^q + ... \]  

(6.53)

where \( z_1, z_2, ... \) are the number of nearest, next-nearest, ... neighbours of atom \( i \). The functions \( \gamma_1^q \) and \( \gamma_2^q \) are defined by

\[ \gamma_1^q = \frac{1}{z_1} \sum_{\rho_1} \exp(iq \cdot \rho_1) = \gamma_1^q \]  

(6.54a)

\[ \gamma_2^q = \frac{1}{z_2} \sum_{\rho_2} \exp(iq \cdot \rho_2) = \gamma_2^q \]  

(6.54b)

and so on, the vectors \( \rho_1, \rho_2, ... \) are the vectors joining the nearest, next-nearest, ... neighbours. For the body-centred cubic lattice the function for the first two neighbours are

\[ \gamma_1^q = \cos \frac{1}{2} a_0 q_x \cos \frac{1}{2} a_0 q_y \cos \frac{1}{2} a_0 q_z \]  

(6.55)

and

\[ \gamma_2^q = \frac{1}{3} \cos a_0 q_x + \cos a_0 q_y + \cos a_0 q_z \]  

(6.56)

where \( a_0 \) is the lattice constant. With these expressions we can rewrite equation (6.52) as

\[ \hbar \omega_q(T) = z_1 J_1(T)(1 - \gamma_1^q) + z_2 J_2(T)(1 - \gamma_2^q) \]  

(6.57)

where

\[ J_i(T) = J_i[1 - C_i(T)/S] \]  

(6.58)

and

\[ C_i(T) = \frac{1}{N} \sum_q (1 - \gamma_i^q) n_q \]  

(6.59)

The factor \( [1 - C(T)/S] \) is usually referred to as the renormalisation factor, \( n_q \) is the Bose factor, equation (6.33) for the renormalised magnon energies. Since \( n_q \) depends on the renormalised magnon energies then \( C(T) \) has to be calculated self-consistently at each
temperature. The integral on the right hand side of equation (6.59) is evaluated by integrating over the first Brillouin zone.

Consider now the nearest neighbour Heisenberg model. We can write the spin wave dispersion as

$$h\omega_q = D(T) q^2$$  \hspace{1cm} (6.60)

where

$$D(T) = 2J Sa^2 \left[1 - C(T)/S\right]$$

$$= D_0 \left[1 - C(T)/S\right]$$  \hspace{1cm} (6.61)

If we expand the equation for $C(T)$, then

$$C(T) = \frac{a^2 v_0}{2\pi^2} \int_0^\infty dq \frac{q^4}{\exp(\beta D_0 q^2) - 1}$$  \hspace{1cm} (6.62)

using the Riemann zeta function we find

$$C(T) = \frac{a^2 v_0}{4\pi^2} \left[\frac{k_B T}{D_0}\right]^{5/2} \frac{\zeta(5)}{\zeta(2)}$$  \hspace{1cm} (6.63)

and the temperature dependence of the stiffness constant is given by

$$D(T) = D_0 \left[1 - \frac{v_0 \xi^2 a^2 \pi}{8 S^2} \left[\frac{k_B T}{4\pi D_0}\right]^{5/2} \zeta(5)\right]$$  \hspace{1cm} (6.64)

We find therefore that the interaction of two or more spin waves gives, to leading order, a temperature dependence to $D$ such that it decreases with $T$ as $T^{5/2}$.

Finally, we make a correction to the magnetisation $\langle S^z \rangle_T$. We can write the magnetisation as

$$\langle S^z \rangle_T = S - \frac{1}{N} \sum_q n_q = S - \frac{1}{N} \sum_q \left[\exp(h\omega_q/k_B T) - 1\right]^{-1}$$
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\[ S - \nu_0 \left( \frac{k_B T}{4\pi D_0} \right)^{3/2} \frac{n(S)}{zS} (1 - C(T)/S)^{-3/2} \]

\[ = S - \nu_0 \left( \frac{k_B T}{4\pi D_0} \right)^{3/2} \left( \frac{3}{2} \right)^{1/2} \left( \frac{3}{2} \right)^{3/2} \]

\[ = S - \nu_0 \left( \frac{k_B T}{4\pi D_0} \right)^{3/2} \frac{n(S)}{zS} \frac{9a^2\pi}{2} \left( \frac{k_B T}{4\pi D_0} \right)^4 \frac{3}{2} \frac{3}{2} \]

(6.65)

Here we find that the interaction of spin waves introduces a $T^4$ term in the magnetisation.

The spin wave dispersion has been calculated for the insulator EuO. This material is an isotropic Heisenberg ferromagnet, therefore a good comparison can be made between theory and experiment. The dispersion has been measured for high q-values by Glinka et al. (1975) using inelastic neutron scattering. The nearest-neighbour and next-nearest-neighbour exchange coefficients have values of $J_1/k_B = 0.602 \pm 0.008K$ and $J_2/k_B = 0.155 \pm 0.014K$ respectively. The calculated and measured dispersions are shown in Figure 6.1. The exchange coefficients used in the present calculations are those above. A fairly good agreement is found between theory and experiment. Thermal expansion effects have not been included, however this correction is expected to have a small effect on the dispersion. There is some disagreement at high temperatures; this is due to dipolar effects which are not taken into account in the theory above.

The results for EuO suggest that the theory fairly accurately predicts the magnon dispersion of Heisenberg ferromagnets for high values of $q$ and high temperatures. These results were obtained in the preliminary stages of the calculation for the Heisenberg model and the model of iron. The spin wave dispersion and magnetisation has been calculated for the nearest-neighbour Heisenberg model using equation (6.57) and equation (6.65), respectively to allow a comparison with the magnon dispersion and magnetisation in the model of iron to be made.
6.4 Spin wave dispersion for iron.

The theory outlined above can be easily applied to the model of iron with non-pairwise exchange interactions. It has already been established that the many-body interactions can be used to give an effective spin Hamiltonian by replacing the exchange interaction in the Heisenberg model by equation (2.30). The exchange interaction in the model of iron is order dependent and so a slight modification is made to the theory. The exchange interaction $l_{ij}(T)$ in the above theory can be replaced with an interaction $l_{ij}(T, S^2)$

$$J_{ij}(T, S^2) = A_{ij} + B_{ij}[S^2(T)]^2$$  \hspace{1cm} (6.66)

Therefore $C_1(T), S^z(T), J_1(T, S^2),$ and $J_2(T, S^2)$ are calculated self-consistently. The exchange interaction defined in equation (6.66) is implicitly renormalised for temperatures greater than zero through the magnetisation parameter $S^2(T)$. One starts by estimating $C_1(T)$ and $C_2(T)$ at temperature $T$. The magnetisation at $T$ is calculated using the first expression in
equation (6.65). The corresponding exchange interactions $J_1(T,S^2)$ and $J_2(T,S^2)$ for this magnetisation are calculated using equation (6.66). New values for $C'_1(T)$ and $C'_2(T)$ are calculated using equation (6.59) and compared with the old values $C_1(T)$ and $C_2(T)$. If the new value is different from the old value we set $C_j(T) = C'_j(T)$ and repeat the calculation otherwise a self-consistent solution for $C_j(T)$ has been found.

It should be pointed out that the parameter used as the magnetisation in equation (2.30) to model the exchange interactions in the model of iron, is the average magnetisation $(S^z)_{\tau}$ found using spin wave theory (first expression of equation (6.65)). Since the exchange interactions found self-consistently using spin wave theory are similar to the interactions found using electronic structure calculations, it may be assumed that $(S^z)_{\tau}$ is a suitable parameter. The non-pairwise exchange interactions do not invalidate spin wave theory since these just go in as parameters, whether they are order dependent or constants.

A more accurate spin wave theory that gives the order in the neighbouring shells of atoms would have to be derived from scratch to model the many-body interactions more accurately. This has not been attempted since the results from the Monte Carlo simulations and from the above spin wave theory show that the physics in the electronic structure calculations is inaccurate rather than any approximations made in the present calculations.

The renormalisation factor for the nearest- and next-nearest-neighbours in the model of iron as a function of temperature is shown in Figure 6.2. In the process $S^z(T)$, $J_1(T,S^2)$, and $J_2(T,S^2)$ are also obtained. The renormalised non-pairwise exchange interaction as a function of order is shown in Figure 6.3. The behaviour is similar to the interactions found in the electronic structure calculations (Figure 2.2). There is a difference near the DLM end since self-consistency in the calculations is difficult to reach in this region (it is near the phase transition). The temperature range available for the calculation is therefore 0 to $0.99T_C$, this is sufficient for the present purposes. The integrals in these calculations are evaluated numerically using standard techniques for multi-dimensional integrals (Press et al, 1985). The spin wave dispersion at $T$ for any value of $\mathbf{q}$ can then be computed using equation (6.57).
Figure 6.2. Renormalisation factor for the nearest- and next-nearest-neighbours (thin and thick line respectively) in the model of iron as a function of temperature.

Figure 6.3. Renormalised non-pairwise exchange interaction as a function of order. Thin line: nearest-neighbour interaction, bold line: next-nearest-neighbour interaction.
The calculated spin wave dispersion for three temperatures is shown in Figure 6.4. Experimentally measured dispersions (Lynn, 1975) for iron are also plotted. Figure 6.5 shows the magnon dispersions for iron with non-pairwise exchange interactions and the nearest neighbour Heisenberg model. One can observe that there is a weak temperature dependence of the magnon dispersion in the model of iron. There is slightly greater temperature dependence of the magnon dispersion in the nearest-neighbour Heisenberg model. The main effect of the non-pairwise exchange interactions on the magnon dispersion is that there is an increase of magnon energies with temperature. The expected decrease in magnon energies (for a Heisenberg type of Hamiltonian), with temperature is compensated for by the increase in the average exchange interaction with increasing temperature. There is a decrease in magnon energies near $T_C$, this is because the exchange interaction falls with temperature in this region (Figure 6.2).

Figure 6.4. Spin wave dispersion in the [110] direction calculated at three temperatures. Crosses correspond to the experimentally measured dispersion (Lynn, 1975).
The magnetisation calculated using spin wave theory is shown in Figure 6.6 for iron with non-pairwise interactions and the nearest neighbour Heisenberg model. It can be observed that the magnetisation in the model of iron decreases more rapidly with temperature than in the Heisenberg model. This is similar to the results found in the Monte Carlo simulations. Again this behaviour can be attributed to the temperature dependence of the exchange interactions. In the region near $T_C$ the magnetisation curves for both models are the same due to the lack of self-consistency in the calculation in this region.

![Figure 6.5. Normalised spin wave dispersion in the Heisenberg model (HM) and iron with non-pairwise exchange interactions.](chart.png)
In conclusion it is found that the magnon energies found in the model of iron do not in fact compare well with experimental results. The expected decrease in magnon energies with temperature is compensated for by the increase in the average exchange interaction with increasing temperature. The magnetisation does fall more rapidly with respect to the Heisenberg model at low temperatures since lower energies are required to excite magnons at these temperatures and the system therefore disorders easily.

The theory does not allow a calculation of magnon energies above $T_C$ and so one cannot conclusively comment on short range magnetic order above $T_C$ using spin wave theory. The measurements of Lynn (1975) did however indicate that the magnon energies are not renormalised any further above $T_C$, so the calculated dispersion at $T_C$ if it were weakly renormalised may indicate short range order. However since the calculated magnon
energies in iron with non-pairwise exchange interactions do not decrease with temperature then one must conclude that the model of iron does not in fact contain the correct physical properties and the observations made in the calculated spin wave dispersions are due to the nature of the exchange interactions rather than short range order.
Chapter Seven.

Can electronic structure calculations explain magnetic short range order in iron above $T_C$?

The picture so far...

This investigation was begun by deriving a model of iron based on the result of electronic structure calculations. The average exchange interaction $J_{ij}$ in the model of iron increases with temperature, Figure 2.2, consequently it becomes increasingly harder for the system to disorder as the temperature is increased. Based on this behaviour, the hypothesis that was put forward was that, in iron with non-pairwise exchange interactions magnetic short range order could exist above the Curie temperature, $T_C$, and that it could be greater than that found in the nearest-neighbour Heisenberg model. In Chapter four the results of a Monte Carlo simulation of our model of iron and the nearest neighbour Heisenberg model were presented. In Chapter five the ground state for the model of iron was investigated using a two-dimensional Ising model, and in Chapter six spin wave theory was used to investigate the effect of the $J_{ij}$ on the magnon energies.

The results indicate that at the important temperatures (around $T_C$) iron with non-pairwise exchange interactions does not behave in a substantially different way from the nearest neighbour Heisenberg model. An effective classical spin Hamiltonian was used in the calculations, this can be different from the nearest neighbour Heisenberg model in two important ways. The exchange interactions may be of long range and oscillate in sign. Such interactions can yield substantial short range order (Shastry et al 1981), however these were not found in the electronic structure calculations of Luchini and Heine (1991). Also the effect of disorder and finite temperature would reduce the amplitude of the longer-range interactions, thereby making this mechanism unlikely. The other is to assume substantial many-atom interactions. While many-atom interactions lead to coarse-grained disorder, they would also strongly distort the magnetisation curves in the ferromagnetic phase. This was
the form used in the present calculations. The principle quantity for the examination of short range order is the real space correlation function, as discussed in Chapter four. Table 7.1 is a summary of the correlation function calculated by Monte Carlo simulation and the extended spherical model (Chana et al, 1991), for the first five neighbours of the BCC lattice. One finds that the nearest-neighbour correlation at $T_C$ is much the same in the nearest-neighbour Heisenberg model as in iron with non-pairwise exchange interactions, even when these have an extreme form. Therefore the conclusion that can be reached from this observation is that the degree of short range order in iron is not greater than in the Heisenberg model.

<table>
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<tr>
<th></th>
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<th>$c(4)$</th>
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<tr>
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<tr>
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<td>0.074</td>
<td>0.058</td>
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<tr>
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<td>0.084</td>
<td>0.064</td>
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<td>0.160</td>
<td>0.134</td>
<td>0.133</td>
<td>0.266</td>
</tr>
</tbody>
</table>

**Table 7.1.** Correlation function at $T_C$ calculated by Monte Carlo simulation and the ESM for the systems described in Chapter four. (I: nearest-neighbour Heisenberg model, II: iron with non-pairwise exchange interactions, III extreme case of non-pairwise exchange interactions.) $c$ is the SRO parameter in the ESM.

The standard Monte Carlo scheme does not allow the ground state to be investigated; however, a modified scheme and a two-dimensional Ising model allows the "motions" of the spins to be observed directly. One does find in such a simulation that, for the extreme case of non-pairwise exchange interactions in iron, clusters of reversed magnetisation form. The results would indicate that the next-nearest-neighbour exchange interaction $J_2$ is fairly important. This interaction establishes the ferromagnetic ground state in iron as observed in the Monte Carlo simulations of the two dimensional Ising model in Chapter five. The effect
of $J_2$ is also noticeable in the calculated Curie temperatures; it reduces $T_C$ considerably. It would have been possible to investigate systems by using different values of the next-nearest-neighbour exchange interaction at the DLM end. There is however no real justification in doing this and simply takes the interactions further away from the original interactions found in the electronic structure calculations. The Monte Carlo results for the BCC lattice would suggest that the clusters of reversed spin do not persist as the temperature is raised and at $T_C$ the short range order in the extreme case is only slightly greater than in the nearest-neighbour Heisenberg model.

A calculation of the spin wave dispersions was carried out for a temperature range of 0 to $0.99T_C$. Although a weak temperature dependence of the magnon energies was observed, as found by Lynn (1975), the magnon energies were found to increase with temperature. This behaviour is easily attributed to the increase in the average exchange interaction with temperature. The results clearly indicate a failure of the model of iron used and in the parameters used in this model.

A simple expression for the Hamiltonian of iron itself does not exist, one has only its second derivative $J_{ij}$. It would require an unfeasible amount of computer time to derive a proper Hamiltonian for arbitrary configurations of the magnetic moments (even in the static approximation) and to calculate the resulting partition function. In the calculation of the statistical mechanics a reasonably large part of the configuration space has been sampled, and the systems sizes have been fairly large. However it is still an approximation to an infinite system. Given a proper Hamiltonian and calculating its partition function for an extremely large configuration space, what the effect would be on the present results and conclusions cannot be commented on.

One possible method of approaching an infinite system is to use the “self-consistent” Monte Carlo method (Müller-Krumhhaar and Binder, 1972). In this method, an "effective surface field" is allowed to act on the free surfaces of the finite system being modelled. This effectively compensates for the interactions with the missing neighbour spins. The magnitude of the surface field is determined by a consistency condition, which requires that
the gradient of the order parameter at the surfaces be zero (Müller-Krumbhaar and Binder, 1972). An attempt to use this method was not made as it was thought that substantially different results from the simulations using the standard method would not be obtained. The approximations made in the calculations of the electronic structure must therefore be considered.

The main approximation made in the calculation of the electronic structure is the static approximation. This is roughly the magnetic equivalent of the Born-Oppenheimer approximation (You and Heine, 1982). The magnetisation of the system is taken as a classical field precessing slowly in comparison with electron hopping, and the energetics calculated are of electrons moving on such a frozen configuration. Although the spin wave stiffness can be calculated successfully from electronic structure data (Luchini and Heine 1989), the physics of the entry of the spin waves into the Stoner continuum at \( q_c \) is missing from this static Hamiltonian. This is important since the theory of Heine and Joynt (1988) predicts short range order on the length scale of \( 2\pi/q_c \). Also above \( q_c \) the magnetic excitations are due to single particle transitions (Stoner spin flips) which will not be included in the electronic structure of static magnetic configurations.

The conclusion that must therefore be reached is that a model of iron with non-pairwise exchange interactions cannot account for the apparent large degree of magnetic short range order indicated by paramagnetic neutron scattering experiments. The experimentally observed correlation function (Brown et al, 1982 and 1983) may result from dynamic or quantum effects, important for wave vectors above \( q_c \) but omitted in the static approximation. Such effects, if they can be expressed as a classical Hamiltonian, would have to lead to effective exchange interactions of a substantially different form from those obtained in the static approximation if the observed correlation functions are to be explained. The conclusion is that electronic structure calculations on static configurations of magnetisation cannot on their own explain the correlation functions observed by neutron scattering.
Although this is a negative result indicating the original model may be wrong, it does provide a valuable pointer to new physics. It has been concluded that the main problem with the calculation is the static approximation, and so to improve the calculations (and our understanding of the original problem) one must go beyond the static approximation, by taking dynamic or quantum effects into account. A more direct numerical calculation of the statistical mechanics from a microscopic viewpoint is required. The quantum Monte Carlo method, outlined in the following chapters, makes fewer approximations and should result in a clearer picture of the physics involved in the magnetism of iron and correlated electron systems in general.
Chapter Eight.

Quantum Monte Carlo simulations of correlated electron systems.

8.1 Statistical mechanics of correlated electron systems.

The conclusion that has been reached thus far in this investigation is that calculations of the electron energies of frozen magnetic configurations do not give a clear picture of the mechanisms leading to the apparent magnetic short range order found in iron above the Curie temperature. In fact one is led to believe that this approach is not accurate for calculating the correlation functions and the statistical mechanics. The main problem in the calculations is in making the so called static approximation. The question then is how can one accurately calculate the statistical mechanics of a correlated electron system such as iron, without making the static approximation. Let us consider how to approach this problem.

Firstly we need to describe a correlated electron system such as iron from a microscopic viewpoint. We have already encountered such a description in Chapter two. There it was used to calculate the electronic properties of iron. However the static approximation was made and the problem was solved using a self-consistent solution based on the Hartree-Fock approximation. The same model can be used and the Hamiltonian (at least the non-magnetic part) can be parameterised in the same way for the present calculations. A quick description of the model is given in section (8.2) before reviewing some of the methods that have been used to solve it in the past in section (8.3).

Once a Hamiltonian has been defined for a correlated electron system this many-body problem needs to be solved. The specific interest is in the statistical mechanics so a many-body partition function for the system needs to be derived. This task is made easier by the use of a functional integral formalism; this replaces the many-body electron-electron interaction with non-interacting electrons interacting only with an auxiliary field. The
functional integral can then be solved using the quantum Monte Carlo method. The quantum Monte Carlo method is a powerful tool for studying quantum mechanical systems and provides an alternative to analytical schemes. The method therefore allows one to concentrate on the physics of the system rather than on mathematical solutions. Also one of the more useful features of the method is that it allows one to set up computer experiments that provide more "probes" to a system than would be available in a real experiment. The simulations give results that can be compared directly with experiment and so allow one to test the validity of a theoretical model. Comparison of experimental results and the calculated physical properties investigated using different system parameters allows one to determine whether a model actually contains the correct physics.

8.2 The Hubbard model.

In the transition metals the electrons responsible for magnetic behaviour reside in the narrow d-band. In the tight-binding approximation, which is appropriate for transition metals, the Hamiltonian for the electrons in such a band is given by the Hubbard model

\[ H = \sum_{i,j,\alpha,\beta,\sigma} (c_{i\alpha \sigma}^\dagger t_{ij\alpha \beta} c_{j \beta \sigma} + h.c.) + U \sum_{i\alpha \beta} n_{i\alpha \uparrow} n_{i\beta \downarrow}. \] (8.1)

The first term is the one-electron nonmagnetic Hamiltonian in the tight-binding approximation with \( t_{ij,\alpha \beta} \) the hopping integral between the orbitals \( \alpha \) and \( \beta \) on sites \( i \) and \( j \) (which assumed to be translationally invariant), \( \sigma \) labels the spin state, \( c_{i\alpha \sigma}^\dagger \) and \( c_{i\alpha \sigma} \) are the creation and annihilation operators respectively, \( n_{i\alpha \sigma} = c_{i\alpha \sigma}^\dagger c_{i\alpha \sigma} \) is the number operator and \( U \) is the Coulomb interaction between the electrons on site \( i \). In this case the electron-electron interaction is defined by \( U \) rather than \( I \) as in the Hamiltonian used in Chapter two. In general \( U \) is the electron-electron repulsion and \( I \) describes the electron exchange. If \( U > 0 \) the electron interaction is repulsive, and \( U < 0 \) corresponds to an attractive electron interaction. The model is ideal for describing magnetic systems, since it is the simplest unified model that interpolates between the itinerant and localised descriptions of metallic magnets. Electrons moving around in the lattice (first term in the Hamiltonian) will lower the energy of the system, however in doing so they have the opportunity to interact with
each other (second term), and the interaction of electrons with opposite spin will increase the energy of the system through the $U$ term. The electron motion will yield an energy gain for the system of the order of the bandwidth $W$, and the electron interaction will result in a loss in the energy of an order $U$. In the 3$d$ transition metals $W = 4$ eV and $U = 1-3$ eV so that $U/W < 1$. In the limit $t_{ij} = 0$ (the atomic limit), the electrons will be fully localised, and for $U = 0$ the Hamiltonian describes a system of itinerant non-interacting electrons. The competition between the two terms in the Hamiltonian will ultimately decide the properties of the system it describes. The model can also describe the Mott conductor-insulator phase transition in metals. Very few exact results are known for this model and in its simplest form it has limitations on its applicability to real systems. In the next section a brief overview of the solutions to this model is given.

8.3 Exact results and limitations of the Hubbard model.

The Hubbard model has been studied extensively yet exact solutions only exist for special limits. Let us limit ourselves to a single band, therefore the orbital index in equation (8.1) can be ignored, also the hopping integral $t_{ij}$ will be the same for both spin directions. The only parameters that can be adjusted in equation (8.1) are $t_{ij}$ and the Coulomb potential $U$. The small-hopping-integral limit, where $t_{ij}$ can be considered as a perturbation has been studied by Anderson (1963). Second order perturbation theory leads to an effective Hamiltonian at half-filling

$$H_{\text{eff}} = -\sum_{ij} \frac{t_{ij}^2}{U} S_i \cdot S_j$$  \hspace{1cm} (8.2)

here $S_i$ and $S_j$ are the spins on sites $i$ and $j$ defined by the operators

$$S_i^z = c_{i\uparrow}^\dagger c_{i\uparrow} - c_{i\downarrow}^\dagger c_{i\downarrow}$$  \hspace{1cm} (8.3a)

$$S_i^+ = c_{i\uparrow}^\dagger c_{i\downarrow}$$  \hspace{1cm} (8.3b)

$$S_i^- = c_{i\downarrow}^\dagger c_{i\uparrow}$$  \hspace{1cm} (8.3c)
so that

\[ S_i \cdot S_j = \frac{1}{2} [ S_i^+ S_j^- + S_i^- S_j^+ ] + S_i^z S_j^z. \]  

(8.3d)

The Coulomb interaction is considered to be much larger than the hopping integral and there is half-filling of the band, therefore only one electron resides on each atom. This model is equivalent to a Heisenberg anti-ferromagnet with an exchange interaction given by the ratio \( \frac{t^2}{U} \).

Nagaoka (1966) has shown that a ferromagnetic state can exist in the Hubbard model; however only for a rather contrived limit. The band is almost half-filled, \( n \ll N \), where \( n = 1 - \frac{1}{N} \) and \( N \) is the number of sites. If \( U \) is considered to be infinite then there is no Anderson type exchange term. The hopping is between nearest-neighbours, denoted \( t \), and an exchange interaction of the type found in the Anderson model above does not exist. The model has been solved for three dimensional cubic lattices and a ferromagnetic ground state exists provided the ratio \( \frac{2t}{U}/(n/N) \) is small.

The model has been solved exactly in one dimension at zero temperature for any number of electrons by Lieb and Wu (1968). They calculated the ground state energy, wave function and the chemical potential using the Bethe ansatz. Their results indicate that the ground state is anti-ferromagnetic for half-filling and insulating for any non zero \( U \), or conducting for \( U = 0 \).

Recently the model has been solved for dimension \( D \rightarrow \infty \), (Metzner and Vollhardt, 1989), using many-body perturbation theory and variational wave functions. This is expected to give new insights into the properties of the model in finite dimensions.

An alternative to having \( U \rightarrow \infty \), is to have a model in which the hopping of the electrons has an infinite range and occurs with equal probability to any site (van Dongen and Vollhardt, 1989). In the general model the kinetic energy part of the Hamiltonian does not commute with the interaction part, however in this limit the two parts commute (i.e do not
Chapter Eight: Quantum Monte Carlo methods.

compete with each other) and so the Hamiltonian can be diagonalized exactly. The ground state is found to be insulating at half-filling and $U > 0$ and is conducting otherwise.

The thermodynamic properties of the one-dimensional half-filled band Hubbard model have been calculated by Shiba and Pincus (1972). They have considered linear chains and rings containing up to six atoms. The eigenvalues and eigenvectors are calculated by exact diagonalisation. These results will form the basis for comparison with the present Monte Carlo results for the one-dimensional systems covered in Chapter nine.

The model in its simplest form has several limitations. It does not take into account long range Coulomb interactions. Although intra-atomic correlations are taken into account inter-atomic correlations are ignored, these obviously have a bearing in metallic magnets. Hybridisation of the electron bands is not accounted for and so the model can only be applied to transition metal compounds where the $sp$-band does not overlap with the $d$-band. Additional terms to account for these interactions have to be added to the interaction part of the Hamiltonian to obtain a more accurate description of multi-band systems and transition metals. The form of a multi-band Hubbard model will be considered in the next chapter.

8.4 Partition function for the Hubbard model.

The Hamiltonian for a correlated electron system such as iron has been defined using the Hubbard model. Although no exact solution exists for all but the most unphysical, or one dimensional cases, the model can be solved using numerical methods. For the present purposes the statistical mechanics of the model are required and so its partition function needs to be able to be evaluated. The topic of this section is the derivation of the partition function in a functional integral representation in contrast to an operator representation. This is a more convenient way of calculating the statistical mechanics of a fermion system since the functional integral can be solved using Monte Carlo techniques.

Let us write the Hamiltonian in equation (8.1) for one band as

$$H = H_{\text{band}} + H_{\text{int}} \quad (8.4a)$$
Chapter Eight: Quantum Monte Carlo methods.

(8.4b) \[ H_{\text{band}} = \sum_{i,j,\sigma} c_{i\sigma}^+ t_{ij} c_{j\sigma} + c_{j\sigma}^+ t_{ij} c_{i\sigma} \]

and

(8.4c) \[ H_{\text{int}} = U \sum_i n_{i\uparrow} n_{i\downarrow}. \]

The grand-canonical partition function of the model is given by the trace over the fermionic degrees of freedom

(8.5) \[ Z = \text{Tr}_f \exp\left[-\beta \left( [H_{\text{band}} + H_{\text{int}}] - \mu \sum_{i,\sigma} n_{i\sigma} \right) \right] \]

where \( \beta = 1/k_B T \), and \( \mu \) is the chemical potential. In general \( H_{\text{band}} \) and \( H_{\text{int}} \) do not commute; however one can separate the two terms by introducing an imaginary time slice sufficiently short so that the commutations of the individual operators can be neglected. The interval \([0,\beta]\) is divided into \( L \) sufficiently small imaginary time periods (Trotter time-slices). The period of a time slice is then \( \Delta \tau = \beta/L \). The partition function can then be expressed as

(8.6) \[ Z = \text{Tr}_f \prod_{l=1}^{L} T \exp\left[-\Delta \tau H_{\text{band}}(\tau_l)\right] \exp\left[-\Delta \tau H_{\text{int}}(\tau_l)\right] \]

where \( l \) is the time slice index. The error in the decomposition is of order \( O(\Delta \tau^2 t U) \). The terms \( H_{\text{band}}(\tau_l) \) and \( H_{\text{int}}(\tau_l) \) represent the non-magnetic and interaction terms of the full Hamiltonian in the time slice \( \tau_l \). The product of the operators over the time-slices is ordered in chronological time denoted by the operator \( T \) in equation (8.6).

The many-body term \( H_{\text{int}}(\tau_l) \) in each time slice can be written in several ways, e.g

(8.7a) \[ U n_{i\uparrow} n_{i\downarrow} = -\frac{U}{2} (n_{i\uparrow} - n_{i\downarrow})^2 + \frac{U}{2} (n_{i\uparrow} + n_{i\downarrow}) \]

(8.7b) \[ = \frac{U}{4} (n_{i\uparrow} + n_{i\downarrow})^2 - \frac{U}{4} (n_{i\uparrow} - n_{i\downarrow})^2 \]

(8.7c) \[ = \frac{U}{2} (n_{i\uparrow} - n_{i\downarrow})^2 - \frac{U}{2} (n_{i\uparrow} + n_{i\downarrow}). \]
The relative merits of these forms have been studied extensively in the literature (Hassing and Esterling, 1973; Amit and Keiter, 1973; Hubbard, 1981). The Hamiltonian in equation (8.1) is not rotationally invariant for more than one-band, therefore presently the form

\[ U n_{i\uparrow} n_{i\downarrow} = \frac{U}{4} (n_{i\uparrow} + n_{i\downarrow})^2 - \frac{U}{3} S_i \]  

(8.8)

is used to make the system invariant to rotation. Here \( S_i \) is the spin operator defined by

\[ S_i = \frac{1}{2} \sum_{\alpha, \beta} c_{i \alpha}^\dagger \sigma_{\alpha \beta} c_{i \beta} \]  

(8.9)

where \( c_{i \alpha}^\dagger \) creates an electron of spin state \( \alpha \) on site \( i \), and \( \sigma_{\alpha \beta} \) is the Pauli spin matrix. Let us now introduce the following short hand

\[ n_i^2 = (n_{i\uparrow} + n_{i\downarrow})^2 \]  

(8.10a)

\[ S_i^2 = S_{i\uparrow} S_{i\downarrow} \]  

(8.10b)

The many-body term in each time slice can then be written as

\[ U n_{i\uparrow} n_{i\downarrow} = \frac{U}{4} n_i^2 - \frac{U}{3} S_i^2 \]  

(8.11)

This term is a many-body operator and so must be transformed to many one-body operators in order to compute the partition function. The transformation used is known as the Hubbard-Stratonovich transformation (Hubbard, 1959); this replaces the two-fermion interaction in each time slice by an interaction between the fermions and an auxiliary field.

Note that most other authors use only one field. The form of the transformation is

\[ \exp(\pi \hat{a}^2) = \int_{-\infty}^{\infty} d\zeta \exp(-\pi \zeta^2 + 2\pi \hat{a} \zeta) \]  

(8.12)

where \( \hat{a} \) is a quantum-mechanical operator and \( \zeta \) is the auxiliary field. The auxiliary field couples to fluctuations of the operator. With the present choice of the interaction term, equation (8.11) there are two operators and so two auxiliary fields need to be introduced. For the two operators, \( n_{i\sigma} \) and \( S_i \), the auxiliary fields couple to the charge and spin.
fluctuations respectively. The importance of these fields is that one can now suitably incorporate both transverse and longitudinal fluctuations in the calculation of the statistical mechanics and therefore in the calculation of the magnetic properties.

Consider now the first term in equation (8.11). Let

\[ a^2 = \frac{-\Delta \tau U n^2_{il}}{4\pi}, \]  

(8.13a)

so

\[ a = i\sqrt{\Delta \tau U} n_{il}, \]  

(8.13b)

therefore

\[ \exp \left( \frac{-\Delta \tau U n^2_{il}}{4} \right) = \int_{-\infty}^{\infty} d\omega_{il} \exp \left( -\pi \omega^2_{il} + i\sqrt{\Delta \tau U} n_{il} \right). \]  

(8.14)

Similarly with

\[ a^2 = \frac{\Delta \tau U S^2_{il}}{3\pi}, \]  

(8.15a)

so

\[ \tilde{a} = \sqrt{\Delta \tau U} S_{il}, \]  

(8.15b)

then

\[ \exp \left( -\frac{\Delta \tau U S^2_{il}}{3} \right) = \int_{-\infty}^{\infty} d^3 \Delta \exp \left\{ -\pi \Delta^2_{il} + 2\sqrt{\frac{\pi \Delta \tau U}{3}} S_{il} \Delta_{il} \right\}. \]  

(8.16)

In these transformations for the site \( i \) in time slice \( l \), \( \omega_{il} \) is a scalar field that couples to charge fluctuations and \( \Delta_{il} \) is a vector field that couples to the spin fluctuations. Further \( \Delta_{il} \) is actually the exchange field the electrons "feel" at each atomic site and is a scaled version of the \( \Lambda \) of Chapter two.

The fully transformed interaction term can now be written as

\[
\exp[-\Delta \tau H_{int}(\tau_i)] = \int_{-\infty}^{\infty} \prod_{i=1}^{N} \left( d\omega_{il} d^3 \Delta_{il} \exp[-\pi (\omega^2_{il} + \Delta^2_{il})]\right)
\]

\[
+ 2\sqrt{\frac{\pi \Delta \tau U}{3}} S_{il'} \Delta_{il} + i\sqrt{\pi \Delta \tau U} n_{il} \omega_{il}\]

(8.17)

where \( N \) is the number of lattice sites.
Using equation (8.17) the partition function can now be written as

\[
Z = \text{Tr}_\tau \left( \prod_{l=1}^L \exp \left( \sum_{i,j,\sigma} c_{i\alpha}^{\dagger} \Delta \tau t_{ij} c_{j\sigma} \right) + \Delta \tau \mu \sum_i n_{ii} \right) \\
\times \int_{-\infty}^{\infty} \prod_{i=1}^N d\omega_i d^3\Delta_{ii} \exp \left[ -\pi (\omega^2_{ii} + \Delta^2_{ii}) + 2\sqrt{\pi \Delta \tau} u S_{ii} \Delta_{ii} + i \sqrt{\pi \Delta \tau} n_{ii} \omega_i \right]
\]

so

\[
Z \approx \text{Tr}_\tau \left( \prod_{l=1}^L \left( \int_{-\infty}^{\infty} \prod_{i=1}^N D[\omega_i] D^3[\Delta_{ii}] \exp \left[ \sum_{ii} -\pi (\omega^2_{ii} + \Delta^2_{ii}) \right] \right) \\
\times \exp \left[ -\Delta \tau H_{\text{band}}(\tau_l) - \Delta \tau H_{\text{int}}(\tau_l, \omega_{ii}, \Delta_{ii}) \right] \right).
\] (8.18)

The term \( H_{\text{int}}(\tau_l, \omega_{ii}, \Delta_{ii}) \) represents the transformed interaction term in the time slice \( \tau_l \). One can show that the fermion trace of the time ordered product in equation (8.18) is given by the determinant of an \( 2NL \times 2NL \) matrix, (a proof is given in Appendix C)

\[
Z = \int D[\omega_{ii}] D^3[\Delta_{ii}] \exp \left[ \sum_{ii} -\pi (\omega^2_{ii} + \Delta^2_{ii}) \right] \det[M]
\] (8.19)

where \( D[\omega_{ii}] \) and \( D^3[\Delta_{ii}] \) denote functional integrals over the auxiliary fields \( \omega \) and \( \Delta \). The matrix \( M \) has the form

\[
M = \begin{pmatrix}
I & 0 & 0 & 0 & B_L \\
-B_1 & I & 0 & 0 & 0 \\
0 & -B_2 & I & 0 & 0 \\
0 & 0 & -B_3 & I & 0 \\
0 & 0 & 0 & -B_{L-1} & I
\end{pmatrix}
\] (8.20)

one can also write

\[
\det[M] = \det[I + B_1 B_{L-1} ... B_1].
\] (8.21)

The matrix \( B_l \) has the form

\[
(B_l)_{ij} = \left[ \exp[-\Delta \tau [H_{\text{band}}(\tau_l) + H_{\text{int}}(\tau_l, \omega_{ii}, \Delta_{ii})]] \right]_{ij}.
\] (8.22)
It is easily shown that the determinant of equation (8.21) is the same as the determinant of matrix $M$ in equation (8.20).

In order to construct the matrix elements in equation (8.22) one separates the sum of the operators in the exponential into an off-diagonal part $H_{\text{band}}(\tau_i)$ and a diagonal part $H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})$ and approximates

$$
\exp\left\{-\Delta \tau [H_{\text{band}}(\tau_i) + H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})]\right\}
= \exp\left\{-\Delta \tau H_{\text{band}}(\tau_i)\right\} \exp\left\{-\Delta \tau H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})\right\}
$$

(8.23)

an improvement on this approximation is made by using the decomposition

$$
\exp\left\{-\Delta \tau [H_{\text{band}}(\tau_i) + H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})]\right\} = \exp\left\{-\frac{1}{2} \Delta \tau H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})\right\} \times \exp\left\{-\Delta \tau H_{\text{band}}(\tau_i)\right\} \exp\left\{-\frac{1}{2} \Delta \tau H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})\right\}.
$$

(8.24)

Now $H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})$ is a matrix that represents the potential energy and $H_{\text{band}}(\tau_i)$ is a matrix that represents the kinetic energy of the system. The matrix $H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})$ is in fact block diagonal and has the form

$$
\exp[H_{\text{int}}(\tau_i, \omega_{ii}, \Delta_{ii})] = \begin{pmatrix}
\exp(h_{ii})_{11} & 0 & 0 & 0 \\
0 & \exp(h_{ii})_{22} & 0 & 0 \\
0 & 0 & \exp(h_{ii})_{33} & 0 \\
0 & 0 & 0 & \exp(h_{ii})_{NN}
\end{pmatrix}
$$

(8.25)

where (for the one-band case)

$$
(h_{ii})_{ii} = \sqrt{\frac{\pi \Delta \tau U}{3}} \sigma_{ii} \Delta_{ii} + i \sqrt{\frac{\pi \Delta \tau U}{3}} \omega_{ii} + \Delta \tau \mu.
$$

(8.26)

Let us write

$$
a_{ii} = \Delta \tau \mu + i \sqrt{\frac{\pi \Delta \tau U}{3}} \omega_{ii}
$$

(8.27a)

and

$$
b = \sqrt{\frac{\pi \Delta \tau U}{3}}
$$

(8.27b)

so

$$
\exp(h_{ii})_{ii} = \exp(a_{ii}) \exp(b \Delta_{ii} \sigma_{ii}).
$$

(8.28)
The second exponential in this expression is the exponential of a $2 \times 2$ matrix. These matrices are complex and the exponential is given by using the identity

$$\exp(r \sigma) = \cosh(r) + \sinh(r) \hat{r} \sigma$$

(8.29)

where $\hat{r}$ is a unit matrix. This identity can easily be derived. Suppose $A$ is a matrix whose square is a unit matrix, so $A^n = 1$ if $n$ is even and $A^n = A$ if $n$ is odd, therefore the Taylor expansion of $\exp(cA)$, where $c$ is a scalar is

$$\exp(cA) = \sum_{n=0}^{\infty} \frac{c^n A^n}{n!} = \sum_{n \text{ even}} \frac{c^n A^n}{n!} + A \sum_{n \text{ odd}} \frac{c^n A^n}{n!} = \cosh(c) + A \sinh(c)$$

so if $r = r \hat{r}$, ($r$ is a scalar) we obtain the identity in equation (8.29).

The explicit form of the Pauli matrix is

$$\vec{\sigma} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \\ i & 0 \\ 0 & -i \end{bmatrix}$$

(8.30)

and the vector $\Delta_{ul}$ is

$$\Delta_{ul} = \Delta_{ul} (\sin \theta_u \cos \phi_u, \sin \theta_u \sin \phi_u, \cos \theta_u)$$

(8.31)

where $\Delta_{ul}$ is the magnitude of the exchange field at site $i$ in time slice $l$. Therefore the product

$$\Delta_{ul} \vec{\sigma}_{ul} = \begin{bmatrix} \cos \theta_u & \sin \theta_u e^{-i \phi_u} \\ \sin \theta_u e^{i \phi_u} & -\cos \theta_u \end{bmatrix}$$

(8.32)

So finally

$$\exp(b \Delta_{ul} \vec{\sigma}_{ul}) = \cosh(\Delta_{ul} \sqrt{\frac{\pi \Delta t U}{3}})$$

$$+ \sinh(\Delta_{ul} \sqrt{\frac{\pi \Delta t U}{3}}) \begin{bmatrix} \cos \theta_u & \sin \theta_u e^{-i \phi_u} \\ \sin \theta_u e^{i \phi_u} & -\cos \theta_u \end{bmatrix}$$

(8.33)

Using this in equation (8.28) one can define $\exp(h_{li})$ as a $2 \times 2$ matrix.
The exponential \( \exp(H_{\text{band}}(\tau_i)) \) has to be calculated numerically. The most accurate method is to diagonalize the matrix and evaluate the product

\[
U_0^{-1} \exp(S_0) U_0 = \exp(H_{\text{band}})
\]

(8.34)

where \( S_0 \) is the spectral matrix formed by the eigenvalues of \( H_{\text{band}}(\tau_i) \), and \( U_0 \) is the matrix of its eigenvectors, these are evaluated using standard numerical methods (e.g. Press et al., 1985). The time slice index is dropped, since the resultant matrix is \( \exp(H_{\text{band}}) \) is the same in each time slice. One can therefore express the \( B_l \) matrix as

\[
(B_l)_{ij} = \begin{bmatrix}
\frac{1}{2} \exp(h_{i1}) & 0 \\
0 & \frac{1}{2} \exp(h_{i2})
\end{bmatrix} \times \exp(H_{\text{band}}) \begin{bmatrix}
\frac{1}{2} \exp(h_{i1}) & 0 \\
0 & \frac{1}{2} \exp(h_{i2})
\end{bmatrix}
\]

(8.35)

The partition function for the one-band Hubbard Hamiltonian has now been defined using the functional integral approach. The statistical mechanics of the Hamiltonian can now be investigated using the quantum Monte Carlo method.

### 8.5 Statistical mechanics of itinerant-electron systems.

The functional integral in the partition function, equation (8.18), can be evaluated using Monte Carlo techniques. We wish to generate a sequence of charge and spin configurations with a suitable probability distribution. This entails the updating of the \( \omega \) and \( \Delta \) auxiliary fields at the lattice sites in each time slice. The new configuration is accepted or rejected according to the ratio of determinants of the matrices \( M \) before and after the update. For a lattice site \( i \) in a time slice \( l \), the direction of the \( \Delta \) field is changed by choosing \( \cos \theta_{il} \) (with \(-1 \leq \cos \theta_{il} \leq 1\)) from a random distribution and then computing

\[
\sin \theta_{il} = \sqrt{1 - \cos^2 \theta_{il}}.
\]
the angle $\phi_d$ is also chosen from a random distribution. This then corresponds to transverse fluctuations in the magnetic moment.

If one assumes a localised magnetic moment picture of an itinerant-electron magnet then one would suppress charge fluctuations and keep the magnitude of the exchange fields constant. The latter suppresses longitudinal fluctuations. If however one chooses not to suppress charge fluctuations and longitudinal fluctuations of the exchange fields then there are two possible ways of sampling the fields. The simplest sampling method is that the value of the $\omega_d$ field is updated by incrementing or decrementing it by a random value. Similarly the magnitude of $\Delta_d$ is updated by incrementing or decrementing it by a random value which corresponds to longitudinal fluctuations in the magnetic moment.

For the one-band case one can suppress charge fluctuations and longitudinal fluctuations of the exchange fields, however for a multi-band system such as iron then charge fluctuations and arguably longitudinal fluctuations in the magnetic moment are important. The second, and preferable sampling method therefore is to somehow couple the charge fluctuations with the longitudinal fluctuations of the exchange fields. This is a more physical approach since the magnitude of the exchange field at a site is due to the difference in the total up and down spin charge at the site. There is however no clearly defined method of achieving this. One possibility is to allow the magnitudes of the exchange fields to have the same values as the charge fields. Another possibility is to introduce three auxiliary fields, two scalar fields that couple to the up and down spin charge fluctuations and a third vector field that couples to the fluctuations in the spin direction. The magnitude of the exchange field could then simply be the difference in the charge auxiliary fields.

In the present calculations of the half-filled one dimensional Hubbard model, the magnitudes of the exchange fields are kept constant and charge fluctuations are suppressed. Therefore the only fluctuations are due to transverse fluctuations in the exchange field. In Chapter nine the system will be investigated in the limit where there are Ising type exchange fields and vector exchange fields. This allows a comparison with the quantum Monte Carlo
calculations of other authors (e.g. Hirsch, 1985). A more detailed account is given in the following chapter.

The sample configuration of the auxiliary fields is accepted or rejected according to the ratio of the updated $M'$ and $M$ matrices

$$R = \frac{\text{det}[M']}{{\text{det}[M]}}. \tag{8.36}$$

This is the "Monte Carlo" in the method, that is one samples the configuration space of the auxiliary fields and a Metropolis algorithm is used to accept or reject the sampled configurations. If the ratio of determinants is greater than a random number selected from a uniform distribution then the change in auxiliary fields is rejected, otherwise it is accepted. The distribution of the auxiliary fields will inherently be Gaussian because of the Gaussian factor in the functional integral.

Since $M$ is a $2NL \times 2NL$ matrix then the calculation of the ratio of determinants (or rather the determinant of $M'$ since one already has $\text{det}[M]$ requires $2NL^3$ operations, this process increases the computation time of the simulation, placing a restriction on the system size and the lowest temperature that can be reached (since more time slices are required at low temperatures). To reduce the computation time of the ratio of determinants a powerful algorithm developed by Blankenbecler \textit{et al} (1981; Scalapino and Sugar, 1981) and White \textit{et al} (1989) has been adapted. Hereafter referred to as BSSW.

Consider the determinant of the $M$ matrix, one can write this as

$$\text{det}[M] = \text{det}[I + B_L B_{L-1}...B_1]. \tag{8.37}$$

This determinant does not change under the cyclic permutation of the $B_t$ matrices (BSSW). Suppose the fields in the $l$th time slice are being updated, one can then write

$$\text{det}[M] = \text{det}[I + B_t,...,B_1 B_L,...,B_{l+1}]$$

$$= \text{det}[I + A(\tau_l)] \tag{8.38}$$
so that
\[ R = \frac{\text{det}[I + A'(\tau)]}{\text{det}[I + A(\tau)]}. \]  
(8.39)

The numerator in this expression can be written as a Green function \( G(\tau) \)
\[ G(\tau) = [I + A(\tau)]^{-1}. \]  
(8.40)

Under the change of the \( \Delta_\tau \)- and \( \omega_\tau \)-fields in this time slice, the product \( A(\tau) \) is updated by
\[ A'(\tau) = [I + \delta(i,l)]A(\tau) \]  
(8.41)

where \( \delta(i,l) \) is a \( 2N \times 2N \) block matrix with one non-zero \( 2 \times 2 \) block element given by
\[ \exp(h')_{ii} = [I + \delta(i,l)] \exp(h)_{ii} \]  
(8.42)

therefore \( \delta(i,l)_{ii} \) is a \( 2 \times 2 \) matrix defined by
\[ \delta(i,l)_{ii} = \frac{\exp(h')_{ii}}{\exp(h)_{ii}} - I \]  
(8.43)

the ratio of determinants can now be written as
\[ R = \frac{\text{det}[I + A'(\tau)]}{\text{det}[I + A(\tau)]} = \text{det}[I + \delta(i,l)A(\tau)] G(\tau) \]
\[ = \text{det}[I + G(\tau) \delta(i,l)A(\tau)] \]
\[ = \text{det}[I + (I + A(\tau))G(\tau) \delta(i,l) - G(\tau) \delta(i,l)] \]
\[ = \text{det}[I + (I - G(\tau)) \delta(i,l)] \]
\[ = \text{det}[I + (I - G(\tau)_{ii}) \delta(i,l)_{ii}]. \]  
(8.44)

The matrix "elements" \( G(\tau)_{ii} \) and \( \delta(\tau)_{ii} \) in equation (8.44) are in fact \( 2 \times 2 \) block matrices, with the spin labels dropped for simplicity. The ratio of determinants can therefore be calculated by evaluating the determinant of a \( 2 \times 2 \) matrix, thereby reducing the computation time. The ratio of determinants resulting from equation (8.44) was checked against the ratio
of determinants calculated explicitly with equation (8.36) and agreement was found between the two results.

If the change in the spin and charge configuration is accepted, then the Green function for the time slice must be updated. This can be achieved through a Dyson equation

$$G'(\tau) = G(\tau) - G(\tau) \delta(i,l) A(\tau) G'(\tau).$$  \hspace{1cm} (8.45)$$

This can be solved easily

$$G'(\tau) = G(\tau) - G(\tau) \delta(i,l) A(\tau) \frac{1}{I + [I + \delta(i,l)] A(\tau)}$$

$$= G(\tau) - G(\tau) \delta(i,l) \frac{[I - G(\tau)] G(\tau)}{[I + A(\tau) + \delta(i,l) A(\tau)] G(\tau)}$$

$$= G(\tau) - \frac{\delta(i,l) [I - G(\tau)] G(\tau)}{G(\tau) [I + A(\tau)] + \delta(i,l) A(\tau) G(\tau)}$$

$$= G(\tau) - \frac{\delta(i,l) [I - G(\tau)] G(\tau)}{I + \delta(i,l) A(\tau) G(\tau)}$$

$$= G(\tau) - \frac{\delta(i,l) [I - G(\tau)] G(\tau)}{I + \delta(i,l) [G(\tau)^{-1} - I] G(\tau)}$$

$$= G(\tau) - \frac{G(\tau) \delta(i,l) [I - G(\tau)]}{[I + [I - G(\tau)] \delta(i,l)]}$$ \hspace{1cm} (8.46)$$

The denominator in the second term of equation (8.46) consists of $2 \times 2$ block matrices. One already has this $2 \times 2$ matrix from the evaluation of the ratio of determinants and in fact in the theory of BSSW the denominator is actually the ratio of determinants. This update process requires $N^2$ operations for a $N \times N$ matrix. The use of the algorithm outlined above reduces the overall computation time since the evaluation of the determinant of the matrix $M'$ in equation (8.36) is no longer required. The updated Green function resulting from the application of equation (8.46) was checked against the explicit calculation of the Green function for the matrix $A'(\tau)$; good agreement was found between the two and so one can be
confident in the use of equation (8.46). It was found that this update equation can be used for several thousand Monte Carlo sweeps without a loss in precision of the Green function. Although at low temperatures or large $U$ it occasionally has to be recalculated from scratch. The theory of BSSW uses the relation

$$G (\tau_{l+1}) = B_l G (\tau_l) B_l^{-1}$$  \hspace{1cm} (8.47)

to advance the Green function to the $l+1$ time slice. However in the present calculations the Green function for the $l+1$ time slice is actually calculated from scratch. The Green function in equation (8.47) can lose precision due to numerical errors and therefore may eventually need to be calculated from scratch.

Finally the time ordered product

$$B_l, \ldots, B_1 B_L, \ldots, B_{l+1}$$

which is required for the calculation of the statistical mechanics of the systems, is updated using the expression

$$[B_l, \ldots, B_1 B_L, \ldots, B_{l+1}] = [I + \delta(i,l)] B_l, \ldots, B_1 B_L, \ldots, B_{l+1}. $$ \hspace{1cm} (8.48)

To check this expression the $B_l$ matrix for the new configuration of auxiliary fields for the $l$th time slice was first evaluated explicitly using equation (8.35). The time ordered product with the new matrix was calculated and compared with the right hand side of equation (8.48). The two were found to be in good agreement, one can therefore be confident in the use of equation (8.48).

The ingredients for a quantum Monte Carlo simulation of a correlated electron system have now been described. The Hamiltonian for the system is given by the Hubbard model in a tight-binding approximation. At the start of the simulation the band matrix is set up and its exponential evaluated using equation (8.34). The auxiliary $\omega_l$- and $\Delta_l$-fields can either have random scalar values and random orientations with random vector magnitudes, respectively; however for the bulk of the present calculations the $\omega_l$ fields have zero values and the $\Delta_l$ fields have ferromagnetic orientations with fixed magnitudes. The $B_l$ matrices
Chapter Eight: Quantum Monte Carlo methods.

for these fields are calculated using equation (8.35) and the Green function for the $l = 1$ time slice is evaluated using equation (8.40). One sweeps through the lattice one time slice at a time choosing lattice sites at random and making a change to the auxiliary fields at the site; however it is possible to use an alternative strategy (see Chapter nine). The system is allowed to relax by performing a defined number of Monte Carlo sweeps before averages of the required thermodynamic quantities are calculated. The choice of accepting or rejecting a particular field configuration is made using a Metropolis algorithm with the weights provided by the ratio of determinants calculated using equation (8.44). After the required number of sweeps for a time slice have been performed the $B_l$ matrices for the current configurations of auxiliary fields are recalculated. The Green function for the next $(l+1)$ time slice must also be evaluated. This ensures that the time ordered product of $B_l$ matrices and the Green functions are kept as accurate as possible. The $B_l$ matrices are cycled such that the matrix for the $\tau_{l+1}$th time slice is at the start of the time ordered product. The time-ordered product for this sequence of $B_l$ matrices is evaluated forming the $A(\tau_{l+1})$ matrix and the Green function, $G(\tau_{l+1})$ for the time slice is calculated using equation (8.40). The lattice is again allowed to reach equilibrium before averages of the thermodynamic quantities for the $l+1$ time slice are taken. The simulation is terminated once the Monte Carlo sweeps for the last time slice have been performed. The thermodynamic quantities are averaged over the time slices giving the required thermodynamics for the temperature $T$.

In the following chapter the Hubbard model in one- and three-dimensions will be examined. Specifically in one-dimension a six atom ring and a BCC lattice in three-dimensions will be investigated. The thermodynamic properties are calculated with and without making the static approximation. The main point of the investigation is the effect of making the static approximation on the thermodynamics. Before looking at specific systems, some of the more general aspects of the quantum Monte Carlo method are discussed, in particular the sign problem and numerical instabilities in the simulation algorithms.
8.6 The sign problem.

A fundamental problem is encountered when the functional integrals to be evaluated are not a positive semi-definite measure. This is generally referred to as the sign-problem. In the auxiliary field method that has been chosen for the current calculations, it originates from the fact that the weight for a given configuration of the auxiliary fields is given by a determinant that can be negative as well as positive. The problem becomes more acute as the temperature of the system is lowered or when the Coulomb interaction or system size is increased. This clearly limits the range of quantum Monte Carlo simulations that can be performed successfully. Let us now examine the sign problem and review the different attempts that have been made in the past to overcome the problem, as well as justifying the approach to the problem in the present simulations.

The expectation value of any quantity can be written symbolically as

$$\langle O \rangle = \frac{\int O(\zeta) \rho(\zeta) \, d\zeta}{\int \rho(\zeta) \, d\zeta}$$

(8.49)

where $\rho(\zeta)$ and $O(\zeta)$ are functions of the auxiliary field variable $\zeta$. The "probability distribution" $\rho(\zeta)$ is not strictly positive except in some special cases: a) the Hubbard model with $U = 0$; b) the one dimensional Hubbard model with $n_\uparrow = n_\downarrow$ (Hirsch et al, 1982); c) the one band model with half-filling. If $\rho(\zeta)$ changes sign, then it cannot be used in the Metropolis algorithm. Further in the present calculations the probability distribution is complex since matrix elements of the matrix $M$ are complex (equation (8.26)). The question then is how can one handle a complex probability distribution and avoid the problem of this distribution changing sign. In the present calculations the simple trick of using the probability distribution $|\text{Re}[\rho(\zeta)]|$ is applied. Normally one would expect the imaginary parts of the distribution to cancel each other out (Jones, private communication). This is not important if the charge fluctuations are suppressed, since then the imaginary parts of the matrix elements are zero and hence one has a real ratio of determinants and probability distribution.
The importance of the sign-problem has been studied numerically in the framework of the Hubbard model (White et al, 1989; Loh et al, 1990; White and Wilkins, 1988). These studies indicate that in general the average sign falls exponentially with inverse temperature and system size. In the one-band Hubbard model the origin of the sign problem at low temperature has been attributed to the exchange of electrons (Loh et al, 1990). The sign problem is not unique to the Hubbard model or quantum Monte Carlo schemes; it would appear that other systems and schemes also suffer from this problem including the Heisenberg model and in any Hamiltonian that comprises non-commutative operators. Recently Samson (1993) and others have made a study of sign problem by proposing a geometrical interpretation. At low temperatures the weight of each path of the functional integral carries a Berry phase factor (Berry, 1984) due to the rotation of a spin in a time dependent field. It is suggested that this phase factor is the origin of the sign problem in the Hubbard model.

In the calculations presented in the following chapter the sign-problem was encountered for non half-filled bands. However this did not occur frequently and was avoided using the above trick. The relevance of the complex probability distribution and origin of the sign problem in a system with scalar and vector auxiliary fields had not been investigated further at the time of writing this thesis.

8.7 Numerical instabilities.

The basis of quantum Monte Carlo simulation is the evaluation of the weights of configurations, which essentially involves the calculation of determinants. The evaluation of the thermodynamic averages also involves matrix operations. As with all computer operations one must not ignore numerical instabilities, particularly so in the present calculations. In mathematical terms, the spectral range of the matrices increases with inverse temperature $\beta$ and number of time slices $L$ (due to the Trotter decomposition). This leads to numerical instabilities in the evaluation of matrix elements and determinants in particular. There is therefore a limit on the lowest temperature and size of the Coulomb interaction $U$ for
which simulations can be carried out, and in the present simulations the limit is $\beta = 4$ and $U = 8$. The error due to the Trotter decomposition is minimised by taking sufficiently small time slices, particularly at low temperatures and high values of $U$. Further improvements have already been discussed (making use of equation (8.24)).
Chapter Nine.

Quantum Monte Carlo study of the Hubbard model.

9.1 The one-band Hamiltonian.

In the previous chapter the Hubbard model and its solution using the functional integral was described. The functional integral is evaluated using the quantum Monte Carlo method. The topic of the present chapter is to study the one-band Hubbard model in one- and three-dimensions and details of how transition metals could be investigated using the method are given. The Hamiltonian for the systems can be written as

\[ H = \sum_{ij\sigma} \epsilon_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + (\text{h.c}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \]  

(9.1)

where

\[ t_{ij} = \begin{cases} 1 & \text{If } i \text{ and } j \text{ are nearest neighbours} \\ 0 & \text{otherwise.} \end{cases} \]  

(9.2)

In this simple case the Hamiltonian describes a single \( s \) band in the tight-binding approximation. The partition function for the Hubbard model was defined in the previous chapter as a functional integral over the scalar and vector auxiliary fields \( \omega \) and \( \Delta \), respectively. The Ising equivalent of the Hubbard-Stratonovich transformation (Hirsch, 1983) will be considered in section (9.3). The main point of the investigation is the effect of the static approximation, the appropriateness of the model in describing itinerant-electron magnets will also be investigated. In section (9.6) the parameterisation of the Hamiltonian for transition metals will be described. The calculation of the ratio of determinants in the Metropolis algorithm outlined in the previous chapter can be broken down to the evaluation of the determinant of a \( 2 \times 2 \) matrix using a Green function approach. The calculation of the magnetic properties will involve the evaluation of the spin up and spin down occupation numbers at a site, this is a computationally intensive operation if a high degree of accuracy is required. In order to reduce the time of computation a parallel algorithm for the evaluation of the ratio of determinants has been used. The side effect of this algorithm is that the
occupation numbers can be calculated on a parallel computer resulting in a reduction of the overall time of computation. The algorithm and its adaptation for the present calculations is described in section (9.8).

9.2 Thermodynamic properties.

The thermodynamic properties of interest are the local magnetic moment and the susceptibility. These can be calculated by evaluating occupation numbers at the atomic sites. The occupation number for the spin state $\sigma$ at a site $i$ can be evaluated as

$$n_{i\sigma} = c_{i\sigma}^+ c_{i\sigma} = \left( B_L \cdots B_1 \frac{1}{I + B_L \cdots B_1} \right)_{i\sigma}$$

$$= \left( A(\tau_i) \frac{1}{I + A(\tau_i)} \right)_{i\sigma}$$

$$= (A(\tau_i) G(\tau_i))_{i\sigma}$$

The occupation numbers can be calculated using equation (9.3c) directly; however since the Green function is updated for each configuration accepted in the algorithm, it is entirely possible that it can lose precision. That is the frequently updated Green function may be very different from a Green function calculated from scratch for the last configuration of auxiliary fields. This obviously means that the occupation numbers calculated using equation (9.3c) may be inaccurate. However one can gain greater accuracy in the calculation of the occupation numbers by using equation (9.3b), which involves a $2N^3$ matrix inversion operation. Therefore by making a sacrifice in computation time one has gained accuracy in the calculation of the occupation numbers. Later in section (9.8) we shall see how the computation time for the evaluation of equation (9.3b) can be reduced by making use of a parallel matrix inversion algorithm. Let us now turn our attention to the calculation of the local moment and susceptibility.
9.2.1 Local magnetic moment.

The magnetic moment at a site $i$ is defined as (Hirsch, 1985)

$$\langle S^2 \rangle = \frac{1}{4} \langle (n_\uparrow - n_\downarrow)^2 \rangle$$

so

$$\langle S^2 \rangle = \frac{1}{4} \langle n_\uparrow \rangle + \frac{1}{4} \langle n_\downarrow \rangle - \frac{1}{2} \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

In the non-interacting electron limit, $U = 0$ then $\langle n_\uparrow \rangle = \langle n_\downarrow \rangle = \frac{1}{2}$ and so $\langle S^2 \rangle = \frac{3}{8}$. In the opposite limit of $U = \infty$, where the local moments are completely localised, $\langle S^2 \rangle = \frac{3}{4}$. The non-interacting limit provides a useful first check of the calculation.

9.2.2 Susceptibility.

The $q$- dependent (zero frequency) magnetic susceptibility is defined as (Hirsch, 1985)

$$\chi(q) = \frac{1}{N} \sum_{i,j} e^{iq \cdot (R_i - R_j)} \int_0^\beta d\tau \langle [n_{i\uparrow}(\tau) - n_{i\downarrow}(\tau)] [n_{j\uparrow}(0) - n_{j\downarrow}(0)] \rangle$$

where $R_i$ is the lattice vector of the atom $i$. We can also define the magnetic structure factor as

$$S(q) = \frac{1}{N} \sum_{i,j} e^{iq \cdot (R_i - R_j)} \langle [n_{i\uparrow} - n_{i\downarrow}] [n_{j\uparrow} - n_{j\downarrow}] \rangle$$

and for $q = 0$ the susceptibility is given by

$$\chi(q = 0) = \beta S(q = 0)$$

$$= \beta \frac{1}{N} \sum_{i,j} \langle (n_{i\uparrow} - n_{i\downarrow}) (n_{j\uparrow} - n_{j\downarrow}) \rangle.$$
Running averages of the local moment and susceptibility are kept in the Monte Carlo simulation. The average magnetic moment and susceptibility for \( N \) atoms and \( M \) measurements in each of the \( L \) time slices at temperature \( T \) are given respectively by

\[
\langle S \rangle_T = \frac{1}{L \times M} \sum_{\nu=1}^{L \times M} S_{\nu} \tag{9.8}
\]

\[
\langle \chi \rangle_T = \frac{1}{L \times M} \sum_{\nu=1}^{L \times M} \chi_{\nu} \tag{9.9}
\]

where

\[
\langle S \rangle_{\nu} = 3 \left\{ \frac{1}{4} \langle n_{\uparrow} \rangle + \frac{1}{4} \langle n_{\downarrow} \rangle - \frac{1}{2} \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle \right\} \tag{9.10}
\]

and

\[
\langle \chi \rangle_{\nu} = \beta \frac{1}{N} \sum_{i,j} (n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow}) \tag{9.11}
\]

also

\[
\langle n_{i\sigma} \rangle = \frac{1}{N} \sum_{i} n_{i\sigma} \tag{9.12}
\]

The occupation numbers are calculated when a Monte Carlo measurement is taken using equation (9.3).

### 9.3 Statistical mechanics of the 1-D half-filled Hubbard model.

The one-dimensional half-filled one-band Hubbard model provides a useful starting point as there are extensive results available for comparison; both for exact solutions (Lieb and Wu, 1968; Shiba and Pincus, 1972) and Monte Carlo simulations (e.g. Hirsch, 1985). There are several points that need to be investigated: firstly a calculation is required to check that the algorithm described in the previous chapter and the computer program actually works; secondly a comparison of vector and Ising auxiliary fields needs to made to examine which approach is more suitable for magnetic systems. The magnetic properties of the Hubbard model can then be investigated. Further its appropriateness in describing itinerant-electron systems can be closely examined and finally the effect of the static approximation has to be examined.
Let us consider the value the chemical potential has for a particular value of $U$.

Suppose the interaction term for one atom is described by

$$H_{int} = U n^\uparrow n^\downarrow. \quad (9.13)$$

The partition function in this case can then be written as

$$Z = 1 + 2e^{\beta \mu} + e^{\beta U} + 2e^{\beta \mu}. \quad (9.14)$$

The first, second and third terms correspond to states with zero electrons, one electron and two electrons respectively. Now the average occupation at the atom is given by

$$\langle n \rangle = \frac{\text{Tr}[e^{\beta \hat{H}} n]}{Z} = \frac{0 + 2e^{\beta \mu} + e^{\beta U} + 2e^{\beta \mu}}{1 + 2e^{\beta \mu} + e^{\beta U} + 2e^{\beta \mu}}. \quad (9.15)$$

So for the extreme limits of $\mu$ we have, $\langle n \rangle \to 0$ as $\mu \to -\infty$ and $\langle n \rangle \to 2$ as $\mu \to \infty$, therefore at half-filling

$$\langle n \rangle = 1 = 0 + 2e^{\beta \mu} + e^{\beta U} + \beta U = 1 + 2e^{\beta \mu} + e^{\beta U} + 2e^{\beta \mu}. \quad (9.16)$$

so

$$e^{\beta U} + 2e^{\beta \mu} = 1$$

thus

$$\mu = \frac{U}{2}. \quad (9.17)$$

This is the value of the chemical potential for a half-filled one-band Hubbard model.

The thermodynamic properties of the one dimensional Hubbard model have been found by exact diagonalisation by Shiba and Pincus (1972) for various values of the interaction $U$. Their results provide a good basis for comparison of the present results. The chemical potential has to be adjusted to give half-filling. The local moment calculated for various values of $U$ is shown in Figure 9.1. One observes that a very good agreement with the exact results is achieved. There is some discrepancy at low temperatures; this is because a larger number of time slices and Monte Carlo steps are required as the temperature decreases. The value of the time slice was taken such that $\Delta t^2 U < 0.1$ so that the error in
the Trotter decomposition of the Hamiltonian is of the order 1 percent. Alternatively following Hirsch (1985) one can also choose $\Delta \tau = 0.25, 0.125,$ and 0.0625 for $U = 2, 4,$ and 8 respectively. The former is chosen in the present calculations in order to minimise the statistical error. The actual number of time slices will then depend on the value of the Coulomb interaction and the temperature of the system at which the simulation is to be performed. For instance in the case $U = 4$ at a low temperature typically $L = 40$ and at higher temperatures $L = 10$. Typically 500 warm-up steps were performed before taking 1000 measurements separated by 2-5 sweeps per time slice. The number of warm-up steps and measurements were increased to 1000 and 2000 per time slice respectively for $U = 8$. As the interaction increases more time slices are required and the algorithm becomes unstable more rapidly at lower temperatures. Therefore the lowest temperature that can be reached increases with increasing interaction. At higher values of $U$ the computation time increases rapidly making it impractical to obtain results for $U > 8$. This is important for the three dimensional case and the multi-band case as the bandwidth in these cases could be large and so large values of interaction are required. However with the parallel algorithm outlined in section (9.5) this impracticality can be overcome. The starting state in the present simulations is with all the exchange fields aligned ferromagnetically in the global $z$-axis. The arguments for such a state are the same as for classical spin Monte Carlo simulations.

Figure 9.1 also shows the results of Monte Carlo simulation by Hirsch (1985) using a discrete Hubbard-Stratonovich transformation (Hirsch 1983). The form of the transformation is

$$\exp(-\Delta \tau U n_{i\uparrow} n_{i\downarrow}) = \text{Tr}_\sigma \exp\left(\lambda \sigma (n_{i\uparrow} - n_{i\downarrow}) - \frac{\Delta \tau U}{2} (n_{i\uparrow} + n_{i\downarrow})\right)$$  \hspace{1cm} (9.18)

with

$$\lambda = 2 \arctanh \sqrt{\tanh(\Delta \tau U/4)}$$  \hspace{1cm} (9.19)

where $\sigma = \pm 1$. The trace $\text{Tr}_\sigma$ is over the discrete fermion degrees of freedom. The auxiliary fields $\sigma$ in this transformation are therefore Ising variables. Such fields can easily be incorporated in the functional integral of the present calculations by simply equating $\omega_d = 0$
and $\Delta_U = 1$, and by restricting $\cos \theta_U$ to $\pm 1$ and $\phi_U = 0$ in the rotation matrix (equation (8.32)). The chemical potential has to be adjusted to make the transformation equivalent to equation (9.18). The result for such a simulation is also included in Figure 9.1. The local moment calculated with discrete vector auxiliary fields agrees fairly well with the exact result. The point here is to justify the choice of fields for the functional integral. Although the discrete transformation does compare well with the exact result for the six-site ring, it is not appropriate for a complete description of the nature of magnetic moments in metallic magnets such as iron, particularly above the Curie temperature where short range order (if it existed) would be described by a smooth variation in the direction of the magnetic moments. The choice of auxiliary fields for the present calculations has been discussed in detail in the previous chapter.

**Figure 9.1.** Local magnetic moment as a function of temperature in the 1D half-filled one-band Hubbard model. The lines for $U = 4$ are (i): the exact result of Shiba and Pincus (1972) and Hirsch (1985); (ii): present calculations with vector fields and (iii): present calculations with Ising vector fields. The other lines are for the present calculations with vector auxiliary fields.
One also observes in Figure 9.1 that the local moment increases gradually as the temperature decreases and the size at the low and high temperatures limits also increases as the interaction $U$ increases. This indicates that the itinerant-electrons begin to form localised moments. The formation of a local moment in an itinerant-electron system is shown much more clearly in the results for the susceptibility, Figure 9.2. One can observe that in the temperature region $T = 1$ to $T = 2$ there is a more rapid increase in susceptibility. It can also be observed that the local moment increases slightly more rapidly in this temperature region. The rapid increase in susceptibility is therefore due to the formation of the local moment in this region. These results would indicate that the Hubbard model is appropriate for the description of itinerant magnets such as iron. Further the assumption that the itinerant-electrons conspire to form local magnetic moments in a material like iron is justified by these results.

**Figure 9.2.** Magnetic susceptibility as a function of temperature in the 1D half-filled one-band Hubbard model. Upper line: $U = 4$ (in the static approximation); middle line: $U = 4$; lower line: $U = 0$. 
9.4 The static approximation.

The calculations of the electronic structure of iron have been made by making the static approximation. In this case the precession of the magnetic moments is slow in comparison to electron hopping; therefore as an electron hops from atom to atom it "sees" a frozen configuration of magnetisation. Incidentally most authors who have made use of the functional integral have made this approximation before calculating the statistical mechanics of the Hubbard model. The quantum Monte Carlo method allows one to calculate the functional integrals without making the static approximation and in the previous section the results of such a calculation have been presented. It is also possible to make the static approximation in a quantum Monte Carlo calculation and this is the topic of the present section.

![Figure 9.3. Local magnetic moment as a function of temperature in the 1D half-filled one-band Hubbard model for $U = 4$. Upper thin line: static approximation; short lower thin line: exact result (Shiba and Pincus, 1972); lower thin line: without making static approximation.](image)
The Trotter time slices in imaginary time can be viewed in this way; an electron at an atomic site on one imaginary time slice will "see" a certain configuration of auxiliary fields, on another time slice an electron on the same site may "see" a different configuration of auxiliary fields. This is precisely what quantum Monte Carlo simulations try to achieve; averages over fluctuations in the auxiliary fields over the entire interval $0 \leq \tau \leq \beta$. One can make the static approximation in the present quantum Monte Carlo simulation by simply making the auxiliary fields in all the time slices have the same values or orientations. Therefore an electron on an atom in one particular time slice will "see" a configuration of auxiliary fields and on another time slice an electron on the same site will "see" the same configuration of auxiliary fields. Therefore the change to the configurations of the auxiliary fields at an atomic site is the same for all time slices. The second requirement in making the static approximation is that an "infinite" number of time slices be used in the simulation; this effectively means that the period of a time slice will be "infinitesimally" small. In fact in a practical simulation a very large ($> 100$) number of time slices is used. Effectively this means that the auxiliary fields are time-independent. In this approximation the electrons are still treated quantum mechanically however now the transverse and longitudinal fluctuations are treated classically. If electron hopping is ignored this approximation then takes us back to the classical systems investigated in Chapter four, using classical Monte Carlo simulations.

The local magnetic moment for $U = 4$ shown in Figure 9.3. The effect of the static approximation is to overestimate the magnetic moment. At low temperatures the value of the local moment is close to the value in the $U = \infty$ limit, even at high temperatures the local moment in static approximation has a larger value. The first implication of the result is the static approximation is one of the main factors that give a larger magnetic moment in calculations than that found by neutron scattering experiments. Now in the Hartree-Fock approximation the magnetic moment and the exchange field are related through

$$\Delta_i = \mathbf{m}_i.$$ (9.20)
therefore a large value of $m$ would result in a large $\Delta$. Once self-consistency is reached the total energy of the system for any set of magnetic moments and exchange fields is given by (Luchini and Heine, 1989)

$$U = \sum_i \left\{ \int_{-\infty}^{E_i} E n_i(E) dE - \frac{1}{4} J m_i^2 \right\}, \tag{9.21}$$

therefore in the static approximation this energy will be overestimated in comparison to the energy with quantum effects taken into account. This implication has a direct bearing on the physical properties calculated using this energy. For instance the spin wave stiffness constant would be overestimated resulting in an overestimated spin wave dispersion. Similarly the exchange interactions fitted to this energy would also be overestimated; if these were used to calculate the Curie temperature in the mean field approximation, this would also be overestimated.

The effect of the static approximation then is to overestimate the calculated magnetic properties of materials. However from this general observation the effect on magnetic short range order above $T_c$ is not so obvious. In order to investigate itinerant systems in greater depth one needs to calculate quantities that can be compared directly with experiment. This will be discussed in section (9.7).

### 9.5 Statistical mechanics of the 3D half-filled Hubbard model.

The decomposition of the Hamiltonian into its band and interaction terms, equation (8.24) allows one to use the same functional integral formulation for a one-dimensional problem and a three-dimensional problem. In fact by parameterising the band matrix appropriately it is possible to study any other system described by a tight-binding Hamiltonian. In this section the results of a calculation on a small system of atoms on a BCC lattice is reported. The lattice consists of 54 atoms and the electron hopping is to the nearest neighbour. The parallel matrix inversion algorithm described in section (9.8) was used to evaluate the occupation numbers.
The magnetic moment for $U = 4$ is plotted against temperature in Figure 9.4. The magnetic moment for the one dimensional lattice from the exact results and the present Monte Carlo calculations is also shown for comparison. The formation of localised magnetic moments is the apparent feature in the three-dimensional lattice.

![Figure 9.4](image)

**Figure 9.4.** Local magnetic moment as a function of temperature in the 1D (thin line) and 3D (bold line) half-filled one-band Hubbard model for $U = 4$.

### 9.6 Transition metals.

The Hubbard model in one and three-dimensions has been investigated using the quantum Monte Carlo method and it is found that the model describes the magnetic properties of itinerant-electron magnets fairly well. The quantum Monte Carlo simulation together with the parallel matrix inversion algorithm allows one to perform practical simulations of large systems. Let us now turn our attention to how the scheme can be used to evaluate the magnetic properties of transition metals.
In order to model different lattices or systems in different dimensions in the present formulation the band part of the Hamiltonian needs to be changed; the interaction part remains the same. We have seen that for a one-band case going from one to three dimensions does not pose any serious problems. In order to study transition metals a $v$-band model is required. This introduces degeneracy in the conduction band; for instance in $3d$ transition metals the fivefold $3d$ band is split into a $t_{2g}$ triplet and an $e_g$ doublet. The degeneracy also introduces interactions beside $t_{ij}$ and $U$. In a one band case the electron hopping process is restricted to the same orbital on different sites, however with more than one band it is possible for an electron to switch orbitals when it hops from one atom to another. This is hybridisation of the bands, whether the $d$ bands or $s,p$-bands. The explicit expression for the inter-band hopping terms has been given by Slater and Koster (1954). In Chapter two the expression for the $d$ bands was given in terms of Pettifor's (1977) scheme.

It is proposed that the hopping parameters be derived from first principle electronic structure calculations, by Fourier transforms of the relevant $s,p,d$ band structures. The LMTO-ASA (linear muffin tin orbital method in the atomic sphere approximation) provides one such method. Recently Yeung and co-workers have developed code for parallel computer systems (Yeung, 1991) allowing a rapid calculation of band structures. The hopping parameters can be derived from the Fourier transform of the band structure,

$$t_{ij} = \frac{1}{N} \sum_k \varepsilon_k \exp\{i k \cdot (R_i - R_j)\},$$

(9.22)

where $R_i - R_j$ is the inter-atomic distance between sites $i$ and $j$.

The magnitudes of the exchange fields can also be derived from band structure calculations. Cooke et al (1980) considered two parameters $\Delta(t_{2g})$ and $\Delta(e_g)$, for the corresponding types of orbital in iron, however they found that to reproduce the correct $t_{2g}/e_g$ nature of the magnetic moment as observed in neutron magnetic form factor measurements, the two parameters have essentially the same value, approximately $0.1420-0.1440$ Ryd.
Consider the simplest case of iron, a model with five $d$ orbitals. This means that the non-magnetic band matrix in the model will be five times the size of a single band matrix. There are two possibilities for the interaction term. The first is to use the same auxiliary fields for each of the five orbitals. This means that the size of the interaction matrix will increase by a factor of five. The other possibility and arguably the more physical approach is to use a separate set of auxiliary fields for each of the bands. This will complicate the simulation since now there will be ten (five for charge and five for spin fluctuations) possible auxiliary field variables that can change during the simulation; five if charge fluctuations are suppressed. Obviously if the $s,p$-bands are also included then the matrix size will increase appropriately. If the hopping integrals are denoted as $t_{ij}^{\alpha\beta}$ where $\alpha,\beta$ label the orbitals and $i,j$ are the atomic sites, the block sub-matrix of off-diagonal terms that define the hopping between sites $i$ and $j$ in the non-magnetic matrix will have the form

![Diagram](image)

In iron there has to be one $s$-orbital, three $p$-orbitals and five $d$-orbitals in the non-magnetic Hamiltonian; therefore a $18 \times 18$ block matrix (for both spin directions) is needed to describe the complete electron hopping. For a "small" system of 54 iron atoms on a BCC lattice therefore the matrices will have dimensions of $972 \times 972$. The large matrix sizes are the restriction of quantum Monte Carlo calculations.

Other interactions are also introduced due to degeneracy in the bands (Acquarone, 1988); for instance on-site exchange and correlation terms between components of the band.
Suppose the degenerate band is composed of $d$ orbitals, labelled $m,l = 1,2,\ldots,d$, there will exist terms such as $U^{ml}$, when $m \neq l$ then this is the inter-orbital correlation, while for $m = l$ the normal intra-orbital correlation $U$ is recovered. There will also exist an inter-orbital exchange interaction $J^{ml}$, expressing Hund's rule and a correlation-induced hybridisation $V^{ml}$, mixing the orbitals $m$ and $l$, provided the $m$ orbital is singly occupied. The Hamiltonian for a transition metal will then be fairly complicated.

The $\nu$-band Hubbard model can also be studied by writing the interaction term as

$$H_{\text{int}} = \frac{U}{4} \sum_i n_i^2 - \sum_i S_i^2$$

(9.23)

where $n_i$ and $S_i$ are the total number and spin operators on site $i$. In this case the exponential in the functional integral is scaled up by a factor of $\nu$. The bands "see" the same auxiliary fields (Samson, 1984). Therefore it is possible to model a $\nu$-band Hubbard model without increasing the matrix size.

At the time of writing this thesis it was not possible to perform a calculation for iron. However the details of such a calculation have been outlined and making use of the parallel matrix inversion algorithm it is not thought that this calculation would present a serious computational problem.

### 9.7 Imaginary time-dependent correlations.

The Monte Carlo sweeps of the lattice in the present simulations are performed in one time slice at a time. The Green function is calculated from scratch for each time slice in this scheme. Let us define this as the "single time slice" scheme. It is possible however to use an alternative scheme. The strategy is to calculate the Green function for each time slice at the start of the simulation. Now instead of choosing sites at random in a particular time slice, the time slice is also chosen at random. This requires that the Green function for each time slice be stored; this is the major drawback of the method since at low temperatures or large $U$ a large number of time slices are required. The advantage of the method is that
correlations between different time slices can be calculated. The scheme was used to perform simulations for the one-dimensional case and the same results as those of the "single time slice" scheme were obtained, this gives us confidence in using the scheme for further calculations. In the simulation a greater number of warm up steps and Monte Carlo sweeps are required. Typically 1000 warm up steps and 10000 Monte Carlo sweeps are required. The thermodynamic quantities are calculated in each time slice after every 5-10 Monte Carlo sweeps. The averages are therefore over the complete number of sites in all the time slices. This type of simulation is equivalent to performing a simulation in a $D+1$ lattice where $D$ is the dimension of the system under investigation. One could argue that this is more representative of a quantum system since fluctuations occur in random time and space, albeit imaginary time.

The main use of time dependent correlation functions is that one can compare them directly with experimental data. In an experiment one is interested in real time correlation functions between operators $A$ and $B$ of the form

$$S_{AB}(t) = \langle A(t)B \rangle$$  \hspace{1cm} (9.24)

and linear response functions of the form

$$\chi_{AB}(t) = i\langle[A(t),B]\rangle.$$  \hspace{1cm} (9.25)

Here $[\_\_]$ is the commutation of $A$ and $B$. Quantum Monte Carlo allows one to calculate imaginary-time correlation functions of the form

$$g_{AB}(\tau) = \langle A(-i\tau)B \rangle = \frac{\text{Tr}[e^{(-\beta H)}A(-i\tau)B]}{Z}.$$  \hspace{1cm} (9.26)

This is usually the imaginary-time Green function. The dynamic correlations are characterised by a spectral density function $A(\omega)$, which is related to the imaginary-time Green function by (von der Linden, 1991; Lovesey, 1980)
\[ G(t) = \int_\infty^\infty d\omega A(\omega) \frac{e^{-\omega t}}{1 + e^{-\beta \omega}} \]  

(9.27)

In order to make a transformation from imaginary time to real time an inverse Laplace transformation from one domain to the other is required. The inverse transformation of equation (9.27) is a ill-posed problem for two reasons; firstly the information for the Green function is only available for a limited set of imaginary times and secondly the data are "noisy". A small change at high frequencies will result in an extremely small change in \( G(t) \) because of the exponential \( \exp(-\omega t) \) in the integral. Conversely a small change in the Monte Carlo data will result in a large change in the spectral density function. The solution to the transformation therefore is not unique.

The problem has been tackled in the past using different models and approaches. The least squares fit has been used to analysis the data from a system of spinless fermions in one dimension (Schüttrler and Scalapino 1985 and 1986). The problem has also been approached using Padé approximants (Hirsch, 1987). The method however that has generated the most interest is based on the maximum entropy approach (Gubernatis et al, 1991). This allows the extraction of real-frequency correlation functions from the Green functions generated by Monte Carlo simulations of many-body systems.

9.8 A parallel matrix inversion algorithm.

The main problem with the quantum Monte Carlo scheme used is that for low temperatures or large values of Coulomb interaction, the computational effort required is extensive. The ultimate aim of the investigation is the study of a three dimensional BCC lattice in the hope of investigating the statistical mechanics of iron from the microscopic viewpoint. The smallest sensible system size in this case is a lattice consisting of 54 atoms. The matrix representing this lattice in each time slice will have dimensions of \( 108 \times 108 \) for a single band Hamiltonian. At high temperatures where fewer time slices are required, this may not present a computational problem; however, when the temperature is decreased the simulation will be impractical due to the greater number of time slices required. Similarly if
more that one band is to be included in the parameterisation of the Hamiltonian the matrix size will increase. However if the matrix operations can be divided among several processors then it is practical to study large systems. In this section an adapted matrix inversion algorithm due to Jones and Yeung (1990 and private communication) is described. The algorithm has been specifically designed with Monte Carlo simulation in mind and provides a rapid method of calculating the ratio of determinants of two arbitrary matrices. However since the calculation of the ratio of determinants for the present Monte Carlo simulations has been reduced to the evaluation of the determinant of a $2 \times 2$ matrix, the algorithm is adapted for the calculation of the occupation numbers.

Suppose we have a $N \times N$ non-singular matrix $M$. Let us now denote the cofactor of the matrix element $M_{ij}$ by $C_{ij}$. We then have the result

$$
\det[M] = \sum_{i,j} M_{ij} C_{ij}. \quad (9.28)
$$

From the expansion theorem for determinants the inverse of a matrix can be written as

$$
M_{ij}^{-1} = \frac{C_{ji}}{\det[M]} \quad (9.29)
$$

Let us now denote the inverse of the transpose of $M$ as $\overline{M}$,

$$
\overline{M} = [M^T]^{-1} \quad (9.30)
$$

we therefore obtain the result

$$
\overline{M}_{ij} = \frac{C_{ij}}{\det[M]} \quad (9.31)
$$

In the Monte Carlo algorithm the change in auxiliary fields at a site will in general involve a "small" change in the row or column of the matrix $M$ (and subsequently in $\overline{M}$). The Sherman-Morrison formula (e.g Press et al, 1985) allows one to calculate the change in the inverse matrix $\overline{M}$ without actually having to perform a further matrix inversion. The matrix inversion algorithm is based on this formulation.
Suppose now the matrix $M$ is changed by replacing the $k$th column by a new column of matrix elements,

$$
\begin{align*}
M_{ik} &\rightarrow M'_{ik} & j &= k \\
M_{ij} &\rightarrow M_{ij} & j &\neq k
\end{align*}
$$

now all columns except the $k$th column in the matrix of cofactors $C$ will change,

$$
\begin{align*}
C_{ik} &\rightarrow C_{ik} & j &= k \\
C_{ij} &\rightarrow C'_{ij} & j &\neq k.
\end{align*}
$$

The matrix elements for a new matrix $\overline{M} = [M'^T]^{-1}$ are now given by (Jones, private communication)

$$
\overline{M}_{jk} = \frac{\overline{M}_{jk}}{Q} \quad (9.32)
$$

$$
\overline{M}_{jq} = \overline{M}_{jq} - \frac{\overline{M}_{jk}}{Q} \sum_{p=1}^{N} \overline{M}_{pq} M'_{pk} & q \neq k \quad (9.33)
$$

where

$$
Q = \sum_{p=1}^{N} M'_{pk} \overline{M}_{pk} = \frac{\text{det}[M']}{{\text{det}[M]}}. \quad (9.34)
$$

The quantity $Q$ in the algorithm is the ratio of determinants of matrices $M'$ and $M$. The ratio of determinants is actually calculated for the column that is being replaced in the matrix $M$.

In the formulation above it is assumed that one already knows $\overline{M}$ and $\text{det}[M]$. In fact this information is not available at the outset; however the algorithm provides the inverse of a matrix $M'$ from the known inverse of another matrix $M$. Now the inverse and determinant of the unit matrix is known, therefore if the above steps are applied $N$ times starting with a unit matrix the inverse of the required matrix can be obtained. Let us now denote the inverse of transpose matrix $\overline{M}$ as $\overline{I}$ indicating that is starting matrix and its determinant by $\text{det}[\overline{I}]$. The first step is to replace the first column of the unit matrix with the first column of the matrix $M$. The $Q$ for this replacement is then calculated and the relevant matrices updated.
The second column of the updated unit matrix is then replaced with the second column of the matrix $M'$ and the process is repeated.

This algorithm easily lends itself to adaptation to a network of parallel processors. In the algorithm outlined above note that to update the $q$th column all that is required is the old $q$th column $I_{pq}$, the new column $M'_{pk}$ and the column vector $I/Q$. Therefore one can update the column $q$ without requiring any information about the rest of the old matrix $I$ except the column $k$. Suppose now we have a parallel network of processors, the main processor is termed the 'Master', $n$ processors are termed the 'Slaves', and there is a terminator processor called the 'Terminus'. The parallel program schematically has the following structure:

```
Master    Slave(1)    Slave(2)    ...    Slave(n)    Terminus
```

The arrows indicate the direction of flow of data in the network. The matrix $I$ is divided into $n$ vertical 'slices' each containing $N/n$ columns. The 'Master' process will distribute the columns of the actual matrix $M'$ whose inverse we require. Each of the 'Slave' processes in succession will take a copy of the current column being distributed and pass it on to its neighbour. After receiving the column $M'_{jk}$ each 'Slave' checks to see if it contains column $k$. If it does then it computes $Q, M'_{jk}$ and broadcasts $M'_{jk}$ to its neighbours on its left and right. If the 'Slave' does not contain $k$ it waits to receive $M'_{jk}$ and then updates its columns according to equation (9.33).

Let us now look at how this algorithm can be adapted to the calculation of occupation numbers in the present Monte Carlo calculations. Suppose we are performing Monte Carlo sweeps for the $l$th time slice. The calculation of occupation numbers requires the evaluation of

$$n_{i\sigma} = \langle A(\tau_l) \frac{1}{I + A(\tau_l)} \rangle_{i\sigma}.$$  (9.35)
If the matrix \( A(\tau_l) \) is distributed by its rows (the algorithm calculates the inverse of the transpose) each of the \( n \) 'Slave' processes will contain \( 2N/n \) rows of this matrix. The denominator of equation (9.35) can be formed easily on each of the 'Slave' processes by adding the appropriate part of the unit matrix to the rows of \( A(\tau_l) \) on the particular processor, so for the \( i \)th 'Slave' process

\[
M_{j,k} = I_{j,k} + A_{j,k}(\tau_l) \tag{9.36}
\]

where \( j' = i \times 2N/n \) and \( k = 1, ..., 2N/n \). Note that the \( M \) matrix on the 'Slaves' is still formed in columns. Now the 'Master' will distribute the \( A(\tau_l) \) matrix by its rows, each of the 'Slave' processes in succession will take a copy of the current row being distributed and pass it on to its neighbour. The 'Slave' will then keep a record of the row and form the respective column of \( M' \) according to equation (9.36). Therefore the first \( 2N/n \) rows of the matrix \( A(\tau_l) \) will be stored on the first 'Slave', the next \( 2N/n \) rows on the second 'Slave' and so on. The 'Slave' processes will then execute the relevant operations of the matrix inversion algorithm until finally each of the 'Slave' processors will have in store rows of \( A(\tau_l) \) and columns of \( [I + A(\tau_l)]^{-1} \). The occupation numbers are then simply calculated by each of the 'Slave' processes performing (in parallel) a vector multiplication of the rows of \( A(\tau_l) \) and columns of \( [I + A(\tau_l)]^{-1} \). The final event in the parallel program is that the last process in the chain, the 'Terminus' process, sends to the 'Slave' process on its left an empty vector of size \( 2N \), the \( n \)th 'Slave' process fills in the last \( 2N/n \) elements of the vector with the results of its previous vector multiplication (the last \( 2N/n \) occupation numbers) and passes the resultant vector to the 'Slave' process on its left. This 'Slave' process repeats the operation until finally a complete vector containing the occupation numbers is returned to the 'Master' process.

The algorithm outlined above therefore allows a rapid calculation of the occupations numbers in the Monte Carlo simulation. Since these need to be evaluated at every 2-5 Monte Carlo sweeps per time slice the overall time of computation is typically 3-5 cpu minutes on a serial computer for \( U = 4 \) and a one-dimensional lattice of six sites. For the BCC lattice with 54 sites the computation time is typically 30 cpu minutes. The use of the algorithm resulted
in a 7-9 times reduction in the overall computation time when 8 'slave' processors (for the BCC lattice calculation) and 9 processors (for the one-dimensional calculation) were used. The number of sites in a BCC lattice scales by a factor of eight (ignoring the case of one unit cell), therefore the corresponding matrices will be divided equally if a number that is factor of eight 'slave' processors is used.

The algorithm has been designed with the calculation of the ratio of determinants for a Monte Carlo simulation in mind. This aspect of the algorithm has not been used since a fast method of calculating the ratio of determinants has already been applied. The method used in the present simulations is due to Blankenbecler et al (1981; Scalapino and Sugar, 1981) and White et al (1989). One can prove that in fact the ratio of determinants calculated in this method is equivalent to that calculated in the method of Jones and Yeung. The point here is that the ratio of determinants can be calculated and the Green function updated on a parallel machine, which should result in an overall reduction of computation time.

Let us define

\[ O = [I + A(\tau)]. \]  
(9.37)

Now the method of Jones and Yeung is based on changes in the column of a matrix \( M \), whereas the method of Blankenbecler et al (1981; Scalapino and Sugar, 1981) and White et al (1989) is based on the change in the row of \( A(\tau) \) and subsequently in \( O \) defined above. Following Yeung (private communication) let

\[ O = M^T \]  
(9.38)

and

\[ \det[O] = \det[M] \]  
(9.39)

therefore changing a row of \( O \) corresponds to changing the column of \( M \). Now

\[ \frac{\det[O]}{\det[O]} = \frac{\det[M]}{\det[M]} = Q \]  
(9.40)
and from equation (9.34)
\[ Q = \sum_{p=1}^{N} M'_{pk} M_{pk} = \sum_{p=1}^{N} O'_{kp} G_{pk} \] (9.41)
where
\[ G = O^{-1}. \] (9.42)

Using equations (9.41) and (8.40) one can show
\[
Q = O'G \\
= [I + A(\tau_{l})]G \\
= [I + A(\tau_{l}) + \delta A(\tau_{l})]G \\
= I + \delta A(\tau_{l})G \\
= I + \delta (G^{-1} - I)G \\
= I + \delta - \delta G. \] (9.43)

Since \( \delta \) is a matrix with one non-zero element one has
\[
Q = 1 + \delta_{ii} - \delta_{ii} G_{ii} \] (9.44)
which is the result from White et al (1989). The formulation above is generalised, however it has been demonstrated that the two different methods do in fact give the same result for the ratio of determinants. The case for spin block matrices has not been derived since this requires a change in the algorithm of Jones and Yeung. This has not been attempted as yet, however it is expected that a similar result would be found. The fact that the ratio of determinants from the methods of White et al (1989) and Jones and Yeung are the same one can expect that if the spin block matrices of the present calculations are treated as general matrices then the ratio of determinants obtained using the method of Jones and Yeung should have the same value as that obtained from equation (8.44).

The update of the Green function must also be shown to be the same in both methods.

Let us first consider the columns of the updated Green function \( G' \) that differ from the column \( k \) that is replaced in the method of Jones and Yeung. We have from equation (9.33)
\[
G'_{jq} = G_{jq} - \frac{G_{jk}}{Q} \sum_{p=1}^{N} G_{pq} O'_{pk}
\]
\[q \neq k\]
\[
= G_{jq} - \frac{G_{jk}}{Q} (O' G)_{kq}
\]
\[q \neq k\]
\[
= G_{jq} - \frac{G_{jk}}{Q} [(I + A(\tau)) + \delta A(\tau)]_{kq}
\]
\[q \neq k\]
\[
= G_{jq} - \frac{G_{jk}}{Q} [(\delta A(\tau)) G]_{kq}. \quad (9.45)
\]

The last term comes about because for \( q \neq k \) the term \( I + A(\tau) \) does not contribute since only the \( k \)th row in \( A(\tau) \) changes. Now \( \delta \) is a matrix with one non-zero element at \( ii \) and so

\[
G'_{jq} = G_{jq} - \frac{[\delta A(\tau)]_{jq}}{Q}
\]
\[q \neq k\]
\[
= G_{jq} - \frac{G \delta (A(\tau) + I - I) G]_{jq}}{Q}
\]
\[q \neq k\]
\[
= G_{jq} - \frac{G \delta (I - G]_{jq}}{Q}. \quad (9.46)
\]

This is the same expression as in White et al (1989). Let us now consider the case for column \( q = k \). From equation (8.46) we have

\[
G' = G - \frac{G \delta (I - G)}{R}
\]
\[
= G_{jk} - \frac{G_{jk} \delta_{ii} (1 - G_{ii})}{R}
\]
\[
= \frac{G_{jk}}{R} \{1 + (1 - G_{ii}) \delta_{ii} - \delta_{ii} (1 - G_{ii})\}
\]
\[
= \frac{G_{jk}}{R}. \quad (9.47)
\]

This equation is equivalent to equation (9.34).

The methods of White et al, 1989 and Jones and Yeung are identical, and so the parallel algorithm due to Jones and Yeung could be used safely to reduce the computation.
time. One also notes that if the unit matrix is subtracted from the matrix $O$ above and the resultant matrix is multiplied by $G$ the occupation numbers can also be computed, so

$$n_i = ((O - I)G)_{ii}$$

(9.48)

this means that occupation numbers can also be calculated in parallel; each of the processors in the chain simply performs a vector multiplication as before.

In this chapter the calculations of the statistical mechanics of a one-band Hubbard model in one and three dimensions have been discussed and presented. This has taken the investigation from classical systems to quantum systems. The details for a calculation of the statistical mechanics of an $v$-band model have also been discussed. In order to reduce the computation time a parallel matrix inversion algorithm has been used, this will prove very useful for larger systems in particular in a calculation for transition metals. The investigation can now be concluded by discussing the insights that have been gained into magnetic properties of itinerant-electron systems.
Conclusions of investigation.

A model of iron has been derived based on results from electronic structure calculations. This is based on an effective classical spin Hamiltonian extracted from such calculations. The exchange interactions in this model are of a non-pairwise nature; that is they are determined by the magnetic order in the atomic shells surrounding the pair of interacting magnetic moments. The unique feature of these exchange interactions is that the larger nearest-neighbour interaction increases with temperature (or magnetic disorder). This suggests that as the Curie temperature is approached in this model of iron, more effort is required to disorder the system any further. It also suggests that as the system goes through the phase transition from the ferromagnetic to the paramagnetic phase any short range order found at $T_C$ should remain in the paramagnetic phase. This should also be larger than that found in the nearest-neighbour Heisenberg model. This was the basis for the hypothesis for large short range order in iron above $T_C$.

In an attempt to investigate this claim a Monte Carlo simulation for the nearest-neighbour Heisenberg model and the model of iron was performed. The short range order can be related to the real space correlation function at $T_C$ and this was the principal quantity for comparison in the investigation. The results indicate that in fact iron with non-pairwise exchange interactions does not behave in a substantially different way from the nearest-neighbour Heisenberg model. The degree of short range order in both models is about the same even with the interactions in an extreme limit (the nearest-neighbour interaction vanishes in the ferromagnetic phase). The only obvious difference is in the magnetisation curves resulting in a stretching of the temperature scale.

The results from the electronic structure calculations and the nature of the exchange interactions also leads one to believe that the disorder could be coarse-grained (Luchini and Heine, 1991), and that the ground state could be broken up into domains of reversed
magnetisation (Heine, private communication). If this was the case then one could expect that these could persist as the temperature of the system was raised and above $T_C$ one could expect short range order on the scale of the size of the blocks of reversed magnetisation. Of course it is possible that this could be an artifact of the Monte Carlo simulation and so care has been taken when running the simulations. When the system is warmed up a ferromagnetic starting state is used, which means that a certain number of Monte Carlo steps have to be performed before measurements of the thermodynamic properties are taken. One possible improvement could actually have been made by using the end configuration of a current temperature as the starting state of the next temperature. This is not really necessary if the system is allowed to reach equilibrium.

To investigate the ground state of the model of iron a two-dimensional Ising model and a modified Monte Carlo scheme was used. The Ising model shows ferromagnetism in the ground state and is described by a Heisenberg spin Hamiltonian. The non-pairwise exchange interactions can therefore be incorporated into the model quite easily. The "motions" of the spins can be observed directly and therefore the formation of blocks of reversed magnetisation can be observed. Such blocks were indeed found to form in the model of iron, however only for cases in which the exchange interactions are extreme. Further it was found that the next-nearest-neighbour interaction is more important than was first thought. It would appear that this interaction establishes the ferromagnetic ground state in the model of iron. The other observation is that the model of iron with non-extreme interactions, i.e with both nearest and next-nearest-neighbour interactions retained, orders (i.e reaches the ferromagnetic state) slightly more rapidly than the nearest-neighbour Heisenberg model (it must conversely disorder more rapidly as well). This again agrees with the conclusion from the standard Monte Carlo simulations, that the main effect of non-pairwise exchange interactions is to stretch the temperature scale.

The experimental interpretation for short range order came from the neutron scattering experiments of Lynn (1975). He found that the spin-wave dispersion was only weakly renormalised as the temperature of iron was increased, and after $T_C$ no further
renormalisation was found. The implication is that in order to support spin waves above $T_c$ then some degree of short range order is needed. From these observations it would indeed appear that this would be greater than in the Heisenberg model. In order to compare with experiment the spin-wave dispersion for the model of iron in the temperature range 0 to 0.99$T_c$ has been calculated using spin wave theory. The expected decrease in magnon energies is compensated for by the increase in the average exchange interactions. This leads to an increase in the magnon energies with temperature. Clearly not the effect we are seeking. The trend in the magnetisation of the model of iron calculated from spin wave theory is similar to that found in the Monte Carlo calculations.

These observations lead one to question the validity of the model of iron, or rather the approximations that have been made when calculating the energetics. The main approximation is the static approximation. This essentially means that the precession of the magnetic excitations is slow compared with electron hopping. Physically this means that an electron hopping from site to site will "see" a frozen configuration of magnetisation. There are justifications for making this approximation; a typical magnetic excitation, a spin-wave will have a lifetime of about $10^{-13}$s, whereas electron hopping occurs on the time scale of about $10^{-15}$s so an electron hopping from an atomic site to another site and then back will "see" the same magnetic configuration during this process.

The static approximation therefore misses out dynamic or quantum effects. Such effects are important for wave vectors above $q_c$, the value at which spin-waves enter the Stoner continuum. If quantum effects could be expressed as a classical Hamiltonian, they would have to lead to effective exchange interactions of a substantially different form to those obtained in the static approximation. This may explain the difference in the calculated and experimentally measured correlation functions.

What is needed then is a calculation of the statistical mechanics of transition metals from a microscopic viewpoint. Such a calculation would incorporate quantum effects and make fewer approximations. The Hubbard model is a fairly accurate description of itinerant-electron magnets and provides the Hamiltonian for a quantum mechanical calculation. The
functional integral and the Hubbard-Stratonovich transformation allows the calculation of the statistical mechanics of many-body systems. The functional integral for a many-body system with scalar and vector auxiliary fields has been derived and evaluated using the quantum Monte Carlo method. Calculations made in the static approximation indicate that the statistical mechanics are substantially different from those obtained from a calculation with quantum effects included.

There are two important conclusions that can be drawn from this investigation: firstly calculations made in the static approximation miss out much of the important physics needed to calculate the statistical mechanics of itinerant-electron systems; and secondly if the statistical mechanics of such systems are to be calculated in a framework that one can believe in, then these need to be performed from a microscopic viewpoint using a quantum Monte Carlo scheme.

**Points for further investigation.**

There are several avenues of further investigation open to us. At the time of writing this thesis it was not possible to investigate transition metals using the quantum Monte Carlo method and so the statistical mechanics of iron based on the method need to be calculated to make the investigation more complete. The path such a calculation might take has been discussed in Chapter nine. The parameters for the Hamiltonian in the calculation could easily be derived from first principles calculations of the band structure of iron. The LMTO-ASA method is one such method. It should also be possible to investigate properties that can be compared directly with experiment by extracting information from the imaginary time-dependent correlation functions quantum Monte Carlo easily allows to be calculated.

The quantum Monte Carlo calculation requires a great deal of computational effort; however the strain can be spread out over several processors. A parallel matrix inversion routine has been adapted for the calculation of the electron occupation numbers of the atoms in an itinerant-electron system and so it should be possible to investigate "large" systems such as, iron with a full compliment of spd bands, within a practical computation time. One
further improvement that could be made is to include multiple updates of the auxiliary fields. The fact that an update is of a long range nature (a complete row or column in the matrices is affected) requires a modified probability distribution. This strategy would reduce the computation time further as many fields could be updated in a single Monte Carlo step. It should also be possible to extend the method to other correlated electron systems such as superconductors, disordered alloys, the Anderson model, Kondo model, the $t$-$J$ model or metallic and magnetic multi-layers currently the focus of much research.

The ground state of correlated electron systems has been the subject of much investigation in recent years using for instance the variational quantum Monte Carlo method (e.g. Ceperley et al, 1977 and Ceperley and Kalos, 1979), and a possibility might be to use quantum Monte Carlo techniques to investigate the excited states of such systems. The sign problem that plagues all quantum Monte Carlo calculations of fermion systems could also be investigated providing numerical support for the geometrical viewpoint offered by Samson (1993).

Another possibility is to take a step back and try to look at the effective exchange interactions in a different light. The method used in the electronic structure calculations is parameterised by many parameters that have to be derived from calculated band structures. A first principles electronic structure calculation is entirely parameter free and therefore would provide a much more accurate framework for the calculation of the effective exchange interactions. The exchange interactions could be derived from susceptibility calculations carried out using the LMTO method (Yeung, private communication), or from the finite temperature band theory of Gyorffy et al (1983). This method allows one to investigate the electronic properties of magnetic configurations. Recently a calculation using spin density functional theory has been made by Peng and Jansen (1991). They have found the exchange interaction to the sixth nearest-neighbour by in iron by fitting the calculated total energy to a Heisenberg Hamiltonian. The total energy is calculated for several anti-ferromagnetic structures and it is assumed that these are representative of the corresponding spin waves (with respect to the ferromagnetic ground state). It should be possible to perform such
calculations for more general magnetic configurations such as the spin spiral. This has in fact already been done by Heine et al (1990) using the LMTO-ASA method. The total energy is again fitted to a Heisenberg model. Therefore it is proposed that the exchange interactions be calculated using the couple method of Luchini and Heine (1991). Although the static approximation would still be made in this scheme, which is in conflict with the conclusions of the present investigation, it does however offer us a opportunity to perform calculations in a scheme that is not so susceptible to the idiosyncrasies of a semi-emperical scheme.
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Appendix A.

Practical random number generators.

Linear congruential method.

The linear congruential method is the most common method implemented on computers to generate random number sequences. The method generates a sequence of integers according to the rule

\[ l_{j+1} = (al_j + c) \mod m \]  (A.1)

Here \( m \) is called the modulus, \( a \) and \( c \) are positive integers called the multiplier and increment respectively. The range of numbers generated is between 0 and \( m-1 \). The sequence will eventually repeat itself, with a period no greater than \( m \). If the parameters \( m, a \) and \( c \) are chosen properly, then the period will have a maximum length \( m \), also each number between 0 and \( m-1 \) will occur at some point, so any initial seed choice of \( l_0 \) can be used (within the range 0 to \( m \)). A real number between 0 and 1 is returned by \( l_{j+1}/m \). The real number is strictly less than 1, but occasionally (at least once in \( m \) calls) exactly equal to 0. The linear congruential method is very fast but has some serious disadvantages when used in Monte Carlo simulations.

On most systems the size of \( m \) is the largest integer that the computer can represent (e.g., \( m = 2^{31}-1 \) for a 32 bit word). For a Monte Carlo simulation this means that the phase space of a dynamic variable will divided into a "comb" of points, so for example the rotation of a spin in say the xy-plane will be "quantized" into steps of \( 2\pi/m \).

There is also a definite correlation between sequential numbers in the random number sequence. Let \( k \) sequential numbers define a point in a \( k \)-dimensional space; that is \( r_1 = \{l_1, l_2, ..., l_k\} \), \( r_2 = \{l_{k+1}, l_{k+1}, ..., l_{2k}\} \) etc... It can be shown that these points lie on a sequence of at most \( m/1 \) \( k \)-1 dimensional planes (Press et al, 1985). For a three
Appendix A: Random number generators.

A dimensional lattice, for example, there will be $2^{31}/3 = 1290$ planes for a 32-bit word and $2^{15}/3 = 32$ planes for a 16-bit word. This places a limit on the lattice size if this is the chosen method for generating random numbers, since for a 32-bit word only 1290 lattice sites can be visited without correlations between lattice sites. If $a, c$ and $m$ are not chosen properly then there will be even fewer planes.

An improved random number generator.

The random number generator used in the Monte Carlo simulations of chapter four and in the evaluation of the functional integrals in chapter nine is based on three linear congruential generators and uses a "shuffling" method suggested by Knuth (1981). The method stores the random number generated by two linear congruential generators (one each for the most and least significant parts of the number) in an array, a third linear congruential generator then picks an element of the array and the value in that element is then the random number returned by the generator. This element in the array is then given another value. The output is also used to generate the next number in the third linear congruential generator.

The period of the complete generators is infinite for all practical purposes. The size of the array and the initial seed value is arbitrary. The disadvantage of using this method is that it is slow in comparison to the simple linear congruential method. However the problem of sequential correlations is effectively eliminated.
Appendix B.

Proof of ferromagnetism in the Ising model.

A simple proof in 2D.

Consider a square lattice. Let each point \( i \) on the lattice be described by a spin variable \( s_i = \pm 1 \). The spins are allowed to interact with only their nearest neighbours through an interaction \( J_{ij} \). Let the energy of the lattice for any configuration \( \{s_i\} \) be

\[
E = \frac{1}{2} \sum_{(i,j)} J_{ij} s_i s_j \tag{B.1}
\]

where

\[
J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ are nearest neighbours} \\ 0 & \text{otherwise}. \end{cases} \tag{B.2}
\]

Now at any temperature \( T \) some of the \( s_i \) will have values of +1 and some of -1. Let us define the boundary between neighbouring spins of opposite sign as a partition point. The partition points can be joined together resulting in a domain wall. This will divide up the lattice into blocks of reversed magnetisation.

The energy of formation of a partition point is \( 2J \). If a domain wall has a length \( L \) then the probability that it exists is

\[
\sim e^{-2JLT}. \tag{B.3}
\]
Suppose now that the lattice is in a ferromagnetic state; the reversal of a spin will cost $8J$ energy units. This comes about because a reversed spin will be surrounded by a square with sides of unit length. The spin reversal will therefore occur with a probability

$$\sim e^{-8J/T}.$$ 

Therefore at sufficiently low temperatures the probability at which this occurs will be extremely small and at $T = 0$ it will never occur. So at low temperatures most of the spins will be aligned in the ferromagnetic direction. This does also imply ferromagnetism at $T > 0$; the proof is after all very simple. A more rigorous argument is given by Peierls (1936) and subsequently by Griffiths (1964) based on the shapes of the reversed blocks of magnetism. The model has been solved in two dimensions by Onsager (1944).
Appendix C.

Trace over fermion operators.

We want to prove the identity

$$\text{Tr} \left( \prod_{l=1}^{L} T \exp \left[ -\Delta \tau \mathcal{H}(\tau_l) \right] \right) = \det \left[ I + \prod_{l=1}^{L} \exp \left[ -\Delta \tau \mathcal{H}(\tau_l) \right] \right] \quad (C.1)$$

where $T$ is the chronological time-ordering operator and the single-particle operators

$$H(\tau_l) = \sum_{ij} c_i^\dagger h(\tau_l)_{ij} c_j. \quad (C.2)$$

The operators $h(\tau_l)$ are arbitrary and the spin index is ignored for simplicity. The proof here follows (von der Linden, 1992). The first step is to prove

$$O = \prod_l T \exp \left[ -\Delta \tau H(\tau_l) \right] = \exp \left[ -\beta \bar{H} \right] \quad (C.3)$$

where $\bar{H}$ is an effective single-particle operator. Let

$$\bar{H} = \sum_{ij} c_i^\dagger \bar{h} c_j. \quad (C.4)$$

Let us now define an arbitrary electron creation operator

$$a_k^\dagger = \sum_i b_{ki} c_i^\dagger \quad (C.5)$$

where $b_{ki}$ is a constant. The evolution of this operator can be defined as

$$\bar{a}_k^\dagger = \bar{a}_k^\dagger (\Delta \tau) = \sum_i \left[ \sum_j \exp \left( -\Delta \tau h(\tau)_{ij} b_{kj} \right) c_i^\dagger \right]. \quad (C.6)$$

Therefore

$$\exp \left[ -\Delta \tau H(\tau) \right] a_k^\dagger = \sum_i \left( \sum_j \left[ \exp \left( -\Delta \tau h(\tau) \right) \right]_{ij} b_{kj} \right) c_i^\dagger \exp \left[ -\Delta \tau H(\tau) \right]. \quad (C.7)$$
The product of single particle operators is then

\[ Oa_i^\dagger = \prod_l T \exp [-\Delta T H(\tau)] \sum_i b_{ki} c_i^\dagger \]

\[ = \sum_i \left( \sum_j \left[ \prod_l T \exp (-\Delta \tau h(\tau)) \right]_{ij} b_{kj} \right) c_i^\dagger O \]  \hspace{1cm} (C.8)

therefore

\[ Oa_i^\dagger O^{-1} = \sum_i \left( \sum_j \left[ \exp (-\Delta \tau \tilde{H}) \right]_{ij} b_{kj} \right) c_i^\dagger = \tilde{a}_i^\dagger. \] \hspace{1cm} (C.9)

The \( O \) can be viewed as a single exponential of an effective single-particle operator \( \tilde{H} \). The matrix elements of \( \tilde{H} \) are defined as

\[ \left[ \exp (-\beta \tilde{H}) \right]_{ij} = \left[ \prod_l T \exp (-\Delta \tau h(\tau)) \right]_{ij}. \] \hspace{1cm} (C.10)

We can now use the effective operator \( \tilde{H} \) to prove the identity in equation (C.1). We have

\[ \text{Tr} \left( \prod_l T \exp [-\Delta T H(\tau)] \right) = \text{Tr} \left[ \exp (-\beta \tilde{H}) \right] \]

\[ = \text{Tr} \left[ \exp \left( \sum_i c_i^\dagger \epsilon_i c_i \right) \right] \]

\[ = \sum_{N_p=1}^{N} \sum n_1 \cdots n_N \delta \left( \sum_i n_i - N_p \right) \langle n_1 \cdots n_N | \exp \left( \sum_i \epsilon_i n_i \right) | n_1 \cdots n_N \rangle. \] \hspace{1cm} (C.11)

Here \( | n_1 \cdots n_N \rangle \) are the eigenstates of \( \tilde{H} \) in the occupation number representation and \( \epsilon_i \) are its eigenvalues. The summation over all possible particle numbers \( N_p \) eliminates the delta function to leading to

\[ \text{Tr} \left( \prod_l T \exp (-\Delta \tau H(\tau)) \right) = \prod_{i=1}^{N} \sum_{n_i} \exp (\epsilon_i n_i) \] \hspace{1cm} (C.12)

making use of the fact that the occupation numbers of fermions can be 0 or 1 we obtain the desired result.
Appendix C: Trace over fermion operators.

\[ \text{Tr} \left[ \prod_l \exp(-\Delta \tau H(\tau)) \right] = \det \left[ I + \exp(-\beta H) \right] \]

\[ = \det \left[ I + \prod_l \exp(-\Delta \tau h(\tau)) \right] \]

This identity can now be used in equation (8.18) to trace out the fermion degrees of freedom in the partition function of the Hubbard Hamiltonian.