THE EFFECT OF DYNAMIC DISTORTIONS ON THE MAGNETIC BEHAVIOR OF TRANSITION METAL CLUSTERS

by

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Abstract

The effect of dynamic distortions on the magnetic behavior of clusters which contain magnetic ions with isotropically coupled spins is studied using the simplifying assumption that the coupling constants are linear in small distortions from the mean cluster configuration. It is found that dynamic distortions may have a particularly pronounced effect on clusters with symmetry equivalent magnetic ions for which the spectrum of magnetic energy states contains degeneracy in addition to that associated with different orientations of the total spin. Dynamic distortions in these clusters can be regarded as a special type of vibrational/magnetic or magnetostrictive coupling.

A dynamic distortion model for the magnetic behavior of clusters which contain equilateral triangles and regular tetrahedra of isotropically coupled ions of $S=1/2$ to $S=5/2$ is derived. Numerical complications associated with matrix methods are avoided by the use of group theory and 'factorable' Hamiltonians which can be usefully simplified by the introduction of intermediate quantum numbers. Distortions are considered in a basis defined by the normal modes of the metal core of the cluster.

The dynamic distortion model for equilateral trimetallic and tetrahedral clusters is tested against magnetic susceptibility data for the clusters $\text{Cu}_6\text{OX}_6\text{L}_4$ (X=halide L=Lewis base) and $\text{M}_3\text{O}(\text{RCOO})_6$ (M = Fe(III) or Cr(III), RCOO =
carboxylate). The dynamic distortion model is shown to provide the most satisfactory interpretation to date for the data for Cu₄Oₓ₆L₄ which exhibit a rather unusual maximum in the moment as a function of temperature. For the trimetallic systems the agreement between the experimental data and the model is excellent but there are difficulties in evaluating the relative importance of static and dynamic distortions.

Infinite Heisenberg linear chains are then examined using numerical extrapolations from finite chains and also the 'Odd/Even' Hamiltonian, which is defined in terms of intermediate spins on the odd and even numbered atoms of the chain. The results of the numerical extrapolation are shown to be consistent with an expression for the ground state energy of the antiferromagnetic chain, \( E_0 = -2S(S+2)n^2-1 \). A phase transition characterised by a discontinuity in the specific heat appears when the Odd/Even Hamiltonian is solved for large numbers of spins; this makes the Hamiltonian more appropriate for 3-D than 1-D systems. The Spin-Peierls transition, in which an infinite chain becomes alternating at a well defined transition temperature, can be regarded as a freezing out of dynamic distortions. It is shown numerically that, for \( S=1/2 \), end effects associated with lattice imperfections are associated with a significant tendency towards dimerisation in chains of as many as several tens of atoms.

Dynamic distortions of high symmetry clusters can be considered as arising from their Jahn-Teller activity and for
$S=1/2$ the matrices for the vibrational/magnetic coupling are identical to those for paramagnetic Jahn-Teller systems. Interpretation of the dynamic distortion model in Jahn-Teller terms highlights the importance of non-magnetic intercluster interactions which provide the symmetry-lowering distortion terms in the dynamic distortion Hamiltonian.
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Notation

$S$ : Spin on an individual ion.

$S'$ : Total spin of cluster.

$S'', S''$ : Intermediate spins.

$S_{ij}$ : $S_i + S_j$

$n$ : Number of magnetic atoms in cluster.

$H_0$ : Spin Hamiltonian for an undistorted system.

$T(n,S)$ : Space in which solutions of Hamiltonian are found.

$R(S',T)$ : Subspace of $T$ of states with total spin $S'$.

$Q(R,\Gamma)$ : Subspace of $R$ of states belonging to the irreducible representation, $\Gamma$.

$\Omega(n,S,S')$ : Dimension of $R(S')$.

$|\psi\rangle$ : Spin state in $T$.

\{\ldots\} : Set

$\Gamma$ : Irreducible representation, I.R.

$P_n$ : Permutation group of order $n$.

$P$ : Permutation group element.

$P(\Gamma)$ : Projection operator onto I.R. $\Gamma$.

$C, \zeta$ : Configuration space of cluster, vector in $C$.

$D, \vec{d}, d_{ij}$ : Distortion space, vector in $D$, component of $\vec{d}$.

$V$ : Distortion Hamiltonian space

$H'(\vec{d})$ : Vector in $V$, distortion Hamiltonian.

$J_{ij}$ : Isotropic exchange coupling between atoms $i$ and $j$.

$K$ : Coulomb orbital interaction term

$\psi, \theta, \phi$ : Angular coordinates.
R,ρ : radial coordinates.

χ : Magnetic susceptibility per mole.

μ : Magnetic moment.

g : g-factor.

h : Planck's constant, $6.6256 \times 10^{-27}$ Js.

$\hbar$ : Planck's constant$/2\pi$ $1.0545 \times 10^{-34}$

k : Boltzmann's constant, $1.3805 \times 10^{-23}$ JK$^{-1}$ = $0.69503$ cm$^{-1}$

1 kJ mol$^{-1}$ = $83.594$ cm$^{-1}$, 1 cm$^{-1}$ = $1.4388$ K

N : Avogadro's constant, $6.02205 \times 10^{23}$

e : Electronic charge, $1.609 \times 10^{-19}$ C.

M : Proton mass, $1.6725 \times 10^{-27}$ kg.

c : Velocity of light, $2.997 \times 10^8$ ms$^{-1}$
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1.1 Historical Introduction

1.1.1 The Magnetic Interaction Hamiltonian

The first satisfactory explanation of the molecular forces causing magnetic phenomena such as ferromagnetism was given by Heisenberg in 1926. Prior to this date theories providing a reasonable qualitative explanation of many magnetic phenomena in terms of magnetic interactions between adjacent particles (Ewing) or in terms of local magnetic fields or 'molecular fields' (Weiss) had been proposed, but no explanation of the magnitude of the molecular forces needed to bring the theories into agreement with experiment was possible. For example, in the Weiss molecular field theory, a field of the form $H + qM$, where $H$ is the applied field, $qM$ is the induced molecular field and $M$ the magnetisation, was postulated. Classically, $q = 4\pi/3$ is expected, but a $q$ of several thousand is necessary to obtain agreement with experiment.

Heisenberg (and Dirac), using the then recently developed theory of quantum mechanics, showed that because of the requirement that the electronic wavefunction of a system must satisfy the Pauli Exclusion Principle, an essentially electrostatic interaction between electrons associated with adjacent atoms, caused by orbital overlap, would be correlated with the electron spins in such a way that the real Hamiltonian of the system could be replaced by an effective spin
Hamiltonian:

\[(1.1) \quad H = -2J \mathbf{S}_1 \cdot \mathbf{S}_2\]

where \(J\) is a (comparatively large) coupling constant arising from orbital overlap and \(\mathbf{S}_1 \cdot \mathbf{S}_2\) represents the scalar product of the spins associated with the two atoms. Dirac showed\(^6\) that, under certain assumptions, the Heisenberg approach can be extended to many electron systems using the spin Hamiltonian:

\[(1.2) \quad H = -2 \sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j\]

where \(J_{ij}\) is the coupling between the total spins on atoms \(i\) and \(j\). Heisenberg, by applying (1.2) and introducing further approximations regarding the number and distribution of the spin states, was able to provide a satisfactory quantum mechanical theory of ferromagnetism in 1928\(^7\).

In 1925 Ising\(^8\) had proposed a different spin Hamiltonian to describe magnetic interactions:

\[(1.3) \quad H = -2 \sum J_{ij} S_{iz} S_{jz}\]

The Ising Hamiltonian is usually regarded as semi-classical, since though the spin operators involved commute, they can only take on the discrete values \(S_z = S, S-1, \ldots, -S\); but it may also arise in real systems with extreme anisotropic coupling\(^9\). The Ising Hamiltonian is typically much easier to solve than the Heisenberg Hamiltonian since it involves scalar, rather than vector, addition of spins. For example, Ising's original paper
contained an exact expression for the zero-field susceptibility of an infinite linear chain of magnetically coupled $S=1/2$ atoms whereas no corresponding solution for the Heisenberg Hamiltonian has yet been obtained.

Despite its limitations as a quantum mechanical model of magnetic interactions, the Ising Hamiltonian has received a large amount of attention, particularly as a model for phase transitions in magnetic lattices; results for the parallel and perpendicular susceptibilities of a variety of infinite 2- and 3-dimensional Ising lattices have been obtained. The mathematical techniques and approximations used in the discussion of infinite lattice systems are often extremely sophisticated but it is clear that neither the Ising nor the Heisenberg model is completely satisfactory. Good experimental examples of Ising lattices are rare, while Heisenberg's theory, though it explains the quantum mechanical origins of, for instance, the Weiss molecular field, suffers from serious defects when applied to infinite lattices, particularly with regard to the neglect of anisotropic contributions to the magnetic exchange which become important near the transition temperature. Phenomena such as hysteresis and domain formation cannot be modelled using the spin Hamiltonian approach.

Magnetic systems involving discrete clusters rather than infinite lattices have been modelled by both Ising and Heisenberg Hamiltonians, but it is now generally accepted that the Heisenberg Hamiltonian is more appropriate, both
because it can be derived in a theoretically satisfactory way and because it gives better fits to experimental data. Mixed, anisotropic Hamiltonians of the form:

\[ H = -2 \sum_{ij} J_{ij} [S_i^z S_j^z + \gamma(S_i^x S_j^x + S_i^y S_j^y)] \]

where \( \gamma=0 \) gives Ising and \( \gamma=1 \) gives Heisenberg exchange, have also been considered\(^\text{15-16} \); anisotropy may arise in the derivation of the spin Hamiltonian when spin-orbit coupling terms are included or when the interacting atoms are nearly orbitally degenerate.

Using Heisenberg's approach, the coupling between two electrons is represented by a scalar, while in equation (1.4) the coupling is represented by a second rank tensor. Moriya\(^\text{17} \) showed that under certain circumstances, the coupling between interacting ions with degenerate or nearly degenerate ground states should be represented by a second rank tensor including off-diagonal antisymmetric elements which tend to cause a perpendicular, rather than parallel or antiparallel, orientation of the interacting spins. The weak ferromagnetism of \( \alpha-Fe_2O_3 \) was shown to be caused by antisymmetric exchange. Antisymmetric contributions to the exchange coupling must vanish if the midpoint between a pair of coupled atoms is a centre of symmetry, as, for example, in infinite linear systems.

### 1.1.2 Introduction to Cluster Magnetochemistry

Until 1960 almost all research into magnetic phenomena was concerned with either the prediction of the properties of
magnetically isolated (paramagnetic) ions using crystal or ligand field theory\textsuperscript{18,19}, or the calculation of the properties of extended lattices of mutually interacting magnetic atoms, usually using the Ising model introduced above. Since 1960 the number of systems involving discrete clusters of magnetic ions has grown enormously. The study of these systems, and also the linear chains characteristic of copper and some other metals has become an important branch of magnetochemistry.

The first evidence for discrete clusters of magnetically interacting ions was obtained by Kambe\textsuperscript{20} in 1950, for iron and chromium carboxylate systems and Bleaney and Bowers\textsuperscript{21} for copper acetate in 1952. In both cases consideration of the magnetic properties led to predictions of the structures; copper acetate was expected to be dimeric, and the iron and chromium systems, trimeric. These predictions were later shown, by X-ray crystallography\textsuperscript{22,23}, to be correct. Many more dimer systems were discovered in the 1950s and 60s\textsuperscript{24-27}; most were found to be adequately described by the simple Heisenberg Hamiltonian. The principal interest with the dimer systems has been the determination of the exchange mechanism, the precise pathway along which the orbital interactions causing spin alignment are transmitted. It was found that interactions involving the ligands bridging between the metal atoms, known as superexchange, rather than direct metal-metal interactions, are usually dominant\textsuperscript{28-29}. Magnetic exchange systems became important to coordination chemists, who were able to investigate empirically the variation in the exchange constant, $J$, with bond
lengths and angles.

In the 1960s systems involving infinite chains of exchange coupled metal atoms (usually copper) were produced. Bonner and Fisher's calculation of the susceptibility of the $S=1/2$ chain by numerical extrapolation from computed results for finite chains, and Fisher's exact solution for the case of infinite spin, provided a theoretical basis for discussion of the results. Like discrete clusters, infinite chains with finite range interactions cannot undergo magnetic ordering above $T=0$; thus they can be usefully discussed with clusters, rather than with the 2- and 3-dimensional lattice systems.

Apart from the trimers discussed by Kambe, comparatively few systems involving clusters of three or more atoms were known until the mid 60's, when several three and four atom clusters were synthesised. Development of cluster chemistry has continued and now there are many clusters of three to six atoms, involving equilateral and isosceles triangle, rhombus, tetrahedral, octahedral, and possibly trigonal bipyramidal configurations of metal ions.

Cluster systems are of particular interest because the use of the molecular approximation in solids which contain discrete clusters allows a detailed study of the modulation of exchange interactions by vibrations. There are many biologically important clusters and small cluster like aggregations of atoms are thought to be be important in heterogenous catalysis.
When discussing magnetic clusters it is usual to assume:

(i) Isotropic exchange within the cluster.
(ii) Intercluster exchange is negligible.
(iii) All coupling constants involved are equal.

The assumption of isotropic coupling is discussed in detail with the derivation of the Heisenberg Hamiltonian in 1.4. Unless intercluster chemical bonds are involved, exchange interactions between clusters are expected to be negligible at all but the lowest temperatures\(^6\). Direct magnetic dipole/dipole interactions are expected to be even smaller; an order of magnitude calculation of the dipole/dipole interactions between clusters is given section 1.4. The assumption of equivalent coupling constants is usually made to avoid the introduction of an excessively large number of parameters when fitting experimental data; direct structural evidence often suggests that the interacting atoms are equivalent.

For many clusters\(^3\)\(^6\)\(^37\) no explanation of the magnetic susceptibility data is possible unless one of the above assumptions is removed. Removal of assumption (i) gives rise to anisotropic or antisymmetric Hamiltonians. Anisotropic Hamiltonians have been used extensively for systems involving chains of copper ions\(^4\)\(^7\)-\(^4\)\(^8\); a theory for Co(II) and Cu(II) clusters involving antisymmetric exchange has been derived by Lines\(^4\)\(^9\)-\(^4\)\(^50\) and applied with some success\(^5\)\(^1\) to clusters of the type Cu\(_n\)OX\(_n\)L\(_n\). Low temperature (<10K) magnetic data sometimes suggest that, when the individual clusters have a magnetic
ground state, very small intercluster interactions may have a significant effect on the magnetic properties. In such cases the intercluster interaction is usually added to the Hamiltonian as a small, molecular field type, perturbation. Interactions presumably extend throughout the crystal lattice and it is surprising that more evidence of phase transitions expected for such interactions has not been found. Although not entirely neglected, the case of non-equivalent coupling constants within the cluster has received comparatively little attention, particularly with regard to non-equivalence caused by dynamic distortions in high symmetry clusters.

1.2 Outline of the Thesis

Most of this work is concerned with effects of dynamic distortions that lower the symmetry of clusters containing up to 6 metal atoms with spins, $S$, of $1/2$ to $5/2$. Two key assumptions are made:

1) That magnetic exchange is adequately described by an intracluster, isotropic (Heisenberg) exchange Hamiltonian.

2) That the coupling constant between each pair of atoms is linear in small changes in the configuration of the cluster.

Assumption 1) is conventional, at least as a first approximation; it is discussed with the derivation of the Heisenberg Hamiltonian given in 1.4. Assumption 2) involves a
two-term Taylor expansion of the coupling, $J_{ij}$, in the distortion, $d_{ij}$, i.e.

$$J_{ij}(d_{ij}) = J_{ij}(0) + d_{ij}\frac{\partial J_{ij}}{\partial d_{ij}}.$$  

In Chapter 2 methods of solution of the Heisenberg Hamiltonian for clusters are discussed. Solution of the Hamiltonian by matrix methods is limited only by the amount of computer time and memory available, but it gives little physical insight if dynamic effects are occurring. A method which involves group theory is shown to be effective even for clusters which exhibit distortion from high symmetry.

In the first part of Chapter 3 a mathematical formalism for describing distortions of clusters is introduced. Distortions are considered in a vector distortion space spanned by the vibrational normal modes; the spin Hamiltonian is considered to lie in a Hamiltonian space linearly related to the distortion space by (1.5). Clusters containing an equilateral triangle of metal ions are examined. It is found that rapid dynamic distortion, or fluxionality, is expected to occur and the system will behave magnetically rather like an isosceles triangle of coupled spins, though its mean configuration will be equilateral triangular. A similar approach can be applied to distortions in the equatorial plane of trigonal bipyramidal clusters.

The dynamic distortion model is extended to clusters containing tetrahedra of coupled spins in Chapter 4. Tetrahedral systems are significantly more difficult to treat than three
atom systems both because of the larger number of spin states and because the distortion space of the tetrahedron spans two irreducible representations. The treatment of fluxionality in tetrahedral systems is more complicated as under some circumstances eigenvalues may become equal for certain orientations of the distortion; this causes the corresponding states to become equivalent. The theoretical development of the dynamic distortion model is concluded with a discussion of the $S=1/2$ octahedron.

In Chapter 5 applications of the dynamic distortion model are discussed using experimental data from the literature. The tetranuclear copper clusters, $\text{Cu}_4\text{OX}_6\text{L}_4$, where $X$ is a halide and $L$ a Lewis base, are considered first; the dynamic distortion model is found to be superior to other models involving intercluster or antisymmetric exchange which have been proposed previously. $\text{M}_3\text{O}^{3-}\text{RCOO}_6^-$ clusters are then considered; it is found that, though the dynamic distortion model gives excellent fits to the magnetic data, the distortion may be caused by ordering of the solvent molecules rather than the magnetic interactions. Finally data for tetrametallic Fe(III) clusters are fitted using the intermediate quantum number approach.

Chapter 6 is devoted to 1-dimensional, linear chain, systems. The infinite chain problem has received an enormous amount of attention from both physicists and chemists, however, no analytic solutions for the thermal properties have been obtained and even the antiferromagnetic ground state energy is
known exactly only for $S=1/2$. The concept of intermediate quantum numbers, which is very useful for cluster systems, is used to develop an approximation to finite and, by extrapolation, infinite chains known as the 'odd/even' model. Though some interesting results are obtained the model is concluded to be less useful than was first hoped. The effect of dynamic distortions on linear chains is then discussed using numerical calculations on finite systems.

In Chapter 7 aspects of the dynamic distortion model such as the nature of the fluxionality, the origin of the distortion term in the Hamiltonian and the role of non-magnetic intercluster interactions, are discussed. It is found that concepts taken from solid state physics, such as coupling of clusters by lattice phonon modes and slowly fluctuating random strains, can be used to improve the physical interpretation of the model derived in Chapters 3 and 4.

The general conclusions of the thesis include:

1) Exchange coupling provides a driving force for distortion in high symmetry magnetic clusters.

2) Distortions caused by 1) can usefully be considered as vibrational/magnetic interactions; it might be expected that such interactions are important in clusters since both have energies $\approx 10-100\text{cm}^{-1}$.

3) Distortions within degenerate normal modes may have a dramatic effect on magnetic behavior. This is usually most
apparent for ferromagnetic clusters since in these systems
dynamic distortions may produce a low spin ground state causing
a rapid decrease in the magnetic moment at the lowest
temperatures.

1.3 The Measurement and Terminology of Magnetism

In magnetochemistry the most fundamental concept is that of
susceptibility, $\chi$. This is a measure of the susceptibility of
the substance to magnetisation induced by an applied field. $\chi$ is
defined by:

\begin{equation}
M = \chi H
\end{equation}

where $M$ is the magnetisation and $H$ is the applied field. In
general, $M$ and $H$ are not parallel, and $\chi$ is a second rank tensor
which can be found by magnetic measurements on a single crystal.

$M$ is defined by:

\begin{equation}
M = -\frac{\partial E}{\partial H}
\end{equation}

where $E$ is the energy of the sample. Thus $\chi$ can be measured by
determining the change in energy as a field is applied. This is
done by measuring the force between the sample and an
inhomogeneous magnetic field. If $\chi > 0$, the sample is attracted
to a magnetic field, if $\chi < 0$, it is repelled.

In general $\chi$ may be field dependent; in this case the zero
field susceptibility, i.e. the limit as the applied field tends
to zero, is usually taken. $\chi$ is usually at least approximately
field independent in systems of magnetochemical interest.
Susceptibility may be expressed per unit volume, per unit mass, or, most commonly, per mole, $\chi_M$.

\[(1.8) \quad \chi_M = \frac{-N}{H} \left( \frac{\partial E}{\partial H} \right)_0 \]

where $N$ is Avogadro's number.

**Paramagnetism**

A paramagnetic substance contains independent ions each associated with one or more unpaired electrons. It is attracted to an applied magnetic field. The simplest form of paramagnetism occurs when each atom can be represented by a single electronic state which does not mix with excited states when the field is applied. Let the electronic angular momentum associated with this state be $\mathbf{J}$, in general $\mathbf{J} = \mathbf{L} + \mathbf{S}$, the sum of the orbital and electron spin contributions. Let the applied field, $\mathbf{H}$, define the unique $z$-axis of the system. When $\mathbf{H} = 0$ all orientations of $\mathbf{J}$ have equal energy which can be taken as $E=0$. On application of the field:

\[(1.9) \quad E = -g\beta \mathbf{H} \cdot \mathbf{J} \]

where '$g$' is the gyromagnetic ratio and $\beta$ is the Bohr magneton, $\frac{e\hbar}{4\pi mc}$. The spin is now quantised such that $J_z = -J, -J+1, \ldots J$, i.e.

\[(1.10) \quad E = -g\beta \mathbf{H} J_z \quad \text{where} \quad \mathbf{H} = |\mathbf{H}| \]

The mean energy of the system, assuming thermal equilibrium is reached is:

\[(1.11) \quad \bar{E} = \frac{\sum E_i \exp(-E_i/kT)}{\sum \exp(-E_i/kT)} \]

\[M = \frac{\sum (\partial E_i/\partial H) \exp(-E_i/kT)}{\sum \exp(-E_i/kT)} \]
Assuming $g\beta HJ << kT$, the exponentials can be expanded using $\exp(-x) = 1 - x$, giving:

\[
\begin{align*}
(1.12) \quad M &= -\frac{g^2\beta^2 HJ(J+1)}{3kT} \\
\text{and} \quad \chi &= \frac{Ng^2\beta^2 J(J+1)}{3kT}
\end{align*}
\]

In this case the system obeys Curie's Law, $\chi T = \text{constant}$.

It is often convenient to discuss magnetic properties in terms of the effective magnetic moment $\mu$ defined by:

\[
\begin{align*}
(1.13) \quad \mu^2 &= \frac{(3k/N)(\chi T)}{} \\
&= 2.828^2(\chi T) \quad (\chi \text{ in c.g.s. units})
\end{align*}
\]

For the simple paramagnet described above $\mu^2 = g^2J(J+1)$ and is constant as the temperature varies. The units of $\mu$ are Bohr Magnetons, $\beta$. In many transition metal ions any orbital angular momentum associated with the electronic state is effectively 'quenched' by the non-spherically symmetric ligand field. This results in a moment given by the 'spin only' formula, $\mu^2 = g^2S(S+1)$. Deviations from Curie Law behavior can be caused by either the influence of excited states of the isolated atoms or by exchange interactions between the ions.

The systems containing isolated ions are considered using the general Van Vleck formula:

\[
\begin{align*}
(1.14) \quad \chi &= \sum \left( \frac{W_i^{(1)})^2}{kT} - 2W_i^{(1)} \right) \exp(-W_i^{(0)}/kT) \\
&\quad \sum \exp(-W_i^{(0)}/kT)
\end{align*}
\]

where the summation is over all states of the ion, $W = W^{(0)} + H W^{(1)} + H^2 W^{(2)}$, and $W^{(1)}$ etc. are found using perturbation
theory.

If only a single, non-degenerate state is occupied, departures from Curie Law behavior are entirely due to the second order Zeeman terms, $W^{(2)}$, also known as Van Vleck's high frequency terms, arising as the ground and excited states interact under the influence of the applied field. The effect of such terms is to add a constant additive term to $\chi$; the magnitude of this 'Temperature Independent Paramagnetism', or 'T.I.P', term can sometimes be estimated from spectroscopic data, and is usually small. If more than one orbital state is thermally occupied, the $W^{(1)}$ terms will be more complicated than they are for the simple paramagnet, and large deviations from Curie's law may be observed. Theoretical calculations for both the magnetic and spectroscopic properties of paramagnets as a function of various ligand field parameters have been made for all the transition metal electron configurations$^{58-59}$. Magnetic exchange systems can usually be described without resort such detailed ligand field calculations, presumably because the metal ions involved have such low local symmetry that orbital degeneracy or near degeneracy does not occur.

**Diamagnetism**

The interaction between an applied magnetic field and closed electron shells in which all spins are paired leads$^{60}$ to a small negative contribution to $\chi$. Standard diamagnetic corrections are usually applied to experimental data before interpretation and need not be considered further here.
Magnetically Concentrated, Dilute, and Condensed systems

It is conventional to refer to systems in which interactions between the ions carrying unpaired spin are important as magnetically concentrated. Those systems in which the ions can be described independently are known as magnetically dilute. In this work the distinction between systems in which there are interactions throughout an extended lattice, leading to a phase transition, and those in which the interactions are localised within small clusters is important. The former will be referred to as magnetically concentrated and the latter as magnetically condensed. Cooperative phenomena are impossible in linear chain systems which can therefore be considered to be condensed, rather than concentrated.

Antiferromagnetism and Ferromagnetism

In the physics literature the term 'ferromagnetism' is usually reserved for magnetically concentrated substances in which a spontaneous ordering of spins throughout the lattice occurs at a well defined temperature, the Curie point. At this point a phase transition associated with the ordering occurs. The definition of antiferromagnetism is similar except that two interpenetrating lattices of equal and opposite spin are involved. More complicated variants of ferro- and antiferromagnetism such as ferrimagnetism, which involves two opposing lattices of unequal spin, are also defined.

In magnetochemistry it is common to consider condensed,
rather than concentrated systems. Because of the lack of phase transitions and associated phenomena, rather weaker definitions of ferro- and antiferromagnetism are often used. A ferromagnetic substance is thus one for which $\mu(T)$ rises as the temperature falls, as a result of exchange interactions between the atoms. Condensed systems with an extremum in $\mu(T)$ thus exhibit ferromagnetic behavior at some temperatures, and antiferromagnetic behavior at others. The difference in terminology is well illustrated by the linear chains; in the magnetochemistry literature such chains are often described as (anti)ferromagnetic though (anti)ferromagnetism in the 'physics' sense is impossible for 1-D systems, whatever the form of the coupling. Since this work is largely concerned with condensed systems the magnetochemistry definition will be used.

In both physics and chemistry interactions characterised by $J > 0$ are described as ferromagnetic, and those with $J < 0$ as antiferromagnetic.

1.4 Derivation of the Heisenberg Hamiltonian

The Heisenberg Hamiltonian (1.1) was extended to many-electron systems by Dirac and applied to ferromagnets by Heisenberg in 1928. In the derivation given below the approximations involved in the spin Hamiltonian approach are stressed. Since the two-electron case usually considered in the derivation is rather a special case, in that the orbital and spin parts of the wavefunction are separable, the three-electron system is also considered in some detail.
1.4.1 The two-electron system

Consider a system with two electrons; assume the electrons are localised on different atoms. The Hamiltonian for the system can be written:

\[(1.15) \quad H = H_1 + H_2 + V\]

where \(H_1\) is the Hamiltonian for atom 1, \(H_2\) is the Hamiltonian for atom 2, and \(V\) represents a small interaction between the atoms. The solutions of \(H_1\) lie in a (Hilbert) space \(1H_1\), those of \(H_2\) lie in \(1H_2\), solutions of \(H\) lie in the direct product space, \(1H = 1H_1 \times 1H_2\), containing all linear combinations of products of states in \(1H_1\) with states in \(1H_2\).

(i) Assume that the ground states for atoms 1 and 2 (ignoring spin) are non-degenerate. Thus they can be represented, in Dirac's notation, by:

\[(1.16) \quad H_1^0|\Psi_1^0> = E_1^0|\Psi_1^0> ; \quad H_2^0|\Psi_2^0> = E_2^0|\Psi_2^0>\]

where \(|\Psi_i^j>\) is the \(j\)-th state above the ground state for atom 'i'.

(ii) Assume \(V\) does not contain the spin explicitly.

(iii) Assume \(|\Psi_1^0>\) and \(|\Psi_2^0>\), which are orthogonal if \(V = 0\), remain orthogonal when perturbed by \(V\), thus \(<\Psi_1^0|\Psi_2^0> = 0\).

Under these assumptions \(|\Psi_1^0\Psi_2^0>\) and \(|\Psi_2^0\Psi_1^0>\), where the first function refers to electron 1 and the second to electron 2, form an orthogonal basis in \(1H\) which is complete enough to allow an
accurate description of the low lying states, those derived from
the ground states of the atoms considered separately. In this
basis:

\[
H = \begin{bmatrix}
K & J \\
J & K
\end{bmatrix}
\]

where \( K = \langle \psi_1^0 \psi_2^0 | V | \psi_1^0 \psi_2^0 \rangle \), \( J = \langle \psi_1^0 \psi_2^0 | V | \psi_2^0 \psi_1^0 \rangle \), and the
energy of the system is defined as zero when \( V \) is zero. \( J \) arises
from the non-zero matrix element of \( V \) occurring when electrons 1
and 2 are interchanged or 'exchanged'. \( J \) is known as the
exchange parameter and the system is said to exhibit electronic
exchange. \( H \) has the solutions:

\[
\begin{align*}
|\Psi_+\rangle &= |\psi_1^0 \psi_2^0 \rangle + |\psi_2^0 \psi_1^0 \rangle, \text{ Energy } = K+J; \\
|\Psi_-\rangle &= |\psi_1^0 \psi_2^0 \rangle - |\psi_2^0 \psi_1^0 \rangle, \text{ Energy } = K-J.
\end{align*}
\]

Before inclusion of the intrinsic spin of the electron,
\(|\Psi_+\rangle\) is symmetric with respect to the exchange of electrons 1
and 2, while \(|\Psi_-\rangle\) is antisymmetric. But the electrons are
indistinguishable fermions and so the total electronic
wavefunction for the system must be antisymmetric with respect
to exchange of any pair of them (the Pauli Exclusion Principle).
For the particular case of two electrons the spin and orbital
functions are separable, i.e. the spin functions:

\[
\psi_+ = \{aa, a\beta + \beta a, \beta \beta\}, \text{ are symmetric}
\]

while \( \psi_- = (a\beta - \beta a) \) is antisymmetric

thus both eigenfunctions of \( H \) lead to acceptable wavefunctions.
\begin{align*}
(1.20) \quad & |\Phi_1> = (|\Psi_1^0\Psi_2^0> + |\Psi_2^0\Psi_1^0>)(a\beta - \beta a) \quad \text{Energy} = K + J; \\
& |\Phi_2> = (|\Psi_1^0\Psi_2^0> - |\Psi_2^0\Psi_1^0>\{\alpha a, \alpha \beta + \beta a, \beta \beta\} \quad \text{K - J}.
\end{align*}

But, defining $S' = (S_1 + S_2)$; $S'^2|\Phi_1> = 0$ and $S'^2|\Phi_2> = 2|\Phi_2>$; $|\Phi_1>$ is associated with spin 0, and $|\Phi_2>$ with spin 1. Thus $V$ can be represented by an equivalent Hamiltonian involving only the electron spin:

\begin{equation}
(1.21) \quad V = K - 2J \ S_1.S_2 - J/2
\end{equation}

The $K$ and $J/2$ terms are constants which can be omitted unless absolute energies are required.

Before considering the three-electron system, one very useful property of the Heisenberg Hamiltonian will be noted. Since $V$ does not contain the electron spin, it must commute with $S'^2$, therefore the eigenfunctions of $H$ must be eigenfunctions of $S'^2$ as long as those of $H_1$ and $H_2$ are, i.e. as long as spin-orbit coupling can be neglected. Similarly the energy of the eigenfunctions cannot depend on the orientation of the total spin, thus the operators $S'_+$ and $S'_-$ applied to a solution of $H$ can only result in states of the same energy. Each solution of $H$ is $(2S'+1)$ degenerate by the orientation of the total spin. One important consequence of this result is that all the eigenvalues of the Heisenberg Hamiltonian can be found by solving in a basis of states having the minimum $z$ component of the total spin, $S'_z$. 
1.4.2 The three-electron system

The two electron system is rather a special case in that all solutions of $H$ in orbital space can be combined with spin functions to produce antisymmetric wavefunctions, thus no solutions of the orbital Hamiltonian are excluded by the requirement that the total wavefunction is antisymmetric. This is not the case for the three-electron system, which can also be used to illustrate the extra approximations needed to extend the Heisenberg Hamiltonian to atoms with spin > 1/2.

Using the same approximations as for $n=2$, an $n!$ dimension subspace of $1H = 1H_1 \cdots 1H_n$ is sufficient to describe the low energy states arising from the interactions of $n$ electrons. Thus for $n=3$, using $'|123>'$ as an abbreviation for $|\psi^0_1(1)\psi^0_2(2)\psi^0_3(3)>$, the basis is:

\[(1.22) \quad \{|123>,|231>,|312>,|213>,|132>,|321>\}\]

Define $J_{12} = <123|V|213>$, $J_{13} = <123|V|321>$, $J_{23} = <123|V|132>$ and $K = <123|V|123>$, terms of the form $<123|V|231>$ can be ignored if orbital overlap is small. The Hamiltonian is:

\[(1.23) \quad H = \begin{bmatrix}
K & 0 & 0 & J_{12} & J_{23} & J_{13} \\
0 & K & 0 & J_{13} & J_{12} & J_{23} \\
0 & 0 & K & J_{23} & J_{13} & J_{12} \\
J_{12} & J_{13} & J_{23} & K & 0 & 0 \\
J_{23} & J_{12} & J_{13} & 0 & K & 0 \\
J_{13} & J_{23} & J_{12} & 0 & 0 & K \\
\end{bmatrix}\]
Though $H$ has 6 eigenfunctions, there are, apart from trivial operations of $S'_+$ and $S'_-$, only three functions which can be correctly antisymmetrised, even when the electron spin is included. The problem is most efficiently solved by defining a basis, including spin, of antisymmetrised functions and reexpressing $H$ in this new basis. Using the antisymmetrizer, $A$, defined by:

$$A = \sqrt{(1/n!)} \sum (-1)^{\chi(P)} P$$

where the $P$ are the permutations of the permutation group $P_n$, the functions: $\Phi_1 = A(123)(aa\beta)$, $\Phi_2 = A(123)(\alpha\beta a)$, and $\Phi_3 = A(123)(\beta aa)$ form an orthogonal basis for solutions of $H$ which satisfy the Exclusion Principle. Explicitly:

$$\Phi_1 = (1a2a3\beta+2a3\beta1a+3\beta1a2a-2a1a3\beta-1a3\beta2a-3\beta2a1a)$$
$$\Phi_2 = (1a2\beta3a+2\beta3a1a+3a1a2\beta-2\beta1a3a-1a3a2\beta-3a2\beta1a)$$
$$\Phi_3 = (1\beta2a3a+2a3a1\beta+3a1\beta2a-2a1\beta3a-1\beta3a2a-3a2a1\beta)$$

in this new basis:

$$H = \begin{pmatrix}
K-J_{12} & -J_{23} & -J_{13} \\
-J_{23} & K-J_{13} & -J_{12} \\
-J_{13} & -J_{12} & K-J_{23}
\end{pmatrix}$$

Apart from the constant $K-(J_{12}+J_{13}+J_{23})/2$, which can be ignored unless absolute energies are required, this is identical to the matrix obtained by applying:

$$H = -2J_{12}S_1 \cdot S_2 - 2J_{13}S_1 \cdot S_3 - 2J_{23}S_2 \cdot S_3$$

to the basis $\{aa\beta, a\beta a, \beta aa\}$ and ignoring orbital and
antisymmetrisation considerations. In this sense the spin Hamiltonian (1.27) is equivalent to the real Hamiltonian for the system.

In the derivation given here it has been assumed for clarity that the electrons are localised on different atoms. This is not essential and the results above also apply to coupling between electrons on the same atom. In this case $H_1$ and $H_2$ can be considered as the central field potentials, while $V$ is the interelectron repulsion term. Hund's first rule, that the ground state of an atom with unpaired electrons is the state of maximum multiplicity, is equivalent to the statement that coupling constants between electrons on the same atom are always large and positive.

The extension of the Heisenberg Hamiltonian to ions with $S > 1/2$ may be illustrated using the 3 atom system described above. Consider the case of two electrons on atom 1 and one electron on atom 2, let the orbitals of atom 1 be $\Psi_1$ and $\Psi_3$ and the orbital on atom 2 be $\Psi_2$. The eigenvalues of (1.27) for general $J_{12}, J_{13}, J_{23}$, are:

\[
(1.28) \quad K - J_{12} - J_{13} - J_{23}
\]

\[
K \pm \sqrt{(J_{12}^2 + J_{13}^2 + J_{23}^2 - J_{12}J_{13} - J_{13}J_{23} - J_{23}J_{12})}
\]

Define $J = (J_{12} + J_{23})/2$; since $J_{13} >> J_{12}$ and $J_{23}$, the square root can be approximated, using the binominal expansion, by $J_{13} - J$. This result is exact if $J_{12} = J_{23}$, for all $J_{13}$, in which case the solutions of $H$ are:
\[(1.29) \quad \psi_1 = (1, 0, -1), \quad \text{Energy} = K + J_{13} - J \]
\[\psi_2 = (1, -2, 1), \quad \text{Energy} = K + J - J_{13} \]
\[\psi_3 = (1, 1, 1), \quad \text{Energy} = K - 2J - J_{13} \]

In both cases, \(\psi_1\) will be of very high energy and can be ignored when considering thermal properties, the system can be represented by two states, that with \(S' = 3/2\) lying \(3J\) above that with \(S' = 1/2\). This result is equivalent to that for the Hamiltonian:

\[(1.30) \quad H = -2J \vec{S} \cdot \vec{S}_2 \text{ where } \vec{S} = \vec{S}_1 + \vec{S}_3, \quad J = (J_{12} + J_{23})/2 \]

describing coupling between a spin 1/2 atom and a spin 1 atom. The high spin Hamiltonian is valid as long as the coupling between electrons on the same atom is much larger than that between electrons on different atoms or as long as all couplings between electrons on a given atom and electrons on another atom are equivalent.

Dirac's approach

By considering the effect of the operators on the basis \{\(|aa>, |a\beta>, |\beta a>, |\beta\beta>\)\} it can be seen that the operators
\[-2J_{12} \vec{S}_1 \cdot \vec{S}_2 \text{ and } (-J_{12}/2)(2P_{12} - 1), \]
where \(P_{12}\) permutes the labels on electrons 1 and 2, are equivalent. Dirac\textsuperscript{65} used this property to show that the Heisenberg Hamiltonian could be extended to a many electron system using (1.2). The Dirac formulation highlights the connection between the coupling operator and permutations of electrons; it is useful when considering the group theoretical methods of solution of the Hamiltonian which
are introduced in Chapter 2.

1.4.3 The Heisenberg-Dirac-VanVleck Model

The Heisenberg Hamiltonian results in a spectrum of magnetic states each of which is an eigenfunction of $S'^2$. In this thesis the corresponding set of eigenvalues will be referred to as the 'magnetic spectrum'. The susceptibility of the system, per atom, is given by applying the formula derived above for the simple paramagnet to each of these states, with the appropriate thermal weighting:

\[
\chi = \frac{(N\beta^2 g^2 / 3nkT) \sum S'(S'+1)(2S'+1)\Omega(S') \exp(-E/kT)}{\sum (2S'+1)\Omega(S') \exp(-E/kT)}
\]

The summation is over all solutions of the spin Hamiltonian. The factor $(2S'+1)$ arises since each state of total spin $S'$ has $(2S'+1)$ degeneracy associated with different values of $S'^z$. A system with non-trivial symmetry may have additional degeneracy; this is represented in the above formula by an $\Omega(S') > 1$. All the assumptions arising in the definition of the Heisenberg model, and the derivation of $\chi$ for the simple paramagnet, apply to (31) which is known as the Heisenberg-Dirac-Van Vleck (HDVV) model. The limitations arising from these assumptions will now be discussed.

1.4.4 Limitations of the HDVV Model

1) The representation of the interacting ions. In the HDVV model the interacting ions are represented by single,
non-degenerate states with an associated spin of maximum multiplicity. In real systems, states other than the ground state may have a significant effect on the exchange. It is useful to consider the cases of orbitally degenerate and orbitally non-degenerate ground states separately.

For systems with an orbitally non-degenerate ground state the principle modifications to the HDVV model occur as a result of spin-orbit coupling and temperature independent paramagnetism. Since T.I.P. is small and constant it can be allowed for by a simple correction to $\chi$; the effects of spin-orbit coupling are more complex, and anisotropic and antisymmetric terms are introduced into the spin Hamiltonian. Order of magnitude calculations on both effects suggest that the $2S' + 1$ degeneracy of the Heisenberg spin states is split by an amount of the order of $(\Delta g/g)^2 J$, where $\Delta g$ is the difference between $g$ and its free electron value of 2.0. Since $\Delta g/g$ is rarely larger than 0.1, orbitally non-degenerate clusters with $J \approx 100 \text{cm}^{-1}$ are not expected to show significant departures from isotropic coupling at temperatures above 1-2K.

For orbitally degenerate or nearly degenerate clusters the situation is considerably more complicated. Thus for a two electron, two atom system in which one atom has a (nearly) degenerate ground state, an enlarged basis of the form:

$$\{|\Psi_1^0\Psi_2^0>, |\Psi_1^1\Psi_2^0>, |\Psi_2^0\Psi_1^0>, |\Psi_2^0\Psi_1^1>\}$$

must be considered. In general there is no reason to suppose that matrix elements such as:
<\psi_1^0\psi_2^0|V|\psi_2^0\psi_1^0> \text{ and } <\psi_1^1\psi_2^0|V|\psi_2^0\psi_1^1>

are equal, and new parameters are introduced. In terms of the spin Hamiltonian, anisotropic and antisymmetric contributions to the exchange may be large and the Heisenberg model may become completely inappropriate. Fortunately, orbital degeneracy is expected to be very rare in clusters, both because the ions in clusters rarely exist in such high symmetry configurations as paramagnetic ions and because of Jahn-Teller effects both within and between the interacting ligand fields. An introduction to JT instability in magnetic clusters is given in the following paragraphs, the discussion is continued in Chapter 3.

The Jahn-Teller theorem\textsuperscript{67} states that any non-linear molecule in an orbitally degenerate electronic state is unstable with respect to distortions which lower the symmetry and remove the degeneracy. The theorem was later extended\textsuperscript{68} to include spin degeneracy (except Kramers degeneracy), with the proviso that any instability caused by spin was expected to be small. The theorem was derived with dilute paramagnets in mind, but may equally well be applied to clusters. Consider a high-symmetry cluster; whatever the precise exchange Hamiltonian, the magnetic spectrum will frequently contain degeneracy associated with the symmetry, which may be removed by small distortions affecting the coupling. This is most easily illustrated by considering a Heisenberg cluster for which the magnetic spectrum contains degeneracy in addition to the \(2S'+1\) degeneracy associated with the orientation of the total spin. Though the Heisenberg Hamiltonian is a spin Hamiltonian, the
real Hamiltonian for the system results from orbital interactions and so the 'strong', orbital Jahn-Teller theorem applies. Distortions which reduce the symmetry and resolve the degeneracy will lower the energy of the cluster. The $2S'+1$ degeneracy associated with isotropic coupling is genuine spin degeneracy, and though it will, in principle, be reduced to Kramers doublets by spin/spin interactions, the effect is unlikely to be significant.

In the Jahn-Teller theorem linear molecules are shown to be exceptional in that they may be stable in an orbitally degenerate state. Magnetic linear chains may, under some circumstances, be similarly resistant to distortion. Also, Heisenberg open chain magnetic spectra are non-degenerate if all coupling constants are equal. Because of these complications, linear chains are considered separately in this thesis, in Chapter 6.

The other approximations inherent in the HDVV model are of relatively minor significance when applied to clusters.

2). The neglect of orbital overlap. Any interaction between orbitals must result in a loss of orthogonality. Some authors, notably Slater, have held that neglect of overlap, and hence multiple exchange terms, undermines the usefulness of the Heisenberg Hamiltonian for magnetic problems. Several later authors disagree. While overlap terms may necessitate modifications if the Hamiltonian is to be applied to infinite systems, for small clusters inclusion of orbital overlap only
causes a second order modification in J, e.g. for two-electron systems, defining \( S = \langle \Psi_1^0 | \Psi_2^0 \rangle \), the energies become:

\[
E = \frac{K \pm J}{1 \pm S^2}
\]

(1.32)

The energy difference is now \( 2(J + KS^2)/(1-S^4) \), rather than \( 2J \), but since \( S'^2 \) remains a good quantum number, the Heisenberg formalism remains intact.

3) \( V \) does not contain spin. Direct spin/spin interactions or molecular field effects introduce additional terms into the Hamiltonian; internal molecular fields cannot occur in clusters, while any direct magnetic interactions are expected to be negligible (this was the original difficulty in the classical theory of ferromagnetism). As an order of magnitude calculation for such direct magnetic forces between clusters consider two unpaired electrons 10Å apart; classically, their mutual potential energy is:

\[
E = -\frac{\mu_1 \mu_2}{r^3} - 3(\mu_1 \cdot \mathbf{r})(\mu_2 \cdot \mathbf{r})/r^5
\]

(1.33)

Taking the first term and using S.I units,

\[
E = -\frac{\mu_0 (\mu_e)^2}{4\pi r^3}
= -\left(\frac{4\pi \cdot 10^{-7}}{4\pi \cdot 10^{-27}}\right)(0.927 \cdot 10^{-23})^2
= 10^{-23} \text{ J} = 10^{-3} \text{ cm}^{-1}
\]

Thus the neglect of direct intercluster dipole/dipole forces is not significant compared to the other approximations involved in the derivation of the Hamiltonian.
4) The inequality $q \beta HS' \ll kT$. This inequality arises from the approximation $\exp(-x) \approx 1 - x$, used to derive the susceptibility of the simple paramagnet. It is expected to be valid for all clusters except for very low temperatures and high fields. However it does set another additional limit to the size of clusters with low-lying, high spin states which can be represented by the HDW model, as in such clusters $S'$ may be very large.

**Summary.** Most of the approximations associated with the derivation of the Heisenberg Hamiltonian are clearly valid for cluster systems. The approximation that the interacting atoms are well represented by a single non-degenerate state is generally considered to be least satisfactory. However it is reasonable to suggest that low ligand field symmetry caused by both the basic structure of clusters and by Jahn-Teller effects, both within and between the interacting ligand fields, should be sufficient to make anisotropic/antisymmetric terms negligible at temperatures of more than a few K. This suggestion is supported by the observation that almost all known clusters can be adequately modelled by the Heisenberg Hamiltonian. In this thesis it is shown that if the effect of dynamic distortion associated with Jahn-Teller instability is considered, the magnetic behavior of many clusters which have previously been considered exceptional can be explained in terms of isotropic exchange coupling.
CHAPTER 2 METHODS OF SOLUTION OF THE HEISENBERG HAMILTONIAN FOR CLUSTERS

2.1 Introduction

The Heisenberg Hamiltonian for clusters of exchange coupled ions:

\[ H = -2 \sum J_{ij} S_i \cdot S_j \]

where \( S_i \) and \( S_j \) are the total spins on the interacting ions, can be solved exactly by matrix diagonalisation, by the introduction of intermediate quantum numbers or by group theoretical methods. The latter two methods are most useful for exact calculations on high symmetry clusters, but they may be combined to give quite accurate approximations for some systems of lower symmetry by correlation between exactly solvable high symmetry configurations. The HDVV equation can be applied to the magnetic spectrum resulting from solution of the Hamiltonian to obtain theoretical predictions of \( \mu \) or \( \chi(T) \), which can then be fitted to experimental data.

The central problem when solving (2.1) for all but the smallest clusters is the large number of spin states involved. The number of states of a cluster of \( n \) atoms of spin \( S \) with total spin \( S' \), \( \Omega(n,S,S') \), is given algebraically by:

\[ \Omega(n,S,S') = \omega(n,S,S') - \omega(n,S,S' + 1) \]

where \( \omega(n,S,S') \) is the coefficient of \( x^{S'} \) in the expression:

\[ (x^S + x^{S-1} + \ldots + x^{-S-1} + x^{-S})^n \]
For $S=1/2$, the coefficients $\omega(n,1/2,S')$ are given by $\omega(n,1/2,S') = n!/[(n/2-S')!(n/2+S')!]$, but for $S>1/2$ no such simple expression can be derived and the $\Omega(n,S,S')$ are most easily found using a branching diagram. The branching diagram is constructed by an iterative procedure which is valid for all $S$; $\Omega(n,S,S')$ is obtained by summing those $\Omega(n-1,S,S'')$ for which $|S'-S''|\leq S$. The diagram is begun by placing '1' at $n=1$ $S'=S$. For $S=1/2$ the branching diagram is:

<table>
<thead>
<tr>
<th>S'</th>
<th>S</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/2</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>5/2</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>4/2</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>3/2</td>
<td>1</td>
<td>46</td>
</tr>
<tr>
<td>2/2</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>1/2</td>
<td>1</td>
<td>42</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>132</td>
</tr>
</tbody>
</table>

# levels 1 2 3 4 5 6 7 8 9 10 11 12
Branching diagrams for $S=1$ to $S=5/2$, up to $n=6$ are given in Table 2.1.
Table 2.1 Branching diagrams for clusters of up to 6 atoms

<table>
<thead>
<tr>
<th>n</th>
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<th>3 ; 4 ; 5 ; 6</th>
<th>S'</th>
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</tr>
<tr>
<td>total</td>
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</tbody>
</table>
2.2 Matrix Methods

The Hamiltonian (2.1) can always be expressed as a matrix using a basis spanning the total spin space of the problem. The set of all possible products of individual atom spin functions which are eigenfunctions of \(S_z\) forms such a basis, e.g. for \(n=3, S=\frac{1}{2}\):

\[
(2.4) \{aaa, aa\beta, a\beta a, \beta aa, \beta a\beta, \alpha a\beta, a\beta \beta, \beta \beta \beta\}
\]

These \((2S+1)^n\) states are eigenfunctions of the Ising Hamiltonian; they will be referred to as the Ising basis. (2.1) is real and symmetric in the Ising basis.

Since \(H\) commutes with the z-component of the total spin, the size of the matrix problem can be reduced by blocking by \(S_z\), i.e. by considering subsets of the Ising basis with different values of \(S_z\) separately. Thus the basis (2.4) can be separated into the blocks \{aaa\}, \{aa\beta, a\beta a, \beta aa\} \{\beta a\beta, a\beta \beta, \beta \beta \beta\}. All eigenvalues of states of \(S_z \geq |S_z'|\) are obtained by solving an \(S_z\) block; by comparing the solutions of each block, the spin associated with each eigenvalue can be found without direct manipulation of the eigenvector. This is useful since it is very much more difficult to find and manipulate the eigenvectors of large matrices than to find just the eigenvalues.

The matrix elements are evaluated by expressing the coupling as:

\[
(2.5) \quad S_i \cdot S_j = S_{iz}S_{jz} + \frac{1}{2} (S_i+S_j-+S_i+S_j-)
\]
where \( S_+ \) and \( S_- \) are shift operators obeying the usual rules for angular momenta. The matrix, \( H \), is a function of the set of \( n(n-1)/2 \) coupling constants \( \{J\} \); the problem can sometimes be further simplified by the use of symmetry in \( \{J\} \).

As well as being used directly to model real magnetic clusters, matrix methods have been used to obtain results for the thermal and ground state properties of infinite systems by extrapolation. This has been most successful for the 1-D, \( S=1/2 \) system, for which Bonner and Fisher were able to obtain accurate expressions for \( \chi(T) \), as well as other properties, as long ago as 1964\(^3\). For \( S>1/2 \) and for 2- and 3-D systems, extrapolation is less useful as the size of the matrix problem prohibits the calculation of a sufficient number of terms. Numerical extrapolations are discussed in more detail in Chapter 6.

Even when applied to small clusters, the size of the matrix problem may make solution impossible. Thus, for \( S=5/2, n=5 \), there are 780 \( S'=1/2 \) basis states and the 780x780 matrix can be diagonalised fairly cheaply. Addition of one more atom increases the matrix size to 4332, and solution is no longer practicable. Even for lower spin clusters any application of matrix techniques in fitting experimental data, requiring large numbers of attempted fits, may be prohibitively expensive. There are also more fundamental objections to the direct matrix approach. Firstly, the set \( \{J\} \) involves too many parameters in all but the smallest clusters and frequently gives rise to ambiguity when experimental data are fitted, in some small \( S=1/2 \) systems it can
be shown that any attempts to define \( \{J\} \) from the magnetic spectrum (and therefore from magnetic susceptibility data) must, in principle, result in ambiguity. Secondly, it is difficult to take into account the effects of changes in \( \{J\} \) caused by dynamic distortions using matrix methods; it is shown in this thesis that the assumption that \( \{J\} \) is constant over time is not justified.

Despite these objections matrix methods have been used, with considerable success, to test hypotheses concerning the structure of magnetic clusters\(^7\)\(^3\)-\(^7\)\(^5\); Hatfield\(^7\)\(^6\) has written a computer program which calculates the magnetic properties of clusters of \( S=1/2 \) ions for all \( \{J\} \), and for all applied fields. I have written a similar program which is useful for general spin as well as general \( \{J\} \), but which only gives zero field magnetic properties; the program uses a standard library subroutine for the matrix diagonalisation. These programs are limited only by time and memory constraints, however these are quite severe for clusters of high spin atoms; practical limits are \( S=1/2, N=12; S=1, n=8; S=3/2 n=6; S=2,5/2, n=5. \) In each case the solution for the largest value of \( n \) given takes of the order of five minutes of CPU time on the Amdahl V8 computer at U.B.C. Experiments with the cluster solving program have provided much of the impetus for the studies of the role of structural distortions on the magnetic properties of clusters described in this thesis.
2.3 The Intermediate Spin Approach and Factorisation

In 1950 Kambe showed that the magnetic behavior of several iron and chromium compounds was consistent with the hypothesis that the compounds contained clusters of three metallic ions in an isosceles triangle configuration. The Hamiltonian for such a system is:

\[ H = -2J (S_1 \cdot S_2 + S_2 \cdot S_3) - 2J' S_1 \cdot S_3 \]

Kambe showed that \( H \) can be solved, without resort to matrix methods, by the introduction of the intermediate quantum number \( S'' = (S_1 + S_3) \), so that \( H \) can be expressed:

\[ H = -JS''^2 - (J'-J)S''^2 + (J+2J')S^2 \]

This formulation is useful because \( S''^2 \) commutes with \( H \), \( S'' \) is a 'good quantum number', and the eigenfunctions of \( H \) can be expressed, in Dirac's notation, by \( \text{kets} |S'S'> \), of energy found from:

\[ S''^2 |S'S'> = S''(S''+1) |S'S'> \]
\[ S''^2 |S'S'> = S''(S''+1) |S'S'> \]

Not all Hamiltonians which can be expressed in terms of intermediate spins can be solved in this way. Thus expression of:

\[ H = -2J (S_1 \cdot S_2 - S_2 \cdot S_3) \]

as \( H = -J(S''^2 - S'''^2 - S^2) \), where \( S'' = S_1 + S_2 - S_3 \), \( S''' = S_1 - S_3 \).

though correct, is not helpful since \([S''^2, S'''^2] \neq 0\). It is now necessary to consider more precisely the conditions under which
intermediate spins may usefully be introduced. This involves consideration of the commutation relations for the terms in the Heisenberg Hamiltonian.

2.3.1 Commutation relations and intermediate spins

Consider the commutator between two terms of the Heisenberg Hamiltonian, \([S_i \cdot S_j, S_k \cdot S_l]\), where \(i \neq j\) and \(k \neq l\). The commutator is clearly zero unless \(i\) or \(j\) equals \(k\) or \(l\). Without loss of generality, assume \(i = 1\), and write:

\[
(2.10) \quad [S_i \cdot S_j, S_k \cdot S_l] = [S_{i\alpha} S_{j\beta}, S_{k\alpha} S_{l\beta}]
\]

where \(\alpha\) and \(\beta\) are dummy subscripts describing the three components of the spins and using the summation convention that if a subscript occurs exactly twice it is summed over. In atomic units (\(\hbar = 1\)) the commutator for spins on the same atom is, \(S_{i\alpha} S_{i\beta} = \delta_{\alpha\beta} i S_i\), where \(\delta_{\alpha\beta}\) is the antisymmetric tensor, thus:

\[
(2.11) \quad [S_{i\alpha} S_{i\beta}, S_{j\gamma} S_{k\delta}] = i \delta_{\alpha\beta} S_{i\gamma} S_{j\delta} S_{k\delta} = i S_i (S_j \times S_k)
\]

by definition of the vector product. For general \(i,j,k,l\) the expression is:

\[
(2.12) \quad [S_i \cdot S_j, S_k \cdot S_l] = \\
i \{(\delta_{il} - \delta_{ik}) S_j \cdot (S_k \times S_l) + (\delta_{jl} - \delta_{jk}) S_i \cdot (S_k \times S_l)\}
\]

The result (2.12) can be used to prove formally that \([H, S_i^2] = 0\). Consider the commutator of a single term in \(H, S_k \cdot S_1\), with \(S_i^2\):
Ignoring the trivial constant, $nS^2$, the commutator is:

$$[S_i S_j, S_k S_l] = 2i \sum_{i \neq j} (\delta_{ik} - \delta_{il}) S_k (S_j S_l)$$

but $\sum (\delta_{ik} - \delta_{il}) = 0$ since $i=k$ and $i=l$ exactly once in each summation over $i$. Thus $S'^2$ commutes with each term, and therefore with the total Heisenberg Hamiltonian.

Now consider the conditions for $[H, S''^2] = 0$, where $S''$ is some spin other than the total spin. Let the system contain $n$ spins, the first $m$ of which contribute to $S''$ i.e.

$$S' = \sum_{i=1}^{n} S_i, \quad S'' = \sum_{i=1}^{m} S_i$$

Consider $[H, S''^2]$; $H$ can be expressed as:

$$H = - \left( \sum_{i \neq j=1}^{m} J_{ij} S_i S_j + 2 \sum_{i=1}^{m} \sum_{j=m+1}^{n} J_{ij} S_i S_j + \sum_{i \neq j=m+1}^{n} J_{ij} S_i S_j \right)$$

$S''^2$ commutes with the first term of $H$ since that term describes a spin system with total spin $S''$. It also commutes with the third term since there are no spins in common. Consider a single term of $S''^2$, say $S_a S_b$, $(1 \leq a \leq m, 1 \leq b \leq m)$:

$$[H, S_a S_b] = -2 \left[ \sum_{i=1}^{m} \sum_{j=m+1}^{n} J_{ij} S_i S_j, S_a S_b \right]$$

$$= -2i \sum_{i=1}^{m} \sum_{j=m+1}^{n} J_{ij} \left( (\delta_{ib} - \delta_{ia}) S_j (S_a S_b) + (\delta_{ja} - \delta_{ib}) S_i (S_a S_b) \right)$$

The second term is zero, since $a, b \leq m < j$, so:
\[(2.18) \ [H, S_a \cdot S_b] = -2i \sum_{j=m+1}^{n} (J_{bj} - J_{aj}) S_j \cdot (S_a \wedge S_b) \]

For \([H, S''^2] = 0\), (2.18) must vanish for all \(a, b\). Since vector addition is involved, each term in each sum over \(j\) must be zero. Thus \(S''^2\) commutes with \(H\) only if the couplings from every spin in \(S''\) to a particular spin not in \(S''\) are equal, for all spins not in \(S''\). In this work a Hamiltonian which can usefully be simplified by the introduction of intermediate quantum numbers will be referred to as 'factorable'. For example, the Hamiltonian:

\[(2.19) H = -2 \{ J(S_1 \cdot S_2 + S_1 \cdot S_3 + S_1 \cdot S_4) + J_2 S_2 \cdot S_3 + J_2 S_2 \cdot S_4 + J_3 S_3 \cdot S_4 \} \]

can be partially factorised by the introduction of \(S'' = S_2 + S_3 + S_4\) to give:

\[(2.20) H = -J[S''^2 - S''^2 - S^2] - 2J_2 S_2 \cdot S_3 - 2J_2 S_2 \cdot S_4 - 2J_3 S_3 \cdot S_4 \]

The 3 spin problem defined by the last 3 terms of (2.20) can be solved independently and the eigenvalues added to those of the first term, according to the value of \(S''\).

2.3.2 Examples of clusters with factorable Hamiltonians

The expression of the Hamiltonian for an isoceles triangle of isotropically coupled spins in terms of intermediate quantum numbers is well known, and several other examples of factorable Hamiltonians have appeared in the literature\(^{40,77}\). The simpler factorable clusters of up to 6 atoms which involve only one non-zero coupling constant are shown in Fig.2.1. The
Fig. 2.1. Examples of small factorable clusters.
corresponding Hamiltonians, in units of \(-J\), are listed below. 

\( S_{ijk} \) denotes \( S_i S_j S_k \).

a) Dimer, \( S' = 2S^2 \);

b) Equilateral triangle, \( S' = 3S^2 \);

c) Tetrahedron, \( S' = 4S^2 \);

d) Trigonal bipyramid, 10 equal coupling constants, \( S' = 5S^2 \);

e) Three membered chain \( S' = S_{13}^2 - S^2 \);

f) \( S'^2 = S_{234}^2 - S^2 \);

g) \( S' = S_{2345}^2 - S^2 \);

h) \( S'^2 = S_{23456}^2 - S^2 \);

i) Trigonal bipyramid, \( S'^2 = S_{15}^2 - 3S^2 \);

j) Open trigonal bipyramid, \( S'^2 = S_{234}^2 - 2S^2 \);

k) Square, \( S'^2 = S_{13}^2 - S_{24}^2 \);

l) \( S'^2 = S_{13}^2 \);

m) Octahedron, \( S'^2 = S_{14}^2 - S_{25}^2 - S_{36}^2 \);

The list above includes only physically reasonable small clusters described by a single coupling constant. Some clusters, such as that with six spins interacting equally with all other atoms in the cluster, \( H = S'^2 - 6S^2 \), are possible, but physically extremely unlikely as it is impossible to arrange six atoms in space in a configuration such that the couplings between a given atom and the remaining five are symmetry equivalent. Example d) also falls into this category.

Linear combinations of the above Hamiltonians are allowed provided that the conditions for factorisation are maintained; thus the Hamiltonian for an isoceles triangle can be expressed in terms of a linear combination of that for the equilateral
triangle and that for the three atom chain. Many more complicated examples exist, for example, a tetrahedron distorted along a three-fold axis can be represented by a combination of c) and f) above, and an octahedron distorted along a four-fold axis by a combination of k) and m). An application in which factorisation is used to define a distortion model for the tetrahedral Cu₄OX₆L₆ clusters by combining c) and k) above is discussed in 5.1.3. Intermediate quantum number Hamiltonians can be used directly where suggested by structural data, or to test structural hypotheses. They are also useful as known points between which correlation of the magnetic spectrum for low symmetry clusters can be carried out with the aid of linear algebra and group theory.

2.4 Group Theory and Magnetic Clusters

Group theory is most powerful when applied to high symmetry clusters having several irreducible representations, but it also provides the most satisfactory formalism for discussion of the non-crossing rule and the Jahn-Teller theorem, which apply to all clusters. When used in conjunction with the intermediate quantum number approach, group theory can frequently provide exact results much more easily than matrix methods.

2.4.1 Magnetic groups

The point group symmetry elements, such as reflections and rotations, operate in ordinary, or 'orbital', space; they are not the symmetry elements required for discussion of the spin
Hamiltonian. Instead, operators which permute electrons leaving the spin Hamiltonian unchanged should be used. The set of such operators will be referred to in this thesis as the 'magnetic group'. The magnetic group of a cluster is a subgroup of a product of permutation groups. The usual definition of magnetic space group elements as those operators which bring the spin density function onto itself is equivalent to the definition above in the case of the Heisenberg model as the electrons are considered to be localised.

The relationship between the spin Hamiltonian and permutation groups is made explicit in Dirac's formalism, which was introduced in Chapter 1. The techniques for group theoretical treatment of clusters will now be introduced using the examples of the $S=1/2$ and the $S=1$ equilateral triangles. Consider a cluster containing an equilateral triangle of $S=1/2$ atoms with exchange coupling, $J$:

\[
H = -2J (S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3)
\]

\[
= -J/2 (2P_{12} + 2P_{13} + 2P_{23} - 3)
\]

$H$ has the symmetry of the permutation group $P_3$. The character table for this group is:

<table>
<thead>
<tr>
<th>$P_3$</th>
<th>123</th>
<th>3{(123)}</th>
<th>2{(123)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>

where standard cyclic notation is used for the permutations, i.e. $(12)3$ changes the numbers 123 into 213, while $(123)$ changes
123 into 231. The brackets, [ ], denote classes and the number of elements in a class is given by the number outside the brackets.

Consider the spin basis \{aa\beta, a\beta a, \beta aa\}; the irreducible representations, 'I.R.s', spanned by the basis are:

\[(2.22) \quad \Gamma\{aa\beta, a\beta a, \beta aa\} = A_1 + E\]

Similarly the I.R. spanned by set of states with \(S'_z=3/2\), i.e. the state (aaa), is \(A_1\). The general expression for the I.R.s spanned by states having a spin of \(S'\) is:

\[(2.23) \quad \Gamma\{S'\} = \Gamma\{S'_z\} - \Gamma\{S'_z+1\}, \quad S'_z \geq 0\]

where \(\{S'_z\}\) includes all basis states with a given value of \(S'_z\). Therefore \(\Gamma\{S'=3/2\} = A_1\) and \(\Gamma\{S'=1/2\} = E\), and the states with \(S'=1/2\) are degenerate. If one of the coupling constants is made different from the other two, the magnetic group becomes \(P_2\) and this degeneracy is split since the I.R., \(E\), correlates with \(A_1 + A_2\) in \(P_2\).

For the \(S=1/2\) triangle the magnetic group, which is isomorphic to \(C_{3v}\), is smaller than the point group, \(D_{3h}\), which contains symmetry elements such as the horizontal mirror plane, which have no counterparts in the magnetic group. In many cases the magnetic group is isomorphic to the point group; if so, it is convenient to use the point group notation for the magnetic group. It is also possible for the magnetic group to be larger than the point group; thus the trigonal bipyramid with 10 equal
coupling constants, d) of Fig. 2.1, has full $P_5$ symmetry, with 120 group elements, whereas its point group is $D_{3d}$ (isomorphic to $P_3\times P_2$) with only 12 elements. The magnetic group of clusters of $n$, $S=1/2$ atoms is always a subgroup of $P_n$.

For $S>1/2$ clusters the additional complication of permutations exchanging electrons on the same atom must be considered in a full group theoretical treatment. In this case the magnetic group is the direct product of the magnetic group of the corresponding $S=1/2$ system with $n$ intra-atomic permutation groups, $P_{2S}$. This can be illustrated by the example of the $S=1$ equilateral triangle. Let orbitals 1 and 2 be on atom A, orbitals 3 & 4 be on atom B, and 5 & 6 on atom C. $H$ can be expressed as:

$$H = -2J'(S_1S_2 + S_3S_4 + S_5S_6) - 2J(S_{12}S_{34} + S_{34}S_{56} + S_{56}S_{12})$$

where $S_{12} = S_1 + S_2$ and $J' >> J$. There are eight permutations leaving the electrons on their original atoms:

$$\begin{align*}
(2.24) & \quad 123456, \quad (12)3456, \quad 12(34)56, \quad 1234(56), \quad (12)(34)56, \\
& \quad (12)(34)(56), \quad (12)(34)(56), \quad (12)(34)(56).
\end{align*}$$

For each of these permutations there are 6 permutations changing the atoms on which the electron pairs are situated but leaving $H$ unchanged; for the first term of (2.23) these are:

$$\begin{align*}
(2.25) & \quad 123456, \quad (12)(35)(264), \quad (13)(24)(56), \quad (15)(24)(56), \\
& \quad (13)(24)(56), \quad (13)(24)(56).
\end{align*}$$

In all there are 48 permutations. The requirement, imposed by $H$, that the three pairs of electrons each remain co-atomic is
very similar to the requirement that opposite corners of an octahedron remain opposite on application of a point group symmetry operator, thus it is not surprising that the magnetic group under discussion is isomorphic to the point group of the octahedron, $O_h$. For example, the element (12)3456 corresponds to a horizontal mirror plane in $O_h$. A similar procedure to that for the $S=1/2$ system can now be followed to find the I.R.s spanned by each spin, though care must be taken to exclude states which involve $S=0$, rather than $S=1$, atoms.

The $S=1$ triangle is the simplest $S>1/2$ cluster for which the group theory is non-trivial, but even in this case the derivation of useful results is tedious. Clearly some simplification is necessary if the method is to be used for more complex systems. Such a simplification can be achieved by considering the atoms, rather than the electrons of the spin Hamiltonian as the 'elementary' particles to be permuted.

When permutations of atoms rather than electrons are considered, smaller and more manageable groups are obtained but some information is lost; in particular, it is possible that a set of degenerate spin states will be represented by more than one I.R. For example, if $P_3$ rather than $O_h$ is used for the $S=1$ triangle the group theory analysis, using basis kets $|S_{z_1} S_{z_2} S_{z_3} >$ is:

\[
\begin{align*}
\Gamma[S_z' = 3] &= \Gamma[|111> ] = A_1 \\
\Gamma[S_z' = 2] &= \Gamma[|110>,|101>,|011> ] = A_1 + E \\
\Gamma[S_z' = 1] &= \Gamma[|100>,|010>,|001>,|11-1>,|1-11>,|-111> ] = 2A_1 + 2E \\
\Gamma[S_z' = 0] &= \Gamma[|10-1>,|1-10>,|01-1>,|0-11>,|-110>,|-101>,|000> ]
\end{align*}
\]
The 3-fold degeneracy of the $S'=1$ states under this Hamiltonian cannot be represented by this subgroup of the full magnetic group.

The advantage of the 'atom based' magnetic group is that it becomes feasible to treat all clusters of up to $S=5/2$, $n=6$, with groups which are independent of $S$. The 'atom based' rather than the full magnetic groups will be used in the rest of this work. The magnetic group for any cluster containing $n$ metal atoms is thus a subgroup of $P_n$. Details of $P_4$, $P_5$ and $P_6$ are given in Table 2.2; the I.R.s spanned by all permutations of sets of objects are listed with the character tables, these lists are useful for calculations such as (2.27), above. Correlation tables between these permutation groups and their subgroups can be used to find the I.R.s spanned by the spin states of any cluster with up to 6 magnetic atoms.
Table 2.2 Character Tables for the groups $P_4, P_5$ and $P_6$.

<table>
<thead>
<tr>
<th>$P_4$</th>
<th>$P_5$</th>
<th>$P_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1234</td>
<td>12345</td>
<td>123456</td>
</tr>
<tr>
<td>8{1(234)}</td>
<td>15{1(23)(45)}</td>
<td>45{12(34)(56)}</td>
</tr>
<tr>
<td>6{12(34)}</td>
<td>20{12(345)}</td>
<td>120{1(23)(456)}</td>
</tr>
<tr>
<td>6{(1234)}</td>
<td>24{(12345)}</td>
<td>144{1(23456)}</td>
</tr>
<tr>
<td>3{(12)(34)}</td>
<td>30{1(23456)}</td>
<td>90{(12)(3456)}</td>
</tr>
<tr>
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$\Gamma\{aaaaa\} = A_1$, $\Gamma\{aaab\} = A_1 + T_2$, $\Gamma\{aabb\} = A_1 + E + T_2$, $\Gamma\{aabbc\} = A_1 + E + T_1 + 2T_2$, $\Gamma\{abcd\} = A_1 + A_2 + 2E + 3T_1 + 3T_2$

$\Gamma\{aaaa\} = A_1$, $\Gamma\{aabb\} = A_1 + G_1$, $\Gamma\{aabc\} = A_1 + 2G_1 + H_1 + I$, $\Gamma\{aabcd\} = A_1 + 3G_1 + 3H_1 + 3H_2 + 3I$, $\Gamma\{abcde\} = A_1 + A_2 + 4G_1 + 4G_2 + 5H_1 + 5H_2 + 6I$. 

$\Gamma\{aaaab\} = A_1 + H_1$, $\Gamma\{aabb\} = A_1 + H_1 + L_1$, $\Gamma\{aabbc\} = A_1 + H_1 + H_2 + L_1$, $\Gamma\{aabbc\} = A_1 + 2H_1 + H_2 + 2L_1 + M_1 + S$, $\Gamma\{aabbcd\} = A_1 + 2H_1 + H_2 + H_3 + 3L_1 + M_1 + 2S$, $\Gamma\{aabbcd\} = A_1 + 3H_1 + 3L_1 + 3M_1 + 5H_2 + 2S$, $\Gamma\{aabbcd\} = A_1 + 3H_1 + 2H_2 + H_3 + 4L_1 + 2S$, $\Gamma\{aabcde\} = A_1 + 4H_1 + H_2 + 3H_3 + 2H_4 + 6L_1 + 3L_2 + 6M_1 + 4M_2 + 8S$, $\Gamma\{abcdef\} = A_1 + A_2 + 5(H_1 + H_2 + H_3 + H_4) + 9(L_1 + L_2) + 10(M_1 + M_2) + 16S$. 
An example of the use of group theory

The group theory for the three atom systems as discussed above did not lead to any results which could not be obtained by other methods. It is obvious from the expression of the spin Hamiltonian for the equilateral triangle as $H=-J(S_1^2-3)$, that all states of the same total spin are degenerate. A more clearly useful example in which group theory and factorable Hamiltonians together give an exact result without resort to matrix methods, will now be discussed.

Consider:

\[ H(\theta) = -2[(S_1.S_2+S_3.S_4)\cos \theta_+ + (S_1.S_3+S_2.S_4)\cos \theta_+ + (S_1.S_4+S_2.S_3)\cos \theta_+] \]

where $\theta_+, \theta_- = \theta \pm 2\pi/3$. This Hamiltonian is important in the discussion of distortions of tetrahedra given in Chapter 4.

For general $\theta$, $H$ has magnetic symmetry $D_2$, while for $\theta=n\pi/3$ the symmetry is $D_{2d}$ and $H$ can be factorised. Consider the Hamiltonian:

\[ H(0) = -2[S_1.S_2+S_3.S_4-1/2(S_1.S_2+S_3.S_4+S_3.S_4+S_4.S_1)] \]

\[ = 1/2 (S'^2-4S^2) - 3/2 (S_{13}^2+S_{2a}^2-4S^2) \]

\[ = 1/2 (S'^2-3S_{13}^2-3S_{2a}^2+8S^2) \]

where $S_{13}=S_1+S_3$ and $S_{2a}=S_2+S_a$. $H$ has the following symmetry:

\[ H(\theta) = - H(\theta+\pi) \]

\[ H(\theta) = P[(13)(24)] H(-\theta) \]

\[ H(\theta+2\pi/3) = P[(1234)] H(\theta) \]
Consider $S=1/2$; from (2.29), the magnetic spectrum of the $S'=1$ states is:

\[(2.31) \mid 111 \rangle = -2, \mid 110 \rangle = 1, \mid 101 \rangle = 1.\]

where the eigenstates are labelled by $\mid S'S_1 S_2 \rangle$. The magnetic spectrum for all $\theta = n\pi/3$ can be found from (2.30) and (2.31). Now consider the I.R.s spanned by $\{S'=1\}$; the necessary group tables are:

\[
\begin{array}{c|cccc}
D_2 & 1 & 2 & 3 & 4 \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
B_1 & 1 & 1 & -1 & -1 \\
B_2 & 1 & -1 & 1 & -1 \\
B_3 & 1 & -1 & -1 & 1 \\
\end{array}
\]

\[
\begin{array}{c|cccc}
D_{2d} & 1234 & 2\{(1234)\} & (13)(24) & 2\{(12)(34)\} & 2\{(13)(24)\} \\
\hline
A_1 & 1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 & -1 & -1 \\
B_1 & 1 & -1 & 1 & 1 & -1 \\
B_2 & 1 & -1 & -1 & 1 & 1 \\
E & 2 & 0 & -2 & 0 & 0 \\
\end{array}
\]

The labelling for the I.R.s, as well as the names of the groups, has been chosen to show clearly the isomorphism with point groups. The correlation table for the two groups is:

\[(2.32) \quad D_2 \quad A_1 \quad B_1 + B_3 \quad B_2 \]

\[
\begin{array}{c|ccc}
D_{2d} & A_1, B_1 & E & A_2, B_2 \\
\end{array}
\]

For $D_2$, the analysis is:

\[(2.33) \quad \Gamma\{S' = 2\} = \Gamma\{|aaaa\rangle\} = A_1 \]

\[\Gamma\{S' = 1\} = \Gamma\{|aaa\beta\rangle, |aa\beta a\rangle, |a\beta a a\rangle, |\beta a a\rangle\} = A_1 + B_1 + B_2 + B_3 \]

\[\Gamma\{S' = 0\} = \Gamma\{|aa\beta \beta, a\beta a\beta, a\beta \beta a, \beta a a\beta, \beta a \beta a, \beta \beta a a\rangle\} = 3A_1 + B_1 + B_2 + B_3 \]

Therefore $\Gamma\{S'=1\} = B_1 + B_2 + B_3$, for all $\theta$, and the eigenfunctions of $H$ are constant as $\theta$ varies. The eigenfunctions can be found
explicitly with projection operators, denoted by \( P(\Gamma) \), thus:

\[
\begin{align*}
(2.34) \quad P(B_1)(aaaa\beta) &= aaaa\beta - a\beta aa + aa\beta a - \beta aaa \\
P(B_2)(aaaa\beta) &= aaaa\beta + a\beta aa - aa\beta a - \beta aaa \\
P(B_3)(aaaa\beta) &= aaaa\beta - a\beta aa - aa\beta a + \beta aaa
\end{align*}
\]

\( H(0) + H(2\pi/3) + H(-2\pi/3) = 0 \); therefore, for each I.R. the sum of the eigenvalues for these 3 Hamiltonians is zero. Further, \( H(\theta) = (2/3)[H(0)\cos\theta + H(2\pi/3)\cos\theta_+ + H(-2\pi/3)\cos\theta_+] \) and so:

\[
(2.35) \quad E(\theta) = (2/3) [E(0)\cos\theta + E(2\pi/3)\cos\theta_+ + E(-2\pi/3)\cos\theta_+]
\]

(2.35) and (2.31) together imply that the \( S' = 1 \) magnetic spectrum, for general \( \theta \), is:

\[
(2.36) \quad E(\theta) = -2 \cos(\theta + 2n\pi/3) \quad n=1,2,3
\]

a result which cannot be obtained by either the group theory or factorisation alone. For \( \theta = n\pi \) the \( B_1 \) and \( B_3 \) states become degenerate and transform as 'E' in the enlarged group, \( D_{2d} \); for other \( \theta = n\pi/3 \), either the \( B_1 + B_2 \) or the \( B_2 + B_3 \) I.R.s combine to form the degenerate I.R.

Now consider the \( S' = 0 \) solutions of \( H \); both functions transform as \( A_1 \) in \( D_2 \) and it is therefore impossible to define the eigenfunctions from group theory alone; however, it is still possible to find some information by applying the non-crossing rule to the magnetic Hamiltonian.

The non-crossing rule applies to the spectrum of eigenvalues of any Hamiltonian and states, simply, that the
eigenvalues associated with eigenvectors of the same symmetry cannot cross as a parameter in $H$ is varied. It is derived as follows. Consider a space spanned by two states of the same symmetry and consider a matrix representation of $H$ in some arbitrary basis for this space. In general, the matrix elements $H_{11}$, $H_{12}$, and $H_{22}$ are all non-zero. Both $H_{11}=H_{22}$ and $H_{12}=0$ are required for degeneracy; it may be possible to choose the variable parameter so that one or other of these conditions hold but the probability of both occurring at the same value of the variable parameter is infinitesimal, therefore the states are never degenerate and cannot cross. The non-crossing rule depends on the Born-Oppenheimer approximation and the assumption that $H$ changes adiabatically, it may break down if non-adiabatic or 'sudden' changes in the variable parameter occur.

As the $S'=0$ states both have the same symmetry in $D_2$ and are non-degenerate in $D_{2d}$, where they transform as $A_1+B_1$, they cannot cross. Since $H(0)+H(2\pi/3)+H(-2\pi/3)=0$, this shows that the eigenfunctions must vary with $\theta$. Further information on the variation of the $S'=0$ energies with $\theta$ is most easily obtained using the linear algebraic results which are derived in the next chapter.
3.1 A Formalism for describing distortions of magnetic clusters

A formalism which can be used to discuss the magnetic effects of coupling constants, \( J_{ij} \), which depend on a distortion coordinate, \( d_{ij} \), will now be developed. As long as \( J_{ij} \) is a sufficiently smooth function of the distortion, it can be expanded as a power series in \( d_{ij} \). Taking the first two terms, \( J_{ij} \) can be approximated by:

\[
J_{ij}(d_{ij}) = J_{ij}(0) + d_{ij} \left( \frac{\partial J_{ij}}{\partial d_{ij}} \right)_0
\]

for small distortions, unless \( \left( \frac{\partial J}{\partial d} \right)_0 = 0 \), in which case the system is in magnetic as well as electronic/steric equilibrium. The nature of the distortion coordinate, \( d_{ij} \), will be discussed in detail; it will be shown that it is best interpreted as a combination of the vibrational normal coordinates of the cluster.

3.1.1 The configuration and distortion spaces

The configuration of a cluster containing \( m \) atoms can be described by a set of \( 3m-6 \) orthogonal coordinates, \( \{c\} \), which can be interpreted as a configuration vector, \( c \), in a vector space, \( C \), the configuration space of the cluster. The basis for \( C \) can be chosen in a variety of ways involving combinations of the bond lengths or angles; one simple choice is to use a set of linearly independent interatomic distances, e.g. for \( m=3 \):

\[
c = (c_{12}, c_{13}, c_{23})
\]
In this work, small distortions from the mean configuration, denoted $c(0) = c_0$, of the cluster are considered in detail. Distortions may be considered as vectors in a distortion space, $D$, closely related to $C$ by $d = c - c(0)$; thus $d(0) = d_0 = 0$.

The vibrational normal modes provide an alternative choice of basis in $D$; transformation between the interatomic distance basis and normal coordinates may be simplified by group theory. As an example, consider distortions of a cluster containing just four equivalent atoms in a tetrahedral configuration. In interatomic distance coordinates the undistorted cluster is represented by:

$$c = (c_{12}, c_{13}, c_{14}, c_{23}, c_{24}, c_{34}) = (1,1,1,1,1,1)$$

$$d = (d_{12}, d_{13}, d_{14}, d_{23}, d_{24}, d_{34}) = (0,0,0,0,0,0)$$

In $T_2$, the point group of the tetrahedron, $\Gamma_d = A_1 + E + T_2$, expressions for the normal coordinates in this basis can be found using projection operators, i.e.

$$P(A_1)(d_{12}) = (1,1,1,1,1,1)$$

$$P(E)(d_{12}) = (2,-1,-1,-1,-1,2)$$

$$P(E)(d_{13}) = (-1,2,-1,-1,2,-1) = E_x$$

$$P(E)(d_{14}) = (-1,-1,2,2,-1,-1), \quad E_y = E(d_{12} - d_{14}) = (1,0,-1,-1,0,1)$$

$$P(T_2)(d_{12}) = (1,0,0,0,0,-1) = T_x, \quad T_2(d_{13}) = (0,1,0,0,-1,0) = T_y,$$

$$P(T_2)(d_{14}) = (0,0,1,-1,0,0) = T_z.$$

The labels $x, y, z$, indicate orthogonality within the degenerate normal modes. $E_x, E_y$, and $T_x, T_y, T_z$, thus form a
Cartesian basis for subspaces of the distortion space. It will often be convenient to work in polar, rather than Cartesian coordinates; distortions in the E subspace of D may be represented by:

\[ d(E) = r (\cos \psi, \cos \psi, \cos \psi, \cos \psi) \]

and distortions in the T2 space by spherical polar coordinates:

\[ d(T_2) = \rho (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta, -\cos \theta, -\sin \theta \sin \phi, -\sin \theta \cos \phi) \]

Any cluster of four atoms can be expressed as a distorted tetrahedron using the above notation. However the concept of normal vibrational modes is valid only for small distortions for which the cluster can be considered as a harmonic oscillator; the energies associated with, say, the T2 modes, will be equal only for small distortions.

The full 3m-6 dimensional distortion space of a cluster is too large to discuss in detail, even for the small dimer Cu2(CH3COO)4, 3m-6=84. However most of the normal modes are of no interest when considering magnetic exchange; for example, the bending and stretching modes of the CH3 groups in copper acetate may clearly be ignored. It might be thought that consideration of all the atoms involved in possible exchange pathways would be necessary to provide an adequate description of the effects of distortion on the magnetic exchange; however, it will be shown below that the formalism is mathematically adequate even if all non-metal atoms are ignored. Thus for all clusters containing
four equivalent metal atoms arranged at the corners of a tetrahedron it is necessary to consider only 6 distortion modes transforming as $A_1$, $E$, and $T_2$. Distortions within $A_2$ or $T_1$ modes can have no effect on the magnetic behavior, while distortions in any of, say, the $E$ modes, affect the magnetism in the same way. In real clusters investigation of the magnetic behavior may indicate that, say, $E$ mode distortions are occurring, however it will, in general, be impossible to determine the relative importance of each of the normal modes transforming as this I.R. This behavior is expected since it is never possible to determine which of several possible exchange mechanisms is important directly from magnetic data. The effect of distortions on the magnetic behavior is best discussed using the concept of the distortion Hamiltonian.

3.1.2 The distortion Hamiltonian

Equation (3.1) relates the magnetic interaction Hamiltonian to the configuration of the cluster. The Hamiltonian for the distorted system can be represented as:

\[ H(d) = H(0) + d \left( \frac{\partial H}{\partial d} \right)_0 = H_0 + H' \]

$H_0$ is a function of $n(n-1)/2$ linearly independent components, $\{J\}$, but because of the constraints imposed by (3.1), $H'$, the distortion Hamiltonian, has only $3n-6$ independent coordinates. $H_0$ can be specified as the origin of a distortion Hamiltonian space, $V$, which is $3n-6$ dimensional and in which $H'$ can be interpreted as a vector. The linear relationship (3.1) also
means that the magnetic group of H' must be isomorphic to a point group. As mentioned above, the full distortion space D, is 3m-6 dimensional, since 3m-6 > 3n-6 each coordinate of a basis in V will, in general, correspond to several coordinates in D. When only normal modes defined by the metal core are considered in D its dimension is 3n-6, and there is a simple one-to-one mapping between D and V. It can now be seen that no information which can be obtained by magnetic susceptibility measurements is lost by considering only distortions of the metal core as contributing to D. The distortions of the metal core are not the real distortions of the cluster but represent them as adequately as is necessary for discussion of the magnetic Hamiltonian.

When n<5 the number of normal modes equals the number of components of \{J\} and the distinction between the n(n-1)/2 degrees of freedom of H and the 3n-6 (3n-5 for n=2, a 'linear' system) degrees of freedom of H' does not arise.

From (3.1), (3.5) and (3.6), the set of distortion Hamiltonian vectors in V can be defined. Thus for the tetrahedron, ignoring the A, distortion which can be taken into \(H_0\):

\[
\text{H}_E^r(r, \psi) = -2Jr \left[ (S_1.S_2+S_3.S_4)\cos \psi + (S_1.S_3+S_2.S_4)\cos \psi + (S_1.S_4+S_2.S_3)\cos (\psi_+) \right]
\]

\[
\text{H}_T^r(\rho, \theta, \phi) = -2J\rho \left[ (S_1.S_2-S_3.S_4)\sin \theta \cos \phi + (S_1.S_3-S_2.S_4)\sin \theta \sin \phi + (S_1.S_4-S_2.S_3)\cos \theta \right]
\]

where \(r_\rho = (d/J)(\partial d/\partial J)_0\) for the relevant normal coordinate. An orthonormal basis in H' can be defined from (3.1) and (3.4) and
Hamiltonians, $H'$, in $V$ can then be expressed as vectors in this basis. It should be noted that orthogonal vectors in $V$ do not, in general, commute.

One immediate advantage of using normal, rather than interatomic distance, coordinates to describe $D$ and $V$ is that $(\partial J/\partial d)_0$ is constrained to be isotropic within each degenerate normal mode. This is because within any degenerate normal mode the vibrational energy is, by definition, independent of the orientation of the distortion vector, i.e. the vibrational force constant, $k$, is constrained by symmetry to be isotropic. Since $k$ and $(\partial J/\partial d)_0$ are tensors of the same kind this implies that $(\partial J/\partial d)_0$ is also isotropic within a degenerate mode. Any anisotropy occurring in $(\partial J/\partial d)_0$ when expressed in, say, interatomic distance coordinates results from differences in the sensitivity of the distortion Hamiltonian vector to distortions within different normal modes. (3.1) is thus better expressed as:

\[
(3.9) \quad J_i(d_i) = J_i(0) + d_i (\partial J_i/\partial d_i)_0
\]

where $J_i$ and $d_i$ are now generalised normal coordinates of the cluster in the sense defined above.

The last vector space which must be discussed is the spin space in which solutions of $H$ are found. A notation for this space will now be defined. The total spin space will be denoted by $T$. $T$ is $\omega(n,S,0)$ or $\omega(n,S,1/2)$ dimensional ($\omega$ as defined in (2.1) and (2.2)) and is, in general, completely unrelated to
C, D and V introduced above. As \( H \) can be solved by blocking by \( S' \) it is convenient to define subspaces, \( R(S') \), of \( T \) by:

\[
(3.10) \quad R(S') = \{ |\psi\rangle \in T : S'^2 |\psi\rangle = S'(S' + 1) |\psi\rangle, \text{ for all } |\psi\rangle \in R(S') \}
\]

\( R(S') \) contains all states of total spin \( S' \); it is \( \Omega(n,S,S') \) dimensional. The \( R(S') \) may sometimes be further reduced by considering subspaces, \( Q(S',\Gamma) \), of states within \( R(S') \) transforming as the I.R., \( \Gamma \).

3.1.3 An application of distortion Hamiltonian formalism

Consider a Hamiltonian of the form:

\[
(3.11) \quad H = H_0 + H' = -J(S'^2 - nS^2) + H'(\theta)
\]

where \( H'(\theta) \) is (i) periodic in \( 2\pi \) in the variable \( \theta \), (ii) \( H'(\pm \theta \pm 2n\pi/3) \) are related by permutations of the magnetic group of \( H_0 \), (iii) the distortion vectors corresponding to \( H'(0) \) and \( H'(\pi/2) \) are orthogonal and (iv) \( H' \) commutes with \( H_0 \). Such distortion Hamiltonians are relatively common in Heisenberg clusters; they occur whenever \( P_3 \) is a subgroup of the magnetic group. \( H'(\theta) \) can be regarded as a vector of constant magnitude in an \( E \) subspace of \( V \). \( H_0 \) can be expressed as a trivial constant which can be taken as zero within each subspace \( R(S') \) of \( T \). Like any other vector in a 2-D space, \( H' \) can be expressed in an orthogonal basis spanning \( R \) as:

\[
(3.12) \quad H'(\theta) = H'(0)\cos\theta + H'(\pi/2)\sin\theta
\]

Let \( \{\lambda\} \) be the set of eigenvalues of \( H' \) and consider a matrix
representation of this Hamiltonian in a basis spanning a given $R(S')$. Choose a basis diagonalising $H'(0)$. Off-diagonal elements of $H'(\theta)$ are clearly proportional to $\sin \theta$ in this basis. Assume first that the magnetic spectrum of $H'(0)$ is non-degenerate. Since $\lambda(\theta)=\lambda(-\theta)$ then $d\lambda/d\theta=0$ at $\theta=0$, but, from the Hellman-Feynmann theorem and (3.12), taking $\lambda=0$ and an eigenvector $|\psi\rangle$ of $H(0)$:

$$d\lambda/d\theta = d/d\theta \langle\psi|H'|\psi\rangle = \langle\psi|H'(\theta+\pi/2)|\psi\rangle = 0$$

and so the diagonal elements of $H'(\pi/2)$ are all zero. If $H'(0)$ is degenerate, the sum of $d\lambda/d\theta$ over the degenerate subspace of $R$ is zero and it is still always possible to choose a basis in which $H'(\pi/2)$ is entirely off diagonal. $H'(\theta)$ can now be expressed as:

$$H'(\theta)_{ij} = a_{ij}[ (1-\delta_{ij})\sin \theta + \delta_{ij}\cos \theta]$$

Now consider the eigenvalues of $H(\theta)$. The determinant $|H-\lambda I|=0$ can be expressed as a characteristic polynomial which is a function of $\theta$:

$$(3.14)$$

$$\begin{vmatrix} a_{11}\cos \theta - \lambda & a_{12}\sin \theta & a_{13}\sin \theta & \ldots & a_{1n}\sin \theta \\ a_{12}\sin \theta & a_{22}\cos \theta - \lambda & a_{23}\sin \theta & \ldots & a_{2n}\sin \theta \\ a_{13}\sin \theta & a_{23}\sin \theta & a_{33}\cos \theta - \lambda & \ldots & \ldots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ a_{1n}\sin \theta & a_{2n}\sin \theta & a_{3n}\sin \theta & \ldots & a_{nn}\cos \theta - \lambda \end{vmatrix} = 0 = \lambda^k + c_1(\theta)\lambda^{k-1} + c_2(\theta)\lambda^{k-2} + \ldots + c_{k-1}(\theta)\lambda + c_k(\theta).$$

where $k=\Omega(S')$. The eigenvalues of $H'$ are now the set of roots $\{\lambda\}$ of the polynomial. The form of the matrix $H(\theta)$ and the symmetry in $\theta$ impose quite strict conditions on the polynomial (3.14). The coefficients, $c(\theta)$, will now be considered in turn.

$$c_1(\theta) = \text{Tr}[H(\theta)]$$
$$\text{but } \text{Tr}[H(\theta)]=\text{Tr}[H(0)]\cos \theta$$
$$\text{and } \text{Tr}[H(\theta)] =$$
\( \text{Tr}[H(\theta+2\pi/3)] \), since these matrices are similar. Therefore \( c_1 = \Sigma \lambda = 0 \) for all \( \theta \).

\( c_2(\theta) \); only terms dependent on \( \cos^2 \theta \) and \( \sin^2 \theta \) contribute to this coefficient. The resulting function can be expressed as \( c_2 = \text{const} + p \cos 2\theta + q \sin 2\theta \), but the polynomial is even in \( \theta \) and therefore \( q = 0 \); also \( c_2 \) is periodic in \( 3\theta \) and therefore \( p \) is zero. Thus \( c_2 \) is constant. An alternative expression of this result can be obtained by considering \( \theta = 0 \), since \( \Sigma \lambda \), the sum of the eigenvalues, is zero, \( (\Sigma \lambda)^2 \) is zero, but \( (\Sigma \lambda)^2 = \Sigma (\lambda^2) + \sum_{i \neq j} \lambda_i \lambda_j = 0 \). By inserting \( \theta = 0 \) into (3.14) it can be seen that

\[
(3.15) \quad c_2(\theta) = \text{constant} = -1/2 \Sigma (\lambda^2)
\]

\( c_3(\theta) \); only terms of the form \( p \cos^3 \theta + q \sin^2 \theta \cos \theta \) contribute to \( c_3 \). These can be represented by \( p' \cos 3\theta + q' \cos \theta \), since \( c_3 \) is even. Clearly \( q' = 0 \) since the polynomial is periodic in \( 3\theta \) and the spectrum is \( \theta \) dependent unless \( p' = 0 \). It can be seen that for \( \theta = 0 \), \( c_3 \) is the sum of all possible different products of three eigenvalues.

\( c_4, c_5 \); Following the same reasoning as above the results are: \( c_4(\theta) = \text{constant} \) and \( c_5(\theta) = p'' \cos 3\theta \).

\( c_6(\theta) \). If \( \Omega(S') \geq 6 \), \( c_6 \) and higher coefficients are involved and the situation becomes more complicated; thus for \( c_6 \):

\[
(3.16) \quad c_6 = p \cos^6 \theta + q \cos^4 \theta \sin^2 \theta + r \cos^2 \theta \sin^4 \theta + t \sin^6 \theta = p' \cos 6\theta + q'.
\]
and there are two coefficients to be determined.

It can be seen that if \( \Omega(S') < 6 \) all coefficients can be determined if the spectrum is known for any one value of \( \theta \); for greater \( \Omega(S') \), two or more symmetry unrelated spectra must be known. For \( \Omega(S') < 6 \) the explicit results are:

\[ \begin{align*}
\Omega(S') &= 1. \quad \lambda = 0, \text{ for all } \theta \\
\Omega(S') &= 2. \quad \lambda^2 \text{-const}=0, \text{ the spectrum is independent of } \theta \\
\Omega(S') &= 3. \quad \lambda^3 - 1/2[\sum \lambda(0)^2] \lambda - [\lambda_1(0)\lambda_2(0)\lambda_3(0)] \cos 3\theta = 0 \\
\Omega(S') &= 4. \quad \lambda^4 - 1/2[\sum \lambda(0)^2] \lambda^2 - c_3 \cos 3\theta \lambda - c_4 = 0 \\
\Omega(S') &= 5. \quad \lambda^5 - 1/2[\sum \lambda(0)^2] \lambda^3 - c_3 \cos 3\theta \lambda^2 - c_4 \lambda - c_5 \cos 3\theta = 0
\end{align*} \]

It is clear that if the number of levels for a given \( S' \) is less than 6, the eigenvalues change monotonically between adjacent values of \( \theta \). For larger \( \Omega(S') \) this is not necessarily the case since harmonic terms of period less than \( 2\pi/3 \) may arise.

3.2 The Jahn-Teller activity of Magnetic Clusters

3.2.1 Application of the Jahn-Teller theorem to systems with magnetic degeneracy

It is now possible to give a detailed discussion of the Jahn-Teller instability of clusters using the group theory of Chapter 2 and the distortion formalism of 3.1. The Jahn-Teller theorem as originally stated\(^7\) is:

"all non-linear molecules are unstable for an orbitally degenerate electronic state"

Some slight modification of the original theorem is
desirable to make the application to magnetic clusters apparent. This is because the magnetic group of the distortion Hamiltonian may not be isomorphic to the point group of the cluster, and also because the states involved are neither spin nor orbital functions but antisymmetrised sums of products of spin and orbital functions, as discussed in Chapter 1. We are concerned here only with the orbital degeneracy which arises when a system containing a number of orbitally non-degenerate atoms is considered as a whole. In the limiting case, when all the atoms are independent, a system of \( n \) independent atoms each of which is orbitally non-degenerate has \( n \)-fold degeneracy when considered as a whole, since the \( n \) atomic orbitals produce \( n \) molecular orbitals of equal energy. Jahn-Teller distortions within the individual ligand fields, which may be important in causing the spin Hamiltonian representation to be valid in the first place, have been discussed in Chapter 1.

The Jahn-Teller theorem is proved by considering all possible matrix elements \( <a|H'|b> \), where \( |a> \) and \( |b> \) are degenerate states and \( H' \) is a perturbation of the Hamiltonian resulting from distortion. Unless all such matrix elements are zero a distortion that splits the degeneracy and lowers the symmetry will occur. Jahn and Teller showed using group theory, by considering all possible I.R.s spanned by \( H' \), \( |a> \) and \( |b> \), that all such matrix elements may be zero only for a linear molecule. \( <a|H'|b> \) may be non-zero only if the I.R.s spanned by the integral include the totally symmetric representation, \( A_1 \).
For magnetic clusters the magnetic, rather than the point group should be considered, since only distortions that lower the symmetry of the spin Hamiltonian can remove degeneracy in addition to the \((2S'+1)'\text{genuine}'\) spin degeneracy. Only the magnetic atoms need be considered when considering instability due to degeneracy in the magnetic spectrum. A system in which each magnetic atom is coupled to, at most, two other atoms, i.e. with a maximum magnetic coordination number of two, can be described as magnetically linear. To illustrate the theorem consider the example of a cluster containing a regular tetrahedron of four equivalent \(S=1/2\) atoms. As shown above, \(\Gamma(H')=E+T_2\); the \(S'=1\) states transform as \(T_2\) in \(P_4\), which is isomorphic to the point group \(T_d\), and the \(S'=0\) states transform as \(E\).

For \(S'=0\), \(\Gamma\langle E|E|E\rangle\) contains \(A_1\), but \(\Gamma\langle E|T_2|E\rangle\) does not, so only \(E\) distortions can affect these states. For \(S'=1\), both \(\Gamma\langle T_2|E|T_2\rangle\) and \(\Gamma\langle T_2|T_2|T_2\rangle\) contain the totally symmetric representation, and the states are split by any distortion. The cluster is unstable with respect to \(E\) and \(T_2\) distortions when in an \(S'=1\) state and unstable with respect to \(E\) distortions when in an \(S'=0\) state.

3.2.2 The magnitude of distortions in magnetic clusters

The method used here to determine the approximate magnitude of distortions due to magnetic symmetry is adapted from the method applied by Teller for spin degeneracy in the second Jahn-Teller paper of 1938\(^6\)\(^7\).
Suppose a cluster exists in a symmetric configuration which is stable when only interactions other than magnetic interactions are considered. The energy dependence on distortion in a normal coordinate, \( d \), can be approximated by \( E = \frac{kd^2}{2} \), where \( k \) is the force constant for the normal mode.

Suppose now that this otherwise non-degenerate state has magnetic degeneracy resulting from isotropic coupling in addition to that associated with the orientation of the total spin. The change in magnetic energy associated with the coordinate, \( d \), can be approximated by \( E' = d(\partial J/\partial d)_0 \). The addition of this energy term will shift the position of the minimum energy along \( d \) by an amount, \( d' \), given by:

\[
(3.18) \quad \frac{\partial}{\partial d} \left[ \frac{kd^2}{2} + d(\partial J/\partial d)_0 \right] = 0, \quad d' = (\partial J/\partial d)_0 / k
\]

It is now necessary to estimate \( (\partial J/\partial d)_0 \) and \( k \). \( k \) can be estimated from the vibrational (infra-red) spectrum. A vibrational state of energy \( E \) has a root mean square distortion, or amplitude of vibration, \( x^2 \), given by \( E = kx^2 \). \( x^2 \) can be estimated from X-ray crystallographic data, from the thermal ellipsoids. If \( \nu \) is the vibrational frequency in \( \text{cm}^{-1} \) and \( \lambda \) is the value of \( (\partial J/\partial d)_0 \) in \( \text{cm}^{-1} \text{Å}^{-1} \); \( (\partial J/\partial d)_0 = 1 \text{cm}^{-1} \text{Å}^{-1} \) means that a distortion of 1Å changes \( J \) by 1cm\(^{-1} \), then:

\[
(3.19) \quad d' = \frac{\lambda x^2}{\nu}; \quad \text{and} \quad \Delta J = \frac{\lambda^2 x^2}{\nu}.
\]

where \( d' \) is in Å, and \( \Delta J \) is in cm\(^{-1} \). Distortion is favoured for 'soft' vibrational modes having a large effect on \( J \). It is clear from the above calculation that any \( (\partial^2 J/\partial d^2)_0 \) terms, neglected
in the discussion so far, merely modify the force constant of the harmonic potential and can have no qualitative effect on the magnetic behavior.

Since \( \lambda, \nu \) and \( x^2 \) may vary in a wide range, two estimates of \( \Delta J \) will be made. First consider clusters involving the Cu-O-Cu exchange pathway. The sensitivity of this pathway has been studied in some detail and reviewed by Melnik\(^8\) who correlated \( J \) with the structure of many dimeric systems. A value of \( \lambda \approx 2000 \text{cm}^{-1} \text{Å}^{-1} \) was obtained. The Cu-O stretching frequency, \( 500 \text{cm}^{-1} \) will be used as an estimate of \( \nu \), and \( x^2 \) can be taken as \( 0.2 \text{Å} \). This gives:

\[
(3.20) \; \Delta J = (2000)^2 (0.2)^2 / 500 = 320 \text{ cm}^{-1}
\]

Thus in these clusters it is possible that \( \Delta J \) is as large or larger than \( J \). Distortions may be associated with dramatic qualitative changes, rather than small perturbations, in the magnetic spectrum. The real \( \Delta J \) in Cu-O-Cu clusters will probably be smaller than indicated by (3.20) since there is no guarantee that the vibrational normal modes exactly correspond to the distortions which have this large effect on \( \lambda \). Also the value of \( \lambda \) was obtained by structural correlations between a series of dimers and it may be an overestimate for \( \partial J / \partial d \) within a single cluster. However this order of magnitude calculation does suggest that the magnetic effects of distortion may be large in Cu-O-Cu containing clusters.

Many clusters have a \( J \) of the order of a few 10s of \( \text{cm}^{-1} \).
and even quite small $\Delta J$ may be significant. Thus for the trimetallic cluster chromium acetate, discussed in 3.3.3, $J=10\text{cm}^{-1}$ and even if $\lambda$ is only $100\text{cm}^{-1}\text{Å}^{-1}$, if there is a $\nu$ with energy $100\text{cm}^{-1}$ then $\Delta J=4\text{cm}^{-1}$. In Chapter 5 it is shown that this is quite sufficient to explain the observed anomalies in both the susceptibility and specific heat data observed for this compound.

It can be seen that the reduced mass corresponding to the cluster vibrations can be calculated from the equations: $E=kx^2$ and $\nu \left(s^{-1}\right) = (1/2\pi) \sqrt{(k/m)}$; in the units used above, $m = 20/\nu x^2$. Substitution of $\nu=500\text{cm}^{-1}$, $x=0.2\text{Å}$ suggests $m=1$. Though the reduced mass of the cluster will be less than the masses of the constituent atoms, it is hardly likely to be as small as this. The resolution of this difficulty is that all vibrational modes of the cluster contribute to $x^2$, the mean square distortion. The largest contributions to $x^2$ are expected to come from the lower energy bending modes of the cluster. The variation of $J$ with bond angle has been studied in copper dimers and it is clear that $\partial J/\partial \theta$ is large for bending as well as stretching modes. The fact that several vibrations contribute to the distortion is related to the result that several normal modes in the full distortion space map onto each normal mode in V. Finally, note that the vibrational energies of any system tend to decrease as the mass of the system increases, thus magnetic distortion effects may be expected to become more pronounced as the mass of the cluster increases.
The discussion given above can only be a crude estimate. However, it does seem clear that distortions associated with thermal vibrations and even the zero point 'motions' may be sufficient to cause significant magnetic effects. An alternative, even more qualitative, way of looking at the problem is to consider that the cluster atoms are coupled by the vibrations in orbital space and by the spins in spin space. As the orbital and spin functions cannot, in general, be separated and both couplings may involve energies of the order of 10-100 cm$^{-1}$, it is entirely reasonable to expect vibrational/magnetic interactions, or coupling, to be important. This latter viewpoint will be shown below to give perhaps the most physically reasonable picture of the dynamic behavior of the distortions. The magnetic forces can be considered as favouring certain phase relationships between orthogonal vibrations making up degenerate normal modes.

Having determined when, and by how much, clusters distort because of magnetic interactions, it is now possible to consider which types of distortions will be important. Consider first a distortion in a non-degenerate normal mode. In this case the magnetic term merely shifts the equilibrium configuration to a new position, which can be taken as redefining an $H_0$ about which thermal motion may occur; however it is clear that the spectrum will average to be that for $H_0$. Under certain circumstances a phenomenon known as exchange striction may occur. This leads to a slight temperature dependence in $J$ and small biquadratic, e.g. $(S_1 \cdot S_2)^2$ terms. Neutron diffraction experiments, in which the
magnetic spectrum is determined directly, are more appropriate than susceptibility measurements to determine the importance of striction. Available results suggest that for clusters biquadratic exchange is usually negligible.

For a degenerate normal mode the situation is much more interesting: \( \mathbf{d}' \) is now a vector with both magnitude and direction, and many if not all values of \( \theta \) will be equally likely. The cluster may move from one distortion to another continuously without passing through \( H_0 \). There is a possibility that the average magnetic spectrum on distortion is different from that of \( H_0 \). The existence of a degenerate mode in the distortion space linearly related to \( V \) (as opposed to the full distortion space including all vibrational normal modes of the cluster) is a necessary and sufficient condition for degeneracy in the magnetic spectrum.

3.3 A Distortion model for Trimetallic Clusters

Only those trimetallic clusters in which the metal atoms are equivalent and lie at the corners of an equilateral triangle have magnetic spectra which exhibit degeneracy in addition to that associated with different orientations of the total spin. This is because only the system with full \( P_3 \) symmetry has a degenerate normal mode; no subgroups of \( P_3 \) contain a degenerate I.R.
3.3.1 Solution of the distortion Hamiltonian

An equilateral triangle has normal modes $A_1$ and $E$. E mode distortions lower the symmetry and are related to a distortion Hamiltonian:

$$H'(r, \theta) = -2Jr(S_1 \cdot S_2 \cos \theta_- + S_1 \cdot S_3 \cos \theta + S_2 \cdot S_3 \cos \theta_+)$$

$H'$ can be solved for $\theta = n\pi/3$ using Kambe's method as introduced in Chapter 2. Thus for $\theta = 0$, taking $Jr = 1$ in this theoretical discussion:

$$H'(0) = (1/2) (S'^2 - 3S_3^2 + 3S_1^2)$$

The solutions of (3.22) are listed in Table 3.1. For $\theta \neq n\pi/3$, $H'(r, \theta)$ has no non-trivial symmetry and thus the eigenvalues obey the non-crossing rule. It is therefore clear even before obtaining the exact solution that a periodic change of $\theta$ will not cause the states to interconvert as long as no transitions associated with non-adiabatic changes occur, i.e., dynamic interconversions between symmetry-related $\theta$ will not in general remove the effects of distortion.
### Table 3.1 Solutions of $H'(\theta=0)$ for the equilateral triangle.

Eigenvectors, $|S',S,>,>_{\alpha}$ are followed by the associated eigenvalues.

| $S$ = 1/2 | $|3/2,1>, 0$ ; $|1/2,1>, -3/2$ ; $|1/2,0>, 3/2$.
|---|---|---|
| $S$ = 1 | $|3,2>, 0$ ; $|2,2>, -3$ ; $|2,1>, 3$ ; $|1,2>, -5$ ; $|1,1>, 1$ ; $|1,0>, 4$ ; $|0,1>, 0$.
| $S$ = 3/2 | $|9/2,3>, 0$ ; $|7/2,3>, -9/2$ ; $|7/2,2>, 9/2$ ; $|5/2,3>, -8$ ; $|5/2,2>, 1$ ; $|5/2,1>, 7$ ; $|3/2,3>, -21/2$ ; $|3/2,2>, -3/2$ ; $|3/2,1>, 9/2$ ; $|3/2,0>, 15/2$ ; $|1/2,2>, -3$ ; $|1/2,1>, 3$.
| $S$ = 2 | $|6,4>, 0$ ; $|5,4>, -6$ ; $|5,3>, 6$ ; $|4,4>, -11$ ; $|4,3>, 1$ ; $|4,2>, 10$ ; $|3,4>, -15$ ; $|3,3>, -3$ ; $|3,2>, 6$ ; $|3,1>, 12$ ; $|2,4>, -18$ ; $|2,3>, -6$ ; $|2,2>, 3$ ; $|2,1>, 9$ ; $|2,0>, 12$ ; $|1,3>, -8$ ; $|1,2>, 1$ ; $|1,1>, 7$ ; $|0,2>, 0$.
| $S$ = 5/2 | $|15/2,5>, 0$ ; $|13/2,5>, -15/2$ ; $|13/2,4>, 15/2$ ; $|11/2,5>, -14$ ; $|11/2,4>, 1$ ; $|11/2,3>, 13$ ; $|9/2,5>, -39/2$ ; $|9/2,4>, -9/2$ ; $|9/2,3>, 15/2$ ; $|9/2,2>, 33/2$ ; $|7/2,5>, -24$ ; $|7/2,4>, -9$ ; $|7/2,3>, 3$ ; $|7/2,2>, 12$ ; $|7/2,1>, 18$ ; $|5/2,5>, -55/2$ ; $|5/2,4>, -25/2$ ; $|5/2,3>, -1/2$ ; $|5/2,2>, 17/2$ ; $|5/2,1>, 29/2$ ; $|5/2,0>, 35/2$ ; $|3/2,4>, -15$ ; $|3/2,3>, -3$ ; $|3/2,2>, 6$ ; $|3/2,1>, 12$ ; $|1/2,3>, -9/2$ ; $|1/2,2>, 9/2$.
H' is of the form discussed in 3.1.3 and thus the results (3.17) apply. This means that expressions for all eigenvalues for states in R(S') with $\Omega(S')<6$ can be found directly from the eigenvalues at $\theta=0$ given above. As an example, consider the $S=3/2$ $S'=3/2$ ($\Omega=4$) eigenvalues. For $\theta=0$ the spectrum is \{-21/2,-3/2,9/2,15/2\}; the polynomial for $\{\lambda\}$ is:

\[(3.23) \quad (\lambda+21/2)(\lambda+3/2)(\lambda-9/2)(\lambda-15/2) = 0\]

or $\lambda^4 - (189/2)\lambda^2 - 216\lambda + (81/16)105 = 0$

Therefore the $\{\lambda(\theta)\}$ are the roots of:

\[(3.24) \quad \lambda^4 - (189/2)\lambda^2 - 216\lambda\cos\theta + (81/16)105 = 0\]

It is now possible to obtain solutions valid for general S without matrix methods (which become rather unwieldy for large S). For if $S' = 3S-2$ ($S>1/2$) there are three states with

\[(3.25) \quad |3S-2,2S>, |3S-2,2S-1>, |3S-2,2S-2>,\]

with energies under $H'(0)$ of:

\[(3.26) \quad (1/2)[(3S-2)(3S-1)+3S(S+1) - 3\{2S(2S+1),(2S-1)2S,(2S-2)(2S-1)\}]
\]

$\Sigma \lambda^2 = -[1+(6S-2)(6S-1)], \lambda_1\lambda_2\lambda_3 = -(6S-1)(6S-2)$

therefore $\{\lambda(\theta)\}$ is given by:

\[(3.27) \quad \lambda^3 - 3(12S^2-6S+1) + (36S^2-18S+2)\cos\theta = 0\]

All similar polynomials for $\Omega(S')<6$ are listed in Table 3.2 The form of the solutions in this table shows that for
$\Omega(S')<6$ the eigenvalues change monotonically as $\theta$ varies between successive $\theta=n\pi/3$. This means that, to a good approximation, a correlation diagram for all $\theta$ can be obtained by joining up eigenvalues which are known for $\theta=n\pi/3$ with smooth, non-crossing, monotonic curves.

The results of Table 3.2 constitute a complete solution for all $S\leq5/2$ except for the $S'=5/2$ states of the $S=5/2$ system. An exact result for $\Omega(S')\geq6$ requires the solution for some $\theta\neq n\pi/3$. An exact numerical solution for $\theta=\pi/2$ gives $\lambda_1 = 5^3.11.7.3^8/2^6$, comparing this with the result for $\theta=0$, $\lambda_1 = 5^4.11.17.29.7/2^6$, allows $c_6$ and $c_6'$ of (3.28) to be determined.

\[
\lambda^6 + c_2\lambda^4 + c_3\lambda^3 \cos \theta + c_4\lambda^2 - c_5 \cos \theta + (5^3.11.7/2^6)(c_6 + c_6'\cos 6\theta) = 0
\]
where $c_2=-3003/4$, $c_3=4576$, $c_4 = 1550835/16$, $c_5=694200$, $c_6=2048$ and $c_6'=-4513$.

The Heisenberg Hamiltonian for any trimetallic cluster can be expressed in distortion vector notation. Thus a cluster with couplings, in interatomic notation, of $J_{12}, J_{13}$ and $J_{23}$ can be expressed in normal coordinates as $J, r, \theta$ where:

\[
(3.29) \quad J = (J_{12}+J_{13}+J_{23})/3 \\
 r = \sqrt{\frac{2}{3} \left\{ (J-J_{12})^2 + (J-J_{13})^2 + (J-J_{23})^2 \right\} } \\
 \theta = \cos^{-1}[(J_{13}-J)/r]
\]

As an example of $(J, r, \theta)$ notation, a linear chain with $J_{12}=J_{23}$, $J_{13}=0$, has $J=r=2J_{12}/3$, and $\theta=0$. 
Table 3.2 Solutions of the trimetallic distortion Hamiltonian

In general, for each $S$, there may be two $S'$ with a given value of $\Omega$, $S'=3S+1-\Omega$ and $2S'+1=\Omega$. Taking $H'=(1/2)[S'^2-3S'^2+3S^2]$, the magnetic spectra are given by the roots of:

$\Omega=1; \lambda = 0$.

$\Omega=2$; a) $S'=3S-1, \quad \lambda^2 - 9S^2 = 0$

b) $S'=1/2, \quad \lambda^2 - (1/16)(6S+3)^2 = 0$

$\Omega=3$; a) $S'=3S-2, \quad \lambda^3 - 3(12S^2-6S+1)\lambda + (36S^2-18S+2)\cos3\theta = 0.$

b) $S'=1, \quad \lambda^3 - 3(3S^2+3S+1)\lambda + (9S^2+9S+2)\cos3\theta = 0.$

$\Omega=4; a) S'=3S-3, \quad \lambda^4 - 9(10S^2-10S+3)\lambda^2 + 27(8S^2-8S+2)\lambda \cos3\theta$

$+ 81(9S^4-18S^3+11S^2-2S) = 0$

b) $S'=3/2, \quad \lambda^4 - (9/8)(20S^2+20S+9)\lambda^2 +$

$(27/2)(2S+1)^2\lambda \cos3\theta + (81/256)(144S^4+288S^3+56S^2-88S-15) = 0$

$\Omega=5, a) S'=3S-4, \quad \lambda^5 - 9(20S^2-30S+13)\lambda^3 + 27(28S^2-42S+16)\lambda^2 \cos3\theta$

$+ 81(64S^3-192S^2+200S^2-88S+16)\lambda - 3^52^4(S-1)^2(2S-1)^2\cos3\theta = 0$

b) $S'=2, \quad \lambda^5 - 9(5S^2+5S+3)\lambda^3 + 27(7S^2+7S+2)\lambda^2 \cos3\theta +$

$81(2S)(2S+1)(2S^2+2S-1)\lambda - 3^5[2S(S+1)]^2\cos3\theta = 0.$

3.3.2 Fluxionality of magnetic distortions

It is now necessary to consider the dynamics, or fluxionality, of the distortions described above. Fluxionality is expected in equilateral triangular systems in which small distortions are produced by internal forces such as exchange coupling, since distortions must occur within a degenerate
normal mode. Thus the symmetry-related configurations corresponding to ±θ±2π/3 are equally likely and liable to interconvert if there is a low energy pathway between them. The solution for S=2 is shown in Fig.3.1. It can be seen that a rotation of the distortion vector for constant r, rather than variation of r for constant θ, provides such a low energy pathway since if r goes to zero there is no distortion and no lowering of the energy of the system. If fluxionality occurs, the mean symmetry of the Hamiltonian will be P₃, and the mean symmetry of the system at least C₃ᵥ.

The S=1/2 system is particularly simple. The results given above show that in the absence of significant anharmonic effects the magnetic spectrum is entirely independent of θ. There is no energy barrier to rotation of the distortion vector in the distortion space and the system will be rapidly fluxional at all temperatures. In terms of a classical picture in which d is a well-defined vector, motion along this pathway can be regarded as a pseudo-rotation. The situation can also be described in terms of the vibrational normal modes as a vibronic coupling in which the two zero point vibrational states with S'=1/2 have cylindrical symmetry but different energies arising out of different but constant phase relationships between the spin and nuclear wavefunctions. It is clear that there is some basis for all S' with Ω(S')=2 in which the matrix representation of H is:

\[
(3.30) \quad H = ±E \begin{pmatrix}
\cosθ & \sinθ \\
\sinθ & -\cosθ
\end{pmatrix}
\]
Fig. 3.1. Spectrum for 3 atom, S=2 system as a function of r. C = chain, E = Equilateral triangle and D = dimer
This matrix has the property that the eigenfunctions 
\( \phi_+ = (\cos \theta/2, \sin \theta/2) \) and \( \phi_- = (\sin \theta/2, -\cos \theta/2) \) change sign if \( \theta \) changes by \( 2\pi \). The eigenfunctions can each be considered as superpositions of functions associated with angular momentum 1/2 just as real p orbitals can be constructed from functions with spin 1. The important difference is that the functions of angular momentum 1/2 are not eigenfunctions of \( H \).

The functions \( \phi_+ \) and \( \phi_- \) do not differ in the sense of the rotation about \( r=0 \) and the expectation value of the angular momentum is zero in each.

As \( S \) increases, an increasing number of states are significantly affected by rotation of the distortion vector. For all \( 2S \) odd, the ground state of the system with \( J<0 \) is a pair of doublets which is split by distortion by an amount independent of \( \theta \) as for \( S=1/2 \). For \( 2S \) even, the non-degenerate, non-magnetic ground state has an energy independent of \( \theta \). For \( S>1/2 \) it is useful to take 'small' \( r \) and 'large' \( r \) separately.

(i) Small \( r \). For small \( r \) (\( r \) less than about 0.2J for \( S=2 \) and \( S=5/2 \), see Fig.3.1.) the ground state lies significantly below the first excited state with an energy separation which is \( \theta \) dependent. Resistance to fluxionality occurs only in excited states, and so fast fluxionality is expected. For the rapidly fluxional system the appropriate time averaged spectrum \( \{ \overline{X} \} \) will be given by:

\[
(3.31) \quad \overline{X}_1 = [\lambda_i(0) + \lambda_i(\pi)]/2
\]

This equation defines the fast fluxionality model for
equilateral triangles of isotropically coupled spins. The spectrum can be obtained explicitly from the results given in Table 3.1, and are listed in Table 3.3. The crucial point is that though $H'(\theta)$ averages out over time to zero, its spectrum does not. This type of result is only possible for distortions occurring within degenerate normal modes.

It was shown above that the electronic parts of the vibronic states carry no angular momentum. At high temperatures excited vibrational states may become involved. These states, which for a two-dimensional well do carry angular momentum, may be pictured as driving the change in $\theta$ associated with fluxionality. In this case a solution of the equations of Table 3.2 with $\cos 3\theta$ replaced by its mean value, zero, might be more appropriate. Fortunately, the difference between this approach and the simple approach of (3.32) is negligible. Thus for $S=1, S'=1$ the fast fluxionality spectrum of $\pm 9/2, 0$ from Table 3.3 would be replaced by $\pm 3/2, 0$.

(ii) Large $r$. For large $r$ ($r > 0.25J$ for $S=2,5/2$) a state for which the energy is dependent on $\theta$ forms the ground state or a low-lying state, at least for some $\theta$. The energy barrier to rotation of the distortion vector may be sufficient to cause the system to remain in a state of well defined $\theta$ for thermal equilibrium to occur. In this case the system can be described as slowly fluxional on the time scale of the magnetic susceptibility measurements. Table 3.1 shows that for $Jr > 0$, $\theta = 2n\pi/3$ are thermodynamically the most stable states of the
system. To a first approximation a system which exhibits slow fluxionality can be considered as being fixed at the stable values of $\theta$ and its magnetic spectrum will be the same as that for the Kambe model (Table 3.1). It is to be expected that if $J<0$ the magnetic moment will be larger at low temperatures for a slowly fluxional system than a rapidly fluxional system since a 'high spin' state is brought closer to the ground state.
Table 3.3 The Spectrum for the Dynamic Distortion Model

As \( \theta \) varies, only the total spin, \( S' \), remains a good quantum number. The calculation of \( \{\lambda\} \) is illustrated by the example of the \( S'=1 \) states of the \( S=1 \) trimer.

For these states \( \{\lambda(0)\} = \{-5, 1, 4\} \) from (i) above thus \( \{\lambda(\pi)\} = \{-4, -1, 5\} \), using the symmetry relation (3.11). and \( \{\bar{\lambda}\} = \{(-5-4)/2, (1-1)/2, (4+5)/2\} = \{-9/2, 0, 9/2\} \).

In the list below, each value of \( S' \) is followed by \( \{\bar{\lambda}\} \):

\[
\begin{align*}
S=1/2. & \quad S'=3/2, \{0\} \quad S'=1/2, \{\pm 3/2\}. \\
S=1. & \quad S'=3, \{0\} \quad S'=2, \{\pm 3\}; \\
& \quad S'=1, \{\pm 9/2, 0\} \quad S'=0, \{0\}. \\
S=3/2. & \quad S'=9/2, \{0\} \quad S'=7/2, \{\pm 9/2\}; \\
& \quad S'=5/2, \{\pm 15/2, 0\} \quad S'=3/2, \{\pm 9, \pm 3\}; \\
& \quad S'=1/2, \{\pm 3\}. \\
S=2. & \quad S'=6, \{0\} \quad S'=5, \{\pm 6\}; \\
& \quad S'=4, \{\pm 21/2, 0\} \quad S'=3, \{\pm 27/2, \pm 9/2\}; \\
& \quad S'=2, \{\pm 15, \pm 15/2, 0\}; S'=1, \{\pm 15/2, 0\}; \\
& \quad S'=0, \{0\}. \\
S=5/2. & \quad S'=15/2, \{0\} \quad S'=13/2, \{\pm 15/2\}; \\
& \quad S'=11/2, \{\pm 27/2, 0\} \quad S'=9/2, \{\pm 18, \pm 6\}; \\
& \quad S'=7/2, \{\pm 21, \pm 21/2, 0\} \quad S'=5/2, \{\pm 45/2, \pm 27/2, \pm 9/2\}; \\
& \quad S'=3/2, \{\pm 27/2, \pm 9/2\} \quad S'=1/2, \{\pm 9/2\}. 
\end{align*}
\]
3.3.3 The trigonal bipyramid

The addition of axial atoms above and below an equilateral triangle results in much more complicated magnetic behavior. Some aspects of the $S=1/2$ system will now be investigated with factorable Hamiltonians. There are two natural choices of parameterisation of the configuration of five atom systems. That in terms of the 'normal modes' (I.R.s spanned by \{d\}) in $P_5$, is useful if the fluxionality was sufficient to make all metal atoms equivalent, as for the halides in $\text{PCl}_5$. That in terms of axial, equatorial and internal $J_a$, $J_e$, and $J_i$, is more useful in the present case where there is no interconversion between axial and equatorial metal atoms. The Hamiltonian for the undistorted system is:

\[
H = -J_e(S_{234}^2 - 3S_5^2) - J_a(S_{23}^2 - S_{234}^2 - S_{15}^2) - J_i(S_{15}^2 - 2S_5^2)
\]

where atoms 1 and 5 are axial and atoms 2, 3 and 4 are equatorial. The solution for $S=1/2$ is given in $|S',S_{234},S_{15}>$ notation in (3.33), the spins and energies have been multiplied by two for convenience.

\[
\begin{align*}
|5,3,2> & : -6J_a - 3J_e - J_i ; |3,3,2> , 4J_a - 3J_e - J_i \\
|3,3,0> & : -3J_e + 3J_i ; |3,1,2> , -2J_a + 3J_e - J_i \\
|1,3,2> & : 10J_a - 3J_e - J_i ; |1,1,2> , 4J_a + 3J_e - J_i \\
|1,1,0> & : 3J_e + 3J_i \\
\end{align*}
\]

Those states with $S_{234}=1/2$ have a two-fold degeneracy which is
split by (3.34) which corresponds to distortion of the equilateral triangle.

\[(3.34) \quad H' = -r(S_{234}^2 - 3S_{24}^2 + 3S^2)\]

(3.34) has eigenvalues of zero for states with $S_{234} = 3/2$ and $\pm 3r$ for those with $S_{234} = 1/2$. The theory for $S = 1/2$ trimetallics now applies to each $S_{234} = 1/2$ pair independently. As the system is now described by four quantum numbers $S', S_{234}, S_{15}$ and $S_{24}$, extremely good experimental data would be necessary to define uniquely the four corresponding $J$ values.

The mapping between the nine normal modes, $2A_1' + 2E' + A_2'' + E''$, and the ten $\{J\}$ is complicated by the existence of two $E'$ modes. (3.34) is just one linear combination of distortion Hamiltonians belonging to this mode which leaves the axial $J$ unchanged. It is also possible to define an distortion Hamiltonian which contains 'axial' terms and can be factored:

\[(3.35) \quad H = -r(S'^2 - 3S_{135}^2 + 2S_{15}^2 - 3S_{24}^2 + 6S^2)\]

This has solutions in $|S', S_{135}, S_{15}, S_{24}\rangle$ notation:

\[|5, 3, 2, 2\rangle, 0; \quad |3, 3, 2, 2\rangle, -5; \quad |3, 3, 2, 0\rangle, 1; \quad |3, 1, 2, 2\rangle, 4; \]
\[|3, 1, 0, 2\rangle, 0; \quad |1, 3, 2, 2\rangle, -8; \quad |1, 1, 2, 2\rangle, 1; \quad |1, 1, 0, 2\rangle, -3; \]
\[|1, 1, 2, 0\rangle, 7; \quad |1, 1, 0, 0\rangle, 3. \]

but (3.35) commutes with (3.32) and (3.34) only if the axial and equatorial $J$ are constrained to equal and in general a proper treatment of the effect of dynamic distortions on the axial coupling requires matrix methods. For the $E''$ mode, which
corresponds to a tilt of the equatorial with respect to the axial atoms no factorable distortion Hamiltonian can be defined. The complications in dealing with the axial E' and E'' modes can be considered as arising from the non-equivalence of the atoms in the static Hamiltonian (3.32). As a result the dynamic distortion method can in general be applied to the trigonal bipyramid only for equatorial distortions.
CHAPTER 4 DYNAMIC DISTORTIONS IN TETRAHEDRAL CLUSTERS.

4.1 Introduction

A theory of dynamic distortions in clusters which contain regular tetrahedra of equivalent magnetic atoms will now be developed. The tetrahedron problem is more complicated than the equilateral triangle problem considered in chapter 3 both because the normal modes span two I.R.s, E and T₂, and because of the larger number of spin states involved. As for the equilateral triangle, distortions of the tetrahedron must occur along a degenerate mode.

The non-linear S=1/2 systems with three or four atoms are the only systems with the property that the number of components in \( \{J\} \) and the total number of spin states (ignoring \( S' \) degeneracy) are equal to the number of normal modes. Thus there is a 1:1 relationship between, say, \( a\alpha\beta \) and \( d_{12} \), and \( a\beta a\beta \) and \( d_{13} \). The matrix problem for the six spin states can be reduced by blocking by \( S' \) to three matrices of order 1, 2 and 3. The application of matrix methods to \( S>1/2 \) would be extremely cumbersome (there are 146 states for \( S=5/2 \)) and it is necessary to use the group theoretical and linear algebraic results introduced in chapters 2 and 3. In this chapter the dynamic distortion model is derived for all \( S\leq5/2 \). In the theoretical discussion it is helpful, initially, to consider E and T₂ distortions separately. It is found that solutions which are complete enough to allow definition of both slow and fast fluxionality models can be obtained for both modes for all spin.
4.2 E-mode distortions of magnetic tetrahedra

The Hamiltonian for the E mode distortion of a tetrahedron was derived in 3.1.2:

\begin{equation}
H'(r,\psi) = -2Jr [(S_1 \cdot S_2 + S_3 \cdot S_4)\cos\psi + (S_1 \cdot S_3 + S_2 \cdot S_4)\cos\psi + (S_1 \cdot S_4 + S_2 \cdot S_3)\cos(\psi)]
\end{equation}

'Jr', which only scales H', will be taken as 1 in the theoretical discussion. The $D_2$ symmetry of $H'(\psi)$ greatly simplifies its solution. It can also be seen that $H'$ is of the form introduced in 3.1.3. and so equation (3.17) can be applied:

\begin{equation}
\Omega(S') = k, \{\lambda\}; \lambda^k - (1/2)\sum \lambda^2(0)\lambda^{k-2} - c_3(\lambda) \lambda^{k-3}\cos3\psi + c_4(\theta)\lambda^{k-4} + c_5(\theta)\lambda^{k-5}\cos3\psi \ldots = 0
\end{equation}

The Hamiltonian (4.1) was introduced in 2.4.2. as an example of the use of group theory. It can now be seen that group theory is unnecessary for the $S=1/2$ case. Equation (4.2) and the results for the factorisable Hamiltonian for $\psi = n\pi/3$ define the exact result immediately:

\begin{equation}
S=1/2; \lambda(S'=2) = 0, \{\lambda(S'=1)\} = -2\cos(\psi+n\pi/3), \{\lambda(S'=0)\} = \pm 3.
\end{equation}

It is useful at this point to introduce the idea of the energy plane. The three $S'=1$ energies can be visualised as being defined by the corners of an equilateral triangle of radius 2. As $\psi$ changes the triangle rotates with the same angular velocity. The second dimension of the energy plane is added for convenience only and has no physical significance.
4.2.1 The $S=1$ system

It can be seen from the branching diagram, Table 2.1, that for $S=1 \Omega\{S'=4,3,2,1,0\} = \{1,3,6,6,3\}$. The first step in solving $H'$ is to write down the solutions for the factorisable $H'(0)$:

\begin{equation}
H'(0) = \frac{1}{2} (S'^2 - 3S''^2 - 3S'^2 + 8S^2)
\end{equation}

In $|S',S'',S'''>$ notation the eigenvectors, and associated eigenvalues, are:

\begin{equation}
|4,2,2>, 0; |3,2,2>, -4; |3,2,1>, 2; |2,2,2>, -7;
|2,2,1>, -1; |2,2,0>, 2; |2,1,1>, 5; |1,2,2>, -9; |1,2,1>, -3;
|1,1,1>, 3; |1,1,0>, 6; |0,2,2>, -10; |0,1,1>, 2; |0,0,0>, 8.
\end{equation}

where each eigenfunction is followed by its energy. States with $S'' \neq S'''$ are doubly degenerate. The solutions of all $H'(n\pi/3)$ can be found from (4.4).

The next stage is to consider the I.R.s spanned by the spin states in the magnetic group $D_2$; the group table was given in 2.4.2. The analysis is:

\begin{align*}
\Gamma\{S'_z=4\} &= \Gamma\{|1111>\} = A_1, \\
\Gamma\{S'_z=3\} &= \Gamma\{|1110>\} = A_1 + B_1 + B_2 + B_3, \\
\Gamma\{S'_z=2\} &= \Gamma\{|1100>\} + \{|111-1>\} = 4A_1 + 2B_1 + 2B_2 + 2B_3, \\
\Gamma\{S'_z=1\} &= \Gamma\{|110-1>\} + \{|1000>\} = 4A_1 + 4B_1 + 4B_2 + 4B_3, \\
\Gamma\{S'_z=0\} &= \Gamma\{|11-1-1> + |100-1>\} + |0000>\} = 7A_1 + 4B_1 + 4B_1 + 4B_1, \\
\Gamma(S'=4) &= A_1, \; \Gamma(S'=3) = B_1 + B_2 + B_3, \; \Gamma(S'=2) = 3A_1 + B_1 + B_2 + B_3,
\end{align*}
\[ \Gamma(S' = 1) = 2B_1 + 2B_2 + 2B_3, \quad \Gamma(S' = 0) = 3A_1. \]

The result for \( S' = 3 \) is the same as that for the \( S' = 1 \) states of the \( S = 1/2 \) system, multiplied by two:

\[ (4.7) \quad E(S' = 3) = -4 \cos(\psi + 2\pi/3) \]

Since \( \Omega(0) < 6 \), equation (3.16) can be applied to the \( S' = 0 \) states; the eigenvalues are the roots of the polynomial:

\[ (4.8) \quad \{ \lambda(S' = 0) \}, \quad \lambda^3 - 34\lambda + 160 \cos^3 \psi = 0 \]

Consider \( S' = 2 \), and consider subspaces \( Q(\Gamma, S') \) separately. \( Q(B_1), Q(B_2) \) and \( Q(B_3) \) are each one dimensional, i.e. spanned by a single state. Though the trace of \( H'(\psi) \) expressed in a basis spanning each \( Q \) is no longer constrained to be zero it must still be periodic and even in \( \psi \) for \( B_1 \), in \( \psi \) for \( B_2 \) and in \( \psi \) for \( B_3 \). Thus \( \lambda(B_2) = \lambda(B_2, \psi = 0) \cos \psi \). Inspection of the set of eigenvalues with \( S' = 2 \), \( \{-7, -1, -1, 2, 2, 5\} \), shows that \( \lambda(B_1) = -2\cos \psi \) is the only possible solution. The 'B' eigenvalues are thus:

\[ (4.9) \quad E(B) = -2\cos(\psi + 2\pi/3) \quad n = 0, 1, 2 \]

This leaves only the \( A_1 \) states. Since \( \text{Tr}[Q(A_1, 2)] = 0 \), (4.2) can be applied and the eigenvalues are the roots of the polynomial:

\[ (4.10) \quad \{ \lambda(A_1) \}, \quad \lambda^3 - 39\lambda + 70\cos^3 \psi = 0 \]

Now consider \( S' = 1 \). Since \( \Gamma(S' = 1) \) includes no I.R.s exactly once the problem is slightly more complicated. In \( D_{2d} \) \( (\psi = 0) \), \( \Gamma(S' = 1) = A_2 + B_2 + 2E \) which indicates that those states which form
degenerate pairs of energy -3 and +6 transform as $B_1 + B_3$ in $D_2$. Therefore the states of energy -9,3 must transform as $B_2$.

Consider $H'(\psi)$ in a basis spanning $Q(B_2,1)$ in which $H'(0)$ is diagonal and hence $H'(\pi/2)$ is off-diagonal. Though the eigenvalues of $H'$ need no longer be periodic in $3\psi$ they must change sign if $\psi$ changes by $\pi$:

$$ (4.11) \quad H' = \begin{bmatrix} -9\cos\psi, & c\sin\psi \\ c\sin\psi, & 3\cos\psi \end{bmatrix} $$

Thus the expression $\lambda^2 + 6\lambda\cos\psi - 27\cos^2\psi - c^2\sin^2\psi = 0$, provides the solutions $\{\lambda\}$ for $Q(B_2,1)$. At $\psi = 2\pi/3$ $\{\lambda\}$ must lie in $\{-9,-3,-3,3,6,6\}$ and have $\Sigma\lambda = 3$; the only solution is $\{\lambda\} = \{-3,6\}$. From this it can be seen that the $B_2$ eigenvalues satisfy:

$$ (4.12) \quad \lambda^2 + 6\lambda\cos\psi - (21 + 6\cos 2\psi) = 0, \quad \lambda = -3\cos\psi \pm \sqrt{(36\cos^2\psi + 15\sin^2\psi)} $$

The solutions for $B_1$ and $B_3$ are identical except that $\psi$ is replaced by $\psi \pm 2\pi/3$.

A correlation diagram for the eigenvalues of the $S=1$ tetrahedron, for $S' = 1$ and $S' = 2$, is given in Fig.4.1.

4.2.2 The $S > 1$ systems

Some general results which are valid for all $S$ will be derived before continuing with explicit results for $S=3/2$, $S=2$ and $S=5/2$.

a) $S' = 4S - 1$. The three states of this spin transform as
Fig. 4.1. Correlation diagrams for E distortion of S=1 tetrahedron. S'=2 (above) and S'=1 (below).
$B_1+B_2+B_3$ in $D_2$. At $\psi=0$ the eigenstates are $|4S-1,2S,2S>, |4S-1,2S,2S-1>$ and $|4S-1,2S-1,2S>$ with energies $-4S, 2S$ and $2S$. Therefore the energies for general $H'(\psi)$ are:

$$\text{(4.13)} \{\lambda(S'=4S-1,\psi) = -4S \cos(\psi+2n\pi/3), n=0,1,2 \}

b) S'=4S-2, S>1/2. This R(S,S') contains six states which transform as $3A_1+B_1+B_2+B_3$ in $D_2$. The spectrum at $\psi=0$, found from the factorisable Hamiltonian, is $\{1-8S,1-2S,1-2S,4S-2,4S-2,4S+1\}$ Application of the argument given in 4.1.1. shows that the three 'B' states have energies:

$$\text{(4.14)} \{\lambda(4S-2,B,\psi) = (4S-2) \cos(\psi+2n\pi/3), n=0,1,2 \}

This leaves the $A_1$ states, of energy $\{1-8S,4S-2,4S+1\}$ to be found from:

$$\text{(4.15)} \{\lambda(4S-2,A,\psi)\} \lambda^3-(48S^2-12S+3)\lambda+(8S-1)(4S-2)(4S+1)\cos3\psi=0

\text{c) } S'=0. There are $2S+1$ states of this spin. The $S'=0$ states are split by an amount $[E(|0,2S,2S>) - E(|0,0,0>)] = 6S(2S+1)$ by 'E' mode distortion. Since this splitting is more than that for any other $S'$, a large enough 'E' distortion will produce a singlet ground state in any isotropically coupled tetrahedral cluster. It will now be shown that all $S'=0$ states transform as $A_1$ in $D_2$ and that they therefore cannot cross.

Consider the I.R.s spanned by sets of four objects in $D_2$. (c.f. Table 2.2):

$$\text{(4.16)} \Gamma\{aaaa\}=A_1, \Gamma\{aab\}=A_1+B_1+B_2+B_3, \Gamma\{aab\}=3A_1+B_1+B_2+B_3,$$
\( \Gamma \{aabc\} = 3(A_1 + B_1 + B_2 + B_3) \), \( \Gamma \{abcd\} = 6(A_1 + B_1 + B_2 + B_3) \)

It can be seen that the number of \( B \), states for any \( R(S') \), which will be denoted \( n(B) \), is equal to the number of \( B_2 \) and \( B_3 \) states. Further, the number of \( A \), states, which will be denoted \( n(A) \), is greater than the number of \( B \), states by an amount depending on the number of sets like \{aaaa\} and \{aabb\} spanned by \{\( S' = S'\)\}-\{\( S'_z = S' + 1\)\}, \( z \) (equation 2.23). Consider \{\( S' = 1\)\}; this set can contain no \{aaaa\} or \{aabb\} sets and thus \( n(A) = n(B) \). Now consider \{\( S' = 0\)\}. If \( 2S \) is even then the set contains, in \( (S_{z_1}, S_{z_2}, S_{z_3}, S_{z_4}) \) notation, an element \((0,0,0,0)\) which contributes one state of I.R. \( A \), in excess of the number of states transforming as \( B \). There are also \( S \) sets of the form \{\( z, z, -z, -z \)\} \( z \) integer, each of which contribute two extra states transforming as \( A \). There are \( 2S + 1 \) more \( A \), states than \( B \), states. But there are exactly \( 2S + 1 \) \( S' = 0 \) states and thus they must all transform as \( A \), therefore they cannot cross. For \( 2S \) odd there are \( S + 1/2 \) sets of the form \{\( z, z, -z, -z \)\}, and \( 2S + 1 \) excess \( A \), states and the result is the same.

This result is very relevant to the magnetochemistry of clusters since it means that fluxionality cannot remove the magnetic effects of 'E' mode distortion on the \( S' = 0 \) states.

The spectra for the \( S' = 0 \) states for \( S = 3/2 \) and \( 4/2 \) can be found from:

\[
\begin{align*}
(4.17) \quad S = 3/2 & \quad \lambda^4 - 3^2 42\lambda^2 + 3^3 64\lambda \cos 3\psi + 3^4 105 = 0 \\
S = 2 & \quad \lambda^5 - 6^2 33\lambda^3 + 6^3 44\lambda^2 \cos 3\psi + 6^4 132\lambda - 6^5 144\cos 3\psi = 0
\end{align*}
\]
Since $\Omega(S=5/2, S'=0)=6$, the exact solution for $S=5/2$ cannot be determined by group theory and factorisation alone.

The method used to show that all $S'=0$ states transform as $A$, can also be applied to higher spins. $\{S'_z\text{=even}\}$ can contain $\{aabb\}$ and $\{aaaa\}$ sets of basis states while $\{S'_z\text{=odd}\}$ cannot. Consideration of the number of 'excess' $A$ states gives the result:

(4.18) If $S'=4S-k$, k even , then $n(A)=n(B)+(k+2)/2$;

$S'=4S-k$, k odd , then $n(B)=n(A)+(k+1)/2$;

The I.R.s for the states of the $S>1$ tetrahedra can now be written down directly given the $\Omega(S')$ from the branching diagram.

(4.19) $S=3/2$. $S'=6, A$; $S'=5, B$; $S'=4, 3A+B$; $S'=3, 3B+A$;

$S'=2, 5A+2B$; $S'=1, 3B$; $S'=0, 4A$.

$S=2$. $S'=8, A$; $S'=7, B$; $S'=6, 3A+B$; $S'=5, 3B+A$;

$S'=4, 6A+3B$; $S'=3, 2A+5B$; $S'=2, 7A+3B$; $S'=1, 4B$;

$S'=0, 5A$.

$S=5/2$. $S'=10, A$; $S'=9, B$; $S'=8, 3A+B$; $S'=7, 3B+A$;

$S'=6, 6A+3B$; $S'=5, 6B+3A$; $S'=4, 9A+5B$; $S'=3, 3A+7B$;

$S'=2, 9A+4B$; $S'=1, 5B$; $S'=0, 6A$.

In each case $\Omega(S') = n(A)+3n(B)$.

Finally it can be seen from the results already obtained that if $S''+S'''$ is even the state $|S', S'', S''\rangle$ transforms as $A$, or
B₂ in D₂ and that if S''+S''' is odd then the state transforms as B₁ or B₃. This result is important since it allows correlation diagrams to be constructed for H'(ψ) even when Ω(S') is too large for exact solution.

The solution for S=3/2 will now be completed, i.e. solutions for S'=3, 2 and 1 obtained. From (4.4) the spectrum for ψ=0 is:

\[
(4.20) \begin{align*}
|3,3,3> & , -15; & |3,3,2> & , -6; & |3,3,1> & , 0; & |3,3,0> & , 3; \\
|3,2,2> & , 3; & |3,2,1> & , 9; & |2,3,3> & , -18; & |2,3,2> & , -9; & |2,3,1> & , -3; \\
|2,2,2> & , 0; & |2,2,1> & , 6; & |2,2,0> & , 9; & |2,1,1> & , 12; & |1,3,3> & , -20; \\
|1,3,2> & , -11; & |1,2,2> & , -2; & |1,2,1> & , 4; & |1,1,1> & , 10; & |1,1,0> & , 13;
\end{align*}
\]

Solutions of H'(ψ=0) for all S>1 are listed in Table 4.1.

For S'=3 n(A)=1, n(B)=3. The λ₁ state must have λ=0 for all ψ. The 3 remaining pairs of degenerate states must be B₁+B₃ pairs which shows that at λ=0 the B₂ spectrum is \{-15,0,3\} at ψ=0 and \{-6,3,9\} at ψ=2π/3. The characteristic polynomial for Q(B₂) is of the form:

\[
(4.21) \quad \lambda^3 + a \cos \psi \lambda^2 + (b + b' \cos 2\psi) \lambda + (c \cos \psi + c' \cos 3\psi) = 0
\]

The only solution is a=12, b=-45, b'=0, c=108 c'=-108.

For S'=2 n(A)=5, n(B)=2. The results for the A and B states are:

\[
(4.22) \begin{align*}
\{\lambda(A)\} & : \lambda^5 - 3^3 31\lambda^3 + 3^3 42\lambda^2 \cos 3\psi + 3^4 72\lambda = 0 \\
\{\lambda(B)\} & : \lambda^2 - 6\lambda + (18\cos 2(\psi + n\pi/3) - 45) = 0
\end{align*}
\]
For $S' = 1$ the 9 eigenvalues can be found from:

\[(4.23) \{\Lambda(B)\} \lambda^3 + 12\cos\alpha \lambda^2 - (428 + 112\cos 2\alpha) \lambda/3 + (656\cos 3\alpha - 1856\cos \alpha)/3 = 0\]

where $\alpha = \psi + 2n\pi/3$, $n = 0, 1, 2$.

As $S$ and $\Omega(S')$ increase exact solution of the spectrum using factorisation and group theory becomes increasingly difficult. When $\Omega(Q, S, S', \Gamma) \geq 6$ the method can no longer provide an exact solution. This failure is not serious since a model for the effect of rapid dynamic distortions on magnetic tetrahedra can be derived without the exact eigenvalues by correlation using group theory and introducing the concept of energy bands.
Table 4.1 Solutions of the $E$ distortion Hamiltonian $H'(\psi,0)$

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4.2.3 Fluxionality in 'E' distorted tetrahedra

Table 4.1 defines the slow fluxionality model for E distorted magnetic tetrahedra. To define a model for fast fluxionality model the the effect of rapid dynamic distortions on the populations of the states must be considered. If a pair of states in a rapidly fluxional system become degenerate as \( \psi \) varies at some \( \psi = n\pi/3 \), then their populations are expected to become equal. The spectrum, for each \( S' \), may be divided into sets of states or bands such that each band contains a set of states for which the eigenvalues cross for some value of \( \phi \). The populations of all states within a band will become equal and the thermal and magnetic properties will now depend on the 'mean' energy, and number of states of each band. In the following discussion the number of bands for each \( R(S,S') \) will be denoted \( B(S,S') \), and the number and mean energy of states in each band as \( N(S,S',n) \) and \( E(S,S',n) \) where \( n=1...B(S,S') \).

\( B(S,S') \) and \( E(S,S',n) \) can be obtained by correlation between the \( \psi = n\pi/3 \) configurations using group theory and the non-crossing rule; the exact values of \( \{\lambda(\psi)\} \) are not essential.

As an example of this notation consider a rapidly fluxional \( S=1/2 \) system. (4.24) defines the fast fluxionality model for this system.

\[
\begin{array}{cccc}
(4.24) & S=1/2 & S' & B & N & E \\
2 & 1 & \{1\} & 0 \\
1 & 1 & \{3\} & 0 \\
0 & 2 & \{1,1\} & \{3,-3\}
\end{array}
\]
The corresponding table for $S=1$ is (see, for example, Fig.4.1):

\[
(4.25) \quad S=1 \quad S' \quad B \quad N \quad E
\]

\[
\begin{array}{cccc}
4 & 1 & \{1\} & 0 \\
3 & 1 & \{3\} & 0 \\
2 & 3 & \{1,4,1\} & \{6,0,-6\} \\
1 & 2 & \{3,3\} & \{5,-5\} \\
0 & 3 & \{1,1,1\} & \{9,0,-9\}
\end{array}
\]

For all $S$, the $S'=4S$ and $S'=4S-1$ states are unaffected by distortion if the fluxionality is rapid. The $2S+1 \ S'=0$ states form $2S+1$ bands since they cannot cross, and the band separation is $3(2S+1)$. It becomes apparent that if $S'$ is odd fluxionality makes all states equivalent, i.e. $B=1$ unless $S'=1$, in which case there are $2S$ bands each of $N=3$. The fast fluxionality spectrum for $S=3/2$ is:

\[
(4.26)
\]

\[
\begin{array}{cccc}
S' & B & N & E \\
6 & 1 & \{1\} & 0 \\
4 & 3 & \{1,4,1\} & \{9,0,-9\} \\
2 & 5 & \{1,4,1,4,1\} & \{15,6.75,0,-6.75,-15\} \\
1 & 3 & \{3,3,3\} & \{13,0,-13\} \\
0 & 4 & \{1,1,1,1\} & \{18,6,-6,-18\}
\end{array}
\]

The results to $S=5/2$ are completed by:

\[
(4.27)
\]

\[
\begin{array}{cccc}
S' & B & N & E \\
8 & 1 & \{1\} & 0 \\
6 & 3 & \{1,4,1\} & \{12,0,-12\} \\
4 & 5 & \{1,4,1,4,1\} & \{21,9.75,0,-9.75,-21\} \\
2 & 7 & \{1,4,1,4,1,4,1\} & \{27,16.5,9,0,-9,-16.5,-27\} \\
1 & 4 & \{3,3,3,3\} & \{24,8,-8,-24\} \\
0 & 5 & \{1,1,1,1,1\} & \{30,15,0,-15,-30\}
\end{array}
\]

\[
\begin{array}{cccc}
S' & B & N & E \\
10 & 1 & \{1\} & 0 \\
8 & 3 & \{1,4,1\} & \{15,0,-15\} \\
6 & 3 & \{1,13,1\} & \{27,0,-27\} \\
4 & 5 & \{1,4,14,4,1\} & \{36,15,0,-15,-36\} \\
2 & 9 & \{1,4,1,4,1,4,1,4,1\} & \{42,29.25,21,6,0,-6,-21,-29.25,-42\} \\
1 & 5 & \{3,3,3,3,3\} & \{38,19,0,-19,-38\} \\
0 & 6 & \{1,1,1,1,1,1\} & \{45,27,9,-9,-27,-45\}
\end{array}
\]
All states except those of R(5/2,4) and R(5/2,6) can be found from:

\[(4.28)\]

\[
S' \text{ even, } S'=0 \quad B=(2S+1) \quad N=\{1\ldots\} \quad \Delta E=6S+3
\]

\[
S'>0 \quad S'=4S. \quad B=1.
\]

\[
S'=4S-2. \quad B=3, \quad N=\{1,4,1\} \quad \Delta E=6S.
\]

\[
S'=4S-4. \quad B=5, \quad N=\{1,4,1,4\ldots\} \quad E=\{12S-3,6S-0.75,0\ldots\}
\]

\[
S'=4S-6. \quad B=7, \quad N=\{1,4,1,4\ldots\} \quad E=\{18S-9,12S-7.5,6S-3,0\ldots\}
\]

\[
S'=4S-8. \quad B=9, \quad N=\{1,4\ldots\} \quad E=\{24S-18,18S-15.75,12S-9,6S-9,0\ldots\}
\]

\[
S' \text{ odd, } S'=1 \quad B=2S \quad N=\{3,\ldots\} \quad \Delta E=6S^2+S-2, \quad S'>1 \quad B=1.
\]

Significant difficulties arise if (4.28) is applied to systems with large $S$. These can be described by considering the classical limit in which (4.1) is divided by $S^2$ and $S$ tends to infinity. In this limit there is a continuum of states of each $S'$ and an energy barrier to rotation of the distortion vector between successive stable configurations of 4. For fast fluxionality there is now just one 'band' and thus all states behave like those with $S'>1$, $S'$ odd in (4.28) and the dynamic distortion has no effect on the magnetic spectrum. The spectrum (4.28) as applied to systems with large $S$ can be regarded describing a situation which is between slow and fast fluxionality. For large $S$ the large number of bands implies an increasingly small band separation (on an $S^2$ scale) and thus an increasing possibility of non-adiabatic transitions between bands, and hence merging of several bands into one. The exceptional behavior of R(5/2,4) and R(5/2,6) noted above can be regarded as a crude representation of this effect. The
modification of the magnetic behavior of E distorted tetrahedra of S=1/2 and other finite spins by fast fluxionality is therefore a purely quantum effect.

The effect of E distortions which are slowly fluxional does not decrease as S increases. Theoretical curves for such distortions for S=5/2 are given in Fig 4.2.

4.3 T-mode Distortions of Magnetic Tetrahedra

The consideration of the effect on the magnetic spectrum of T₂ mode distortion is more complicated than for the E mode both because two non-trivial coordinates must be considered and because no non-trivial symmetry is maintained for all orientations of the T₂ distortion vector. Though the procedure would be long and involved, both the three fold and the four fold 'rotation' axes within T₂ could be considered and an essentially complete correlation diagram for the space obtained. The approach followed below is somewhat less complete; only interconversions between low energy configurations in T₂ are considered in detail.

4.3.1 The T₂ distortion Hamiltonian

The T₂ distortion Hamiltonian \( H'(\rho, \theta, \phi) = H'(x,y,z) \) was defined in chapter 3.

\[
H'_{T}(\rho, \theta, \phi) = -2J\rho \left[ (S_{1}.S_{2}-S_{3}.S_{4})\sin\theta\cos\phi+(S_{1}.S_{3}-S_{2}.S_{4})\sin\theta\sin\phi \right. \\
\left. + (S_{1}.S_{4}-S_{2}.S_{3})\cos\theta \right] \\
= -2J\rho \left[ x(S_{1}.S_{2}-S_{3}.S_{4})+y(S_{1}.S_{3}-S_{2}.S_{4})+z(S_{1}.S_{4}-S_{2}.S_{3}) \right]
\]
Fig. 4.2. Moments of E distorted $S=\frac{5}{2}$ tetrahedron; from top to bottom, $\lambda=2, 3, 4, 5$ and 6.
where \( x^2 + y^2 + z^2 = 1 \). The \( J_\rho \) term, which only scales \( H' \), will be taken as 1 in the theoretical discussion.

The result \( \Sigma \lambda^2 = \text{constant} \) applies to \( H'(T_2) \) just as to \( H'(E) \); it is proved in a similar way. If \( H'(T_2) \) is expressed as
\[
H'(x,y,z) = xH_1 + yH_2 + zH_3,
\]
where \( H_1 = H'(1,0,0) \), \( H_2 = H'(0,1,0) \) and \( H_3 = H'(0,0,1) \), \( H'^2 = x^2H_1 + y^2H_2 + z^2H_3 + 2(xyH_1H_2 + yzH_2H_3 + zxH_3H_1) \). Since \( H_1, H_2 \) and \( H_3 \) are similar (they are related by permutations which are elements of \( P_3 \)) \( \text{Tr}[H_1] = \text{Tr}[H_2] = \text{Tr}[H_3] \), i.e. \( \text{Tr}[H'(x,y,z)^2] = \text{Tr}[H_1^2] = 2 \text{Tr}[H_1H_2 + H_2H_3 + H_3H_1] \). But \( H'(x,y,z) \) is similar to \( H'(-x,y,-z) \), \( H'(-x,-y,z) \) and \( H'(-x,-y,-z) \) thus \( \text{Tr}[H_1H_2] = 0 \) and \( \text{Tr}[H'^2(x,y,z)] = \text{Tr}[H_1^2] = \Sigma \lambda^2 = \text{constant} \).

An exact solution for \( S=1/2 \) valid for all \( x,y,z \) can be obtained comparatively easily. For \( S'=0 \) \( <E|T_2|E> \) does not contain the totally symmetric representation and the states are unaffected by \( T_2 \) distortion. For \( S'=1 \) the characteristic polynomial can be expressed as:

\[
(4.30) \quad \lambda^3 - c_2(r)\lambda - f(x,y,z) = 0
\]

where the coefficient of \( \lambda^2 \) is zero as \( H(T_2) \) is traceless and \( c_2 \) is proportional to \( r^2 \). \( f(x,y,z) \) is symmetry related to \( f(-x,y,z) \), i.e. \( f(x,y,z) = f(-x,-y,z) \). Thus \( f(x,y,z) = -f(-x,y,z) \) and \( f(0,y,z) = 0 \). Therefore \( f(ax,y,z) = af(x,y,z) \) for all \( a \) and, by permutation of \( x,y,z \) \( f(ax,\beta y,\gamma z) = a\beta \gamma f(x,y,z) \) for all \( a,\beta,\gamma \). Therefore \( f(x,y,z) \) is proportional to \( xyz \). The complete solution can now be obtained from any particular
solution. Taking \( x=y=z=1/\sqrt{3} \), for which the solution, obtained by factorisation (see (4.31)) is \( 1/(\sqrt{3})\{4,-2,-2\} \), \( \Sigma \lambda^2 = 8 \Rightarrow c_2 = -4 \), \( f(x,y,z) = -16/3\sqrt{3} = c_3/3\sqrt{3} \), \( c_3 = -16 \). The result is easier to visualise if the characteristic equation is expressed:

\[
(\lambda - \lambda_0 \cos \theta)(\lambda - \lambda_0 \cos \theta)(\lambda - \lambda_0 \cos \theta) = 0
\]

where \( \theta = \cos^{-1}(-3\sqrt{3}xyz) \) and \( \lambda_0 = 4/\sqrt{3} \). Thus, as for the E mode, rotation of the distortion vector corresponds to a rotation of the \( S'=1 \) triangle in the energy plane, in this case the behavior of the eigenvalues is more complicated as the rotation is three dimensional.

For all \( S \), the ground state of \( H'(x=y=z=-1/\sqrt{3}), a=0 \), is the lowest possible energy state of the system, this Hamiltonian will be denoted \( H'^0 \). \( H'^0 \) can be factorised:

\[
(4.32) \quad H'^0 = 1/\sqrt{3} \left( S'^2 - 2S'^2 + 2S^2 \right)
\]

where \( S''=S_2+S_3+S_4 \). \( H'^0 \) has \( P_3 \) symmetry with magnetic group elements \{E,P(23),P(24),P(34),P(234),P(243)\} and its associated distortions produce tetrahedra with point group symmetry \( C_{2v} \). The eigenvalues of \( H'(-1,-1,-1) \) for all \( S \leq 5/2 \) are listed in Table 4.2.

It can be seen from the table that, in contrast to 'E' mode distortions, 'T' mode distortions split the \( S'=2S \) states by the largest amount and leave the \( S'=0 \) states unchanged.
Table 4.2 Solutions of the T distortion Hamiltonian \( H'(-1,-1,-1) \)

The degeneracy of a state \(|S',S''\rangle\) is equal to the number of total spin = \(S''\) states of the corresponding three atom system, \(\Omega(3,S,S'')\). The energies should be divided by \(\sqrt{3}\) before comparison with other eigenvalues of (4.29) which requires \(x^2+y^2+z^2=1\).

\[
\begin{align*}
S &= 1/2, \\
|2,3/2\rangle, &\quad 0, & |1,3/2\rangle, &\quad -4, & |1,1/2\rangle, &\quad 2, & |0,1/2\rangle, &\quad 0. \\
S &= 1, \\
|4,3\rangle, &\quad 0; & |3,3\rangle, &\quad -8; & |3,2\rangle, &\quad 4; & |2,3\rangle, &\quad -14; \\
|2,2\rangle, &\quad -2; & |2,1\rangle, &\quad 6; & |1,2\rangle, &\quad -6; & |1,1\rangle, &\quad 2; \\
|1,0\rangle, &\quad 6; & |0,1\rangle, &\quad 0. \\
S &= 3/2, \\
|6,9/2\rangle, &\quad 0; & |5,9/2\rangle, &\quad -12; & |5,7/2\rangle, &\quad 6; & |4,9/2\rangle, &\quad -22; \\
|4,7/2\rangle, &\quad -4; & |4,5/2\rangle, &\quad 10; & |3,9/2\rangle, &\quad -30; & |3,7/2\rangle, &\quad -12; \\
|3,5/2\rangle, &\quad 2; & |3,3/2\rangle, &\quad 12; & |2,7/2\rangle, &\quad -18; & |2,5/2\rangle, &\quad -4; \\
|2,3/2\rangle, &\quad 6; & |2,1/2\rangle, &\quad 12; & |1,5/2\rangle, &\quad -8; & |1,3/2\rangle, &\quad 2; \\
|1,1/2\rangle, &\quad 8; & |0,3/2\rangle, &\quad 0. \\
S &= 2, \\
|8,6\rangle, &\quad 0; & |7,6\rangle, &\quad -16; & |7,5\rangle, &\quad 32; & |6,6\rangle, &\quad -30; \\
|6,5\rangle, &\quad -6; & |6,4\rangle, &\quad 14; & |5,6\rangle, &\quad -42; & |5,5\rangle, &\quad -18; \\
|5,4\rangle, &\quad 2; & |5,3\rangle, &\quad 18; & |4,6\rangle, &\quad -52; & |4,5\rangle, &\quad -28; \\
|4,4\rangle, &\quad -8; & |4,3\rangle, &\quad 8; & |4,2\rangle, &\quad 20; & |3,5\rangle, &\quad -60; \\
|3,4\rangle, &\quad -16; & |3,3\rangle, &\quad 0; & |3,2\rangle, &\quad 12; & |3,1\rangle, &\quad 18; \\
|2,4\rangle, &\quad -22; & |2,3\rangle, &\quad -6; & |2,2\rangle, &\quad 6; & |2,1\rangle, &\quad 14; \\
|2,0\rangle, &\quad 18; & |1,3\rangle, &\quad -10; & |1,2\rangle, &\quad 2; & |1,1\rangle, &\quad 10; \\
|0,2\rangle, &\quad 0. \\
S &= 5/2, \\
|10,15/2\rangle, &\quad 0; & |9,15/2\rangle, &\quad -20; & |9,13/2\rangle, &\quad 10; & |8,15/2\rangle, &\quad -38; \\
|8,13/2\rangle, &\quad -8; & |8,11/2\rangle, &\quad 18; & |7,15/2\rangle, &\quad -54; & |7,13/2\rangle, &\quad -24; \\
|7,11/2\rangle, &\quad 2; & |7,9/2\rangle, &\quad 24; & |6,15/2\rangle, &\quad -68; & |6,13/2\rangle, &\quad -38; \\
|6,11/2\rangle, &\quad -12; & |6,9/2\rangle, &\quad 10; & |6,7/2\rangle, &\quad 28; & |5,15/2\rangle, &\quad -80; \\
|5,13/2\rangle, &\quad -50; & |5,11/2\rangle, &\quad -24; & |5,9/2\rangle, &\quad -2; & |5,7/2\rangle, &\quad 16; \\
|5,5/2\rangle, &\quad 30; & |4,13/2\rangle, &\quad -60; & |4,11/2\rangle, &\quad -34; & |4,9/2\rangle, &\quad -12; \\
|4,7/2\rangle, &\quad 6; & |4,5/2\rangle, &\quad 20; & |4,3/2\rangle, &\quad 30; & |3,11/2\rangle, &\quad -42; \\
|3,9/2\rangle, &\quad -20; & |3,7/2\rangle, &\quad -2; & |3,5/2\rangle, &\quad 12; & |3,3/2\rangle, &\quad 22; \\
|3,1/2\rangle, &\quad 28; & |2,9/2\rangle, &\quad -26; & |2,7/2\rangle, &\quad -8; & |2,5/2\rangle, &\quad 6; \\
|2,3/2\rangle, &\quad 16; & |2,1/2\rangle, &\quad 22; & |1,7/2\rangle, &\quad -12; & |1,5/2\rangle, &\quad 2; \\
|1,3/2\rangle, &\quad 12; & |0,5/2\rangle, &\quad 0.
\end{align*}
\]
The path followed by a distortion vector rotating in the $T_2$ space is not uniquely defined as it was for 'E' mode distortions and a more precise understanding of the potential well and of time considerations would be necessary to obtain a detailed description of the motion. Plausible suggestions for the behavior of both the slow and fast fluxionality systems are considered below, and the problem will be discussed again in Chapter 7.

Consider first the slowly fluxional cluster. The system will spend most time in one of the four low energy configurations, $(-1,-1,-1), (-1,1,1), (1,-1,1), (1,1,-1)$, denoted $\{(-1,-1,-1)\}$. $\{(-1,-1,-1)\}$ defines a tetrahedron in the $T_2$ space. The high energy configurations $(-1,-1,1), (-1,1,-1), (1,-1,-1)$ and $(1,1,1)$, denoted $\{(1,1,1)\}$, define a tetrahedron which opposes $\{(-1,-1,-1)\}$ i.e. the points $\{(1,1,1)\} + \{(-1,-1,-1)\}$ define a cube in $T_2$. If the system has just enough energy to interconvert between members of $\{(-1,-1,-1)\}$ it may be represented as following paths such as $(-1,-1,-1), (-1,0,0), (-1,1,1), (0,0,1), (1,-1,1)$, along the edges of the tetrahedron $\{-1,-1,-1\}$.

Consider now the rapidly fluxional cluster. If the interconversion is rapid the distortion vector may be associated with an angular momentum making it tend to follow a great circle in $T_2$. Only two points from the set $\{(-1,-1,-1)\}$ can lie on a great circle and a great circle through a point in $\{(-1,-1,-1)\}$ must also pass through a point in $\{1,1,1\}$. The system can be
pictured as precessing (perhaps discontinuously) between great
circles defined by two points from \{1,1,1\}. At very high
temperatures all great circles will be associated with
approximately equal free energy and essentially free precession
will occur.

The correlation of the spin states for the great circle
through \( (1,1,1) \) and \( (1,-1,-1) \) will now be considered. The path
can be parameterised by: \( x = \cos \beta \), \( y = z = \sqrt{2} \sin \beta \) and will be
denoted \( P(\beta) \):

\[
(4.34) \quad H'(\beta) = 2(S_1 S_2 - S_3 S_4) \cos \beta + \sqrt{2}(S_1 S_3 + S_1 S_4 - S_2 S_4 - S_2 S_3) \sin \beta
\]

\( H' \) can be factorised both when \( |x| = |y| = |z| \) (giving \( H'^0 \)) and when
\( y = z = 0 \):

\[
(4.33) \quad H'(-1,0,0) = 2(S_1 S_2 - S_3 S_4) = S_{12}^2 - S_{34}^2
\]

\( H'(-1,0,0) \) will be denoted \( H' \). The six Hamiltonians which are
symmetry related to \( H' \) define the corners of an octahedron in
\( T_2 \). They are associated with \( C_{2v} \) distortions of the cluster.

For \( S = 1/2 \), only the \( S' = 1 \) states are affected by \( T_2 \)
distortion. The exact solution, which can be obtained from
(4.30), is plotted in Fig.4.3. If the system has no angular
momentum and is slowly fluxional only that part of the
correlation diagram between \( (1,-1,-1) \) and \( (1,1,1) \) is involved.
States in \( \{1,1,1\} \) may interconvert with an energy barrier of
only \( \sqrt{(16/3)} - 2 \approx 0.31 \); it is to be expected that the system
will rock back and forth 'slowly' between \( \{1,1,1\} \). The spectrum
Fig. 4.3. Correlation diagram for $S=1/2$ tetrahedron for $T_2$ distortion.
is divided into two bands, one containing the ground state and the other containing the two excited states. If the cluster exhibits fast fluxionality it will be unable to avoid passing through (or near to) a point in \{-1,-1,-1\}. It can be seen from Fig. 4.3 that the fluxionality will cause all the states to become equivalent.

It can be seen from the above discussion that the ground state of a T\textsubscript{2} distorted tetrahedron may exhibit considerable resistance to fluxionality since there is no loss of energy relative to the undistorted system the fluxionality becomes rapid.

Group theory can be applied to the problem of correlating the magnetic spectrum for the path P(\beta) but is less useful than for the 'E' mode distortions since only a single symmetry element, P(34), is maintained for all \beta; this gives a magnetic group P\textsubscript{2}. For S=1/2 the three S'=1 states for \beta=0 can be expressed, in |S',S\textsubscript{12}, S\textsubscript{34}> notation as |1,1,1>, |1,0,1>, which transform as A\textsubscript{2}, and |1,1,0>, which transforms as A\textsubscript{1}. The single A\textsubscript{1} state must have energy \(\lambda=\lambda(\beta=0)\cos\beta=2\cos\beta\). The energies of the two A\textsubscript{2} states can be found by writing:

\[(4.35) \lambda^2 + c_1(\beta) \lambda + c_2(\beta) = 0\]

Since Tr[R(S'=1)]=0 \(c_1=2\cos\beta\). \(c_2\) can be expressed \(c_2=d+e \cos\beta\).

At \(\beta=0\), (4.33) is \(\lambda^2+2\lambda=0\) indicating that d=−e. The angle \(\beta=\cos^{-1}(1/\sqrt{3})\) will be denoted \(\beta_0\). At \(\beta=\beta_0\), \(\lambda^2+\sqrt{4/3}\lambda+8/3=0\) is obtained which shows that the full solution is:
(4.36) $\lambda^2 + 2\cos\beta \lambda - 4\sin^2\beta = 0$, $\lambda = -\cos\beta \pm \sqrt{(\cos^2\beta + 4\sin^2\beta)}$

4.3.2 $S > 1/2$ systems

For $S > 1/2$ problems arising from the incompleteness of the atom based magnetic groups, discussed in chapter 2, arise for the first time. The equivalence of the three atoms at $\beta = \beta_0$, which allows the Hamiltonian to be factorised by the introduction of an intermediate spin consisting of three individual spins, may give rise to a degeneracy greater than the dimension of the largest I.R. (E) in $P_3$; one result of this is an apparent breakdown of the non-crossing rule at $\beta = \beta_0$. Apart from this difficulty, application of factorisation is now very similar to that for the 'E' mode and a detailed calculation will be given only for $S = 1$.

For $S = 1$, the $S' = 3$ states behave in the same way as the $S' = 1$ states of the $S = 1/2$ system; the general result for $S' = 4S - 1$ for all $S$ is just (4.30) multiplied by $2S$. The $S' = 0$ states are unaffected by $T_2$ distortion. As for the 'E' mode, the calculation for $S' = 1, S' = 2$ is somewhat more complicated. Consider $S' = 1$. At $\beta = 0$ the states are $|1, 2, 2\rangle, |1, 1, 2\rangle$ and $|1, 1, 0\rangle$, which transform as $A_1$, and $|1, 2, 1\rangle, |1, 1, 1\rangle$ and $|1, 0, 1\rangle$, which transform as $A_2$. $\{\lambda(A_1)\} = \{-4, 0, 2\}$, $\{\lambda(A_2)\} = \{4, 0, -2\}$. Clearly the solution for $A_1$ will also give the solution for $A_2$. Writing:

\begin{equation}
\lambda^3 + 2\lambda^2 \cos\beta + (c_1 + c_2 \cos 2\beta)\lambda + (c_3 \cos 3\beta + c_4 \cos\beta) = 0
\end{equation}

$\beta = 0 : \lambda^3 + 2\lambda^2 - 8\lambda = 0$

$\beta = \beta_0 : \lambda^3 + \sqrt{(4/3)} - 20\lambda/3 + \sqrt{(64/3)} = 0$
The solution is:

\[(4.37) \lambda^3 + 2\lambda^2 \cos \beta - (7 + \cos 2\beta) \lambda + 3(\cos \beta - \cos 3\beta) = 0. \]

For \(\beta = 0\), the \(S' = 2\) states are \(|2, 2, 2>, |2, 1, 2>, |2, 0, 2>, |2, 2, 0>, A_1, \) and \(|2, 2, 1>, |2, 1, 1>, A_2\). The two \(A_2\) states can be found in the same way as those for \(S = 1/2\) \(S' = 1\). The result is \(\lambda = 2\cos \beta \pm \sqrt{(4\cos^2 \beta + 6\sin^2 \beta)}\) The four \(A_1\) states have energies \(\{\lambda\} = \{6, 0, -2, -6\} \) at \(\beta = 0\) and \(\sqrt{3}\{-14, -2, 6, 6\} \) at \(\beta = \beta_0\). Writing:

\[(4.38) \lambda^4 + 4\lambda^3 \cos \beta + (b + b' \cos 2\beta) \lambda^2 + (c \cos \beta + c' \cos 3\beta) \lambda + (d + d' \cos 2\beta + d'' \cos 4\beta) = 0\]

\[\beta = 0 \quad \lambda^4 + 4\lambda^3 - 37\lambda^2 - 144\lambda = 0\]
\[\beta = \beta_0 \quad \lambda^4 + 4\lambda^3 \cos \beta_0 - (128/3)\lambda^2 + 80\lambda \cos \beta_0 + 112 = 0\]

The solutions for \(b\) and \(b'\), and for \(c\) and \(c'\) are obtained as before but for the coefficient of \(\lambda^0\) more information is necessary to define \(d, d'\) and \(d''\). If the path \((1, 0, 0), (0, 1, 0), (-1, 0, 0), (0, -1, 0)\), where the points are related by a \(C_4\) axis is considered, it can be shown that the point \((1, 1, 0)\) has two \(A_2\) eigenstates with \(\lambda = 0\). Thus \(d + d' + d'' = d - d' + d'' = 0\), \(d' = 0\) and \(d = 63, d'' = -63\). The solution for general \(\beta\) can now be written:

\[(4.39) \lambda^4 + 4\lambda^3 \cos \beta + (5\cos 2\beta - 41) \lambda^2 - (60\cos \beta + 84\cos 3\beta) \lambda + 63(1 - \cos 4\beta) = 0\]

The result for \(S = 1\) \(S' = 2, 1\), is shown in Fig. 4.4., again only that part of the correlation diagram between \((1, -1, -1)\) and \((1, 1, 1)\) is needed for slow fluxionality. As with \(S = 1/2\), if the fluxionality is rapid the effect of \(T_2\) distortion is removed from the spectrum.
Fig 4.4. Correlation diagrams for $T_2$ distortion of $S=1$ tetrahedron. $S'=2$ (above) and $S'=1$ (below).
If this approach is continued for $S>1$ it is found that the effect of $T$ distortion is entirely removed from the magnetic spectrum of any spin if the fluxionality is rapid. This can be seen by correlating between $H(-1,-1,-1)$ and $H(1,1,1)$ (see Table 4.2). Even if the non-crossing rule applied for all states it is clear that since the number of highest energy states of a given spin is never equal to the number of lowest energy states there can be only one 'band' for each value of $S'$.

The dynamic distortion model for $T_2$ distorted tetrahedra of general spin can thus be summarised by: (i) Slow fluxionality, $H'=H'(-1,-1,-1)$, a factorisable Hamiltonian, (ii) Fast fluxionality, $H'=0$.

4.3.3 General distortions of tetrahedra

As $H'(E)$ and $H'(T)$ do not, in general, commute, the results derived in 4.2 and 4.3 do not amount to a complete solution for general distortions. Such a solution would involve all six variables of $\{J\}$ and would be rather complicated even though, for example, a $T_2$ distortion can always be ignored in the calculation of the $S'=0$ energies.

For fast fluxionality, $E$ distortion lowers the symmetry of the system and splits both the $T_2$ mode and the degeneracy which favours the $T_2$ distortion; similarly significant $T_2$ distortion splits the $E$ mode. Thus the two types of distortion can be envisaged as competing, each will tend to 'quench' the other, and therefore consideration of the general distortion
Hamiltonian is unlikely to be necessary.

For both E and T₂ slow fluxionality the magnetic spectrum retains some degeneracy and hence there is a possibility of secondary distortion. The slow T₂ system retains a C₃ axis and therefore an E mode. This is not the original E mode but one derived from the two components of the T₂ mode orthogonal to the original distortion, and so results such as the lack of splitting of the S' = 0 states still apply. The E mode of the slow E distorted system is also derived from the original T₂ mode and so in this case effects associated with T₂ distortion might occur. Thus for S = 1/2, such a secondary distortion would move the low energy triplet closer to the singlet ground state.

4.4 Temperature Dependent Fluxionality (TDF)

The discussion in this and the preceding chapter has shown that there is typically an energy barrier to rotation of the distortion vector of a high symmetry magnetic cluster within a degenerate normal mode. This energy barrier tends to divide the potential well of the cluster into 3 smaller wells for E distortion and 4 smaller wells for T distortion, in each case the secondary wells are related by symmetry operations of the undistorted cluster.

Two extreme types of behavior associated with these energy barriers have been defined. Thus in slow and fast fluxionality the lifetime of the distorted configurations are, respectively, long and short compared to the rate at which the magnetic
spectrum attains thermal equilibrium. Since the lifetimes of a distorted configuration may depend on its thermal energy it is reasonable to expect that, under suitable circumstances, a transition from slow to fast fluxionality as the temperature increases, i.e. temperature dependent fluxionality, or TDF, may occur. As such behavior cannot be modelled, using the Heisenberg-Dirac-VanVleck approach, by a temperature independent spectrum it is necessary to define a new model which provides a connection between the low and high temperature forms.

A somewhat tentative model for TDF will now be derived. The model as applied to $S=1/2$ tetrahedra will be tested against experimental data in chapter 5.

Factors which determine the type of fluxionality include 1) The rate at which the magnetic spectrum attains thermal equilibrium, 2) The relative magnitudes of the vibrational force constant and $\partial J/\partial d)_{0}$, since these affect the shape of the potential well, and 3) the magnetic spectrum itself. Thus a system with a spectrum which includes a low-lying triplet state is expected to have a larger energy barrier to interconversion than one in which the triplets are well removed from the ground state. A full treatment of the above factors would be both very complicated and somewhat redundant since the values of many of the important parameters, such as the relaxation rates between states of the same spin, and between states of different spin, are not known. As $S'$, but no intermediate quantum number, is a constant of the motion for rotation of the distortion vector,
the relaxation rate within a set of states of the same $S'$ can be assumed to be much faster than that between sets of states of different spin. In other words, spin-lattice relaxation is expected to be most effective for states of the same $S'$. Because of this it is possible to consider clusters of different $S'$ separately. As the energy barriers to interconversion depend on $S'$ so, in general, will the rates of fluxionality.

For each cluster with a given $S'$ it is possible to define a low temperature partition function, $f_0$, and a high temperature function, $f_1$. All that is required to apply the HDVV formalism to fit magnetic data is a total partition function, $f$, which changes smoothly from $f_0$ at low temperature to $f_1$ at high temperature. It is possible to define an 'effective' fraction in the slowly fluxional form, $p$, and write:

$$f = pf_0 + (1-p)f_1$$

(4.40)

It is now necessary to choose a form for $p$ such that $p=1$ at low temperature and $p=0$ at high temperature. One simple form is:

$$p = \exp(-T/\epsilon)$$

(4.41)

where the $T$ in the numerator of the exponential can be regarded as corresponding to the thermal energy of the system which must overcome an energy barrier of height $\epsilon$. Fast fluxionality corresponds to $\epsilon=0$, $f=f_1$ for all $T$; slow fluxionality corresponds to $\epsilon \gg \delta$ since in this case $f_1$ becomes close to $f_0$ before $p$ varies significantly from 1.
For the simplest example of a TDF system, the $S=1/2$ tetrahedron, in which only the triplet states are affected by fluxionality, application of (4.40) gives a TDF triplet partition function, with respect to the mean triplet energy:

\[(4.42) f_3 = 3p\{2\exp+\delta/T +\exp(-2\delta/T)\} + 9(1-p)\]

where $3\delta$ is the triplet splitting in the magnetic spectrum for slow fluxionality.

It must be admitted that the above form for $p$ is far from unique, it was originally suggested by the expression for transition probability due to tunnelling through a simple potential barrier, which has an energy in the numerator of an exponential. It may be that tunnelling as well as thermal activation over the energy barrier is significant in the present case since even though the large effective mass will tend to reduce tunnelling the distances involved are very small. Also the concept of 'effective' proportion of clusters which exhibit slow and fast fluxionality, though satisfactory for a treatment of magnetic data because the partition function is just a simple number, may be inadequate where experiments which measure the magnetic spectrum more directly, such as e.s.r., are involved. Thus, while the fast and slow fluxionality models are theoretically satisfactory, a decision on the above model for TDF must be postponed until the experimental data are considered in the next chapter.
4.5 Dynamic Distortions of Octahedra

The magnetic group of the undistorted cluster is isomorphic to $O_h$, the point group. The normal modes are $\{A_1g + E + T_2g + T_1u + T_2u\}$ and the Hamiltonian, $H_0$, contains independent 'exterior' and 'interior' couplings, $J_e$ and $J_i$ between adjacent and opposite atoms. In general there is no reason to assume $J_i=0$; indeed, if the cluster contains an exchange active central atom the pathways corresponding to $J_e$ and $J_i$ are of equal length.

$$H_0 = -J_e (S'_2 - S_{13}^2 - S_{25}^2 - S_{36}^2) - J_i (S_{14}^2 + S_{25}^2 + S_{36}^2 - 6S^2)$$

Atom $n+3$ in (4.43) is opposite atom $n$. As for the tetrahedron, the magnetic spectrum contains degeneracies associated with the E and T modes which can be expected to be removed by dynamic distortions.

As for the trigonal bipyramid the lack of full permutation group symmetry (unless $J_e=J_i$) severely limits the number of factorable distortion Hamiltonians which commute with $H_0$. Some aspects of the $S=1/2$ system will now be investigated.

The spectrum of (4.43) for $S=1/2$ is given in (4.44). The states may be denoted most simply by $|S'S_1S_{25}S_{36}\rangle$ but in the present discussion it is useful to introduce $S_{1346}=S_{14}+S_{36}$ and use the notation $|S'(S_{1346}S_{14}S_{36})S_{25}\rangle$, in which the spins in parenthesis lie in an equatorial plane of the octahedron. This latter notation gives a unique description of each state.
Note that there are two sources of degeneracy in the system: if $S_{1a}=S_{25}=S_{36}=1$ the combination of the three angular momenta results in a degeneracy found from the branching diagram for $N=3, S=1$; if $S_{1a}, S_{25}$ and $S_{36}$ are not equal there is degeneracy related to interchanges of these pairs of spins.

The only factorable distortion Hamiltonian which modifies the external $J$ and commutes with $H_0$ is:

\[(4.45) \quad H' = \frac{r}{2} \left( S'^2 - 3S_{1a}^2 + 2S_{1a}^2 + 2S_{36}^2 - S_{25}^2 \right)\]

with solutions (in units of $r$):

\[(4.46) \quad \begin{array}{c|c}
3(211)1> & 0 \\
2(211)1>, |2(111)1> & -3, +3 \\
1(211)1>, |1(111)1>, |1(011)1> & -5, 1, 4 \\
0(111)1> & 0 \\
2(211)0>, |2(110)1>, |2(101)1> & -2, 1, 1 \\
1(111)0>, |1(110)1>, |1(101)1> & 2, -1, -1 \\
0(011)0>, |0(110)1>, |0(101)1> & 4, -2, -2 \\
1(000)1>, |1(110)0>, |1(101)0> & 0, 0, 0 \\
0(000)0> & 0.
\]

\[(4.45) \text{ and the two Hamiltonians related by permutation of the axes of the octahedron sum to zero; they are E mode distortion vectors. The general distortion Hamiltonian for this mode can be}\]
written:

\[(4.47) \quad H'(\theta) = \cos \theta \left( S_2 S_3 + S_3 S_5 + S_5 S_6 + S_6 S_2 \right) + \cos \theta \left( S_1 S_3 + S_3 S_4 + S_4 S_6 + S_6 S_1 \right) + \cos \theta \left( S_1 S_2 + S_2 S_4 + S_4 S_5 + S_5 S_1 \right)\]

The 8 symmetry elements associated with permutations of one or more of the pairs of spins \((14), (25), (36)\), which form a group isomorphic to \(D_{2h}'\), are maintained throughout (just as \(D_2\) symmetry is retained for all \(E\) distortions of the tetrahedron). The states with \(S_{14} = S_{25} = S_{36} = 1\) transform as \(A_g\) in \(D_{2h}\) and those with one of \(\{S_{14}, S_{25}, S_{36}\}\) equal to zero, as \(B_{1u} + B_{2u} + B_{3u}\); those with two of \(\{S_{14}, S_{25}, S_{36}\}\) equal to zero transform as \(B_{1g} + B_{2g} + B_{3g}\) and the state with \(S_{14} = S_{25} = S_{36} = 0\) transforms as \(A_u\). Analysis shows that all eigenstates except those transforming as \(A_g\) are independent of \(\theta\). The groups of three \(\theta\) independent eigenstates in \((4.46)\) therefore rotate in the energy plane with \(\theta\) in the same way as the \(S'=1\) states of the \(S'=1/2\) tetrahedron.

It can be seen that for (this) \(E\) mode distortion fast fluxionality leaves the magnetic spectrum unchanged except that the states with \(S_{14} = S_{25} = S_{36} = 1\) behave like the corresponding states of the \(S'=1\) triangle. For slow fluxionality the \(S'=1\), not the \(S'=0\), states exhibit the largest splitting and if \(J_e > 0\), \(J_1 = 0\) the ground state is \(S'=3\) for \(r<2\) and \(S'=1\) for \(r>2\), never \(S'=0\) or \(S'=2\).

The internal \(J\) can be varied independently of both each other and the external \(J\) with the distortion Hamiltonian:
\[(4.48) \quad H'' = xS_{14}^2 + yS_{25}^2 + zS_{36}^2 - 2(x+y+z)S^2 \]

which commutes with \( H_0 \) and \( H' \). If \( x=y=z \) \( H \) has the symmetry of \( H_0 \), for \( x+y+z=0 \) \( H'' \) lies in the E mode, i.e.:

\[(4.49) \quad H'' = S_{14}^2 \cos \theta + S_{25}^2 \cos \theta + S_{36}^2 \cos \theta. \]

The assumption that \( J \) is linear in the distortion constrains the magnitude of the distortion \( (4.48) \) to be proportional to that of \( (4.45) \); that there is such a constraint is clear from the fact that there is only one E mode. \( (4.49) \) does not affect the states with \( S_{14}=S_{25}=S_{36} \). The remaining states have energies:

\[(4.50) \quad |2(211)0>, |2(110)1>, |2(101)1> = -2,1,1 \]
\[|1(111)0>, |1(110)1>, |1(101)1> = -2,1,1 \]
\[|0(011)0>, |0(110)1>, |0(101)1> = -2,1,1 \]
\[|1(110)0>, |1(101)0>, |1(000)1> = 2,-1,-1 \]

Application of \((3.17)\) shows that fast fluxionality completely removes the effect of distortion of the form \((4.49)\). Where \( J_1 \) and \( J_e \) are at least approximately equal, consideration of distortion Hamiltonians based on the C\(_3\) axis, such as:

\[(4.51) \quad H = 2S'^2 - 5S_{12}^2 - 5S_{45}^2 + 18S^2 \]

and

\[(4.52) \quad H = S_{12}^2 - S_{45}^2 \]

would give some idea of the effects of T mode distortions on the spectrum. \((4.51)\) results from \( T_{2g} \) distortion and \((4.52)\) from a combination of \( T_{1u} \) and \( T_{2u} \) distortions. It can be seen that
$T_{2g}$ distortion is associated with a large singlet splitting and may produce a singlet ground state in a system with $J_e > 0$, $J_i = 0$. This approximate method would be essential for treatment of distorted high-spin clusters, as the large number of states ($6^6$ for $S=5/2$) makes matrix solution impracticable even if the matrix is blocked by $S_z$. 
CHAPTER 5 APPLICATIONS OF THE DYNAMIC DISTORTION MODEL.

Dynamic distortion effects are expected to be most pronounced in clusters which exhibit (i) high symmetry and (ii) coupling constants which are very sensitive to distortion. At least a three fold axis relating equivalent metal atoms is necessary so that the distortion Hamiltonian spans a degenerate normal mode and the Heisenberg magnetic spectrum contains degeneracy in addition to that associated with the total spin. The requirement for large \( \langle \delta J/\delta d \rangle_0 \) suggests that distortion effects are particularly likely in complexes which contain oxide or halide bridges, since exchange associated with these bridges has been shown to be very susceptible to small changes in configuration.

The clusters \( \text{Cu}_8 \text{OX}_6 \text{L}_3 \) \(^{37,87-110}\) (where \( X \) is a halide and \( L \) is a Lewis base), and \( \text{M}_3 \text{O} \langle \text{RCOO} \rangle_6 \) \(^{35-36,111-131}\) (where \( M \) is Fe(III) or Cr(III) and \( \text{RCOO} \) a carboxylate) satisfy both the above requirements. An interpretation of the magnetic behavior of these clusters is given in 5.2 and 5.3 after a discussion of alternative models in 5.1. It is found that the dynamic distortion model is the best available for the copper clusters, but for the trimetallic complexes the situation is much less clear. In at least one case, that of the intensively studied compound \( [\text{Cr}_3 \text{O} \langle \text{CH}_3 \text{COO} \rangle_6 ] \text{Cl.6H}_2 \text{O}, \) a non-magnetic phase transition\(^{117,128}\) is the likely to be the dominant cause of the observed magnetic and thermal behavior.

The application to tetrahedral Fe(III) clusters discussed
in 5.4 is somewhat tentative and is included largely to indicate the potential of the factorisable Hamiltonian method in the treatment of large, high spin, clusters in which the fluxionality is expected to be slow. For both the triangle and the tetrahedron the static, undistorted Hamiltonian has the simple form:

\[(5.1) \quad H_0 = -J (S'^2 - nS^2)\]

and all distortion Hamiltonians commute with \(H_0\).

In principle, lower symmetry systems may also exhibit distortions associated with magnetic effects, and such effects may show some dynamic character whenever there are states of the same total spin which lie close enough in energy to be regarded as quasi-degenerate. Thus in the cubane-like \(\text{Cu}_n\text{O}_n\) clusters\(^{132-138}\), the magnetic interactions favour the frequently pronounced separation into a pair of ferromagnetic dimers which are weakly antiferromagnetically coupled, as such an interaction lowers the energy of the ground state singlet. However, since there are expected to be at least two \(J\) values in such a system, magnetic distortion effects cannot easily be separated from the presumably larger electronic and steric contributions. Even so, the technique of fitting the susceptibility data to the magnetic spectrum rather than to particular \(J\) values, which is introduced in the discussion in 5.2, may still be useful as it avoids ambiguity in the derived parameters.
5.1 Introduction to Cu₄OX₆L₄ clusters

The Cu₄OX₆L₄ complexes typically exhibit a maximum in the magnetic moment \( \mu(T) \) in the region 20–50K which cannot be fitted by a simple Heisenberg model with one \( J^{50,51,95,101,104} \). Structural determinations on several of the complexes indicate either exact or almost exact tetrahedral point group symmetry\(^{37,88,100}\), and some complexes occur in a tetrahedral point group\(^{88,90}\). The structure consists of an oxygen centred copper tetrahedron with edge-bridging halides; the copper atoms are trigonal bipyramidally coordinated, the axial position opposite the oxygen being occupied by a ligand, L. About two dozen of these complexes, which show a characteristic infra-red absorption at about 500 cm\(^{-1}\), have been synthesised\(^{89,91,99}\); magnetic measurements have been reported on about half of them, sometimes in conjunction with e.s.r. studies\(^{101,105}\). The experimental data discussed in this chapter are principally those of Dickinson\(^{101,105}\) and Wong\(^{51}\).

The characteristic maximum in the moment of the Cu₄0 complexes implies, assuming temperature independent exchange constants, that the magnetic spectrum contains a highly magnetic state which lies just above a non-magnetic, or slightly magnetic, ground state. Such a spectrum might conceivably arise from non-isotropic contributions to the exchange, intercluster exchange, or static distortions, possibilities which are discussed below, as well as from dynamic distortions. The antisymmetric and intercluster exchange models, which differ
strikingly from the distortion model in that the non-magnetic ground state arises from a splitting of the Heisenberg quintet, as opposed to a splitting of the Heisenberg singlets, are discussed first.

5.1.1 The Antisymmetric exchange model

The $S'=1$ and $S'=2$ states of the regular tetrahedral Heisenberg cluster with $S=1/2$ exhibit 9- and 5-fold degeneracy, respectively, which must clearly be reduced by spin-orbit (and spin-spin) interactions as there are no I.Rs of dimension greater than three in $T_d$. In the Lines model, spin-orbit coupling terms are included in the spin Hamiltonian by the addition of antisymmetric exchange terms:

$$(5.2) H = -J(S'^2 - 3) + \sum_{i<j} D_{ij} (S_i \times S_j)$$

Anisotropic terms, $S_i \Gamma_{ij} S_j$, which are expected to be even smaller than $D$, are neglected. This representation of spin-orbit coupling terms was introduced by Moriya, who also derived certain symmetry rules which constrain the vectors, $D$, for the Cu₄ system to lie along the diagonals of the cube which is defined by the tetrahedron of Cu₄ atoms. As the $D$ are not parallel, $H$ commutes with neither $S'^2$ nor $S'_z$ and the solutions of (5.2) are somewhat complicated. However, the essential feature of the model, the splitting of the $S'=2$ Heisenberg state, which is the ground state for $J > 0$, can be seen by a straightforward symmetry argument.

The Cu₄OX₆L₄ cluster as a whole can be regarded as defining
an inverted transition metal crystal field. The $S'=2$ states before the addition of the crystal field can be denoted $^5S$. If the $T_d$ crystal field due to the configuration of the copper atoms is added, the five fold degenerate state splits into $E+T_2$. It is found that in this case, as in ordinary tetrahedral transition metal complexes, the non-magnetic $E$ doublet lies lowest. For small $D$, the splitting of the quintet is considerably smaller than that of the triplets as its orbital state is non-degenerate.

In order to explain the experimental data with this model, a quintet splitting of several tens of wavenumbers is required. The parameter $D$ is expected to make a contribution to the magnetic energy of the order of only $(g-2)^2 J / g^2$ for orbital singlets. Lines model therefore involves the assumption of an orbitally degenerate ground state, $E$. While such a ground state is by no means impossible for copper in a trigonal field (in which the ground state may be $A$ or $E$ depending on the relative strengths of the axial and equatorial ligands), it would be very unusual and there is no convincing supporting evidence. Spectroscopic data on other trigonal bipyramidally coordinated copper species such as $\text{CuCl}_5^{3-}$ suggest a singlet ground state with the lowest $E$ state at an energy of about 8000 cm$^{-1}$ $^{139,140}$. It is also true that dynamic Jahn-Teller effects acting on an $E$ state would tend to quench any orbital angular momentum and hence reduce the spin orbit coupling.

While it provides fairly good fits to several sets of
magnetic data, Lines model has several drawbacks:

1/ It does not fit all available data, failing for both the anionic clusters which have a low moment at 20K and clusters such as Cu₆OCl₆(3-quinuclidinone)₄ which have a very high moment at this temperature. Also, correlation between the derived parameters and the chemical and physical nature of the complex is difficult. 2/ The model typically predicts a somewhat sharper maximum than is observed experimentally, and it has been suggested that the good fits presented in the original paper were to some extent artifacts of systematic experimental error. 3/ Most significantly, recent detailed single crystal e.s.r. studies on Cu₆OCl₆(OP(C₆H₅)₃)₄, which is a typical compound of the group, show that the zero field splitting of the S' = 2 state is small (about 0.5 cm⁻¹) and that a ground state singlet, lies 14 cm⁻¹ below the quintet. The results of this study make the Lines model untenable, at least for this compound. It had been difficult to reconcile the results of earlier e.s.r. studies on powdered samples, which indicated normal g-factors, with the orbitally degenerate model and its associated high g-values (e.g. 2.37 for Cu₆OCl₁₀⁴⁻)¹⁵. In view of the above difficulties, it can be concluded that antisymmetric exchange does not contribute significantly to the unusual magnetic behavior of Cu₆OX₆L₄ complexes.
5.1.2 The intercluster exchange model

In the intercluster exchange model for Cu₄OX₆L₄, the ground state quintet is split by a symmetry-lowering molecular magnetic field which arises, in the molecular field approximation, from weak isotropic exchange between clusters. The derivation of the standard molecular field result, in which the kT in the denominator of the HDVV equation is replaced by kT-θ, (exactly as the susceptibility of weakly coupled paramagnets tend to follow a Curie-Weiss rather than a Curie law), involves several approximations. Each pairwise interaction between Cu₄ clusters involves 16 coupling constants, between each possible pair of metal atoms; if these are all small compared to the intracluster coupling they can be well approximated by an average coupling J' multiplied by an intercluster coordination number z'. This is the same approximation as involved in applying the Heisenberg model to the S=2 dimer (c.f. chapter 1.3), the intracluster couplings here play the role of the strong ferromagnetic couplings between orbitals on the same atom in the dimer. The coupling between clusters, which is assumed to extend throughout the lattice, can therefore be represented by a term -z'J'Sᵢ·Sⱼ where Sᵢ and Sⱼ are now the total spins of separate clusters, as long as z'J'<<J. Sᵢ=Sⱼ=2 for the ground states of Cu₄OX₆L₄ clusters with J>0.

The molecular field approximation involves writing:

\[ (5.3) \quad Sᵢ·Sⱼ = Sᵢz<Sⱼz> \]
i.e. each cluster experiences a field due to the rest of the clusters, \( <S_j z> \). Though this approximation suffers from the theoretical weakness that isotropic coupling cannot give rise to a special direction \( z \), and hence a molecular field, above the magnetic phase transition temperature, the model is useful as it does produce a splitting of the quintet into states of low spin and high spin, just as would be expected in a solution of the isotropic problem. However, the model must be used with care as a phase transition at \( T=\gamma'J' \) is an essential feature of any model which involves coupling throughout a 3-D lattice; the simple Curie-Weiss type expression for the susceptibility is expected to become inaccurate in this temperature range, which is often precisely the temperature range at which interesting magnetic behavior occurs.

With the exception of \( \text{Cu}_4\text{OCl}_6(3\text{-quinuclidinone})_4 \), for which the intercluster model results in a good fit\(^{10}\) to the susceptibility data with \( \gamma'J' = 0.3 \text{cm}^{-1} \), fits to magnetic data for \( \text{Cu}_4\text{OX}_6\text{L}_4 \) complexes using this model are frequently poor, and sometimes involve a ratio \( \gamma'J':J \) which is large enough to affect seriously the validity of the derivation (e.g. \( \text{Cu}_4\text{OCl}_6(\text{OP}(\text{C}_6\text{H}_5)_3)_4, \gamma'J' = -12\text{K}^{50}, J=40\text{K} \)). As no evidence of a magnetic phase transition has ever been observed in \( \text{Cu}_4\text{OX}_6\text{L}_4 \) complexes it seems reasonable to assume that the value of \( \gamma'J' \) found for the 3-quinuclidinone complex represents an upper bound for the magnitude of intercluster exchange in these systems.
5.1.3 The static distortion model

The purpose of this section is to show that a relatively simple model, in which the Heisenberg Hamiltonian is solved for certain fixed, factorisable distortions, can give good fits to some but not all of the experimental data. This simple approach has the advantage that it can be relatively easily adapted to larger clusters, such as the trigonal bipyramid and octahedron, but it also has the disadvantage that no real understanding of the fluxionality pathway is obtained. The factorisation approach is useful because the lowest energy static configuration is always factorisable. The model can be interpreted both as a genuine static distortion model, in which the permanent distortions are too small to be observed in X-ray studies, or as a slow fluxionality model, since if there is a low energy barrier to interconversions between distortions related by the symmetry operations of $P_a$ then fluxionality must occur.

Many factorable distortion Hamiltonians can be defined for the tetrahedron. Thus, taking a three fold axis ($T_2$ distortion and $C_{3v}$ symmetry):

\[(5.4) \quad H' = J'[S'^2 - 2(S_1 + S_2 + S_3)^2 + 2S_2^2]\]

and hence, treating the spins $S_1$, $S_2$ and $S_3$ as an equilateral triangle:

\[(5.5) \quad H' = J_1(S_1 + S_2 + S_3)S_4 + J_2(S_1 + S_2)S_3\]

can be factorised. However, given the striking resemblance of
the experimental moment data for the Cu₄OX₆L₄ complexes to those for a pair of ferromagnetic dimers which are weakly antiferromagnetically coupled, it is natural to consider a distortion Hamiltonian based on the two fold axis first. The Hamiltonian:

\[ H = -J_1(S_1^2 - 3) - (J_2 - J_1)(S_{13}^2 + S_{24}^2 - 3) - xJ_2(S_{13}^2 - S_{24}^2) \]

where \( S_{13} = S_1 + S_3 \) and \( S_{24} = S_2 + S_4 \), which contains the maximum number of parameters for this kind of factorisation, has energies:

\[ |2,1,1>, -2J_1 - J_2; |1,1,1>, +2J_1 - J_2; |0,1,1>, +4J_1 - J_2; \]
\[ |1,1,0>, J_2(1 - 2x); |1,0,1>, J_2(1 + 2x); |0,0,0>, +3J_2. \]

The arrangement of coupling constants corresponding to (5.6) is shown in Fig. 5.1. \( J_1 > 0, J_2 < 0 \) corresponds to a pairwise antiferromagnetic distortion of a ferromagnetic tetrahedron and \( D_{2d} \) symmetry; if \( x \neq 0 \) the symmetry is reduced to \( C_{2v} \). The parameter \( x \) affects only the triplet states as it corresponds to a \( T_2 \) distortion in addition to the \( E \) distortion \( (J_2 - J_1) \). It is significant as for values of \( x \approx 1 \) a triplet is brought close to the ground state.

The results of a least squares fit to this model, are presented in Table 5.1. the notation \((X,L)\) is used as shorthand for Cu₄OX₆L₄, and the following abbreviations for the ligands L, are introduced: py - pyridine, pyo - pyridine-N-oxide, tmu - tetramethylurea, dmos - dimethylsulphoxide, 3-quin - 3-quinuclidinone, TPPO - triphenylphosphine oxide. The counter
Fig. 5.1. Static distortion coupling constants for the copper tetrahedron.
ion for both ionic complexes, (Cl, Cl⁻) and (Cl, Br⁻), is NMe₄⁺.

Table 5.1 Fits to the static distortion model

<table>
<thead>
<tr>
<th>Complex</th>
<th>J₁/cm</th>
<th>J₂/cm</th>
<th>x</th>
<th>J</th>
<th>g</th>
<th>FIT†</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cl, Cl⁻)</td>
<td>200</td>
<td>-135</td>
<td>0.94</td>
<td>90</td>
<td>2.10</td>
<td>0.068</td>
</tr>
<tr>
<td>(Cl, Br⁻)</td>
<td>220</td>
<td>-148</td>
<td>0.96</td>
<td>100</td>
<td>2.07</td>
<td>0.068</td>
</tr>
<tr>
<td>(Br, py)</td>
<td>45</td>
<td>-28</td>
<td>0.94</td>
<td>21</td>
<td>2.21</td>
<td>0.038</td>
</tr>
<tr>
<td>(Cl, pyo)</td>
<td>210</td>
<td>-106</td>
<td>0</td>
<td>105</td>
<td>2.14</td>
<td>0.031</td>
</tr>
<tr>
<td>(Cl, tmu)</td>
<td>190</td>
<td>-97</td>
<td>0</td>
<td>95</td>
<td>2.04</td>
<td>0.09</td>
</tr>
<tr>
<td>(Cl, dmso)</td>
<td>280</td>
<td>-141</td>
<td>0</td>
<td>150</td>
<td>2.11</td>
<td>0.029</td>
</tr>
<tr>
<td>(Br, dmso)</td>
<td>195</td>
<td>-98.8</td>
<td>0</td>
<td>100</td>
<td>2.25</td>
<td>0.027</td>
</tr>
<tr>
<td>(Cl, 3-quin)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Cl, TPPO)</td>
<td>30.7</td>
<td>-18.5</td>
<td>0.895</td>
<td>14</td>
<td>2.10</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>-2.0</td>
<td>43.2</td>
<td>0</td>
<td>13</td>
<td>2.10</td>
<td>0.045</td>
</tr>
</tbody>
</table>

† FIT = R.M.S. deviation of the calculated from the experimental moments, i.e. the least squares fitting routine minimised Σ(μₗcalc - μₗobs)².
‡ No acceptable fit could be obtained for this complex.

A value of FIT of about 0.02-0.04 B.M. is expected from the scatter in the experimental data. It can be seen that this model gives adequate fits to some but not all the compounds. In general the shapes of the moment curves corresponding to the best fits are qualitatively similar to those obtained on the antisymmetric exchange model, this can be seen by comparing the theoretical curves of Fig.5.2 with those of ref 50. Thus both
Fig. 5.2. Moments calculated from static distortion model with $J_1=-100\text{cm}^{-1}$ and, from top to bottom, $-J_2=100, 102, 106, 112, 160$ and $200\text{cm}^{-1}$. 
models give a poor fit for (Cl,tmu) and a very poor fit (FIT > 0.10) for (Cl,3-quin). This latter compound has an exceptionally large maximum moment, $\mu>2.6B.M.$, which strongly suggests a quintet ground state with no low lying low spin states, and yet the moment decreases at low temperatures. Introduction of Hamiltonians such as (5.4) and (5.5) does not yield a better fit and only the dynamic distortion and intercluster models can explain the behavior. The behavior of the experimental curves at low temperatures for the ionic complexes (Cl,Cl\textsuperscript{−}) and (Cl,Br\textsuperscript{−}) suggests that these samples may have been contaminated with a monomeric species.

The fits to the remaining five compounds are more satisfactory, although it is noticeable that the theoretical curve for (Cl,TPPO) gives a systematically low moment in the range 20-60K. Two fits for (Cl,TPPO) are presented; it can be seen by reference to equation (5.7) that these correspond to essentially identical spectra. This ambiguity is characteristic of the model, i.e. similar pairs of fits can be derived for all compounds in Table 5.1; and is associated with rotations of the distortion vector. In general the fits obtained are extremely insensitive to either $J_1$ or $J_2$ alone but very sensitive to the quantity $J_1+2J_2$, which is typically small and negative and results in a ground state singlet which lies just below the quintet. For example, for (Cl,pyo) comparably good fits are obtained with the $J_1,J_2$ parameter sets 150,-76; 210,-106; 270,-136cm\textsuperscript{−1}. $J_1+2J_2=-2cm\textsuperscript{−1}$ in every case. Because of this the magnitude of the derived parameter $J=(4J_1+2J_2)/6$ must be
regarded as only a crude estimate. Similarly the fits are extremely insensitive to x unless x=1, in which case a triplet lies near the ground state.

The complexes apparently fall into two groups, those for which the fit with $J_1>0$ and $J_2<0$ gives $x=0$, and those for which for this choice of $J_1$ and $J_2$ gives $x=1$; it is difficult to interpret this feature without reference to the dynamic distortion model. Taking all the results together, it can be said that the static distortion model leads to fits which are at least as good as those obtained with the antisymmetric exchange model, and has the advantage that if some kind of slow fluxionality is invoked there is no contradiction with e.s.r. data. However there are enough questions and difficulties arising out of the fits to experimental data to make it clear that the model is still far from providing a complete explanation for the observed magnetic behavior.

5.2 The dynamic distortion model for Cu$_4$OX$_6$L$_4$

5.2.1 The magnetic spectrum

The magnetic spectrum for this system was derived in chapter 4. It is summarised in Table 5.2.

<table>
<thead>
<tr>
<th>Distortion</th>
<th>Slow</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>singlet and triplet splitting</td>
<td>singlet splitting</td>
</tr>
<tr>
<td>$T_2$</td>
<td>triplet splitting</td>
<td>no splitting</td>
</tr>
</tbody>
</table>
The spectrum for slow fluxionality is expected to include a degenerate pair of triplets well removed from the ground state. For fast fluxionality rotation of the \( S' = 1 \) energy triangle in the energy plane produces equivalent triplets. The exact solutions for static \( E \) and \( T_2 \) distortions (equations (4.3) and (4.31)) are:

\[
(5.8) \quad \text{E distortion}
\]
\[
H'(r, \psi) = -2r \left[ (S_1 \cdot S_2 + S_3 \cdot S_4) \cos \psi + (S_1 \cdot S_3 + S_2 \cdot S_4) \cos \psi + (S_1 \cdot S_4 + S_2 \cdot S_3) \cos \psi \right]
\]
\[
E(S' = 0) = \pm 3r; \quad E(S' = 1) = -2r \cos (\psi + n\pi/3), \; n = 0, 1, 2; \quad E(S' = 2) = 0.
\]

\[
(5.9) \quad \text{T}_2 \quad \text{distortion}
\]
\[
H(\rho, \theta, \phi) = -2\rho \left[ x(S_1 \cdot S_2 - S_3 \cdot S_4) + y(S_1 \cdot S_3 - S_2 \cdot S_4) + z(S_1 \cdot S_4 - S_2 \cdot S_3) \right]
\]
\[
E(S' = 0) = E(S' = 2) = 0 \quad E(S' = 1) = -4/\sqrt{3} \cos (\alpha + n\pi/3), \; \cos 3\alpha = -3\sqrt{3}xyz.
\]

where \( x = \rho \sin \rho \cos \phi, \; y = \rho \sin \theta \sin \phi \) and \( z = \theta \cos \theta \).

Given the simplicity of the Table 5.2 it is clear that any attempt to define six independent \( J \) from the magnetic spectrum must result in ambiguity. The three 'constraints' of i) a Landé rule on the average energies for each \( S' \), ii) an arbitrary energy zero and iii) the degeneracy of two of the triplets, mean that at most three parameters are necessary to describe the spectrum. In the case of pure \( E \) or \( T_2 \) distortion, or fast \( E \) fluxionality, this number is reduced to two by a further constraint, and for fast \( T_2 \) fluxionality only \( J \) is defined.
In view of the impossibility of uniquely defining six $J$ an alternative procedure has been used to fit the data. Three parameters, chosen for convenience, have been used to define a magnetic spectrum, which is then interpreted according to Table 5.2. The most convenient choice of parameters in this case is one based on energy differences between the quintet, which is always at low energy and the other spin states, since this leads to the most reliable convergence of the least squares fitting routine. The parameterisation is illustrated on a typical spectrum in Fig.5.3.

The procedure of fitting to a magnetic spectrum rather than an explicit Hamiltonian avoids both the introduction of spurious $J$ and the associated ambiguity in the derived parameters. It is useful for all small $S=1/2$ clusters $(n<6)$, even those with a static distortion from high symmetry. Thus, for $n=3$ there are three $J$ but only two parameters necessary to define the spectrum and for $n=5$ there are ten $J$ and only eight parameters. For $S>1$ the magnetic spectrum becomes more complex and even for $S=1$ it may be possible to fit to an explicit Hamiltonian, though the results must still be interpreted with care and examined for possible ambiguity.

5.2.2 Treatment of data

The experimental data of Dickinson and Wong have been fitted to magnetic spectra of the type predicted by the distortion model using a least squares program. Where no temperature independent spectrum could produce a satisfactory
Fig. 5.3. Parameterisation of spectrum used for fitting data to the dynamic distortion model.
fit a temperature dependent triplet partition function:

\[(5.10) f = 3p\{2\exp(\delta/T+\exp(-2\delta/T))\} + 9(1-p)\]

as derived in 4.5, was introduced. The model was found to give good fits to all the experimental data of Dickinson and Wong.

The fits are illustrated in Fig.5.4 and Fig.5.5, the corresponding spectra are given in Fig.5.6, and the resulting parameters are tabulated in Table 5.3. For the complexes \((\text{Cl},\text{Cl}^-)\) and \((\text{Br},\text{Br}^-)\) the fits remain poor at low temperatures, either because of some temperature dependence in the energy of the low lying triplet, or, more simply, the presence of monomeric impurity. In all cases the fits are as good or better than those given by any other model even where, for complexes which exhibit fast fluxionality, such as \((\text{Cl},\text{pyo})\), fewer parameters were used. 'g' was included as a variable parameter in all cases except two, the values for \((\text{Cl},3\text{-quin})\) and \((\text{Cl},\text{TPPO})\) having been found by e.s.r. to be 2.16 and 2.10 respectively.
Fig. 5.4. Dynamic distortion model fits to Cu₆OX₆L₆ data. In order of increasing theoretical moment at 200K, symbols are + -(Cl,Br), □ -(Cl,C1), △ -(Br,py), ○ -(Cl,pyo), ✶ -(Cl,dmso) and ◊ -(Br,dmso).
Fig. 5.5. Dynamic distortion model fits to Cu$_4$OX$_6$L$_4$ data. In order of increasing theoretical moment at 200K, symbols are Δ - (Cl,tmu), □ - (Cl,TPPO), + - (Cl,3quin).
Fig. 5.6. Magnetic spectra of the Cu₄OX₄L₄ complexes. Parentheses indicate states removed by fluxionality.
Table 5.3 Distortion model parameters for Cu₄OX₆L₄ complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Spectrum parameters (cm⁻¹)</th>
<th>J</th>
<th>g</th>
<th>Fluxionality</th>
<th>Distortion</th>
<th>FIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cl,Cl⁻)</td>
<td>Δ₁=−135, Δ₃=−116</td>
<td>&gt;100</td>
<td>2.08</td>
<td>E+T₂</td>
<td>Slow</td>
<td>0.066</td>
</tr>
<tr>
<td>(Cl,Br⁻)</td>
<td>Δ₁=−145, Δ₃=−132</td>
<td>&gt;100</td>
<td>2.04</td>
<td>E+T₂</td>
<td>Slow</td>
<td>0.066</td>
</tr>
<tr>
<td>(Br,py)</td>
<td>Δ₁=−22, Δ₃=−18.5</td>
<td>22</td>
<td>2.20</td>
<td>E</td>
<td>Slow</td>
<td>0.037</td>
</tr>
<tr>
<td>(Cl,pyo)</td>
<td>Δ₁=−5.0, Δ₃=300</td>
<td>75</td>
<td>2.13</td>
<td>E</td>
<td>Fast</td>
<td>0.026</td>
</tr>
<tr>
<td>(Cl,dmso)</td>
<td>Δ₁=−3.8, Δ₃=400</td>
<td>100</td>
<td>2.09</td>
<td>E</td>
<td>Fast</td>
<td>0.030</td>
</tr>
<tr>
<td>(Br,dmso)</td>
<td>Δ₁=−5.4, Δ₃=250</td>
<td>60</td>
<td>2.27</td>
<td>E</td>
<td>Fast</td>
<td>0.018</td>
</tr>
<tr>
<td>(Cl,tmu)</td>
<td>Δ₂=−16, Δ₃₃=95, ε=30</td>
<td>25</td>
<td>2.13</td>
<td>T₂</td>
<td>TDF</td>
<td>0.020</td>
</tr>
<tr>
<td>(Cl,3-quin)</td>
<td>Δ₁=−1.4, Δ₃=2.6</td>
<td>25</td>
<td>2.16</td>
<td>T₂</td>
<td>TDF</td>
<td>0.035</td>
</tr>
<tr>
<td>(Cl,TPPO)</td>
<td>Δ₁=−14.0, Δ₃₃=38, Δ₃=−10.3</td>
<td>10</td>
<td>2.10</td>
<td>E</td>
<td>TDF</td>
<td>0.028</td>
</tr>
</tbody>
</table>

The parameters Δ correspond to the energy differences in Fig.5.3.

These results can be interpreted according to the distortion model as follows:-

(Br,dmso),(Cl,pyo),(Cl,dmso). The singlet ground state and low lying quintet indicates that the system corresponds physically to a pair of ferromagnetic dimers in which rapid fluxionality removes the low lying triplet states. The small singlet/quintet separation indicates weak antiferromagnetic coupling between the dimers. In (Br,py) the situation is similar, except that fluxionality is slow, i.e. a low lying triplet state is 'frozen out'.

(Cl,Cl⁻),(Cl,Br⁻). In the anionic clusters a large singlet
splitting (E distortion) occurs but the low energy of the lowest triplet compared with that expected for pure E mode distortion indicates that significant $T_2$ distortion also occurs. The fluxionality is slow. The three excited states not represented on Fig.5.6 are of such high energy that they are not significantly populated even at 300K and thus cannot be fixed by magnetic data; $J$ cannot be defined from these three states but is probably greater than 100 cm$^{-1}$.

$(Cl,tmu),(Cl,3$-quin$)$. In these complexes no temperature independent spectrum gives acceptable fits to the experimental data. This is most marked for $(Cl,3$-quin$)$ for which the moment of 2.65 BM at 20K implies that (unless $g$ is unrealistically large) only the quintet state can be occupied, i.e., the system must have a quintet ground state well separated from excited states. If the spectrum were temperature independent, no decrease in $\mu(T)$ below 20K would occur. Application of the TDF model derived above, i.e. introduction of a triplet ground state at low temperatures, was found to give excellent fits to the data, thus providing some experimental justification for the model. At $T<20K$, the triplet ground state and low lying quintet indicates that $T_2$ distortion is dominant; the complexes may be considered as consisting of ferromagnetic trimers with weak antiferromagnetic coupling to the remaining copper atom in the cluster. The system undergoes slow fluxionality at low temperatures and fast fluxionality above about 20K. The singlets are represented as degenerate in Fig.5.6 as no improvement in fit is obtained by introducing a singlet splitting parameter.
(Cl,TPPO). The slow E-fluxionality model gives a nearly satisfactory fit to this data, c.f. 5.1.3, but an entirely satisfactory fit is only obtained if the triplets are allowed to exhibit TDF. In general a singlet ground state TDF model would involve 5 parameters: $\Delta_1, \Delta_3, \Delta_{33}, g$ and $\epsilon$, too many to give a meaningful result. It is fortunate that a recent e.s.r. study on this complex has determined $g=2.10$ and $\Delta_1=-14.0 \text{cm}^{-1}$; this reduced the number of parameters to an acceptable number, three. It is also reassuring to find that the best fit if $g$ and $\Delta_1$ are allowed to vary freely yields the parameters: $g=2.11$, $\epsilon=14 \text{cm}^{-1}$, $\Delta_3=-10.9 \text{cm}^{-1}$, $\Delta_{33}=35 \text{cm}^{-1}$, $\Delta_1=-14.5$; i.e. values for $g$ and $\epsilon$ very close to those found by e.s.r.

On this interpretation the experimental data for the neutral complexes can be summarised as indicating that distortion splits the ferromagnetic tetrahedron into ferromagnetic subclusters (i.e. two pairs of ferromagnetically coupled atoms or a monomer and three ferromagnetically coupled atoms) between which weak antiferromagnetic coupling occurs.

5.2.3 Discussion of results

The following trends are noticeable in the results:

1) The complexes with bridging bromides, (Br,py) and (Br,dms), have the highest g-values. The neutral chloride bridged complexes have $g=2.12 \pm 0.04$.

2) The large $J$, poor fit, and lack of the moment maximum in the ionic complexes suggests that these might most usefully be
treated as a separate class of compounds. Their slow fluxionality may be due either to a large $\Delta$, associated with the large $J$ or to the influence of the counter ions in the crystal lattice.

3) (Br, dmso), (Cl, pyo) and (Cl, dms0), in which the donor atom is oxygen and steric interactions between ligand atoms and the halide octahedron are probably insignificant, all exhibit fast fluxionality at all temperatures. In contrast, (Cl, tmu), (Br, py) and (Cl, 3quin), in which the donor atom is nitrogen and in which steric interactions are definitely significant (they have been noted in the X-ray studies of (Br, py) and (Cl, 3quin)) all exhibit slow fluxionality at least at low temperatures. There is an apparent correlation between either (or both) the nature of the donor atom or the steric interactions, and the rate of fluxionality. In this context it is significant that the other TDF compound (Cl, TPPO) has an oxygen donor and a small possibility of significant steric interactions. However it would be unwise too read too much into this single result as this ligand is unusual in its large mass and high P-O bond order. It is interesting to re-examine the available structural data in the light of the above observations.

The X-ray data typically show r.m.s. distortions associated with vibrations of about 0.2Å. Such displacements are very probably small enough compared to the typical Cu-Cu distance of about 3.0Å to make the assumption that $J$ is a linear function of the distortion valid. Though there is a significant
problem in finding molecules for a fair comparison, it can be
said that thermal ellipsoids of this size are not anomalously
large. Thus is it probably more correct to picture the magnetic
interactions as imposing certain phase relationships, such as
$\pi/2$ out of phase vibrations in the two orthogonal modes which
comprise the E mode, on the vibrations of the system rather than
to picture the magnetic interactions as perturbing a system
which is essentially fixed or static.

Few $\text{Cu}_4\text{OX}_5\text{L}_4$ complexes have cubic space group symmetry. In
cases in which the distortion produces a reduction in the
symmetry of the Cu-Cu linkages, i.e. excluding reduction in
symmetry due to the structure or orientation of L, the static
distortion may affect the magnetism. However even in this case
fluxionality may still occur. The static distortion field will,
in general, favour one of the otherwise symmetry equivalent
distortions; nevertheless, for $T>0$ the remaining minima will
still have thermal populations and interconversions between them
may give rise to dynamic effects such as singlet splittings
which are larger than those expected on the static model and
equivalence of the triplets.

A treatment of susceptibility data within the Heisenberg
formalism, as above, cannot lead directly to a determination of
the relative importance of the oxide and halide magnetic
exchange pathways. Even so, some information may be obtained
indirectly by comparisons, both between the $\text{Cu}_4$ clusters and
with other systems. Displacement of the central oxygen atom
transforms as $T_2$ (i.e. as a displacement) in $T_d$ and leads only to $T_2$ distortions of $J$ if $J$ is linear in the distortion. Displacement of the copper and chlorine atoms may lead to either $E$ or $T_2$ distortions. Given the preponderance of $E$ distortions in Table 5.3 it would seem that distortion of the Chloride octahedron is most likely to be the cause of the observed magnetic behavior. The copper atoms are expected to be relatively fixed both because of their larger mass and strong bonds to oxygen and the ligands.

Clearly either the halide or oxide pathway or both must be associated with a $J>0$. Standard correlations would suggest that the Cu-X-Cu contribution is positive since the halide bridge angle is close to 90°, the perfect angle for ferromagnetic coupling via orthogonal p-orbitals. The Cu-O-Cu pathway is more difficult to assess; the contribution cannot be large and negative as would be expected from the formula\(^2\):

$$(5.11) \ 2J \ (\text{cm}^{-1}) = 7555 - 77.6\theta$$

since this would result in a negative net $J$ for the tetrahedral angle $\theta=109°$. The discrepancy is not surprising as the oxygen in question is in a very different environment from that in the dimers which were used to obtain the formula. Both a small positive and small negative $J$ associated with the oxide pathway are possible. Further comments on this topic are made in 5.4.2. after discussion of some other M-O-M containing clusters.
5.2.4 Conclusions

The rival models for Cu₄OX₆L₄ are not entirely mutually exclusive, however each possible mechanism does tend to suppress the others. Thus dynamic distortion removes the high symmetry of the copper environment, suppressing any orbital effects, while strong spin/orbit coupling would remove the degeneracy which is the driving force for dynamic distortion. In both cases the production of a non-magnetic ground state would suppress intercluster exchange. In this sense one or other of the possible interactions is expected to dominate.

For the following reasons I conclude that, though small contributions from non-isotropic and intercluster exchange interactions cannot be ruled out, the primary cause for the rather unusual magnetic behavior of Cu₄OX₆L₄ complexes is dynamic distortion.

1) When considering magnetic exchange in clusters it is usual to assume isotropic exchange, intracluster exchange and equivalent coupling constants. One of these assumptions must be removed to fit the experimental data for Cu₄OX₆L₄. The removal of the assumption of equivalent coupling constants is the most natural as distortions resulting from magnetic exchange can be expected in these compounds. In contrast, there is no obvious intercluster exchange pathway and little evidence for an orbital doublet ground state.

2) Only the parameters obtained using the distortion model can be correlated with the physical and chemical nature of the
clusters.

3) The model provides a simple physical picture of the magnetic behavior of these compounds.

4) Only the distortion model is capable of giving good fits to all available experimental data.

5.3 \([\text{M}_3\text{O} (\text{RCOO})_6]^+\) clusters

Clusters of the form \([\text{M}_3\text{O} (\text{RCOO})_6]^+\), where \(\text{M}\) is chromium or iron typically exhibit an equilateral triangular arrangement of metal atoms and thus may, under suitable circumstances undergo dynamic distortions which affect the magnetic spectrum as described in Chapter 3. In the case of \(\text{M} = \text{Cr}\), the experimental work has been largely directed towards a very thorough investigation of a single compound, \([\text{Cr}_3\text{O} (\text{CH}_3\text{COO})_6]\text{Cl}.6\text{H}_2\text{O}\), by susceptibility\(^{111}\) and heat capacity\(^{112-117}\) measurements and by e.s.r\(^{122}\) and optical spectroscopy\(^{118-129}\). In contrast, for \(\text{M} = \text{Fe}\), many systems have been investigated but only in a rather incomplete way; the magnetic susceptibility data for these clusters\(^{35-36,120}\) are only occasionally supplemented by e.s.r\(^{127}\) and Mossbauer\(^{120}\) data. Partly because of this difference the cases \(\text{M} = \text{Cr}\) and \(\text{M} = \text{Fe}\) will be considered separately.

The distortion Hamiltonian used in the following discussion is:

\[
(5.12) \quad H = -J \left[ (S_1^2-3S^2) + \frac{\lambda}{2}(S_1^2-3S_2^2+3S_3^2) \right]
\]

The corresponding spectrum, Table 3.1, is modified to that of
Table 3.3 by fast fluxionality.

5.3.1 Chromium acetate. \([\text{Cr}_3\text{O(CH}_3\text{COO)}_4\text{Cl}.6\text{H}_2\text{O}]\)

It is perhaps rather unfortunate that this compound has become the most intensively studied polymetallic \((n>2)\) cluster, since its rather interesting magnetic and thermal behavior may be associated with properties of the waters of hydration rather than with the \(\text{M}_3\) cluster itself.

The compound was first studied by Wucher in 1955. The magnetic susceptibility data\(^{111}\) down to 2K were fitted to an isosceles triangle model with \(J=11\text{cm}^{-1}\), \(r=0.16\). On the same model the heat capacity data\(^{112}\) indicated a similar \(J\) but \(r=0.08\). Uryu suggested that apparent inconsistency in the value of \(r\) could be due to a small temperature dependence; the specific heat is sensitive at very low temperatures to the splitting of the \(S'=1/2\) states, whereas the susceptibility is just that due to \(S'=1/2\) until higher spin states are thermally occupied. Significant intercluster magnetic exchange was conclusively disproved by a susceptibility experiment to 0.3K which showed no departures from Curie-Weiss behavior\(^5\) \(\theta=0.13\text{K}\). Given this, the \(S'=1/2\) splitting must be due to either spin-orbit coupling, introducing non-isotropic exchange terms, or an intercluster interaction other than a direct exchange interaction, or dynamic distortion.

The key experiments on this cluster to date are those of Sorai et al\(^117\), who redetermined the specific heat over a wide
temperature range, and Ferguson and Gudel\textsuperscript{119}, who obtained the optical (electronic) spectrum. The heat capacity data, which differ significantly at low temperatures from those obtained by Wucher, exhibit a broad maximum at 3.5K which cannot be reproduced by an arrangement of two Kramers doublets. The presence of more than two doublets implies the existence of two types of cluster, and hence an intercluster interaction, at least at very low temperatures. Measurements of the heat capacity to room temperature showed a peak due to a first order phase transition at 211K, with \( \Delta H = 3322 \text{ J mol}^{-1} \); there was an increase in the number of infra-red transitions below this temperature. The phase transition was ascribed to an ordering of crystalline water, an idea now supported by structural data\textsuperscript{128}. The corresponding anhydrous compound does not show a transition. The \( \Delta H \) is clearly far too large to be associated with the magnetic interactions. Sorai made the entirely reasonable assumption that the ordering associated with the phase transition creates equal amounts of two types of cluster, and obtained a fit to the low temperature specific heat for \( J = 10.5, \lambda = 0.1 \) and \( J = 10.5, \lambda = -0.03 \). The two cluster model was supported by the optical spectroscopy\textsuperscript{119}, which can be resolved below \( T = 40K \) and assigned with parameters consistent with those obtained from the heat capacity measurements.

As a result of these experiments it would seem that the \( S' = 1/2 \) splitting in these clusters is probably largely due to the reduction of symmetry and ordering at 211K rather than to any more complicated effects, such as dynamic distortions
associated with magnetic interactions. Though papers on this system have appeared since the heat capacity and optical results were published, invoking antisymmetric exchange\(^{123}\) and intercluster exchange\(^{125}\) between pairs of clusters, they would seem to be somewhat redundant. It is possible that dynamic effects contribute significantly to the total distortion in this cluster but, as in the 'dimerised' Cu\(_6\)O\(_4\) cubane clusters, separation of magnetic from non-magnetic effects is not feasible at present.

5.3.2 [Fe\(_3\)O(RCOO)\(_6\)]\(^+\) clusters

The iron clusters are particularly suitable for magnetic measurements. The \(^6\)S ground state of Fe\(^{3+}\) means that \(g\) is likely to be very close to 2.0 and need not be included as a variable parameter in fitting to magnetic data; also, \(J\) is typically larger than for the Cr system and the magnetic spectrum extends over a much larger energy range. Mossbauer as well as susceptibility measurements can be used to detect magnetic ordering.

The experimental data of Earnshaw\(^{35}\), Duncan\(^{36}\) and Long\(^{120}\) have been fitted to the dynamic distortion model defined above using a least squares program. It was found that the slow (isosceles) and fast fluxionality models give almost identical, and essentially perfect, fits to all the data. This is illustrated for Fe\(_3\)O(CCl\(_3\)COO)\(_6\)(H\(_2\)O)\(_3\)Cl.H\(_2\)O \(^{120}\) in Fig.5.7. The parameters and fits obtained using the distortion model are compared to those obtained using the isosceles model in Table
Fig. 5.7. Fits to experimental data for complex L4. The theoretical curves, in order of increasing moment at 20K, correspond to an isosceles triangle with $\lambda < 0$, fast fluxionality, and an isosceles triangle with $\lambda > 0$. 
As indicated in Table 5.4, the isosceles model always gives rise to two minima in FIT as the two J values are varied, as was noted by Long (see Fig. 3 of ref. 120). The ambiguity arises from the similarity of the spectrum with λ>0 to that with λ<0. Thus for every fit with J_{12}=J_{23}<J_{13}, there is another similarly good fit with J_{12}=J_{23}>J_{13}. The fast fluxionality model is in a sense superior to the static model in this case since no attempt is made to define θ and this ambiguity is avoided.
Table 5.4 Static and dynamic distortion model fits to Fe₃(RCOO)₆⁺ data

<table>
<thead>
<tr>
<th></th>
<th>Equilateral Triangle</th>
<th></th>
<th>Isoceles Triangle</th>
<th></th>
<th>Dynamic Distortion</th>
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<td>J</td>
<td>λ&lt;0 FIT</td>
<td>J</td>
<td>λ&gt;0 FIT</td>
</tr>
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<td>0.017</td>
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<tr>
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<td>0.38</td>
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<tr>
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<td>25.2</td>
<td>0.33</td>
<td>0.008</td>
<td>24.6</td>
</tr>
<tr>
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<td>27.6</td>
<td>0.35</td>
<td>0.017</td>
<td>26.8</td>
</tr>
<tr>
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<td>0.040</td>
<td>27.5</td>
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<td>0.020</td>
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</tr>
<tr>
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<td>27.6</td>
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<td>27.6</td>
</tr>
</tbody>
</table>

† The formulae as given in the original papers (E, ref. 35; L, ref. 120; D, ref. 36) are:
E1 : [Fe₃(C₆H₅CO₂)₆](C₆H₅CO₂)₃·3H₂O  
E2 : [Fe₃(CH₂ClCO₂)₆(OH)₂].ClO₄·4H₂O  
E3 : [Fe₃(C₆H₅CO₂)₆(OH)₂].ClO₄·3H₂O  
E4 : [Fe₃(CH₃CO₂)₆(OH)₂].Cl·4H₂O  
E5 : [Fe₃(C₆H₅CO₂)₆(OH)₂].C₆H₅CO₂  
E6 : [Fe₃(CCl₃CO₂)₅(OH)₃](CCl₃CO₂)·7H₂O  
E7 : [Fe₃(C₆H₅CO₂)₅(OH)₃].C₆H₅CO₂·H₂O  
L1 : [Fe₃O(HCOO)₆(H₂O)₃]OH·2HCOOH  
L2 : [Fe₃O(CH₃COO)₆(H₂O)₃].Cl·5H₂O  
L3 : [Fe₃O(CH₂ClCOO)₆(H₂O)₃].Cl·5H₂O  
L4 : [Fe₃O(CCl₃COO)₆(H₂O)₃].Cl·H₂O  
L5 : [Fe₃O(C₆H₇COO)₆(H₂O)₃].C₆H₇O₂·2H₂O  
L6 : [Fe₃O(C₇H₅COO)₆(H₂O)₃].C₇H₅O₂·6H₂O  
D1 : [Fe₃(HCOO)₆(OH)₂].OH·2HCOOH  
D2 : [Fe₃(CH₃COO)₆(OH)₂].NO₃·5H₂O  
D3 : [Fe₃(C₆H₅COO)₆(OH)₂].NO₃·2H₂O  
D4 : [Fe₃(CH₂ClCOO)₆(OH)₂].NO₃·4H₂O  
D6 : [Fe₃(CCl₃COO)₆(OH)₂].NO₃·3H₂O

5.3.3 Discussion of results

As in the case of Cr₃O(CH₃COO)₆Cl·6H₂O most of the Fe₃O compounds contain molecules which are not part of the cluster and it is possible that their ordering may contribute to the observed distortion. In some cases it is not even possible to write down a structural formula in which the molecule can have a three-fold symmetry axis, as the number of solvent molecules is not a multiple of three. On the other hand there is no correlation between the amount of solvent and λ as might be expected if solvent ordering were the dominant effect. Also the changes in the magnetic spectrum produced by the distortion are much larger in Fe₃ than in Cr₃. Thus the splitting of the S'=1/2 states is about 8cm⁻¹ in Cr₃ and about 80cm⁻¹ in Fe₃. In several Fe₃ complexes λ is great enough to bring an S'=3/2 state close to the ground state and thus the moment might exhibit a minimum and rise to ½ towards T=0. This difference in the amount of distortion makes it reasonable to suggest that the causes of
distortion here are not identical to those for the chromium acetate.

One of the features of the results obtained with both the distortion and isosceles models is the constancy of J and λ. Only six of the 18 clusters have J outside the range -30±3 cm⁻¹ and similarly only five have λ outside the range 0.16±0.04. In five out of six clusters with unusual J and in four of the five with λ > 0.2, R involves a phenyl group. Though a size effect seems to be occurring it is unlikely that simple steric interactions within the cluster are significant here. Attempts to correlate J and λ with the chemical nature of these clusters are hampered by the number of variables: R, the nature of the anion and the numbers of water and other molecules in the lattice.

For the compounds with large λ and data down to 20K (L4,L5,L6) μ(T) is slightly larger at low temperatures than expected on the fast fluxionality model (Fig.5.7). This may indicate a tendency towards slow fluxionality at the lowest temperatures.

In conclusion, though the fits to magnetic data for the Fe₃O clusters are excellent, the physical interpretation of the results presents great problems and the relative importance of steric and magnetic, dynamic and static distortions has not been determined. An analysis of the heat capacity between 4.2 and 300K and lower temperature magnetic measurements would be useful in this respect. I would suggest that the dynamic, rather than the isosceles model be used in future fits to experimental
magnetic data because the new model gives a unique 'best fit' and results in an unambiguous J.

5.3.4 Factors affecting the importance of dynamic distortion

For dynamic distortion effects to be observed, the JT type energy change associated with distortion must be greater than that associated with non-magnetic types of ordering. The following differences between the Fe₃O, Cr₃O and Cu₄O clusters may be significant.

1/ Though the M₃ core has equilateral triangular symmetry, the chromium cluster has a rather low space group symmetry at room temperature. Cu₄ clusters typically have rather higher space group symmetry and some are exactly cubic.

2/ The M₃ clusters considered above are ionic. Ionic bonding between clusters, via the anions, might be expected to be stronger than Van der Waals coupling in the neutral Cu₄ systems. It is noticeable that the two anionic Cu₄ systems behave quite differently from the others and that their magnetic susceptibilities suggest larger distortions which are not removed as the temperature is increased.

3/ M₃ clusters typically contain a number of water, or acid (RCOOH) molecules; in some of these high symmetry is stoichiometrically impossible, in the others disorder of the molecules of crystallisation may make a high symmetry arrangement unlikely. The Cu₄ clusters typically contain no non-cluster molecules.
4/ It may be intrinsically more difficult to pack the 'inherently 2-dimensional' equilateral triangle clusters in a highly symmetrical 3-dimensional lattice, than to pack the 'inherently 3-dimensional' tetrahedral Cu₄ clusters.

5/ The coordination sphere of copper(II) is known for its "plasticity" and hence may be particularly sensitive to fluxionality.

In addition to the above factors which influence the tendency of the cluster to undergo a phase transition independent of magnetic effects, differences in the relative magnitudes of ∂J/∂d and the force constants may be relevant.

5.4 Tetranuclear Fe(III) clusters

Tetrahedral Fe₄ complexes are important in several areas; Fe₄ "cubane"-like groups occur in ferredoxins; there are several polynuclear iron-tungsten clusters which often contain a large number of metal atoms arranged in linked tetrahedra and mixed valence. Fe(III),Fe(II) complexes also occur. Given the biological interest it is surprising that the simple Fe₄-carboxylate-methoxide complexes have not been more intensively studied. The data for two such compounds, Fe₄O(CH₃COO)₁₀, and Fe₄(CH₃COO)₆(OCH₃)₆, are discussed below. The interpretation given must be regarded as somewhat tentative as magnetic data are available only down to about 100K, but it is hoped that the results will have some predictive value for the moment at lower temperatures. The treatment also illustrates
how the factorisable distortion method makes the fitting and interpretation of magnetic data feasible for larger clusters.

Though there are no reports of X-ray studies on Fe₄O(CH₃COO)₁₀ and Fe₄(CH₃COO)₆(OCH₃)₆, the structural formulae, infra-red and Mossbauer data suggest an approximately tetrahedral Fe₄ core, which is carboxylate bridged and, by analogy with the Cu₄O systems, oxygen centred in the case of compound Fe₄O(CH₃COO)₁₀. The fits to magnetic data presented below suggest distortions which might be static or slowly fluxional; fast fluxionality is unlikely in S=5/2 tetranuclear systems unless the distortion is very small. The appropriate Hamiltonians for E and T₂ distortions are:

\begin{align*}
(5.13) \quad H(E) &= -J \left( S'^2 - 70 \right) - J' \left( S'^2 - 3(S_{13}^2 + S_{24}^2) + 70 \right) \\
(5.14) \quad H(T) &= -J \left( S'^2 - 70 \right) - J' \left( S'^2 - 2S_{12}^2 + 17.5 \right)
\end{align*}

5.4.1 Treatment of data

Fe₄O(CH₃COO)₆. The moment for this neutral cluster is qualitatively similar to that for the neutral Cu₄O species, though the variation with temperature is small the behavior can be regarded as similarly unusual as there is a maximum, or at least decrease in slope of \( \mu \) vs \( T \) with decreasing temperature. This behavior cannot be fit to a model with one \( J \) as such a model predicts an increasing slope with decreasing \( T \) in this range. As might be expected from the lack of low temperature data, fits to both \( E \) and \( T \) models can be obtained, and are summarised in Table 5.5. The addition of the second
parameter, $J'$, improves the least squares fit by about a factor of 10. All the fits to two parameters are essentially perfect.

Table 5.5 Fits to magnetic moment data for Fe$_4$O(CH$_3$COO)$_6$

<table>
<thead>
<tr>
<th></th>
<th>E $J'&gt;0$</th>
<th>J'&lt;0</th>
<th>J'&gt;0</th>
<th>J'&lt;0</th>
<th>T No distortion</th>
</tr>
</thead>
<tbody>
<tr>
<td>J (cm$^{-1}$)</td>
<td>1.48</td>
<td>1.22</td>
<td>1.35</td>
<td>1.05</td>
<td>0.644</td>
</tr>
<tr>
<td>J'</td>
<td>3.38</td>
<td>-2.24</td>
<td>10.55</td>
<td>-4.68</td>
<td>-</td>
</tr>
<tr>
<td>FIT</td>
<td>0.010</td>
<td>0.008</td>
<td>0.011</td>
<td>0.008</td>
<td>0.072</td>
</tr>
</tbody>
</table>

The existence of two fits for both E and T$_2$ models is associated with a rotation of the distortion vector in the appropriate space, the situation is analogous to that found with the isosceles triangle model for M$_3$O. Thus for the E distortion the ratio of $J'<0:J'>0$ is close to the value $-11/7$ which is associated with identical singlet ground state energies; the ratio for the T$_2$ model is similarly close to $-8/3$.

For the chosen sign convention, $J'<0$ is the thermodynamically stable configuration for both E and T$_2$ distortions; thus the other fits can be disregarded. An encouraging feature of the remaining fits is that J is quite well defined, $J=1.15\pm0.1$cm$^{-1}$, even though the distortion mode is not. J is about twice the value obtained on the one parameter model. In Fig.5.8 the theoretical curves associated with the E and T$_2$ fits have been extended to T=10K. The curves are strikingly different as the T$_2$ distortion results in an S'=$5$ ($\mu_{\text{eff}}=\sqrt{30}$) ground state whereas for E distortion the ground state is a singlet. The curves can be regarded as alternative predictions for the low temperature moment.
Fig. 5.8. Distortion model fits to data for Fe$_4$O(CH$_3$COO)$_5$ (above) and Fe$_4$O(CH$_3$COO)$_5$(OCH$_3$)$_6$. 
Fe₆(CH₃COO)₆(OCH₃)₆. Though this compound is expected to have 6 carboxylate bridges as did the previous cluster, there cannot be a central oxygen atom. The fits to the moment indicate that J is significantly more antiferromagnetic. Variation of J' with the E-model results in no improvement in fit. Two fits are obtained on the T-model; taking the one associated with J'<0 the result is:

\[
(5.15) \text{T-distortion, } J = -4.38, \quad J' = -2.526, \quad \text{FIT}=0.020
\]

No distortion, \( J = -3.85, \quad \text{FIT}=0.080 \)

For \( J<0 \), any \( |J'| > 3|J|/8 \) produces an \( S'=5 \) ground state. Thus the moment is expected to exhibit a minimum and rise towards the limiting value of \( \sqrt{3}0 \) at \( T=0 \), as shown on Fig.5.8.

5.4.2 Discussion of results

Comparison between the J values obtained both for Fe₆, and for the other clusters discussed in this chapter suggests several comments concerning the nature and relative importance of the various possible exchange pathways in the polymetallic clusters. The change in sign of J in the two Fe₆ complexes suggests that the oxygen centred M-O-M pathway is quite strongly ferromagnetic. It should be remembered here that, as Heisenberg exchange involves just one orbital on each atom, a J of \( 1\text{cm}^{-1} \) in Fe implies an exchange integral, \( \langle 12|V|21 \rangle \), of \( 25\text{cm}^{-1} \) since there are five electrons on each atom. This point is discussed more fully in 6.5.1. The exchange integral in the Fe₆ clusters is therefore comparable with that found in some Cu₄O (while
that in the M₃O systems is very large). This positive contribution to J suggests that the M-O-M pathway in oxygen centred tetrahedra involves an sp³ hybridised oxygen and an orthogonal exchange pathway. pathway orthogonal.

A comparison between the Fe₃ and Fe₄ systems, which both contain carboxylate bridges suggests that the dominant contribution to the (J<0) exchange in Fe₃O is a very strongly antiferromagnetic M-O-M pathway. This suggests that the oxygen atom avoids the sp² hybridisation which would make such a pathway orthogonal. There is some supporting evidence for this assertion as the oxygen atom is rarely found exactly in the M₃ plane.

With these results in mind, the magnetic data for the compound formulated as Fe₅O(O₂CMe)₁₂(O₂CMe), for which conductivity, solubility and mass spectrum suggested a trigonal bipyramid of Fe atoms, was investigated. Fitting to an axial Jₐ, an equatorial Jₑ, and an internal Jᵢ with the Hamiltonian:

\[ \text{(5.16)} \ H = -Jₑ (S'²-3S²) - Jₐ (S'²-S'²-S'²) - Jᵢ (S'²-2S²) \]

though leading to considerable ambiguity suggested axial and equatorial J of about -15cm⁻¹. However just as good a fit was obtained to the trimetallic distortion model with parameters J=-28.5, r=-0.29, which are typical for equilateral Fe₃O complexes. Because of the more normal J found in the fit to the triangular model the magnetic data can be said to support a
trimetallic rather than a pentametallic structure for this complex.

The role of the M-X-M pathway in Cu₄ clusters is somewhat harder to define. As the central oxygen is sufficient to cause J>0, J might be of either sign, though a large antiferromagnetic contribution is unlikely. A small ferromagnetic contribution to J associated with the M-X-M angle of about 90° would be consistent with the correlations observed in other systems.
CHAPTER 6 LINEAR MAGNETIC SYSTEMS.

6.1 Introduction to Linear Chains

The linear magnetic chain is of general theoretical interest as it is one of the simplest many-body systems in which quantum effects play a vital part. Essentially complete exact or numerical solutions have been obtained for $S=1/2$ which have no counterparts in 2 or 3 dimensions. The mathematics of the 1-D magnetic problem is closely related to that of many other problems of interest in physics: e.g. 2-D ferroelectrics, field theoretical models, realistic fluids and 1-D organic conductors such as TCNQ (tetracyanoquinodimethane). The Peierls type transition, in which a regular chain becomes an alternating chain is an obstacle to the production of high temperature superconductors. Magnetic chains are of great interest in chemistry both because, like all exchange coupled systems, changes in the magnetic behavior on substitution of both ligands and metals can give insight into bonding and coordination, and because they can be used to investigate the phenomenon of polymerisation in transition metal chemistry.

Both finite and infinite chains are considered in this chapter. Only systems which are linear in the 'chemical' sense i.e. those with a maximum 'magnetic coordination number' of two are discussed, 'Ladder' type and similar more complicated structures which would be considered linear in solid state physics, since they may be infinite in only one
dimension, are excluded. Only chains which are, at least initially, before distortion, defined by just one coupling constant will be considered.

There are several reasons for considering linear chains separately in this thesis. First, the linear systems are intermediate between true clusters, e.g. the three atom chain can be considered as a cluster, and, as the chain length increases, the infinite lattice systems. The mathematical treatment of the infinite magnetic chain is simplified by the absence of a phase transition at $T>0$ for finite range interactions$^{34}$. Second, the metal atoms in magnetic chains typically have higher symmetry than those in (other) clusters. This is relevant to the discussion in chapter 1, where it was argued that the intrinsically low symmetry of the crystal fields of cluster atoms would be an important factor in removing any degeneracy in the ground state and making the Heisenberg model of magnetic exchange more valid. As a consequence of their higher symmetry, chain systems exhibit magnetic anisotropy more frequently than clusters and are often modelled with the anisotropic Hamiltonian:

$$ (6.1) \quad H = -2J \sum_{i=j+1} a S_{i z} S_{j z} + \beta (S_{ix} S_{jx} + S_{iy} S_{jy}) $$

The XY ($a=0, \beta=1$)$^{153,154}$, the Ising$^{8,155}$ ($a=1, \beta=0$) and the Heisenberg ($a=\beta=1$)$^{156-162}$ limits of 6.1 are all of theoretical interest.

The third reason for considering chains separately is that
whichever the nature of the exchange coupling, linear systems are exceptions to the Jahn-Teller theorem. In terms of the assumption that $J$ is linear in distortions, $J = J(0) + d(\partial J/\partial d)$, only the non-degenerate longitudinal vibrations of the chains affect the magnetic spectrum and though the chain has many degenerate transverse vibrational modes, these are magnetically irrelevant. In terms of group theory the magnetic symmetry of any open chain can be no more than $P_2$, a group with no degenerate I.R.s; as a direct consequence of this the spectrum of the open magnetic chain can never contain degeneracy in addition to that due to the total spin. However the Jahn-Teller theorem does not predict that linear systems are stable, only that they need not be unstable with respect to distortions which lower the symmetry. A brief historical survey of the aspects of magnetic chain theory and experiment which are of interest to magnetochemists will now be given.

As a result of its intrinsic theoretical interest the magnetic chain Hamiltonian was studied even before experimental examples were known. The first development was Ising's solution of the $\alpha=1, \beta=0$, Hamiltonian for the infinite chain (1925). The spin wave theory developed by Bloch, which can be applied to 2- and 3-D systems as well as chains, was found to be very useful, particularly for low temperature properties. Bloch obtained the result that the low temperature heat capacity of the Heisenberg chain is proportional to $T^{3/2}$. The antiferromagnetic ground state energy of the $S=1/2$ chain, $E_0 = 0.5-2\ln2$, was calculated by Hulthén in 1938. Comparatively
few advances in the determination of the thermodynamic properties of chains were made until 1960.

On the experimental side, Cu(NH$_3$)$_4$SO$_4$·H$_2$O, $J=-5$ cm$^{-1}$, which contains $\text{Cu-H}_2\text{O-Cu-H}_2\text{O-}$ chains, was the first compound to be recognised as magnetically linear, by Watanabe and Haseda in 1958$^{165}$. Several more examples followed$^{166,167}$ and now, though copper infinite chains are still the most common, infinite chains containing a wide variety of transition metal ions are known$^{168,169}$. Considerably fewer systems containing finite chains, such as Co$_4$($\text{C}_5\text{H}_7\text{O}_2$)$_8$, are known$^{170}$; again copper is the metal most frequently involved$^{171,172}$.

From the point of view of magnetochemists the two most important contributions to linear chain theory were made by Fisher$^{33}$ in 1963, who obtained an exact solution for $\chi(T)$ of the classical (S=$\infty$) chain, and Bonner and Fisher$^{32}$, who used numerical extrapolation from finite systems to determine $\chi(T)$ for the S=1/2 infinite chain in 1964. Bonner and Fisher's result was expressed in a polynomial form suitable for the fitting of data by Hall$^{173}$ and by Jotham$^{174}$. Baker has developed series expansions in T and 1/T for the susceptibility of the S=1/2 chain for both $J<0$ and $J>0$$^{175}$. With the development of faster computers numerical calculations have continued to play a role. Weng made some calculations on S=1 systems in 1968$^{156}$, but the most accurate results are those of Blöte$^{160,161}$ who made extensive calculations on the specific heat of S=1/2 chains, including those with axial anisotropy, in 1975. Majumdar$^{158}$ and
later Hatfield\textsuperscript{162} have performed similar calculations to obtain exact results for the magnetic susceptibility of finite chains. With the comparatively powerful computer at UBC it has been possible to improve some of the earlier extrapolations. The results of this work are discussed in 6.2.

One of the conclusions of the numerical work is that extrapolation from results for small finite chains results is difficult and unreliable. No results as accurate as Bonner and Fisher's result of 1964 have been obtained for $S>1/2$. In section 6.3 an alternative approach in which the true spin Hamiltonian is approximated by a Hamiltonian which involves intermediate spins, the 'odd/even' Hamiltonian, which can be easily solved for large numbers of atoms, $N$, for all $S$, is used. The results of this work are discussed in 6.3.

Finally, the stability of both finite and infinite Heisenberg chains is considered in 6.4. Though the tendency to dimerisation of the infinite chain has recently received a great deal of attention, the effect of magnetic instability on long but finite chains has so far been ignored.

6.2 The antiferromagnetic ground state energy

The ground state of an antiferromagnetic Heisenberg chain is not a simple Ising type ordered state and the calculation of its energy and properties is not trivial. Hulthén obtained an exact expression for the ground state energy, $E_0 = 0.5-2\ln2 = -0.886294$, for $S=1/2$ in 1938 but until numerical extrapolation
became feasible the best result for $S>1/2$ was that of spin wave theory, given to first and second order by Anderson$^{176}$ and Kubo$^{177}$.

Bonner and Fisher found in the course of their work on finite $S=1/2$ systems that a plot of $E_0$ of finite rings of $n$ atoms against $1/n^2$ gave rise to two very nearly straight lines, for $n$ even and $n$ odd, which intersected near $1/n^2=0$ at an energy within 1% of the exact value obtained by Hulthén. Having demonstrated this result they went on to extrapolate for the thermal properties of the linear chains using a similar technique.

Numerical extrapolations for the ground state energy for $S>1/2$ have been carried out by Weng, Majumdar and Blöte but some modifications of the original Bonner-Fisher method are necessary as the lines on a plot of $E_0(n)$ v $1/n^2$ no longer intersect near $1/n^2=0$. Despite this difficulty it is generally believed that numerical extrapolation is the most reliable method for determining the properties of $S>1/2$ chains. I have re-examined the numerical extrapolations for $S>1/2$ and obtained results for somewhat larger systems than previous authors. The results are consistent with the expression:

$$(6.2) \quad E_0(S) = -2S(S+2\ln 2-1)$$

which is given some theoretical basis in 6.2.1. A summary of some results for $E_0(S)$ is given in Table 6.1 where 'SW' refers to the spin wave expression $E_0 = 2S(S+0.363+0.033/S)$ obtained
by Anderson and Kubo.

Table 6.1 Results for $E_0(S)$ for Heisenberg chains

<table>
<thead>
<tr>
<th>$S$</th>
<th>1/2</th>
<th>2/2</th>
<th>3/2</th>
<th>4/2</th>
<th>5/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st order SW</td>
<td>0.863</td>
<td>2.726</td>
<td>5.589</td>
<td>9.452</td>
<td>14.315</td>
</tr>
<tr>
<td>2nd order SW</td>
<td>0.929</td>
<td>2.792</td>
<td>5.655</td>
<td>9.518</td>
<td>14.38</td>
</tr>
<tr>
<td>Weng$^{156}$</td>
<td>0.886</td>
<td>2.810</td>
<td>5.734</td>
<td>9.658</td>
<td>14.58</td>
</tr>
<tr>
<td>Majumdar$^{158}$</td>
<td>-</td>
<td>2.808±0.004</td>
<td>5.70±0.06</td>
<td>9.40±0.8</td>
<td>14.20±1.0</td>
</tr>
<tr>
<td>Blöte$^{161}$</td>
<td>-</td>
<td>2.8059±0.0002</td>
<td>5.67±0.02</td>
<td>9.52±0.04</td>
<td>14.38±0.08</td>
</tr>
<tr>
<td>Hulthén$^{164}$</td>
<td>0.88629</td>
<td>2.772</td>
<td>5.659</td>
<td>9.545</td>
<td>14.43</td>
</tr>
<tr>
<td>(6.2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The spin wave expansion in powers of $1/S$ is variational to first order but not beyond. There are significant problems of convergence for low spin; for example, the second order result for $S=1/2$ is worse than the first order result and the expansion may be asymptotic rather than convergent. Weng obtained the expression $E_0 = 2S(S+0.424-0.019/S)$ from calculations on $S=1$ rings only; Bonner-Fisher type extrapolation was used to obtain $E_0(S=1)$ and then the results for $S=1/2$ and $S=1$ were used to obtain the coefficients in his expression. Weng's results differ from the others by more than 1% for the higher spins suggesting that this technique is not very accurate. Majumdar obtained results for only relatively small systems and the error bounds on his results, except for $S=1$, are correspondingly large. This leaves Blöte's results as the most accurate for general $S$. Blöte considered both rings and chains in his extrapolation and made calculations for all $S = 1$ to $S = 5/2$.

(6.2) is in agreement with the previous results except for $S=1$ where the difference of 1% is well outside Blöte's error.
bounds. A detailed discussion of the extrapolation for \( E_0(S=1) \) and a comparison with that for \( E_0(S=1/2) \) is given in 6.2.2.

6.2.1 Theoretical considerations

It will now be shown by consideration of the Hamiltonian (6.3) that equation (6.2) is theoretically reasonable, though a formal proof has not been obtained.

\[
(6.3) \quad H = \lim_{n \to \infty} \frac{2}{n} \sum_{i=1}^{n} S_i \cdot S_{i+1}
\]

The Hamiltonian (6.3) can be used to describe two similar but distinct systems: (a) a ring of \( n \) atoms with an \( n \)-fold axis of symmetry and boundary conditions \( S_{n+1} = S_1 \); (b) a chain of \( n+1 \) atoms with \( S_i = 0 \) for all \( i > n+1 \). As \( n \to \infty \) the differences in the ring and chain ground state energies induced by the differences in the boundary conditions for the two systems tend to zero. In this discussion deviations of \( E_0(n) \) from \( E_0(n=\infty) \) are of no interest.

Consider the eigenvalue problem \( H \phi_0 = E_0 \phi_0 \), where \( \phi_0 \) is the ground state eigenfunction, as a matrix problem in the basis set of the Ising states of the system with \( S_z = 0 \). The basis contains both the Ising ground states \(|S,-S,S,-S,S,-S...> \) and \(|-S,S,-S,S,-S,S...>\); take the first of these and call it \( \psi(0) \). The rest of the states can be ordered by the number of operations of \( S_i S_{i+1} \) or 'flips', needed to produce them from \( \psi(0) \). All off diagonal matrix elements of \( H \) arise from such spin flips.
The notation \( \psi(1,i) \), for a state related to \( \psi(0) \) by one spin flip at position \( i \); \( \psi(2,i,j), i<j \) for a state related to \( \psi(0) \) by two flips at positions \( i \) and \( j \), \( \psi(3,i,j,k) \) etc., will be used. Thus the other Ising ground state is \( \psi(n/2,1,3,5,7...) \) for \( S=1/2 \) and \( \psi(nS,1,1,...,3,3,3...,...) \) for general \( S \). The sets \{\( \psi(M) \), \( M=0,1,2 \) etc.\} form blocks within the matrix, and the elements of each block are related by spin flips only to those in adjacent blocks.

Consider that part of \( \phi_0 \) which involves states near to \( \psi(0) \), i.e. from \{\{\( \psi(M) \), \( M=0(1) \}\}. \( \phi_0 \) can be written:

\[
(6.4) \quad \phi_0 = \psi(0) + \sum_i b(i) \psi(1,i) + 1/2 \sum_{i,j} c(i,j) \psi(2,i,j) + \ldots
\]

where the summation takes into account the fact that for each \( S \) there are some combinations of spin flips which are not allowed; thus for \( S=1/2 \) neither \( \psi(2,i,i) \), a 'multiple flip', nor \( \psi(2,i,i+1) \), an 'adjacent' flip, exist. General expressions for the matrix elements can be obtained, e.g:-

\[
(6.5) \quad \langle \psi(0) | H | \psi(0) \rangle = -2S^2
\]
\[
\langle \psi(1,i) | H | \psi(1,j) \rangle = (-2S^2 + O(S/n)) \delta_{ij}
\]
\[
\langle \psi(2,i,j) | H | \psi(2,k,l) \rangle = (-2S^2 + O(S/n)) \delta_{ik} \delta_{jl}
\]
\[
\langle \psi(0) | H | \psi(1,i) \rangle = \langle \psi(1,i) | H | \psi(2,i,j) \rangle = 2S/n \text{ for all } i,j.
\]

thus:

\[
(6.6) \quad H\phi_0 = \left[-2S^2 + (2S/n) \sum b(i) \right] \psi(0)
\]
\[
+ \sum_i \left[b(i)(-2S^2+O(S/n)) + (2S/n)(1+ \sum_j c(i,j)) \right] |\psi(1,i)\rangle
\]
\[
+ \sum_{i,j} \left[c(i,j)(-2S^2+O(S/n)) + 2S/n (b(i)+ \sum_k d(i,j,k)) \right] |\psi(2,i,j)\rangle
\]
Premultipling gives:

\( \langle \psi(0) | H | \phi(0) \rangle = E_0 = -2S^2 + (2S/n) \Sigma b(i) \)

\( \langle \psi(1,i) | H | \phi(0) \rangle = b(i)E_0 = b(i)[-2S^2 + O(S/n)] + (2S/n)(1+\Sigma c(i,j)) \)

\( \langle \psi(2,i,j) | H | \phi(0) \rangle = c(i,j)E_0 = c(i,j)(-2S^2 + O(S/n)) + 2S/n (b(i)+b(j)+ \Sigma d(i,j,k)) \) etc.

Quantities which are \( O(S/n) \) will now be neglected except where multiplied by quantities \( O(n) \), i.e. though the result is intended to be valid for general \( S \), \( S \) is not as large as the infinite \( n \). Therefore:

\( E_0 = -2S^2 + (2S/n) \Sigma b(i) = -2S^2 + (2S/nb(i)) \Sigma c(i,j) \)

Now consider \( S=1/2 \), for which \( E_0 = 2ln2-0.5 \). For a closed ring \( b(i) = b(0) \exp(-2\pi i/n) \); either \( \Sigma b(i) = 0 \) or the \( b(i) \) are all equal, \( b(i) = b \). Thus from (6.7), \( b = 1-2ln2 \). For the states with two flips, the first flip destroys the symmetry and so the \( c(i,j) \) vary, but their sum is a function of the \( b(i) \) only, from (6.7):

\( (1/n) \Sigma c(i,j) = (1-2ln2)^2 \) for all \( i \) (ring).

and \( (1/n^2) \Sigma c(i,j) = (1-2ln2)/n \Sigma b(i) = (1-2ln2)^2 \) (chain)

To make further progress it is necessary to consider the differences between the coefficients \( b,c,... \) induced by the different boundary conditions for the rings and chains. Coefficients and functions for chains will be written as a prime, e.g. \( b'(2,i,j) \). Consider \( S=1/2 \) and write:
where the symbol \(||\) refers to a chain end. For both \(\psi'(0)\) and \(\psi(1,i)\) a unique point in the system is defined. At this point the states having one extra spin flip at or adjacent to the initial point vanish as no flip is possible between the ends of a chain and no flip is possible at or adjacent to a first flip in a ring. Expressed as boundary conditions on the coefficients of the remaining flips, these conditions are identical, i.e.:

For a chain the \(b'(i)\) satisfy
\[
b'(i) = b'(i+1) = 0
\]
for a ring the \(c(i,j)\) satisfy
\[
c'(i,i) = c'(i,i+1) = 0
\]

It is known that \(\Sigma b'(i) = \Sigma b(i)\), since \(E'_0 = E_0\) and therefore it is expected that:

\[
(6.11) \quad \Sigma c(i,j) / b(i) = \Sigma b'(i) = \Sigma b(i) = n(1-2\ln2)
\]

exactly as found above. Though the boundary conditions imposed by the end effects/spin flip have a large effect on the individual coefficients \(b'(i)\) and \(c'(i,j)\), the sum of these coefficients with respect to the end or flip is unchanged. i.e. although one flip affects the coefficients of the next spin it does not affect their sum - but it is the sum which is important in the equations for \(E_0\) such as (6.7). Therefore the coefficient of a typical basis state in \(\phi_0\) will be 'b' raised to the power of the number of flips in the state. This argument can be
extended to as many flips as necessary, e.g.

\[(6.12) \sum c(i,j) / b = \sum c'(i,j) / b'(i) = \sum d(i,j,k) / c(i,j)\]

and will only break down when the number of flips is \(O(n)\) - at which point the chain has been 'divided' into finite lengths. Thus for large \(n\) the expression can be made true for an arbitrarily large number of sets \(\{|\psi(M)|\}\).

Now consider solving the \(S > 1/2\) problem, not in the Ising basis corresponding to \(S\) but in the basis \(B\), derived from the \(S = 1/2\) basis by replacing:

\[|a_\alpha a_\beta a_\alpha a_\beta a_\beta a_\alpha a_\beta a_\beta| \text{ with } |S,-S,S,-S,-S,-S,-S\rangle\]

and \[|a_\alpha a_\beta a_\alpha a_\beta a_\beta a_\alpha a_\beta a_\beta| \text{ with } |S,-S,S,-S,-S,-S+1,-S,-S\rangle\]

The basis \(B\) does not include the multiply and adjacently flipped states which do exist for \(S > 1/2\); it is not complete. Consider the effect on \(E_0(S)\) of ignoring these states, i.e. setting coefficients such as \(c(i,i)\) and \(c(i,i+1)\) to zero. In the above discussion it was shown that for \(S = 1/2\) this was formally equivalent to breaking the ring, which has no effect on \(E_0\). For \(S > 1/2\) the flipped state \(|...S,-S+1,S-1,S...\rangle\) is equivalent to only a partial ring opening and will produce even less disturbance. Therefore imposing this boundary condition, i.e. using the basis \(B\), will have no effect on \(E_0\) expressed as the solution of an arbitrarily large section of the matrix which involves states in the sets \(\{|\psi(M)|\}\) where \(M < n\) for any spin. Thus \(E_0(S)\) is the solution of a matrix for which the matrix elements have been given in (6.5). It can be seen by
adding $2S^2$ times the identity to this matrix, dividing by $S$ and ignoring $(S/n)$ terms, that the lowest eigenvector is independent of $S$. Since it is known for $S=1/2$ it follows that:

$$E_0(S) = -2S^2 - 2Sb = -2S(S+2\ln2-1)$$

The above approach is far from rigourous, and has several weaknesses. First, the total number of states increases as $(2S+1)^n$ and the above approach assumes that all extra states for $S>1/2$, i.e. the vast majority, have no effect on the eigenvector since they occur in sets $\{\psi(M)\}$ where $M=O(n)$. However it is not proved that states with $O(n)$ flips have no effect on $E_0$. If this were the only difficulty (6.2) would be an upper bound for $E_0$ since it arises from an incomplete basis. However if states with $O(n)$ flips are important then the spin variation in the diagonal matrix elements might be significant. Thus the diagonal element of $\psi(1,i), |...S,-S+1,S-1,-S...>$, is $-2S^2+(8S-2)/n$. The $-2/n$ type terms could contribute a negative term to $E_0$ which would decrease with $S$.

In view of these difficulties, (6.2) can only be regarded as tentative. The contradiction between (6.2) and numerical extrapolations for $E_0(S=1)$ provides an incentive for further study of numerical extrapolation.

6.2.2 Numerical Extrapolation

As $S$ increases the size of the basis of the matrix problem increases very rapidly and correspondingly fewer terms in the sequence $E_0(n)$ can be obtained. As (6.2) contradicts Blöte's
result for $S=1$, this spin will be considered in detail.

For $S=1$ the lines on a Bonner-Fisher plot are not straight and do not intersect near $1/n^2=0$. Blöte found that if the results for even $n$ were plotted against $1/n^3$ and the results for odd $n$ against $1/n^2$ intersection near $n=\infty$ was obtained. The estimate of $E_0(S)$ obtained was "critically" dependent on the assumption that this theoretically rather unexpected behavior continued.

Following Blöte, I have used both open chains and closed rings to obtain series for numerical extrapolation. The advantage of rings is that the cyclic symmetry can be used to reduce greatly the size of the matrix to be solved. However 'mismatch seam' effects due to the periodic boundary conditions of the problem may sometimes give misleading results for small $n$. For open chains convergence to $n=\infty$ is more frequently monotonic. The matrix for the chains can be easily banded, reducing to some extent the memory and CPU time required for solution. Calculations on $S=1/2$ and $S=1$ are significantly simpler than those for $S>1$ since all off-diagonal matrix elements are equal for these spins, and therefore only the positions of the elements need to be stored.

The results for $S=1/2$ and $S=1$ rings and chains are presented in Tables 6.2 and 6.3. The columns 'F1', 'F2' and 'F3' replace plots of $E/n$ against $1/n$, $1/n^2$ and $1/n^3$. Thus in Table 6.2 for $S=1/2$ $F1(2)=0.75$ is the intercept on $1/n=0$ drawn from the points corresponding to $n=3$ and $n=1$. $E_0$ is considered as a
positive quantity, i.e. $|E_0|$, throughout.

The results for rings will be considered first. Classically, $E(n) = E_0$ for $n$ even but for $n$ odd the mismatch in spin is evenly divided into $n$ intervals of misalignment, $\pi/n$, causing an energy change of $-2JS^2\{1-\cos(\pi/n)\} = -JS^2\pi^2/n^2$ for $n$ not too small. This is the theoretical basis of the Bonner-Fisher method. Inspection of Table 6.2 shows that for $S=1/2$ the behavior is exactly as expected even for quite small $n$; the sequence $F2$ is approximately constant for $n>3$. 


Table 6.2 The ground state energy of S=1/2 and S=1 rings.

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<tr>
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<th>F2(n)</th>
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### Table 6.3 The ground state energy of $S=1/2$ and $S=1$ chains.

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#### S=1

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It appears that F2 forms two sub-sequences for odd and even n which approach the known limit monotonically from below and above for odd and even n. The final values in the table, F2(14) and F2(15) imply the result E_o=0.88634±0.00001, a result which is accurate to 0.005%. Extrapolation through n=16 and n=20 raises the lower bound even closer to the exact value. For S=1/2, F1 forms sub-sequences converging in the same way as F2 but convergence is much slower and the result less useful; the F3 sub-sequences also converge but in the opposite sense to those for F1 and F2, i.e. from above and below for odd and even n. This change in the sense of the convergence between F2 and F3 suggests that for some a between 2 and 3, Fa might give an even better result.

With the available data it is found that the crossover occurs between 2.016 and 2.017. For a=2.0166 both sub-sequences are monotonic but converge to a result 0.886296 < E_o < 0.886299 which is incorrect as the lower bound is larger than the exact result. It is clear that unless the behavior at large n is exactly that assumed in any given extrapolation the extrapolation must eventually fail and the attempt to refine the value of E_o by varying a is unreliable.

Now consider S=1. F1(S=1) behaves as F1(S=1/2) and suggests 2.775<E_o<2.907. F2 also behaves as F2(S=1/2) but the sequence is not as constant nor is convergence as rapid. F2 suggests 2.795<E_o<2.832. Once again the sense of convergence is reversed for F3 and the sequences suggest 2.8074<E_o<2.8027, a
nonsensical result. The situation here must be analogous to that for $a=2.0166$ for $S=1/2$ in that at least one of the sequences must reverse for larger $n$. This reversal of apparently monotonic sequences seriously undermines the basis for numerical extrapolation using arbitrary exponents, $a$.

With the available data for $S=1$, contradictions are obtained for all $a>2.7$ where the most 'refined' estimate for $E_0$ is 2.797. For both $S=1/2$ and $S=1$ the values for $E_0$ obtained by simple plotting are too large if $a$ is too large. The question arises, what is the largest 'safe' value of $a$? It would seem that since logarithmic, $1/\log(n)$, terms cannot be ruled out no value of $a$ is entirely safe and all Bonner-Fisher type plots might fail by indicating an $E_0$ larger than the correct one. Thus, though the upper bounds for $E_0$ defined above are almost certainly correct the lower bounds are suspect.

Now consider the results for chains, listed in Table 6.3. Classically $E(n)$ tends to $E_0$ as $1/n$. The column $E/(n-1)$ is included as it might be thought that division by the number of interactions was more appropriate in this case. The sub-sequences for odd and even $n$ are monotonic increasing for both $S=1/2$ and $S=1$ and monotonic decreasing for $E/(n-1)$. By varying $\beta$ in $E/(n-\beta)$ a more refined value can be obtained but the 'best' $\beta$ varies with $S$ and as with the rings the correctness of the refined result is in doubt.

For chains the convergence of $E/n$ is much slower for $S=1$ than for $S=1/2$; thus $E_0(S=1/2,n=4)$ is 91.4% of the exact $E_0$
whereas \( n=8 \) is needed for \( S=1 \) to obtain similar accuracy. It appears that \( O(S/n) \) terms as discussed in 6.2.1 may be important, creating an added difficulty in extrapolations to all \( S>1/2 \). Only \( F1 \) is useful in extrapolation as \( F2 \) and \( F3 \) do not form two sub-sequences which converge from above and below. \( F1 \) suggests \( 0.8850<E_0<0.8905 \) for \( S=1/2 \) and \( 2.7699<E_0<2.7974 \) for \( S=1 \). For \( S=1/2 \) the exact value is significantly nearer to the lower limit than to the upper limit.

One more example of the dangers of numerical extrapolation will be given. Classically, \( E(n)=E_0-2S^2/n \). If \( 2S^2/n \) is added to the second column of Table 6.3 a sequence which is monotonic from below for odd and even \( n \) is obtained for both \( S=1/2 \) and \( S=1 \). For \( S=1 \) the sequence suggests \( 2.7692 < E_0 < 2.7789 \), apparently the best result yet. Testing this result on \( S=1/2 \) gives \( 0.8891<E_0<0.8952 \), which is incorrect and once again too high. However the upper bound is genuine, for \( S=1/2 \) at least.

A variety of further transformations, both on the raw data and on the sequences \( F1,F2,F3 \) have been tried. A feature of this work has been that the apparent limit is strongly dependent on the transformation applied, and since this kind of behavior is worse than useless the results are not presented in detail. In general the difficulty of obtaining reliable results by series transformations suggests that logarithmic terms may be important for large \( n \).

It therefore appears that the lowest power of \( n \) consistent with a useful result should be used in the extrapolation. Since
F1 has a theoretical basis for chains (classical approximation) but not for rings, F1 of chains will be taken as the most reliable result for S=1. Thus:

\[(6.15) \quad 2.7699 < E_0(S=1) < 2.7974\]

(6.15) does not imply that (6.2) is correct but it does seem that previous extrapolations to E0 by Weng, Majumdar and Blöte are incorrect. The conflict between (6.2) and numerical extrapolations has been removed.

Cautious attempts to define bounds for E0(S>1) have been made. Results for finite rings with totally symmetric ground states are given in (6.16), results for chains are listed in Table 6.4. New results, for both rings and chains, are underlined.

(6.16) Rings
\[
\begin{align*}
S=3/2, \ n=8 & \quad 5.732511; \\
S=2, \ n=6 & \quad 9.721564; \\
S=5/2, \ n=8 & \quad 14.52762 \\
\end{align*}
\]
\[\underline{n=8} \quad 9.630467.\]
Table 6.4 The ground state energy of S > 1 chains

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
S = 3/2 & n & E & E/n & F1(n) & F2(n) \\
\hline
2 & 7.500000 & 3.750000 & 6.000000 & 4.500000 & 4.153846 \\
3 & 12.000000 & 4.000000 & 5.431181 & 4.870787 & 4.710675 \\
4 & 18.362362 & 4.590591 & 5.718267 & 5.073917 & 4.876667 \\
5 & 23.436534 & 4.687307 & 5.575896 & 5.181774 & 5.057314 \\
6 & 29.514154 & 4.919026 & 5.678951 & 5.265766 & 5.133092 \\
7 & 34.794436 & 4.970634 & 5.616229 & 5.317428 & 5.220519 \\
8 & 40.746612 & 5.093326 & 5.667361 & 5.362543 & 5.263043 \\
9 & 46.129158 & 5.125462 & & & \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
S = 2 & n & E & E/n & F1(n) & F2(n) \\
\hline
6 & 49.285120 & 8.214187 & 9.551885 & 8.839118 & 8.610248 \\
7 & 58.309994 & 8.329999 & & & \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|c|c|}
\hline
S = 5/2 & n & E & E/n & F1(n) & F2(n) \\
\hline
2 & 17.500000 & 8.750000 & 15.000000 & 11.250000 & 10.384615 \\
7 & 87.821137 & 12.545877 & & & \\
\hline
\end{array}
\]

For the limited data available, the results (6.16) appear to behave as for the lower spins. The sequence F1 and the sequence \( E_0(n) + 2S^2/n \) were considered in an attempt to estimate \( E_0 \). The results for lower and upper bounds for \( E_0 \) are:

(6.17) \[
\begin{align*}
S & \quad 3/2 & \quad 2 & \quad 5/2 \\
F1 & \quad 5.616, 5.679 & \quad 9.220, 9.599 & \quad 14.01, 14.48, \\
E + 2S^2/n & \quad 5.586, 5.669 & \quad 9.439, 9.610, & \quad 14.29, 14.50,
\end{align*}
\]

The estimates of \( E_0 \) from (6.17) are:

(6.18) \[
\begin{align*}
E_0: S = 3/2, & \quad 5.647 \pm 0.031; \\
S = 2, & \quad 9.52 \pm 0.08; \\
S = 5/2, & \quad 14.38 \pm 0.10.
\end{align*}
\]

For \( S = 2 \) and \( S = 5/2 \) the estimate is the same as Blöte's, for \( S = 3/2 \) it is somewhat lower. All numerical estimates are
consistent with (6.2).

In conclusion, numerical extrapolation is consistent with the result $E_0 = 2S(S+2+1)n^2-1$ suggested by theoretical considerations, however in view of the extreme uncertainty associated with the numerical estimates the result cannot be regarded as proved. Numerical extrapolation is most, even anomalously, satisfactory for $S=1/2$, for which $E_0$ is known exactly anyway; its usefulness decreases rapidly as $S$ increases both because of the increased difficulty in obtaining sufficient members of the sequences and because terms $O(S/n)$ are important for finite $n$.

6.3 The Odd/Even Approximation

In 6.2 it was shown that it is difficult to obtain accurate numerical extrapolations for the low temperature properties of $S>1/2$ chains. An alternative approach in which the Hamiltonian is approximated before solution will now be introduced.

6.3.1 Approximations to the Heisenberg Hamiltonian

The quantum mechanical theory of magnetic interactions was first applied to real systems by Heisenberg in 1928. A model for ferromagnetism in infinite systems was derived by making certain approximations about the distribution of the spin states.

Heisenberg considered an infinite lattice of atoms each
coupled to a number of nearest neighbours, \( z \). The mean energy, per atom, of all states with a given value of \( S' \) is given by \( W(S') = -(zJ/n)S'^2 \). For \( S=1/2 \) the standard deviation, \( \Delta \), of the energies about \( W(S') \) can also be calculated; Heisenberg obtained the result:

\[
(6.19) \quad \Delta^2(S') = J^2 z (n^2 - 4S'^2)(3n^2 - 4S'^2)/(8n^2)
\]

The total number of states with total spin \( S' \), \( \Omega(S') \) can be calculated from \( \Omega(S') = \omega(S') - \omega(S'+1) \), where \( \omega(S') = n!/[(n/2-S')!(n/2+S')!] \), as in Chapter 2. Since \( S' \) is large for low energy ferromagnetic states Stirling's approximation can be used. Assuming a Gaussian distribution of states, the partition function and hence the thermal and magnetic properties as a function of temperature can then be calculated. Heisenberg obtained an expression for the Curie point, \( T_0 = 2J/k(1-[1-8/z]) \). Thus a real Curie point is predicted only if \( z \geq 8 \). Later calculations have shown that though 1-D, \( z=2 \), and 2-D, \( z=4 \), systems do not have a Curie point, systems with \( n=6 \) may. However, given the number of approximations involved this approach is surprisingly successful.

For \( S>1/2 \) the standard deviation of the energies of states with total spin \( S' \) cannot be calculated and there is no simple expression for \( \Omega(S') \). Heisenberg made the 'still cruder' assumption that all states of the same spin have the same energy. This led to an expression for the Curie point \( T_0 = 2Jz 2S(S+1)/3k \). This approximation is much less adequate that that for \( S=1/2 \), and incorrectly predicts ferromagnetic Curie points.
for all lattices, irrespective of z.

In 1966, Earnshaw applied Heisenberg's 'cruder' approximation, that all states of the same S' are degenerate, to model the finite antiferromagnetic cluster and chain systems which were then being synthesised\textsuperscript{30}. The approximation was hoped to be valid for $S>1/2$ linear chains, for which no numerical extrapolations corresponding to Bonner and Fisher's result were available. The application to finite systems will be referred to in this thesis as Earnshaw's approximation. Earnshaw's approximation involves replacing the correct Hamiltonian for the system by:

$$ (6.20) \ H = -\frac{zJ}{(n-1)} [S'^2 - nS^2] $$

where $z$ is now the 'average coordination number'. In a linear chain $z=2(n-1)/n$ and thus $H= -(2J/n) (S'^2 - nS^2)$. The eigenvalues of (6.20) can be inserted into the HDVV formula in the usual way. Earnshaw published a table giving the $\mu(T)$ for antiferromagnetic chains of $n=3-10$, $S=1/2-5/2$.

Unfortunately the simplification of the exact spin Hamiltonian by (6.20) is even less satisfactory for chains and clusters than for infinite systems. (6.20) is only accurate if all coupled atoms are equivalent as in the equilateral triangle or tetrahedron. For other systems the difference between the energies of states having the same spin may be at least as large as that between states of different spin, as can be verified by inspection of the exact results of 6.2. For example the Earnshaw
model suggests that all odd n antiferromagnetic chains will have a ground state of spin 1/2 or 0 whereas exact results show that the ground state spin is $S$.

Another serious failing of the Earnshaw approximation as applied to antiferromagnetic systems is that as $n$ increases, the ground state energy per atom tends to zero and the specific heat vanishes at all temperatures; also the temperature at which the maximum in the antiferromagnetic susceptibility occurs tends to zero for large $n$. The only contribution to the antiferromagnetic ground state energy for large systems comes from the splitting of states of the same $S'$. It can be seen from (6.19) that as $S'$ decreases $\Omega(S')$ increases. The inadequacy of Earnshaw's approach was pointed out by Barraclough in 1968.

Since neither Earnshaw's approximation nor numerical extrapolation for the magnetic properties of linear chains of $S > 1/2$ is entirely satisfactory, I have investigated a simple Hamiltonian involving intermediate quantum numbers as an approximation to these systems. The atoms of the chain are considered to be numbered consecutively and two intermediate spins representing the spins on the odd numbered and the even numbered atoms are introduced. The true spin Hamiltonian is approximated by:

$$\text{(6.21)} \quad H = -cJ (S'^2 - S''^2 - S''') = -2cJ S''.S'''$$

where $S'' = S_1 + S_3 + S_5 + \ldots.$ and $S''' = S_2 + S_4 + S_6 + \ldots.$
where \( c \) is a scaling factor analogous to the \( z/(n-1) \) of Earnshaw's approximation, it is equal to the real number of interactions divided by the number implied by (6.21) with \( c=1 \). The worst aspects of Earnshaw's approximation are now removed. States of the same \( S' \) split by an amount which increases as \( S' \) increases, the antiferromagnetic ground state has non-zero energy and the ground state spin for odd chains is now predicted correctly. In view of these improvements it was thought worthwhile to investigate the approximation (6.21), which will be known as the odd/even approximation, in some detail. For linear chains the scaling factor, \( c \), is given by:

\[
(6.23) \quad \frac{4}{n+1}, \quad n \text{ odd}; \quad \frac{4(n-1)}{n^2}, \quad n \text{ even}.
\]

The Earnshaw approximation is exact only for the 2 membered chain, the odd/even approx is exact for \( n = 2 \) and 3. As \( n \) tends to infinity the antiferromagnetic ground state for the chain tends to \(-2S^2\) per atom, the same as the classical value.

Eigenstates of the odd/even Hamiltonian can be expressed as kets \(|S',S'',S'''>\) of degeneracy equal to the product of the degeneracies associated with the half chains \( \Omega(n,S,S',S'',S''') = \Omega(n/2,S,S'').\Omega(n/2,S,S''') \) where \( \Omega(n/2,S,S') \) is found from the branching diagram. A program which calculates the susceptibility and specific heats of OE systems using these degeneracies, the energies from (6.21) and the HDDV formula is therefore straightforward. Results for all \( n,S \) up to \( S'=250 \) have been obtained.
6.3.2 Results of the odd/even approximation

The susceptibility and specific heat of OE systems for \( S=1/2, \ S=1 \) and \( S=5/2 \) antiferromagnets have been calculated. The results are plotted in Figs. 6.1 to 6.6 and listed in Table 6.5. Some data relevant to the discussion of these results are listed below. The 'natural' units, \( (N\beta^2/3k)=1 \), where \( n \) is Avogadro's number, \( k \) is Boltzmann's constant and \( \beta \) is the Bohr magneton, and \( g=2 \) for \( \chi \); and \( R \) (the gas constant) = 1 for the specific heat, are used throughout. The results are presented normalised for linear chains; as explained above, they may easily be transformed to apply to 2-D or 3-D systems. This 'adaptability' is one of the weaknesses of this approach as solutions for 2- and 3-D systems can in no way be obtained from solutions for 1-D by scaling.
Fig. 6.1. Susceptibility of Odd/Even $S=1/2$ chains. From bottom to top at $T/J=0.5$ $N=2, 4, 8, 16, 32, 64, 128, 256$ and 512.
Fig. 6.2. Susceptibility of Odd/Even $S=1$ chains. From bottom to top at $T/J=0.5$ $N=2, 4, 8, 16, 32, 64, 128$ and 256
Fig. 6.3. Susceptibility of Odd/Even S=5/2 chains. From top to top at $T/J = 3.0$ $N = 2, 4, 8, 16, 32$ and 64.
Fig. 6.4. Specific Heat of Odd/Even $S=1/2$ chains. In order of increasing maxima, $N=2, 4, 8, 16, 32, 64, 128, 256$ and 512.
Fig. 6.5. Specific Heat of Odd/Even $S=1$ chains. In order of increasing maxima, $N=2, 4, 8, 16, 32, 64, 128$ and 256.
Fig. 6.6. Specific Heat of Odd/Even $S=5/2$ chains. In order of increasing maxima, $N=2,4,8,16,32$ and 64.
Table 6.5 Susceptibility and Specific Heat results for the Odd/Even approximation for antiferromagnetic chains

<table>
<thead>
<tr>
<th>S</th>
<th>( n )</th>
<th>( x_{\text{max}} )</th>
<th>( T(x_{\text{max}}) )</th>
<th>( C_{\text{max}} )</th>
<th>( T(C_{\text{max}}) )</th>
<th>( E(1.0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>2</td>
<td>1.2071</td>
<td>1.247</td>
<td>0.5117</td>
<td>0.703</td>
<td>-0.601</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.1139</td>
<td>1.173</td>
<td>0.4636</td>
<td>0.714</td>
<td>-0.597</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.1827</td>
<td>1.034</td>
<td>0.4825</td>
<td>0.743</td>
<td>-0.487</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>1.2634</td>
<td>0.967</td>
<td>0.5764</td>
<td>0.752</td>
<td>-0.405</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>1.3294</td>
<td>0.946</td>
<td>0.7001</td>
<td>0.772</td>
<td>-0.341</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>1.3785</td>
<td>0.947</td>
<td>0.8299</td>
<td>0.803</td>
<td>-0.286</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>1.4138</td>
<td>0.955</td>
<td>0.9518</td>
<td>0.836</td>
<td>-0.236</td>
</tr>
<tr>
<td></td>
<td>256</td>
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<td>0.964</td>
<td>1.0588</td>
<td>0.867</td>
<td>-0.192</td>
</tr>
<tr>
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<td>0.894</td>
<td>-0.154</td>
</tr>
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</tr>
<tr>
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<td>4</td>
<td>1.3262</td>
<td>2.293</td>
<td>0.5696</td>
<td>1.591</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.3141</td>
<td>2.347</td>
<td>0.7105</td>
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<tr>
<td></td>
<td>16</td>
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<td>1.4320</td>
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<td>1.3852</td>
<td>2.236</td>
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</tr>
<tr>
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<td>2.573</td>
<td>1.5098</td>
<td>2.326</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
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<td>1.8615</td>
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<td>8.17</td>
<td>0.7217</td>
<td>5.79</td>
<td></td>
</tr>
<tr>
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<td>8</td>
<td>1.3888</td>
<td>9.38</td>
<td>0.9625</td>
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<td></td>
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<tr>
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<td>1.1947</td>
<td>6.87</td>
<td></td>
</tr>
<tr>
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<td>32</td>
<td>1.4024</td>
<td>10.56</td>
<td>1.4053</td>
<td>8.62</td>
<td></td>
</tr>
<tr>
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<td>1.4227</td>
<td>10.88</td>
<td>1.5886</td>
<td>9.25</td>
<td></td>
</tr>
</tbody>
</table>
The susceptibility, $\chi$, is characterised by:

a/ A smooth, rounded maximum for which $\chi\approx 1.5$ for all $S$

b/ $\chi$ tends to approximately 1.0 as $T$ goes to 0, for all $S$. At high temperatures $\chi$ is proportional to $S(S+1)/T$.

The smooth, rounded maximum is qualitatively correct for the linear chain. However the result is quantitatively poor. Comparing the OE and exact results for the antiferromagnetic $S=1/2$ chain:

(6.22)

<table>
<thead>
<tr>
<th></th>
<th>$\chi_{\text{max}}$</th>
<th>$T(\chi_{\text{max}})$</th>
<th>$\chi(T=0)=\chi_0$</th>
<th>$\chi_{\text{max}}/\chi_0$</th>
<th>$C_{\text{max}}/R$</th>
<th>$T(C_{\text{max}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact</td>
<td>0.8815</td>
<td>1.282</td>
<td>0.6079</td>
<td>1.450</td>
<td>0.350</td>
<td>0.962</td>
</tr>
<tr>
<td>OE</td>
<td>$\approx 1.5$</td>
<td>$\approx 1.0$</td>
<td>$\approx 1.0$</td>
<td>$\approx 1.5$</td>
<td>-</td>
<td>$\approx 1.0$</td>
</tr>
<tr>
<td>$S=\infty$</td>
<td>1.204</td>
<td>0.2382</td>
<td>1.0</td>
<td>1.204</td>
<td>1.0</td>
<td>0</td>
</tr>
</tbody>
</table>

The susceptibility is overestimated at low temperatures because of the inadequate representation of the ground state as an ordered $\alpha\beta\alpha\beta\alpha\beta$ state with energy $-0.5$. Thus for $S=1/2$ the OE energy spectrum is more compressed than the exact spectrum ($E_0=-0.88$) and more magnetic states are occupied at low temperatures. If this compression of the spectrum by a factor of 1.38 is taken into account the result is improved but is still by no means accurate. The similarity of the $\chi$ vs $T$ curves for all spin suggests that $\chi_0$ and $\chi_{\text{max}}$ may be relatively simple functions of $E_0$.

The specific heat is characterised by:

a/ Low temperature, $C$ tends to $1/n$. 

b/ Intermediate T. As n increases a lambda shaped maximum forms at a temperature which varies with spin.

c/ High T. C proportional to $1/nT^2$.

The decrease as $1/n$ at the extremes suggests that if n were increased further the specific heat would show an increasingly large and sharp maximum associated with some kind of phase transition; the maximum specific heat may even be unbounded for infinite n. This behavior is quite unlike that of the real linear chain which exhibits a smooth specific heat at all temperatures. It is clear that some of the essential features of the chain Hamiltonian are lost if intermediate quantum numbers are introduced, because such quantum numbers incorrectly imply a degree of long range interaction.

Careful investigation of the susceptibility near the temperature associated with the maximum in the specific heat does not show any anomaly, though it is possible that the slope may be discontinuous at or near the maximum in $\chi$ for infinite n.

It can be seen that the OE approx is less than satisfactory as an approximation for the calculation of the thermodynamic properties of Heisenberg linear chains. It is not unusual in this respect since the linear system provides a severe test for any model\textsuperscript{179}. Despite this failure the OE Hamiltonian is not without interest as it gives some indication of the effect of particle size on magnetic phase transitions for which most mathematical treatments assume an infinite number of atoms.
The magnetic interactions in any real sample will be limited by microcrystal boundaries and other imperfections and it has been suggested that the proportion of such defects is \( \approx 1\% \) in linear chains\(^{180}\), leading to a mean chain length \( \approx 100 \). As expected finite size decreases the temperatures of the specific heat and susceptibility maxima. The variation of the maximum specific heat with \( n \) is nearly logarithmic for a considerable range of \( n \) but for large \( n \) appears to be even slower. It is relevant in this context that specific heats of more than \( 2R \) are rarely observed in practice.

There is a connection here with calculations on antiferromagnetic chains with random lengths\(^{181}\) or with random exchange couplings\(^{182}\). The frequently observed tail in the susceptibility of 'infinite' linear systems may be due to randomness rather than paramagnetic impurity. Sensitivity to impurities and imperfections is "one of the basic topological characteristics of pure 1-dimensional systems"\(^{183}\).

6.4 Dynamic Distortions and Linear Chains

Effects associated with non-zero \( (\partial J/\partial d)_o \) may occur in linear systems as well as in clusters. As a result of the non-degeneracy of the magnetic spectrum of the finite Heisenberg linear chains, the changes associated with small distortions tend to be quadratic rather than linear in the distortion coordinate. Second order effects associated with coupling between magnetic and elastic forces, i.e. \( (\partial J/\partial d)_o \), are often referred to as striction effects\(^{184-186}\), and have been observed
in several 3-dimensional lattice systems as well as in dimers.

In infinite chains first-order changes in the spectrum may occur as the system can be considered as equivalent to an infinite ring. The spin-Peierls transition, in which the ring becomes alternating (incipient dimerisation) at a well defined transition temperature, and which has recently been an area of vigourous research\textsuperscript{187-189}, can be regarded as a 'freezing out' of such dynamic distortions. The mathematical techniques used in spin-Peierls transition theory are typically much more sophisticated than those for the dynamic distortion model, as the full 3-dimensional lattice phonon field must be considered rather than merely the local normal modes of a small cluster.

6.4.1 Dimetallic systems

Dimetallic systems have the unique property that the distortion Hamiltonian must be proportional to the static Hamiltonian. The magnetic term in the Hamiltonian can therefore be associated with a shift in the potential minimum of the vibrational harmonic oscillator associated with the distortion; this shift is typically dependent on $S'$ and thus leads to a slight rearrangement of the energy levels. As they are degenerate the wavefunctions can be written as Born-Oppenheimer products $|n>|S>$, where $|n>$ is a vibrational and $|S>$ a spin function, and treated by perturbation theory. Lines\textsuperscript{83} developed such a model and found that striction effects can be included in the spin Hamiltonian by the addition of a biquadratic $(S_1.S_2)^2$ term. Later work\textsuperscript{190} showed that, because the distortion terms
commute with H, the Lines Hamiltonian has a relatively simple exact solution, which can be expanded in increasing powers of $(S_1.S_2)$. The striction Hamiltonian (assuming J is a function of the position but not the momentum of the nuclei) is:

\[
(6.24) \quad H = \pi^2/2 + \omega^2 \xi^2/2 - J_0(1+A\xi+B\xi^2)\tau
\]

where $\xi$, $\pi$ and $\omega$ are the coordinate, momentum and frequency of the normal mode, $A=(1/J_0)\partial J/\partial \xi$, $B=(1/J_0^2)\partial^2 J/\partial \xi^2$, and $\tau=2S_1.S_2$. Similar dimers typically indicate that J is nearly linear for quite a large range away a rather sharp turning point of maximum J and thus that B is usually small. The sign convention for J in (6.24) is opposite to that used in refs 83 and 221, and a conventional factor of 2 is included in $\tau$. In the perturbation theory approach H is expressed as:

\[
(6.25) \quad H_0 = \pi^2/2 + \omega^2 \xi^2/2 - J_0 \tau \quad V = -J_0(A\xi+B\xi^2)
\]

and solved in the usual way. The exact solution makes use of the fact that $\tau$ is a constant for each $S'$ and that striction does not couple terms of different $S'$. H can therefore be expressed as:

\[
(6.26) \quad H = \pi^2/2 + \Omega^2(\xi-\delta)^2 + C
\]

where $\Omega^2=\omega^2-2J_0B\tau$, $\delta=-(J_0A/\Omega^2)\tau$ and $C=-J_0\tau-(J_0A/\Omega)^2\tau^2/2$.

Therefore:

\[
(6.27) \quad E(n,S') = \hbar\Omega(n+1/2) + C
\]

the result, up to second order in $\tau$ is:
Thus the Lines model gives rise to both biquadratic terms and a temperature dependence of \( J \). Experimentally, the large temperature dependence of \( J \) for dinuclear copper cryptates has been explained in terms of such striction or 'exchange elasticity' which is enhanced by the "quite specific non-rigidity" of the cryptate cavity\(^1\).\(^9\)

The effect on (6.28) of including terms other than \( J\tau \) which may depend on the strain coordinate will now be considered. First consider \( S=1/2 \); referring to equation (1.21), the full Hamiltonian is:

\[
(6.29) \quad H = K - J/2 - 2JS_1.S_2 = K - J(\tau+1/2)
\]

In general \( K \), as well as \( J \), will be a function of the distortion:

\[
(6.30) \quad K = K_0 (1 + A'\xi + B'\xi^2) \quad \text{where} \quad A' = (1/K)\partial K/\partial \xi)_0
\]

\( A' \) may, in general be different from \( A \), though it is reasonable to expect them to be similar as they both arise from some form of orbital overlap. Following Lines' treatment \( H \) may be written:

\[
(6.31) \quad H_0 = \pi^2/2 + \omega^2\xi^2/2 + K_0 - J(\tau+1/2)
\]

\[
V = \xi[K_0A' - J_0A(\tau+1/2)]
\]

The \( B \) and \( B' \) terms will be reintroduced in (6.35). The second order change in energy is now:
(6.32) $\Delta E = -(1/2\omega^2) [K_0 A' - J_0 A(t+1/2)]^2$

$(t+1/2) = +1$ and $-1$ for the triplet and singlet for $S=1/2$.

If $K_0 A' = 0$ both the singlet and triplet energies are reduced by $J_0^2 A^2/\omega^2$ i.e. there is no change in the singlet-triplet splitting. If $K_0 A' = J_0 A/2$ Lines' result is obtained. If $K_0 A' \gg J_0 A$ the levels again suffer a shift in energy but the energy difference remains constant. It can be seen that $J_0 A \approx K_0 A'$ is needed in order for striction to have a significant effect on the singlet-triplet splitting in $S=1/2$ dimers.

For general $S$, the equation equivalent to (6.29) is $H = K - J(t+2S^2)$, a result most conveniently demonstrated by perturbation theory:

Consider a pair of atoms each with $n$ electrons, $(S=n/2)$. Let the exchange interaction between pairs of electrons on the same atom be $J'$ and suppose that just one pair of orbitals on different atoms are coupled with an exchange integral $J''$. The problem can be solved by expressing $H$ as a matrix in an Ising basis blocked by $S'_z$. Clearly $\{A(a_1, a_2, \ldots, a_n), (a_1, a_2, \ldots, a_n)\}$, where $A$ is the antisymmetriser and the subscripts denote atoms 1 and 2, is an eigenfunction with $S' = n$ and an eigenvalue $E = K - n(n-1)J' - J''$.

Now consider the basis of $2n$ states with $S'_z = n-1$, such as $\{A(a_1, a_2, \ldots, a_n), (a_1, a_2, \ldots, a_n)\}$. If $J'' = 0$ the matrix can be separated into two blocks of size $n$. Each diagonal element is $E_0 + (n-1)J'$ and each off-diagonal element in each block is $-J'$. There are two low energy solutions for this $S'$, $\psi(S' = n) = |(1, 1, \ldots, 1)_1, (1, 1, \ldots, 1)_2>$ and $\psi(S' = n-1) = |(1, 1, \ldots, 1)_1(-1, -1, \ldots, -1)_2>$; if $J'' = 0$
these have energy $E_0$. If $J''$ is now applied as a perturbation one obtains:

\[(6.33) \langle \psi(S' = n) | V | \psi(S' = n) \rangle = 0, \quad \psi(S' = n - 1) | V | \psi(S' = n - 1) \rangle = 2J''/n \]

Having defined an absolute energy and an energy difference, the rest of the spin spectrum follows from the Landé interval rule.

In terms of the Hamiltonian, $H = -J\tau$, the splitting between the $S' = n$ and $S' = n - 1$ states is $2Jn = 2J''/n$; therefore $J = J''/n^2$. The energies found above can now be expressed as $E(S' = n) = K - n^2J$, $E(S' = n - 1) = K - J(n^2 - 2n)$, where the term in $J'$ is ignored as it is unaffected by striction. Thus the general result is:

\[(6.34) H = K - J(\tau + 2S^2) = K - J[S'(S' + 1) - 2S]\]

This result is not dependent on the details of the coupling between the two atoms; if more than one pair of orbitals are coupled, $J''$ is replaced by a sum of such integrals. The perturbation, and hence the Heisenberg, treatment is useful as long as $J' \gg J''$. This is expected to be the case as the $J'$ are the strong positive couplings which give rise to Hund's first rule. It is interesting to note that the spins $S$ on the constituent atoms remain good quantum numbers only when all $J'$, and all $J''$, are equal. The result $J = J''/n^2$ shows that, for example, a measured $J$ of $30 \text{cm}^{-1}$ in an $S = 5/2$ system implies an exchange integral between orbitals of $750 \text{cm}^{-1}$ if just one orbital on each atom is involved in the exchange.

It can be seen that the rest of the solution for the Lines
model can now be followed except that, assuming A=A' and B=B' for simplicity, \( \tau \) must be replaced by \( (\tau+2S^2-K_0/J_0) \). Thus,

\[
(6.35) \ H = \pi^2/2 + \omega^2\xi^2/2 - J_0(1 + A\xi + B\xi^2) (\tau+2S^2-K_0/J_0)
\]

has the solution corresponding to (6.27); when this is expanded in \( \tau \) new terms are added to \( J \):

\[
(6.36) \ J = J_0[1 + \{(<n>+1/2)\hbar B/\omega\} + (J_0/\omega)^2[A^2 + hB^2(v+1/2)/\omega](2S^2-K_0/J_0)]
\]

Thus the first order striction parameter A, as well as B, causes a change in the magnetic spectrum which results in a small difference between the experimentally measurable value of \( J \) and the static exchange integral \( J_0 \).

6.4.2 Three atom chains

In the three atom chain there are two normal modes, the symmetric and antisymmetric stretch, which may be associated with striction effects. The striction Hamiltonian corresponding to (6.24) is:

\[
(6.37) \ H = \pi_0^2/2 + \omega_0^2\xi_0^2/2 - J_0(1+A\xi_0)(\tau_1+\tau_3+c) + \pi_1^2/2 + \omega_1^2\xi_1^2/2 - J_0(1+A\xi_1)(\tau_1-\tau_3)
\]

where \( c=(2S^2-K_0/J_0) \) is a constant which appears only for the totally symmetric vibration. Applying (6.28) (and ignoring \( c \)) gives:

\[
(6.38) \ \Delta E = -(J_0^2A^2/2) [(\tau_1+\tau_3)^2/\omega_0^2 + (\tau_1-\tau_3)^2/\omega_1^2)]
\]

\[
= -(J_0^2A^2/2^2)[(1/\omega_0^2+1/\omega_1^2)(\tau_1^2+\tau_3^2) + (1/\omega_0^2-1/\omega_1^2)(\tau_1\tau_3+\tau_3\tau_1)]
\]
(If the two pairwise couplings $\tau_1$ and $\tau_3$ are treated separately, i.e., the two pairwise interactions are treated as dimers, only the first term is obtained; in general $\omega_1 \neq \omega_0$ and this procedure is incorrect). In the idealised case of vibrational coupling between three metal atoms of equal mass, $\omega_1^2 = 3\omega_0^2$.

The case of $S=1/2$ will be considered first. As well as being simplest case in terms of the number of spin states, it has the special property that $\tau^2 = 3/4 - \tau$ and $(\tau_1 \tau_3 + \tau_3 \tau_1) = \tau_2$. Thus the first term in (6.38) merely scales $H$ and adds a trivial constant, and the second has the same effect as a next-nearest neighbour exchange $\tau_2$, which is expected to have $J>0$; i.e. $H$ can be expressed most simply as:

$$ (6.39) \quad H = -J(\tau_1 + \tau_3) -J'\tau_2 $$

where $J' = (J_0A/2)^2(1/\omega_0^2 - 1/\omega_1^2)$ is expected to be small and positive. The spectrum of (6.39) consists of a quartet at $E_a = -J-J'$ and doublets at $E_2 = 3J'/2$ and $2J-J'/2$. Defining $J'' = J+J'/2$ these can be re-expressed as $E_a = -J''$, $E_2 = 3J'/2$ and $2J''-3J'/2$, this shows that if $J>0$ striction decreases the doublet splitting compared with that of the static chain while if $J<0$ this splitting is increased.

It is interesting to compare the above result with that obtained by simply solving $H$ for the range of possible distortions and averaging the resulting magnetic spectrum, as in the dynamic distortion model. Clearly 'A' mode vibrations merely scale $J$; the asymmetric distortion terms can be included by
writing:

\[
(6.40) \quad H = -J(\tau_1 + \tau_3) - xAJ(\tau_1 - \tau_3) = J \begin{bmatrix}
-Ax & 1+Ax & 0 \\
1+Ax & -1 & 1-Ax \\
0 & 1-Ax & Ax
\end{bmatrix}
\]

where the matrix basis is \{aa\beta, a\beta a, \beta aa\} and \(x\) is an asymmetric distortion parameter. \(H\) has eigenvalues \(E(S' = 3/2) = J, E(S' = 1/2) = 3(AJx)^2/2, -2J - 3(AJx)^2/2\). This spectrum has the same form as that obtained on the striction model except that \(<x^2>\) replaces the term in the frequencies. The Lines and dynamic distortion approaches are expected to yield equivalent results for all systems in which the magnetic spectrum contains only degeneracy due to the total spin.

Biquadratic and bilinear exchange effects cannot be separated for the 3 atom \(S = 1/2\) system as again there is only one energy difference (that between the mean of the \(S = 1/2\) energies and the \(S = 3/2\) energy in the magnetic spectrum) to define \(J\), and so the idea of deviations from a Landé interval rule has no meaning. In general, for \(S > 1/2\) such a separation is possible but it may be extremely difficult to distinguish biquadratic from next nearest neighbour exchange given only, say, susceptibility data. This state of affairs is not of merely theoretical interest as several 3-atom \(S = 1\) nickel chains exist\(^{192,193}\) and several of these have been fitted to a next-nearest neighbour exchange Hamiltonian.
6.4.3 Infinite chains

As the chain length increases the discrete vibrational spectrum characteristic of small molecules is replaced by a continuous phonon spectrum. The spectrum contains low energy modes which correspond to waves of long wavelength throughout the 3-D lattice as well as higher energy vibrations associated with significant local distortions.

Deviations from the equivalent J are often discussed in terms of the Hamiltonian:

\[(6.41) \quad H = -2J \sum_i (S_i \cdot S_{i+1} + aS_i \cdot S_{i-1})\]

In this work a slightly different notation:

\[(6.42) \quad H = -2J \sum_i [(1+a)S_i \cdot S_{i+1} + (1-a)S_i \cdot S_{i-1}]\]

will be used as \(a\) can now be related via \((\partial J/\partial a)\) to a shift of the odd numbered atoms with respect to the even numbered ones and the spectrum of \(H\) is now symmetric in \(a=0\).

Alternating chains, e.g. Cu(NO₃)₂·2·5H₂O, are characterised by a temperature independent \(a\neq 0\) in (6.42). In contrast spin-Peierls (SP) systems exhibit \(a=0\) above a well defined transition temperature, below which \(a\) increases to a maximum, usually less than 0.2, at \(T=0\). In general \(a\neq 0\) separates an \(S'=0\) state from the continuous spectrum of the infinite system, i.e. creates an energy gap, and \(\mu=0\) at \(T=0\) in both alternating and SP chains. A noticeable 'knee' in the
susceptibility at the transition temperature, somewhat similar in appearance to that for long and even Odd/Even chains, Figs. 6.1 to 6.3, is characteristic of the SP transition.

The causes of alternation and SP behavior are not yet completely understood. Alternation may in at least some cases be associated with a non-magnetic, structural phenomenon such as the stacking of the polymer units, but the SP transition is thought to be caused by interaction between the magnetic couplings and the 3-D (to produce static ordering) phonon field. In the language of this thesis the behavior can be described as the freezing out of a dynamic distortion which, because it is not along a degenerate normal mode, does not affect the susceptibility above the transition temperature. For classical spins there is no decrease in the ground state energy as \( a \) varies from zero. As there must be some decrease in energy to drive the transition, SP behavior is thus an essentially quantum phenomenon.

Solitons\textsuperscript{196-197}, or non-linear excitations which are able to travel along chains without, in principle, loss of energy, have also been observed in chains in neutron diffraction studies. This has aroused a great deal of interest as the whole area of non-linear physics has been the subject of intense study in recent years. It might be possible to adapt the soliton formalism to cluster systems, using periodic boundary conditions associated with rotation of the distortion vector around the normal mode, but it is unlikely that the concept
would be useful in clusters as small as trimers or tetrahedra as the travelling wave soliton typically extends across several metal atoms.

SP/alternation phenomena are typically investigated assuming periodic boundary conditions in either infinite, or in a few numerical calculations, finite rings\textsuperscript{194-198}. For rings \(\delta E_0/\delta a\), where \(E_0\) is here defined as the ground state energy per atom, is zero by symmetry. Some numerical calculations on open chains will now be discussed. These show that for antiferromagnetic \(S=1/2\) chains a significant tendency to dimerisation associated with non-zero \(\delta E/\delta a\) remains for chains of at least several tens of atoms. In view of the extremely delicate nature of the SP transition (only about half a dozen examples are known out of hundreds of linear systems) and the significant proportion of atoms which are expected occur in chains of less than 100 atoms because of lattice defects\textsuperscript{180}, it would seem that these end effects may significantly influence the SP transition.

End effects have been considered previously only in rather different contexts; they cause an increase in susceptibility at very low temperatures\textsuperscript{182} and lower the 3-D ordering temperature associated with interchain interactions\textsuperscript{183}.

Consider the distortion Hamiltonian:

\[
(6.43) \ H = -2J \ [\ (1+a/2)S_1 \cdot S_2 \ + \ (1-a)S_2 \cdot S_3 \ + \ (1+a/2)S_3 \cdot S_4] \\
\]
in which \(a\) corresponds to a shift of the central atoms with
respect to fixed outer atoms. The coefficients of (6.43) are chosen to be orthogonal to the totally symmetric stretching mode of the chain. The condition \( \Sigma J_{ij} = 0 \) in this and subsequent examples ensures that \( (\partial E_0 / \partial a)_0 \) per atom tends to zero in the limits of either large \( n \) or classical spin. Introducing the notation \( H = \{ J_{12} / J, J_{23} / J, J_{34} / J, \ldots \} \), (6.43) can be written as \( \{ 1 + a/2, 1 - a, 1 + a/2 \} \). For \( S = 1/2, J > 0 \), the ground state quintet energy is independent of \( a \) and there is no tendency to dimerisation, as in closed rings; for \( J < 0 \) the singlet energies are, in units of \(-J\), and to first order in \( a \):

\[
(6.44) E_0 = -1.5 \pm \sqrt{3(1+a/2)}
\]

and dimerisation is clearly favoured. For longer chains numerical calculations are needed. Some results for \( \partial E_0 / \partial a \) for \( S = 1/2 \) Hamiltonians of the form \( H = \{ 1 + a, 1 - 2a, 1 + 2a, \ldots, 1 + 2a, 1 - a \} \) obtained by solving for \( a = \pm 10^{-6} \) and \( a = 0 \) are:

\[
(6.45) n=2, 0.0; n=4, 0.21651; n=6, 0.24132; n=8, 0.23995; n=10, 0.23182; n=12, 0.22288; n=14, 0.21410; n=16, 0.20587;
\]

Though \( (n-2) \) orthogonal distortion Hamiltonians can be defined, that leading to alternation has the largest \( (\partial E_0 / \partial a)_0 \) and the others will not be considered. The most interesting feature of (6.45) is that \( (\partial E_0 / \partial a)_0 \) decreases only very slowly towards the limit, zero, as \( n \) increases; inspection of the last few terms given above suggests that the decay is even slower than that of \( 1/\log(n) \).

The spin variation of this phenomenon is also of interest
as in the classical limit \( (\partial E_0/\partial a)_0 = 0 \) for all \( n \). Some results for \( n=4 \), are in units of \(-J\):

\[
\begin{align*}
(6.46) \quad S=1/2, & \quad 0.21651; \quad S=1, & \quad 0.30430; \quad S=3/2, & \quad 0.37581; \\
& \quad S=2, & \quad 0.45670; \quad S=5/2, & \quad 0.54142; \quad S=3, & \quad 0.62766; \\
& \quad S=7/2, & \quad 0.71460; \quad S=4, & \quad 0.80195.
\end{align*}
\]

The high spin results can be obtained most simply by solving the 'three' atom Hamiltonian \( H=\{2+2a,1-2a,0\} \) which, since it is related to (6.43) by the addition of the 'T_2' distortion \( \{1+a/2,0,-1-a/2\} \), which leaves the \( S'=0 \) energies unchanged, has the same ground state energy. The sequence (6.46) indicates that for the four-atom chain \( (\partial E_0/\partial a)_0 \) is proportional to \( S \) for large \( S \) and thus that the limit as \( S \) tends to infinity is zero only on a \( 1/S^2 \) scale.

For \( S=1 \) the sequence corresponding to (6.45) is:

\[
(6.47) \quad N=4, \quad 0.30430; \quad N=6, \quad 0.25526; \quad N=8, \quad 0.19951; \quad N=10, \quad 0.15674
\]

Now consider odd chains; these have an even number of interactions. Consider the Hamiltonian of the form \( \{1-a,1+a,1-a,\ldots,1+a,1-a\} \); to maintain \( \Sigma J = 0 \) the chain must contain two adjacent couplings of \( 1+a \). These will be placed in the centre of the chain for \( n=4m+1 \) (\( m \) integer) and displaced by one atom from the centre for \( n=4m+3 \). For example the Hamiltonians for \( n=7 \) and \( n=9 \) are \( \{1-a,1+a,1-a,1+a,1+a,1-a\} \) and \( \{1-a,1+a,1-a,1+a,1+a,1-a,1+a,1-a\} \). The sequences equivalent to (6.45) and (6.47) are:
(6.48) \( S = 1/2 \) \( n = 3, \ 0.0; \ n = 5, \ 0.15716; \ n = 7, \ 0.15016; \ n = 9, \ 0.16553 \)
\( n = 11 \ 0.15700; \ n = 13 \ 0.15766; \ n = 15 \ 0.15059. \)

\( S = 1 \) \( n = 3, \ 0.0; \ n = 5, \ 0.21849; \ n = 7, \ 0.18070; \ n = 9, \ 0.16391. \)

(There is alternation within the sequences (6.48) as the Hamiltonian of the distorted system can have \( P_2 \) symmetry only for \( n = 4m+1, \ m \) integer). It can be seen that though there is no first order energy change associated with simple alternation, distortions in which the end pairs become more strongly antiferromagnetically coupled at the expense of the remaining interactions are energetically favoured. In this sense the ends of finite odd, as well as even, chains of finite spin can be regarded as sources of incipient dimerisation.

Though \( E_0 \) is larger for \( S = 1 \), \( (\partial E_0 / \partial a)_0 \) is smaller for all but the shortest chains and decreases much more rapidly. It can be said that quantum end effects remain important for long chains for \( S = 1/2 \) but rapidly become unimportant for \( S > 1/2. \)

In view of the comments made in section 6.2 a detailed interpretation of (6.45) to (6.48) is not given. However it does seem that real 'infinite' \( S = 1/2 \) chains which contain a finite number of atoms can be said to have an innate tendency towards alternation. In comparing chains with clusters it can be said that clusters retain a tendency to distort even for high spin because of magnetic frustration\(^{199} \) associated with their triangular faces. (A frustrated system is one in which no energetically favourable alignment of spins is possible.)
Frustration is impossible in linear systems for which first order changes associated with a distortion which preserves the sum \(\{J\}\) can arise only from quantum effects.

The above analysis is far from exhaustive; the SP transition occurs at \(T>0\) and thus the effects of distortion on excited states could also be considered. \(\left(\frac{\partial E}{\partial a}\right)_o\) tends to zero in the limit of high temperature as well as in the limits of large \(S\) and \(n\). The development of a theory explaining the existence of a well defined transition point, and hence some mechanism for transmission of alternation from the comparatively short chains throughout the lattice would require a treatment of 3-D lattice interactions.
Most of this chapter is concerned with a re-examination of high symmetry magnetic clusters from a perspective somewhat closer to solid state physics than that of the rest of the thesis. The JT idea, which applies to all clusters with suitable degeneracy in the magnetic spectrum, is introduced by a discussion of concepts such as fluxionality, tunnelling and vibronic coupling.

The dynamic distortion model as presented in chapters 3 and 4 is based on a 'molecular' view of solids. As such it is open to criticism because it makes no explicit reference to the non-magnetic intercluster interactions which are the real cause of any decrease in the symmetry of the spin Hamiltonian and hence, by their fluctuation, the rotation of the distortion vector. In 7.2 it is shown that a fuller treatment, involving features such as slowly fluctuating random strains to explain the reduction of the degeneracy associated with the Jahn-Teller active clusters, would add little to the model already derived. Suggestions for future experiments to supplement magnetic susceptibility data for these clusters are made in 7.3, and the conclusions of the thesis are summarised in 7.4.

7.1 Introduction

7.1.1 Fluxionality

The term fluxionality was coined by Doering and Roth in 1963 to describe the magnetic equivalence observed in the n.m.r
spectrum of the hydrocarbon bullvalene\textsuperscript{200}. It has been widely applied in cluster chemistry to describe the equivalence of ligands bonded to the metal core\textsuperscript{201-202} and, more recently, applied in inorganic chemistry to describe apparent changes in the stereochemistry of ligand fields with temperature\textsuperscript{203}. Slightly different definitions of fluxionality have been associated with each of these applications. Thus, Doering's implied definition\textsuperscript{204} of a fluxional system was one in which the molecular Born-Oppenheimer potential has several geometrically equivalent minima separated by low energy barriers. A fluxional cluster has been defined\textsuperscript{205} as one in which there exist low lying states through which a permutation of equivalent ligands can be effected. The application to temperature dependent stereochemistry arises since the occupation of these low-lying states depends on the temperature.

Fluxional systems are often discussed in terms of a molecule in a particular configuration either tunnelling or interconverting via excited states between the symmetry related potential minima\textsuperscript{206}. Tunnelling is favoured for particles of low effective mass, as in ammonia\textsuperscript{207}, and thin potential barriers; the first of these factors works against tunnelling in magnetic clusters, the second favours tunnelling. The rate of fluxionality is the rate at which a molecule initially prepared in a state which is localised with one minimum is transformed to a state or states localised within other minima. However, as long as $H$ is time independent, stationary state solutions exist and it is clear from the variational theorem that a molecule
which is localised near one potential minimum, for which fluxionality involves real motion, has an energy greater than that of the ground state. In this sense the concepts of fluxionality and tunnelling fit rather awkwardly into quantum chemistry as most quantum treatments of molecules focus on the eigenstates of H, states in which, by definition, there is no real motion, dynamic distortion or permutation of ligands.

Fluxionality and tunnelling only arise when the wavefunctions under discussion are the eigenfunctions of a Hamiltonian which is not the full Hamiltonian of the system. Partial Hamiltonians are used:

(a) where the Born-Oppenheimer potential has several well-defined minima and for many purposes it is only necessary to consider one of these.

(b) where interactions between the molecule and its surroundings are important.

As an example of a potential surface with several minima, consider a square molecule with 4 equivalent atoms in a non-degenerate electronic state. Such a molecule has 3-fold configurational degeneracy since atom 1 can be bonded to atoms 2 & 3, 2 & 4 or 3 & 4. These configurations can be pictured as arising from E mode distortion of a parent, higher energy configuration of full tetrahedral symmetry. The three square configurations correlate with the ground state and two lowest vibrations of the parent molecule. The molecule is only square
to the extent that tunnelling matrix elements between the three configurations can be ignored. The lowest three eigenfunctions of the full Hamiltonian for the system transform as $A_1+E$ in $P_4$ and the degenerate $E$ state lies lowest. In each eigenstate of the full Hamiltonian the expectation value of the configuration is $T_d$. In this extreme sense any molecule with $n$ equivalent atoms and less than $P_n$ symmetry if only proper rotations are included can be described as fluxional. Such a molecule has an inversion mode if the inclusion of improper rotations enlarges the symmetry group.

It is clear that to be useful, the word fluxionality must always be qualified by the reference to the time scale on which the configuration, or distortion from the parent high symmetry system, is to be measured. For example, in the application to magnetic clusters the time scale is that on which the magnetic spectrum attains thermal equilibrium.

Interactions between a molecule and its surroundings may be important when external fields are applied, perhaps in the course of some measurement. More important in the present discussion, they are an essential feature of any treatment of the molecules in the solid state. The treatment of such interactions provides a meeting ground between solid state physics, which typically treats atomic lattices before considering the 'molecular problem'\textsuperscript{208}, and coordination chemistry.
The distinction between partial Hamiltonians (a) and (b) is an important one. Variation in the molecular eigenvalues can occur only in case (b). In terms of fluxionality, it is likely that intermolecular interactions will have a dominant effect on any fluxionality in solid state compounds such as inorganic compounds with temperature dependent stereochemistry. In both cases (a) and (b) reference to 'fluxional molecules' is somewhat misleading, for (a) because eigenstates with no real motion exist and for (b) because such fluxionality is not an intrinsic property of the molecule.

7.1.2 Vibronic coupling

The eigenstates of a Hamiltonian which involves only electronic coordinates and momenta lie in a space which can be labelled $H_e$; similarly the eigenstates of a nuclear Hamiltonian lie in $H_n$. The eigenstates of a Hamiltonian which involves interactions between electrons and nuclei lie in the direct product space, $H_e \ast H_n$, which contains all sums of products of functions in $H_e$ with functions in $H_n$. A vibronic state is an eigenfunction of the Hamiltonian which cannot be adequately expressed as a single product of an electronic and a nuclear wavefunction.$^{209}$

Born and Oppenheimer$^{210}$ showed that the error involved in representing the eigenfunction corresponding to a non-degenerate eigenvalue by a single product state is negligible. The BO approximation is useful because the electron mass is very much less than that of the nuclei; the nuclear momenta therefore have
a negligible effect on the electronic parts of the wavefunction and the nuclei only respond to the average field due to the electrons. In the BO approximation the Hamiltonian without nuclear momenta is solved to yield eigenstates in which the nuclear positions appear as parameters. The electronic energies for each nuclear configuration can then be considered to define a nuclear potential which can be solved to yield the vibrational states of the system.

The BO approximation breaks down for degenerate electronic states as JT type terms which do not commute with the rest of the Hamiltonian are introduced, in this situation small changes in nuclear configuration cause large changes in the electronic parts of the eigenfunctions. In Jahn-Teller theory this difficulty is overcome by the introduction of vibronic states which are linear combination of several product states, obtained by solution of an appropriate eigenvalue problem. JT theory can therefore be regarded as providing a correction to the BO approximation for degenerate states.

7.2 Symmetry, Degeneracy and the Jahn-Teller Effect

7.2.1 The properties of Jahn-Teller systems

The most frequently studied JT systems are those in which a transition metal ion in a degenerate orbital state, either E or T, is JT-active with respect to a normal mode of its ligand field, e.g. an E or T mode of an octahedral or tetrahedral complex. Significant extension of the original JT theorem
is necessary to provide a description of all static and dynamic aspects of the coupling between the electronic and nuclear wavefunctions which occurs in such complexes.

Phenomena associated with ground state electronic degeneracy have been described in terms of static\textsuperscript{214}, dynamic\textsuperscript{215}, cooperative\textsuperscript{216}, dynamic cooperative\textsuperscript{217}, weak or strong\textsuperscript{218} and local\textsuperscript{219} effects. In the context of the present work it is most useful to distinguish between dilute JT systems, in which interactions between JT centres are negligible, and concentrated JT systems, in which interactions between JT-active centres are important and may lead to a cooperative phase transition. The similarity to the terminology of magnetism is deliberate and JT effects in general can be usefully discussed in a spin Hamiltonian formalism\textsuperscript{220}.

In a system containing just one JT-active centre and no external field, no 'distortion' and no removal of essential degeneracy can take place. JT effects can, however, still be observed in the form of a quenching of orbital angular momentum, the Ham effect,\textsuperscript{221,222} and increased absorption for forbidden infra-red transitions\textsuperscript{223}. No distortion can occur because all eigenstates must transform according to I.Rs of the original point group. This situation is analogous to that in intramolecular fluxionality as in ammonia, in which both of the ground state eigenfunctions transform according to I.Rs of the planar point group. (Vibronic coupling does not occur in this case as the 'distortion' part commutes with the rest of the
Hamiltonian.) No reduction in the essential degeneracies occurs because the electronic degeneracies are replaced by vibronic degeneracies, as will be discussed below. Essential degeneracy in this context refers to that which arises when several states are symmetry related and span the same I.R. Thus a molecule with an E electronic state and with one vibrational quantum in an E normal mode has 4-fold degeneracy, E*E, but 1+2+1 (A_1+E+A_2 in O_h) essential degeneracy. The 4-fold degeneracy is an accidental result of applying the harmonic approximation.

The degeneracy and symmetry of dilute JT systems can only be reduced by external fields. As a result of the shape of the JT potential surface, a small stress may be associated with a large strain, i.e. the system is very sensitive to such fields. If a system contains more than one JT-active centre, the centres may provide external fields for each other, and a permanent static distortion may occur. There is even the possibility of 'condensed' JT systems along the lines of magnetic clusters. In the limit as the number of interacting centres becomes infinite a cooperative phase transition, characterised by discontinuities in the first or second derivatives of the free energy with respect to an order parameter, and driven by the JT effect, may occur. Such phase transitions can be characterised, by analogy to magnetic phase transitions, as (anti)ferrodistortive. As static JT distortion is a result of interactions between the metal atoms and the lattice it is often difficult to separate JT effects from crystal packing effects not related to the electronic
Coupling between an E electronic state and an E mode is conventionally denoted \( E^*\epsilon \), that between a T state and an E mode is denoted \( T^*\epsilon \), and that between a T state and a T mode, \( T^*\tau \). The matrices which define the BO surface for these systems are independent of the particular states and modes involved and are:

\[
(7.1) \quad E^*\epsilon, \quad H(x) = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad H(y) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},
\]

\[
T^*\epsilon \quad H(x) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}, \quad H(y) = \begin{bmatrix} \sqrt{3} & 0 & 0 \\ 0 & -\sqrt{3} & 0 \\ 0 & 0 & 0 \end{bmatrix},
\]

\[
T^*\tau; \quad H(x) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0.1 & 0 \end{bmatrix}, \quad H(y) = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad H(z) = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},
\]

The \( E^*\epsilon \) system has been studied in most detail, and is relevant to octahedral copper(II). The eigenfunctions of the JT contribution to the potential surface:

\[
(7.2) \quad \begin{bmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{bmatrix}, \quad \psi_+ = (\cos\theta/2, \sin\theta/2), \quad \psi_- = (\sin\theta/2, -\cos\theta/2)
\]

have eigenvalues, \( \pm 1 \) which are independent of \( \theta \). The full electronic potential has cylindrical symmetry and is known as the 'Mexican hat'\(^{227}\). It can be shown that the solutions to
the total Hamiltonian can be adequately represented by vibronic states consisting of just two BO product states:

(7.3) \[ \Psi = \psi_+ \phi_+ + \psi_- \phi_- \]

where \( \phi_+ \) and \( \phi_- \) are non-orthogonal nuclear functions and \( \psi_+ \) and \( \psi_- \) are now electronic momentum states of the form \( \exp(\pm ip\theta/2) \). The electronic parts of \( \Psi \) have the unusual characteristic that they change sign as \( \theta \) changes by \( 2\pi \); since the total function must be single valued the nuclear parts must undergo the same change in sign. The change in sign is characteristic of systems with half-integral spin associated with a nuclear angular momentum quantum number \( j \). For each solution with \( m_j > 0 \) there is one with \( m_j < 0 \) and thus all vibronic states are doublets and no essential degeneracy is removed. In other words, the apparent splitting in (7.2) is removed when nuclear effects are included. Anharmonic effects destroy the cylindrical symmetry of the Mexican hat but the three fold axis remains. In this case the system can be pictured as tunneling between three potential minima, leading in the limit to a three fold degeneracy associated with a static distortion.

Because of the rather peculiar boundary conditions associated with the change of sign as \( \theta \) changes by \( 2\pi \), the ground state is a doublet, \( E \), even when anharmonic effects are included. There is an interesting correspondence with the configurational degeneracy of the square molecule discussed in 7.1.1.

\( T^e \) coupling is rather less interesting as, in the absence of spin/spin coupling, the eigenstates of \( H(JT) \) commute with
the rest of the Hamiltonian. Each is therefore associated with a
different 2-D harmonic oscillator potential and the three fold
degeneracy is not removed.

T*r coupling is the most complex form. The potential has T_d
symmetry. Relatively complete numerical calculations for the
eigenvalues have been performed^{228-229}. If there is no JT
interaction the three-D harmonic oscillator potential has
spherical symmetry and the ground and lowest excited states have
angular momentum J=0 and J=1 with degeneracy 2J+1 multiplied by
the electronic degeneracy, three. For large JT interaction the
potential is divided into four separate 2-D wells. The lowest
vibrational functions in each have a number of vibrational
quanta, n=0 and n=1 with degeneracy n+1 multiplied by the
configurational degeneracy, four. The three-fold ground state
degeneracy is retained for all values of k.

7.2.2 Application to magnetic clusters

For high symmetry metal clusters the matrices (7.1) apply
as long as each R(S') (see 3.1.1) contains each I.R. at most
once. This is the case for small S=1/2 systems, including the
octahedron. In general R(S') contains at least some I.R.s more
than once and more complicated forms of coupling such as (E+E)*ε
and (T+T)*τ are introduced. This would correspond, in the theory
of JT paramagnets to a situation in which there are several
low-lying states, each with electronic degeneracy.

The relationship between the above approach, which involves
the magnetic group of the undistorted cluster, and the approach used in Chapters 3 and 4 will now be explored by taking the specific example of Cu$_4$OX$_6$L$_6$. Consider first the S' = 0 states which transform as E in P$_4$. Though their degeneracy is not removed by the JT effect as discussed above the levels may become shifted in energy. Decrease in energy of the singlets affects the magnetism by increasing the partition function. The same effect is obtained in the dynamic distortion model by a singlet splitting.

As the S' = 1 and S' = 0 states of the Cu$_4$OX$_6$L$_6$ cluster are essentially distinct JT systems it is likely that the JT shift in their energies will be different. Such a difference would result in a breakdown of the Landé interval rule which applies to the mean energy for each spin. It is interesting to note that a treatment of the data for Cu$_4$OCl$_6$(TPPO)$_4$ using a Hamiltonian with the degeneracy maintained and without the Landé rule$^{105}$ gives a reasonable fit to a spectrum with both singlets 10cm$^{-1}$ above the ground state and the triplets at 85cm$^{-1}$. This approach breaks down at low temperature and is not consistent with e.s.r. data$^{107}$ which puts the singlets at 14cm$^{-1}$.

Strictly speaking, the Hamiltonian for an isolated Cu$_4$O cluster is a single well-defined operator which has P$_4$ symmetry associated with identical coppers and eigenvalues with the corresponding degeneracy which, by definition, are time independent. Thus concepts such as rotation of the S' = 1 triangle introduced in 4.1 cannot apply. The distortion Hamiltonians H$_e$
and $H_{e}$ cannot arise from internal effects; they must arise from those non-magnetic interactions between clusters which are an essential feature of the solid state. Thus $H_{e}$ and $H_{t}$ are better interpreted as resolved components of phonon modes than as internal vibrations of the cluster.

The basic picture on the JT approach is that of a cluster which is undistorted (and has degeneracy) above a transition temperature, $T'$. Below $T'$ a static distortion to lower symmetry occurs. A transition temperature must always exist in (undiluted) ground state JT systems. Systems such as $\text{Cu}_4\text{OX}_6\text{L}_4$ for which $J > 0$ exhibit excited state JT activity and the situation may be much more complicated. Studies of $\text{TmPO}_4$, in which the JT activity is in a doublet at $\approx 44K$ have resulted in the development of concepts such as "dynamic random JT effects"\textsuperscript{230} in which "slowly fluctuating random strains"\textsuperscript{231} considerably modify the behavior above $T'$ removing sharp discontinuities in the temperature dependence of, for example the e.s.r. spectrum. As another example, Mossbauer\textsuperscript{232} studies on FeCr$_2$O$_4$ show that the quadrupole splittings, which arise from distortion in this cubic crystal, are observed even above $T'$, and decrease only slowly to zero at high temperature. Even in classic, ground state JT phase transitions there may be significant short range order above $T'$. It may be that the magnetic spectra of $\text{Cu}_4\text{O}$ clusters behave in a similar way as no discontinuities in $\mu(T)$ have ever been observed. Any slow removal of distortion at high temperature would be difficult to observe as $\mu$ might be close to its limiting value $\sqrt{3}(g/2)$ before
significant changes occur.

The theory of slowly fluctuating random strain goes far beyond magnetochemistry, and the same kinds of problems as are encountered in a thorough treatment of spin-Peierls transitions, e.g. the continuum of phonon modes and partial ordering, are involved. However it can be seen that the introduction of this idea resolves the apparent contradiction between the JT activity of Cu₄O and the removal of degeneracy in high symmetry clusters at all temperatures, which is the basis for the dynamic distortion model.

This treatment also suggests an alternative explanation of temperature dependent fluxionality. \( \epsilon \), formerly an activation parameter, can be interpreted as a phase transition temperature below which a static ordering, which might be observable by X-ray, occurs. On a very simple molecular field type treatment the ordering parameter and hence the 'proportion of distorted triplet' (see 5.2.2) is given by:

\[
(7.4) \quad p = \left\{ 1 - \frac{T}{\epsilon} \right\}^{1/2}
\]

Series expansion of \( T<<\epsilon \) gives a \( T \) in the numerator just as expansion of the ad hoc expression \( \exp(-T/\epsilon) \) introduced in chapter 4. Fitting the data using (7.4) gives slightly poorer but qualitatively good fits. Since perfect agreement could hardly be expected on such a simple model it can be said that the phase transition may in some cases provide an alternative interpretation of TDF.
In conclusion, treatment of 3-D interactions throughout the lattice would be necessary to provide an entirely satisfactory theoretical interpretation of the unusual behavior of \( \text{Cu}_n \text{OX}_6 \text{L}_a \) and similar clusters. For magnetochemists such a treatment would add little to the dynamic distortion model developed in chapters 3 and 4. In some respects, such as the temperature independence of (most of) the magnetic spectra and the absence of explicit parameters describing strain effects in detail, the dynamic distortion model is actually more useful, even though it might offend a Jahn-Teller 'purist' as it makes no explicit reference to intercluster interactions.

7.3 Suggestions for further experiments

It has become increasingly clear in the course of this thesis that magnetic susceptibility data, even when supplemented by room temperature X-ray studies, cannot lead to an unambiguous interpretation of magnetic interactions in high symmetry clusters of magnetic ions. Mossbauer and e.s.r. studies may provide additional information on the ground state and perhaps on fluxionality but even where these techniques are possible further experiments may be necessary.

As intercluster magnetic exchange can be ruled out in most cases, the biggest single problem in applying the dynamic distortion model is in the determination of the relative importance of static distortions which may arise from non-magnetic effects and genuine dynamic distortions throughout the temperature range. To this end more low temperature X-ray
studies, particularly below $\epsilon$ of TDF clusters would be useful.

Specific heat measurements could test for the presence of a phase transition, as in Cr$_3$O, and the magnitude of any $\Delta H$ observed would indicate whether or not the transition could be magnetically induced. The specific heat is typically much more sensitive than the susceptibility to phase transitions, see, for example, Figs. 6.1 to 6.6 for the Odd/Even approximation. Clusters which have very high symmetry at room temperature would be particularly interesting for specific heat and low temperature X-ray studies as if they are indeed JT-active some symmetry lowering transition must occur above $T=0$.

Specific heat measurements can also, in principle give information on the spins and energies of low-lying states in the magnetic spectrum. Thus for Cu$_4$O, the triplet above a doublet of the antisymmetric exchange model, the blurred quintet of the intercluster model and the quintet above a singlet of the dynamic distortion model should be distinguishable. Fluxionality of the low lying triplet might complicate such an experiment.

Perhaps the most useful experiments would be those in which the magnetic spectrum was measured directly. To date two such experiments are available. Optical spectroscopy$^{233-234}$ has the advantage of comparative simplicity but the transitions which give information about the magnetic properties are not always well resolved. Inelastic neutron scattering$^{235}$ (INS) from clusters, a technique which has been pioneered by Gudel and co-workers, would seem more promising for, say, the Cu$_4$Ox$_6$L$_4$ and
Fe₃O(RCOO)₆⁺ systems. INS has already been applied to some Cu₄O₄ cubane type clusters and found to give results consistent with purely isotropic exchange²³⁶. As a relatively short timescale experiment, INS might give new information about triplet fluxionality in the Cu₄OX₆L₄ systems.

As interactions between clusters are essential to the dynamic distortion model, dilution experiments, in which the clusters are doped in a non-magnetic, non-JT-active host lattice, perhaps of similar clusters such as Mg₄OBr₆²³⁷, would be of interest. Dilution experiments are carried out routinely in paramagnetic JT systems²³⁸-²³⁹. Cu₄OX₆L₄ clusters have already been doped into the pores of a cross linked polystyrene¹⁰⁵; the effective moment for Cu₄OCl₆(TPPO)₆ was found to decrease monotonically with temperature and the 'hump' found as in the pure compound was absent. This indicates either a larger, perhaps static, distortion, possibly associated with the packing of the cluster in the very dissimilar host or, less likely, a reversal in the sign of J.

7.4 Conclusion

(1) High symmetry clusters with exchange pathways which are highly sensitive to small changes in cluster configuration exhibit dynamic distortion effects which may modify, as in Cr₃O(CH₃COO)₆Cl.6H₂O, or dominate, as in Cu₄OX₆L₄, any static distortions associated with non-magnetic effects. Such clusters exhibit either ground or excited state Jahn-Teller activity and the dynamic distortion may be 'frozen out' at low temperature to
yield a symmetry-reduced (anti)ferrodistorted structure.

(2) Group theory and factorisation can be combined to produce a powerful technique for solving the spin Hamiltonians of isotropically coupled clusters which exhibit either static or dynamic distortions from high symmetry.

(3) Application of the dynamic distortion theory considerably reduces the number of known clusters for which Heisenberg intracluster exchange fails to provide an adequate explanation. The few anomalous clusters remaining, such as $\text{Ni}_4(\text{OCH}_3)_4(\text{acac})_4(\text{CH}_3\text{OH})_4$ exhibit ferromagnetic intercluster exchange and magnetic ordering at low temperature.

(4) The situation in infinite linear systems is complicated by (i) the lack of Jahn-Teller activity, (ii) the difficulties inherent in the mathematics of infinite systems. These difficulties are not circumvented by approximations such as the Odd/Even approximation and even numerical extrapolation from finite chains is unreliable for $S>1/2$. The application of dynamic distortion formalism to linear chains leads to a new approach to exchange striction and a suggestion that end effects may be a significant factor in alternation phenomena such as the spin-Peierls transition.
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