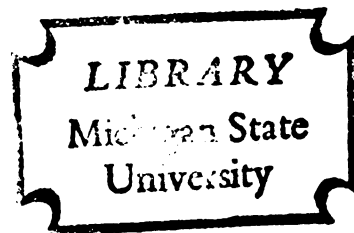A STUDY OF THE EFFECT OF CRYSTAL-FIELD
ANISOTROPY ON MAGNETICALLY ORDERED
SYSTEMS

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
JOHN F. DEVLIN
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This is to certify that the

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ABSTRACT

A STUDY OF THE EFFECT OF CRYSTAL-FIELD ANISOTROPY
ON MAGNETICALLY ORDERED SYSTEMS

By

John F. Devlin

A study has been made of the effect of crystal-
field anisotropy on magnetically ordered systems by using
the Green function techniques. The anisotropy was repre-
sented by a term $D(S^z)^2$ added to the usual Heisenberg
Hamiltonian.

For a spin S system we have found a convenient
set of operators, 2S in number, which are appropriate
for completely solving, within the Green function form-
alism, a system of non-interacting spins in a crystal-
line field environment. The inclusion of exchange coupling
between the spins introduced higher order Green func-
tions. These higher order Green functions were found to
be only higher order exchange Green functions, and not
higher order anisotropy Green functions. Therefore
there was no need to approximate any of the anisotropy
functions. We have found an approximation scheme which
reduces the higher order Green functions to lower order

ones, thereby decoupling the set of equations. This scheme is a generalization of the random phase approximation (RPA). For D=0, our set of equations reduces to the set obtained by Tahir-Kheli and ter Haar when they used the random phase approximation. Our technique is valid for any size spin system, and also for antiferromagnetic as well as ferromagnetic systems.

We have numerically solved the necessary set of equations for the spin S=1, ferromagnetic and antiferromagnetic systems with simple cubic and body centered lattices, and for the spin S=3/2 ferromagnetic system with a simple cubic lattice. The decoupling approximation we have presented here is superior to those that were used in the earlier work on this subject. The transition temperature $T_c(D)$ as a function of the crystal-field parameter D is finite for all values of D. Our particular decoupling approximation shows that $T_c(D)$ depends more strongly on D, for low anisotropy, than does the molecular field theory (MFT). For anisotropies of the order of the exchange, J, or smaller, our results are equivalent to those of Lines. At the transition temperature the ensemble averages of the different powers of S^z as predicted by our RPA calculation and as predicted by the MFT are the same. The temperature dependence of these ensemble averages, below T_c, shows a greater variation with changes in D/J than does the MFT prediction. For very large anisotropies our results

approach those of the MFT, and at $D/J = \infty$ both theories agree **exactly**. This is to be contrasted with the earlier single excitation schemes which predict $T_c = \infty$ at $D/J = \infty$.

A STUDY OF THE EFFECT OF CRYSTAL-FIELD ANISOTROPY

ON MAGNETICALLY ORDERED SYSTEMS

By

John F. Devlin

A THESIS

Submitted to
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DEDICATION

To my wife, Patricia, who spent four long years in a town she cared little about, listening to a subject she knew nothing about, waiting for me to get a decent job, I dedicate this thesis.

ACKNOWLEDGMENTS

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1. INTRODUCTION

A magnetically ordered system may be defined as a
system in which the ensemble averages of the magnetic
moment operators, $\underset{\sim}{\mu}_i$, or equivalently the spin operators,
$\underset{\sim}{S}_i$, associated with the lattice sites labeled by the index
i, are non-zero, even when there is no external magnetic
field. Since the ensemble average is obtained by taking
the trace of the product of $\underset{\sim}{S}_i$ and the density operator,
exp $(-H/\kappa T)$, one first needs to know the Hamiltonian, H,
of this system before attempting to calculate any of these
statistical mechanical quantities. However, for such a
system the true Hamiltonian is much too complicated to
ever be of any direct use. One generally resorts to using
a Hamiltonian which is appropriate only for the spins of
the system, and not for the whole crystal, and all its
constituents. The spin Hamiltonian, as it is called,
is rarely, if ever, derived from first principles; rather
it is a construct of reasonable and convenient forms of
quantum mechanical spin operators. The assumption most
frequently made is that the spin Hamiltonian depends only
linearly or bilinearly on the spin operators. In fact,
for systems in which there is no external magnetic field
one invokes time reversal invariance of the Hamiltonian

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to say that products of an odd number of spin operators cannot appear at all, since the $\underset{\sim}{S_i}$ change sign under time reversal, whereas H cannot.

The allowed forms of the spin operators are generally of two distinct types: single ion terms and exchange terms. The single ion spin Hamiltonian is of the form,

$$H_{SI} = -g\mu_\beta \sum_i \sum_\alpha H_o^\alpha S_i^\alpha + \sum_i \sum_{\alpha,\beta} A_i^{\alpha\beta} S_i^\alpha S_i^\beta, \qquad (1.1)$$

where the index i is for the lattice sites, and α and β represent the components of the spin operator vector. The coefficients g and μ_β are the gyromagnetic ratio and the Bohr magneton respectively. The first term is the Zeeman term, and it is just the interaction of the spins with the external magnetic field, $\underset{\sim}{H_o}$. The second term represents the splitting of the low lying energy levels of the system due to the presence of a crystalline electric field around each ion[1]. This term has the information of the symmetry about each ion included in the parameters $A_i^{\alpha\beta}$.

The interaction between the spins may be written as,

$$H_I = -\sum_i \sum_j \sum_\alpha \sum_\beta J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta. \qquad (1.2)$$

The coupling coefficient $J_{ij}^{\alpha\beta}$ is commonly refered to as the exchange energy or exchange integral. A special case of the Hamiltonian is the much used Heisenberg-Dirac Hamiltonian,

$$H_{HD} = -\sum_i \sum_j J_{ij} \underset{\sim}{S_i} \cdot \underset{\sim}{S_j}, \qquad (1.3)$$

where we now assume $J_{ij}=J_{ji}$ and $J_{ii}=0$. This is a completely isotropic Hamiltonian, i.e. the αth component of the total spin vector commutes with H_{HD} for all α, whereas it does not necessarily do so for the Hamiltonian H_I. As such, H_{HD} presents a problem in trying to describe a magnetically ordered system. By the symmetry of H_{HD}, $<S_i^\alpha>=$ Trace $(S_i^\alpha \exp(-H/\kappa T))$ should be the same for all α. But this can only be if $<S_i^\alpha>=0$ for all α. Hence in attempting to describe any magnetically ordered system with the Hamiltonian H_{HD} one must include terms which are anisotropic, i.e. terms which produce a preferred direction in space along which the spins may align. Two simple alternatives are possible at this point: we may include terms of the form, $J_{ij}^\alpha S_i^\alpha S_j^\alpha$ in which J_{ij}^α is different for different α, or else we may include terms like $D_i^\alpha (S_i^\alpha)^2$ where the D_i^α are different for different α. The first possibility is merely a more complicated form of exchange and has a weaker theoretical basis than even H_{HD} itself. The second possibility is more reasonable since, as we have already mentioned, it may be present when the effects of crystalline field are taken into account.

In this thesis we will be concerned only with a spin Hamiltonian that has cylindrical symmetry. The preferred direction will be the z axis. Then the appropriate Hamiltonian for our problem, within the limits we have already set, is as follows:

$$H = -\sum_i \sum_j J_{ij}\underset{\sim}{S}_i \cdot \underset{\sim}{S}_j - \sum_i D(S_i^z)^2, \tag{1.4}$$

where we have set the external magnetic field to zero
since it will not be needed for any of our calculations.
We have also assumed that the crystal field parameter D is
the same at each lattice site.

The physical effect of the crystal field anisotropy
term is clear: spin states with large absolute values of
the quantum number, m_s, corresponding to the eigenvalue of
the z component of the spin operator, will have the lower
energies (assuming $D \geq 0$) and hence they will be more highly
populated than spin states with small $|m_s|$ values. This is
completely equivalent to saying that the z direction is
preferred over the x and y directions. Note that the
Hamiltonian we have chosen makes no statements about pre-
ferences between the x and y directions, hence $<S_i^x> = <S_i^y> = 0$.
Furthermore, the ensemble average of any function of S_i^x must
be the same if S_i^x is replaced by S_i^y.

Once the spin Hamiltonian has been established for a
given system, the next problem is to determine the transi-
tion temperature, i.e. the temperature above which the system
is no longer ordered when the external field is set to zero.
In order to do this exactly for a many-body system, either
one has to be able to write the Hamiltonian as a sum of
one-particle Hamiltonians or else one has to diagonalize
the Hamiltonian completely. Because of the presence of the
exchange term in (1.4) it is not possible to write it as a
sum of one-particle Hamiltonians. The second alternative
is then to try to diagonalize H exactly. No one has ever

done this except for some trivial one-dimensional lattices, and some N-particle lattices where N is a very small integer. Therefore one must rely on some sort of approximation scheme for obtaining a reasonable estimate of transition temperature. We shall discuss five previous attempts at obtaining this temperature from (1.4) before we present our own method. Each of these theories is derivable by appropriate "decoupling approximations" from the Green function technique, which will be discussed in a later chapter.

2. THE MOLECULAR FIELD THEORY

The molecular field theory (MFT) is by far the simplest of all the effective field theories to apply. It is clear from (1.4) that the Hamiltonian for a single spin $\underset{\sim}{S}_i$ is of the form,

$$H_i = \{-2 \sum_j J_{ij} \cdot \underset{\sim}{S}_j\} \cdot \underset{\sim}{S}_i - D(S_i^z)^2. \qquad (2.1)$$

The factor of 2 appears because we are no longer double counting over all lattice points as we did in (1.4). H_i would be a one-particle Hamiltonian if the quantity in braces were a real number rather than a quantum mechanical operator. This leads us to try and replace it by its ensemble average,

$$\sum_j J_{ij} \underset{\sim}{S}_j \rightarrow \sum_j J_{ij} \langle S_j^z \rangle. \qquad (2.2)$$

This replacement is equivalent to saying that each spin interacts with an effective magnetic field,

$$H^{eff} = 2 \sum_j J_{ij} \langle S_j^z \rangle / g\mu_\beta, \qquad (2.3)$$

instead of with the individual spin operators $\underset{\sim}{S}_j$. Since $\langle S_i^z \rangle$ is independent of the lattice site index i for a ferromagnetic lattice, we denote $\bar{S} = \langle S_i^z \rangle$. We also make the definition $J(0) = \sum_j J_{ij}$. Then the new Hamiltonian is,

$$H_i = -2\bar{S} \, J(0) S_i^z - D(S_i^z)^2. \qquad (2.4)$$

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The eigenvalues of this Hamiltonian are,

$$E_m = -2\bar{S} J(0) m - Dm^2, \qquad (2.5)$$

where the allowed values of the azimuthal quantum number m are,

$$m = S, S-1, \ldots, -S+1, -S. \qquad (2.6)$$

Then the ensemble average of S_i^z becomes,

$$\langle S_i^z \rangle = \bar{S} = \{\sum_m m \exp[(2\bar{S}J(0)m + Dm^2)/\kappa T]\}/$$
$$\{\sum_m \exp[(2\bar{S}J(0)m + Dm^2)/\kappa T]\}. \qquad (2.7)$$

For any arbitrary power of S_i^z, we have,

$$\langle (S_i^z)^n \rangle = \{\sum_m m^n \exp[(2\bar{S}J(0)m + Dm^2)/\kappa T]\}/$$
$$\{\sum_m \exp[(2\bar{S}J(0)m + Dm^2)/\kappa T]\}. \qquad (2.8)$$

At the transition temperature $\bar{S}=0$, since this is the temperature at which the magnetic ordering vanishes. By expanding the exponentials in the limit $\bar{S} \rightarrow 0$, one may obtain the following expression for the transition temperature according to the MFT,

$$\kappa T_c = 2J(0) [\sum_m m^2 \exp(Dm^2/\kappa T_c)]/[\sum_m \exp(Dm^2/\kappa T_c)]. \qquad (2.9)$$

where we have defined T_c to be the transition temperature, or, more commonly, the Curie temperature. This expression can also be written as,

$$\kappa T_c = 2J(0) \langle (S_i^z)^2 \rangle |_{T=T_c} \qquad (2.10)$$

Two special cases of (2.9) are as follows,

for D=0, $\quad T_c = 2S(S+1)J(0)/3$, $\hspace{2cm}$ (2.11)

for D=∞, $\quad T_c = 2S^2 J(0)$. $\hspace{2.5cm}$ (2.12)

Graphs of $T_c(D)/T_c(0)$ versus D/J are plotted in Figures 1, 2, and 7 in Chapter 7. $T_c(D)$ is the Curie temperature for finite D and $T_c(0)$ is for D=0. The exchange integral in this case is between nearest neighbors only. The variable J(0) which appears in all the equations then reduces to J(0)=zJ, where z is the number of nearest neighbors. (z=6 for a simple cubic lattice, and z=8 for a body centered cubic lattice.)

In chapter 5, we shall again present the MFT, but this time as a decoupling approximation within the Green function formalism.

3. THE GREEN FUNCTION TECHNIQUE

The method of double-time temperature-dependent Green functions was first applied to the problem of ferromagnetism by Bogolyubov and Tyablikov[2],[3]. Since that time a large number of problems in ferromagnetism, antiferromagnetism, and ferrimagnetism have been solved by this technique[4]-[9]. We will present here only a very brief outline of the method. (See Zubarev[10] for complete details and example problems.)

The retarded double-time temperature-dependent Green function is defined as,

$$<<A(t);B(t')>> = -i\theta(t-t')<[A(t),B(t')]>, \qquad (3.1)$$

where $\theta(t-t')$ is the unit step function, singly pointed brackets denoting the ensemble average as usual, and doubly pointed brackets denoting the Green function. The equation of motion of this Green function is,

$$i\frac{d}{dt}<<A(t);B(t')>> = \delta(t-t')<[A(t),B(t)]>$$

$$\qquad (3.2)$$

$$+<<[A(t),H];B(t')>>.$$

Fourier transforming over the time variable t into the energy variable E ($\hbar=1$) gives,

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$$E<<A;B>>_E = \frac{1}{2\pi} <[A,B]> + <<[A,H];B>>_E, \qquad (3.3)$$

where the E subscript on the double brackets denotes the Fourier transformed Green function. Once equation (3.3) has been solved for $<<A,B>>_E$, the double-time correlation function $<B(t')A(t)>$ can be written down quickly with the aid of the Spectral Theorem [10]:

$$<B(t')A(t)> = i \lim_{\varepsilon \to 0} \int_{-\infty}^{+\infty} \frac{<<A,B>>_{E=\omega+i\varepsilon} - <<A,B>>_{E=\omega-i\varepsilon}}{\exp(\omega/\kappa T)-1}$$

$$X \quad \exp(-i\omega(t-t')) \, d\omega. \qquad (3.4)$$

There are two main difficulties to be overcome for every statistical problem to be solved by the Green function method: (1) The operators A and B have to be chosen very carefully, as not all choices are convenient and useful. (2) Once A and B are chosen, one needs to solve the equation (3.3) for $<<A,B>>_E$. This last step is a non-trivial task since the Green function $<<[A,H];B>>$ is also an unknown. If the equation for $<<[A,H];B>>$ is written down one finds that it, in turn, depends on the Green function $<<[[A,H],H];B>>$ which is also an unknown. Hence there is really a whole hierarchy of Green function equations implied by (3.3). For any given system with a many-body Hamiltonian it is impossible to solve the complete hierarchy of equations exactly. Approximate solutions to (3.3) may be obtained only by decoupling the chain of equations so as to reduce it to a much smaller number of equations. In general these decoupling approximations all assume the form of

writing a selected higher order Green function as a linear combination of lower order Green functions. Then all the Green functions which are of higher order than the one selected are ignored completely. The problem of decoupling is thus reduced to deciding at which point the hierarchy is to be truncated, and to decide just what the coefficients in the linear expansion should be.

Since the chosen higher order Green function is written as a <u>linear</u> combination of the lower order ones, this finite set of equations will be a set of linear equations. The solutions for any one Green function in the set of N equations will then be of the form of a polynomial of degree N-1 in the variable E, divided by a polynomial of degree N in E. A partial fraction expansion will then yield a Green function which has, at most, N simple poles in the complex E plane. For a real physical problem these poles will always lie on the real axis. The limit-taking process inside the integrand of (3.4) is easily performed using the identity,

$$\lim_{\varepsilon \to 0} \{\frac{1}{E-E_o+i\varepsilon} - \frac{1}{E-E_o-i\varepsilon}\} = -2\pi i \delta (E-E_o). \qquad (3.5)$$

The following corollary to the Spectral Theorem will be of use in later calculations: when the Green function $<<A,B>>_E$ has the form,

$$<<A,B>>_E = \frac{1}{2\pi} \sum_i \frac{A_i}{E-E_i} \qquad (3.6)$$

where the E_i are the poles, and the A_i their residues, the equal-time correlation function of B and A has the form,

$$\langle BA \rangle = \langle B(t)A(t) \rangle = \sum_i \frac{A_i}{\exp(E_i/\kappa T)-1}. \tag{3.7}$$

4. THE SINGLE EXCITATION THEORIES

All of the early attempts at solving the ferromagnetic system described by the Hamiltonian (1.4) were single excitation theories, i.e. their first order Green functions were approximated by a single simple pole on the real axis. This is the most elementary of all approximation schemes. The choices for the operators were: $A=S_g^+$ and $B=B_h$, where g and h denote lattice sites (not necessarily the same) and B_h is some function of S_h^- and S_h^z. The complete equation of motion of the Green function is obtained by working out the commutator of S_g^+ and H, and then inserting this into (3.3). The result is,

$$E<<S_g^+;B_h>> = F\delta_{g,h}/2\pi + 2\sum_i J_{ig}<<(S_g^+S_i^z-S_g^zS_i^+);B_h>>$$

$$+ D<<(S_g^+S_g^z-S_g^zS_g^+);B_h>>, \qquad (4.1)$$

where $F\doteq<[S_g^+,B_g]>$, and $\delta_{g,h}$ is the Kronecker delta function. For convenience we have also dropped the subscript E on the Green function. Note that both of the Green functions on the right hand side of (4.1) are of higher order.

Two very effective decouplings of the exchange term Green function have been made, one by Tyablikov[3], the other by Callen[5]. The Tyablikov decoupling is more

commonly referred to as the random phase approximation (RPA). These decouplings are as follows:

Tyablikov Decoupling (RPA):

$$<<S_i^+ S_g^z ; B_h>> = <S_g^z> <<S_i^+ ; B_h>> \text{ for } i \neq g, \qquad (4.2)$$

Callen Decoupling:

$$<<S_i^+ S_g^z ; B_h>> = <S_g^z> <<S_i^+ ; B_h>> -$$

$$\frac{1}{2S^2} <S_i^z> <S_g^+ S_i^-> <<S_g^+ ; B_h>> \text{ for } i \neq g. \qquad (4.3)$$

The reason that these are valid approximations is that for ordered systems one can neglect, to a high degree of accuracy, the correlations between the operators S_i^+ and S_g^z where $i \neq g$. Hence it is reasonable to factor out the operator S_g^z and replace it by its ensemble average. The second term in the Callen decoupling is included to overcome the defects of the RPA at very low temperatures. For zero crystal field anisotropy (D=0) both of these give good results over the whole temperature range $0 \leq T \leq T_c$. The Callen decoupling is better in the low temperature range in that it agrees more closely with Dyson's[11] exact spin wave results than does the RPA. On the other hand the RPA comes closer to getting the transition temperature T_c as predicted by the accurate high temperature series expansion methods[12], than the Callen decoupling does.

The decoupling of the crystal field term (4.1) has historically not been as easy nor as reliable as the decoupling of the exchange term. The basic problem is

that the operators in the left side of the Green function all refer to the same lattice site g. In this case the fluctuations of S_g^z are not uncorrelated with the fluctuations of S_g^+. In fact these operators must be intimately correlated if the identity $S(S+1) = (S_g^z)^2 + \frac{1}{2}(S_g^- S_g^+ + S_g^+ S_g^-)$ is to hold at all times. Basically there have been three attempts at approximating this Green function so as to give rise to a single excitation theory. Simply stated the three decouplings are,

Narath[13]:

$$<<(S_g^+ S_g^z + S_g^z S_g^+);B_h>> = 2<S_g^z><<S_g^+;B_h>>, \qquad (4.4)$$

Anderson and Callen[7]:

$$<<(S_g^+ S_g^z + S_g^z S_g^+);B_h>> = 2<S_g^z><<S_g^+;B_h>>$$
$$-\frac{1}{2S^2} <S_g^z><(S_g^- S_g^+ + S_g^+ S_g^-)><<S_g^+;B_h>>, \qquad (4.5)$$

Lines[15]:

$$<<(S_g^+ S_g^z + S_g^z S_g^+);B_h>> = \phi_g <<S_g^+;B_h>>, \qquad (4.6)$$

where,

$$\phi_g = \frac{<3(S_g^z)^2 - S(S+1)>}{<S_g^z>} \quad \text{for } B_h = S_h^-, \qquad (4.7)$$

and

$$\phi_g = \frac{<2(S_g^z)^4 + 3(S_g^z)^3 - (2S^2 + 2S - 1)(S_g^z)^2 - S(S+1)S_g^z>}{<(S_g^z)^3 - (S_g^z)^2 - S(S+1)S_g^z>}$$

$$(4.8)$$

$$\text{for } B_h = S_h^z S_h^-.$$

Plots of $T_c(D)/T_c(0)$ versus D/J for each of these decouplings

are contained in Figures 1, 2 and 7. In each case the exchange term Green function was decoupled by the RPA.

In the limit $D/J \to \infty$, each of these single excitation decouplings predicts an infinite transition temperature. This is clearly an unphysical result. For extremely large anisotropy the effective spin states at each site become $|S\rangle$ and $|-S\rangle$, and only transitions between these two states can occur. The intermediate spin states, such as $|S-1\rangle$ and $|-S+1\rangle$, are simply not populated at all because they are so widely separated in energy from the states $|S\rangle$ and $|-S\rangle$. A system with only two effective spin states still has a finite, though larger, transition temperature than a system with some populated intermediate states. Therefore, the prediction of $T_c = \infty$ is completely erroneous. These single excitation decouplings are, at best, valid only for very small anisotropy.

The Narath and Anderson and Callen decouplings also contain another fallacy. Both predict $\langle (S_g^z)^2 \rangle = S(S+1)/3$ at, and above T_c. But this can only be true for an iso-tropic system which has $D=0$. Lines's results do not suf-fer from this defect for $D \geq 0$; he has $\langle (S_g^z)^2 \rangle \geq S(S+1)/3$ at and above T_c.

5. THE MANY-EXCITATION SOLUTION FOR

A FERROMAGNETIC SYSTEM

A. The Non-Interacting Spin Problem

Once it has been established that the single excita-
tion approximations to the crystal field Green function
will not work, one is tempted to try and use the higher
order Green functions generated by the equation of motion
of the lower order Green functions. To illustrate how this
might be done we will consider the case of a lattice of
non-interacting spins, which has the Hamiltonian,

$$H = \sum_i H_i,\tag{5.1}$$

where

$$H_i = -g\mu_\beta H_o S_i^z - D(S_i^z)^2.\tag{5.2}$$

As we saw with the MFT Hamiltonian (2.4), this problem can
be solved very easily. H_i is already in diagonal form, hence
$\exp(-H_i/\kappa T)$ is quickly written down and one can then find
all the relevant ensemble averages for this system. For
example, for a spin S=1 system the results are,

$$\bar{S} = \frac{\exp(g\mu_\beta H_o/\kappa T) - \exp(-g\mu_\beta H_o/\kappa T)}{\exp(-D/\kappa T) + \exp(g\mu_\beta H_o/\kappa T) + \exp(-g\mu_\beta H_o/\kappa T)},\tag{5.3}$$

$$(S_i^z)^2 = \frac{\exp(g\mu_\beta H_o/\kappa T)+\exp(-g\mu_\beta H_o/\kappa T)}{\exp(-D/\kappa T)+\exp(g\mu_\beta H_o/\kappa T)+\exp(-g\mu_\beta H_o/\kappa T)}. \quad (5.4)$$

It is also enlightening to solve this problem by the Green function technique. That this can be done exactly within the Green function formalism is almost obvious. The set of all possible linearly independent spin operators associated with a lattice site i for a given size spin S, is a closed set under commutation with the Hamiltonian H_i in (5.2). Hence as we attempt to generate the higher order Green functions $<<[A,H_i];S_i^->>$, we must eventually return to the lower order Green functions. Therefore we will only have a finite number of operators to work with, and correspondingly only a finite number of Green functions. As an illustration of this, consider, again, a spin S=1 system. For the first Green function choose $A=S_i^+$, and $B=S_i^-$. Then,

$$E<<S_i^+;S_i^->> = 2\bar{S}/2\pi + g\mu_\beta H_o<<S_i^+;S_i^->>$$
$$+ D<<(S_i^z S_i^+ + S_i^+ S_i^z);S_i^->>. \quad (5.5)$$

Now writing down the equation of motion of the higher order Green function that appears above we have,

$$E<<(S_i^z S_i^+ + S_i^+ S_i^z);S_i^->> = Z/2\pi + g\mu_\beta H_o<<(S_i^z S_i^+ + S_i^+ S_i^z);S_i^->>$$
$$+D<<S_i^+;S_i^->>, \quad (5.6)$$

where $Z = <[(S_i^z S_i^+ + S_i^+ S_i^z),S_i^-]>$.

This second equation has closed the set of equations upon itself. The solutions for the Green functions in these equations are,

$$<<S_i^+;S_i^->> = \frac{1}{2\pi} \left\{ \frac{S+Z}{E-g\mu_\beta H_o-D} + \frac{\bar{S}-Z}{E-g\mu_\beta H_o+D} \right\}, \quad (5.7)$$

$$<<(S_i^z S_i^+ + S_i^+ S_i^z);S_i^->> = \frac{1}{2\pi} \left\{ \frac{\bar{S}+Z}{E-g\mu_\beta H_o-D} \right.$$
$$\left. - \frac{\bar{S}-Z}{E-g\mu_\beta H_o+D} \right\} \quad (5.8)$$

Then using the corollary to the Spectral Theorem (3.6) we have,

$$<S_i^- S_i^+> = (\bar{S}+Z)/(\exp((g\mu_\beta H_o+D)/\kappa T)-1)$$
$$+ (\bar{S}-Z)/(\exp((g\mu_\beta H_o-D)/\kappa T)-1) \quad (5.9)$$

$$<S_i^-(S_i^z S_i^+ + S_i^+ S_i^z)> = (\bar{S}+Z)/(\exp((g\mu_\beta H_o-D)/\kappa T)-1)$$
$$+ (\bar{S}-Z)/(\exp((g\mu_\beta H_o+D)/\kappa T)-1) \quad (5.10)$$

But since,

$$<S_i^- S_i^+> = 2-\bar{S}-<(S_i^z)^2>, \quad (5.11)$$

$$Z = 4 - 2<(S_i^z)^2>, \quad (5.12)$$

$$<S_i^-(S_i^z S_i^+ + S_i^+ S_i^z)> = 2+\bar{S} - <(S_i^z)^2>, \quad (5.13)$$

equation (5.9) and (5.10) are really two coupled equations in the two unknowns $\bar{S}$, and $<(S_i^z)^2>$. If we solve for these unknowns, we obtain the expressions (5.3) and (5.4) just as we had hoped to do. The point of this alternative derivation

was to learn how to deal with crystal field anisotropy in the Green function technique. It has essentially told us how to choose the operators, and hence the Green functions, for any size spin system.

For a spin S system we will need 2S different operators for the operator A in (3.3). The most convenient set is as follows:

$$A_g^1 = S_g^+, \tag{5.14}$$

$$A_g^i = \left\{ A_g^{i-1}, S_g^+ \right\}_+ \qquad \text{for } 2 \leq i \leq 2S, \tag{5.15}$$

where the braces $\{,\}_+$ denote the anticommutator. Though the set $\{A_g^i\}$ contains only 2S operators it is still closed under commutation with the Hamiltonian in (5.2), since the following commutation relations hold,

$$[A_g^i, S_g^z] = -A_g^i \qquad \text{for all } i, \tag{5.16}$$

$$[A_g^i, (S_g^z)^2] = -A_g^{i+1} \qquad \text{for all } i \leq 2S-1, \tag{5.17}$$

and

$$[A_g^{2S}, (S_g^z)^2] = -\sum_{j}^{2S-1} a_j A_g^j, \tag{5.18}$$

where the coefficients a_j depend on the particular size of the spin of the system. By defining the Green functions to be $G^i(E) = \langle\langle A_g^i; S_g^- \rangle\rangle$, the equations of motion are,

$$(E - g\mu_\beta H_o) G^i(E) - D G^{i+1}(E) = z_i/2\pi, \qquad \text{for } i \leq 2S-1, \tag{5.19}$$

$$(E - g\mu_\beta H_o) G^{2S}(E) - D \sum_{i=1}^{2S-1} a_j G^j(E) = z_{2S}/2\pi, \tag{5.20}$$

where $z_i = <[A_g^i, S_g^-]>$.

Or, if we write this in matrix form we have,

$$
\begin{vmatrix}
E-g\mu_\beta H_o & -D & & & & \\
& E-g\mu_\beta H_o & -D & & & \\
& & E-g\mu_\beta H_o & \cdot & & \\
& & & \cdot & -D & \\
& & & & \cdot & \\
-a_1 D & -a_2 D & -a_3 D & \cdots & & E-g\mu_\beta H_o
\end{vmatrix}
\begin{vmatrix}
G^1(E) \\
G^2(E) \\
G^3(E) \\
\cdot \\
\cdot \\
G^{2S}(E)
\end{vmatrix}
= \frac{1}{2\pi}
\begin{vmatrix}
z_1 \\
z_2 \\
z_3 \\
\cdot \\
\cdot \\
z_{2S}
\end{vmatrix}
$$

(5.21)

This can even be shortened to,

$$(E \underset{\sim}{I} - \underset{\sim}{H}_{CF}) \cdot \underset{\sim}{G}(E) = \underset{\sim}{z}/2, \qquad (5.22)$$

where $\underset{\sim}{I}$ is the identity matrix, the column vector $\underset{\sim}{G}(E)$ has components $G^i(E)$, and $\underset{\sim}{z}$ has components z_i.

As we noted in the spin 1 case the ensemble averages $<S_g^- A_g^i>$ and the z_i are just linear combinations of the moments $<(S_g^z)^n>$. Hence equation (5.21) completely determines these moments for all temperatures.

This process of solving for the moments, $<(S^z)^n>$, via the Green function technique is certainly not any easier than directly diagonalizing the Hamiltonian H, but it is very revealing. Suppose we add an exchange term to the Hamiltonian which we will denote as H_E, for the time

being. We can again write down the set of equations for
the 2S Green functions as in (5.19) and (5.20), but now
there will be extra terms of the form $<<[A_g^i, H_E]; S_h^->>$
associated with each of these equations. These exchange
terms are not completely determined within this set of
equations, i.e. they are higher order Green functions.
The only way the exchange terms can be known within this
set of 2S equations is if we reduce them to lower order
Green functions by an approximation scheme. In this way
we will be able to determine the moments when there are
exchange interactions present. Note that in this process
we will only need to approximate the Green functions asso-
ciated with the exchange. Hence, we may state that: the
decoupling of the crystal field Green function in (4.1)
is completely unnecessary. The real problem in trying to
extract statistical information from an interacting system
of spins with crystal field anisotropy present is in de-
coupling all of the exchange term Green functions, which
arise from using a set of spin operators for the A opera-
tor in (3.3) rather than the single operator S_g^+.

B.   The Exchange Term Decoupling

In this section we will present the decoupling of the
exchange term for an arbitrary size spin system. For con-
venience we will temporarily neglect the crystal field
anisotropy. The Heisenberg-Dirac Hamiltonian (1.3) can
be written as,

$$H_E = -\sum_i \sum_j J_{ij} [S_i^z S_j^z + \tfrac{1}{2}(S_i^+ S_j^- + S_i^- S_j^+)].\qquad(5.23)$$

Since the RPA is one of the most convenient and reasonably accurate decoupling approximations used in determining the transition temperature we would like to be able to decouple each of the Green functions $<<[A_g^i, H_E]; S_h^->>$ so as to obtain the RPA as originally stated in (4.2).

It will first be necessary to define two new sets of operators $\{B_g^i\}$ and $\{C_g^i\}$, as follows,

$$B_g^i = [A_g^i, S_g^+] \qquad \text{for all } i, \qquad (5.24)$$

$$C_g^i = [A_g^i, S_g^-] \qquad \text{for all } i. \qquad (5.25)$$

In the usual matrix representation, the spin angular momentum operators A_g^i are non-diagonal, more specifically their only non-zero elements are on the diagonal just above the main diagonal of the matrix. Therefore by the definition (5.24) the $\{B_g^i\}$ matrices have their only non-zero elements on the second diagonal above the main diagonal. Hence the ensemble averages of the $\{A_g^i\}$ and $\{B_g^i\}$ operators must vanish at all temperatures:

$$<A_g^i> = <B_g^i> = 0 \qquad \text{for all } i. \qquad (5.26)$$

Next we note that the operators $\{C_g^i\}$ are diagonal, and also that the quantities Z_i defined in the previous section are of the form $Z_i = \{C_g^i\}$. Since the $\{C_g^i\}$ are diagonal they can be written as linear combinations of the powers of the matrix S_g^z and the identity matrix I. One can also show

that for i odd the matrices $\{C_g^i\}$ can be written solely as linear combinations of the odd powers of S_g^z, and if i is even, the $\{C_g^i\}$ can be written solely as linear combinations of the even powers of S_g^z. These relations will be useful later when we consider antiferromagnetic systems.

Using (5.16), (5.24), and (5.25), the commutator of A_g^i with the Hamiltonian H_E in (5.23) yields,

$$[A_g^i, H_E] = -\sum_f J_{fg}(-2A_g^i S_f^z + B_g^i S_f^- + C_g^i S_f^+), \qquad (5.27)$$

where we have made use of the facts that $J_{fg} = J_{gf}$, $J_{ff}=0$, and operators located at lattice sites g and f automatically commute unless g=f. Hence we have separated the Green function $<<[A_g^i, H_E]; S_h^->>$ into three parts: $<<A_g^i S_f^z; S_h^->>$, $<<B_g^i S_f^-; S_h^->>$ and $<<C_g^i S_f^+; S_h^->>$. Taking our initiative from the RPA as stated in (4.2), we try decouplings of the form:

$$<<A_g^i S_f^z; S_h^->> = <S_f^z><<A_g^i; S_h^->>, \qquad (5.28)$$

$$<<B_g^i S_f^-; S_h^->> = 0 \qquad (5.29)$$

$$<<C_g^i S_f^+; S_h^->> = <C_g^i><<S_f^+; S_h^->> = z_i <<S_f^+; S_h^->>. \qquad (5.30)$$

The first and third decouplings are rather obvious: we have factored out the powers of S_g^z and replaced them by their ensemble averages. In effect, then, we are saying that the powers of S_g^z are uncorrelated with the operators A_f^i, where g and f are different lattice sites. Since the operators A_f^i are strictly non-diagonal they represent

fluctuations which are transverse to the quantization axis z. The powers of S_g^z, of course, correspond to longitudinal fluctuations. Hence it is not unreasonable to expect the longitudinal fluctuations at site g to be almost completely uncorrelated with the transverse fluctuations at site f≠g, as long as we are in, or near, the ordered state where the predominant correlation between the spins is a longitudinal-longitudinal correlation. The decoupling of (5.29) is less obvious, but nevertheless reasonable. If we attempt to factor out either the operator B_g^i or S_f^- and replace it by its ensemble average, we get zero because $\langle B_g^i \rangle = \langle S_f^- \rangle = 0$ as we stated earlier. Both of the operators B_g^i and S_f^- correspond to transverse correlations and therefore the Green function in (5.29) represents transverse-transverse correlations which are much smaller than even the transverse-longitudinal correlations at the transition temperature. Clearly, then, this Green function is negligible.

The equations of motions are then,

$$E\langle\langle A_g^i; S_h^-\rangle\rangle = \delta_{g,h} Z_i/2\pi + 2\sum_f \langle S_f^z\rangle J_{fg} \langle\langle A_g^i; S_h^-\rangle\rangle$$
$$- \sum_f Z_i J_{fg} \langle\langle S_f^+; S_h^-\rangle\rangle.$$

(5.31)

The sum over all the lattice sites f complicates somewhat the process of obtaining a solution of (5.31). This can be overcome by assuming that the magnetic ions all lie on a Bravais lattice. (If this is not the case one must introduce the concept of sublattices. This procedure will

be discussed in the section on antiferromagnetism.)

Secondly one must assume that the Green functions $<<A_g^i;S_h^->>$

and the exchange integrals J_{gh} depend only on the difference,

$R_g - R_h$, in their spatial coordinates rather than on the

individual coordinates, R_g and R_h. Then we may Fourier

transform as follows,

$$G^i(k,E) = \sum_{R_g-R_h} <<A_g^i;S_h^->> \exp(ik\cdot(R_g-R_h)), \qquad (5.32)$$

$$J(k) = \sum_{R_g-R_h} J_{gh} \exp(-ik\cdot(R_g-R_h)), \qquad (5.33)$$

$$<S^-(k)A^i> = \sum_{R_h-R_g} <S_h^-A_g^i> \exp(-ik\cdot(R_h-R_g)). \qquad (5.34)$$

The inverses of these transforms are,

$$<<A_g^iS_h^->> = \left(\frac{1}{N}\right)\sum_k G^i(k,E) \exp(-ik\cdot(R_g-R_h)), \qquad (5.35)$$

$$J_{gh} = \left(\frac{1}{N}\right)\sum_k J(k) \exp(ik\cdot(R_g-R_h)), \qquad (5.36)$$

$$<S_h^-A_g^i> = \left(\frac{1}{N}\right)\sum_k <S^-(k)A^i> \exp(ik\cdot(R_h-R_g)). \qquad (5.37)$$

where N is the number of magnetic ions on the Bravais

lattice. The sums over k are over all points in the first

Brillouin zone of the lattice. Then defining $\bar{S}=<S_g^z>$,

we have,

$$E\ G^i(k,E) = z_i/2\pi + 2\bar{S}J(0)G^i(k,E)-z_iJ(k)G^1(k,E). \qquad (5.38)$$

This may be written in matrix form as,

$$
\begin{vmatrix}
E-2\bar{S}(J(0)-J(k)) & & & & \\
Z_1 J(k) & E-2\bar{S}J(0) & & & \\
Z_2 J(k) & & E-2\bar{S}J(0) & & \\
& & & \ddots & \\
Z_{2S}J(k) & & & & E-2\bar{S}J(0)
\end{vmatrix}
\begin{vmatrix}
G^1 \\
G^2 \\
G^3 \\
\cdot \\
\cdot \\
G^{2S}
\end{vmatrix}
= \frac{1}{2\pi}
\begin{vmatrix}
2\bar{S} \\
Z_2 \\
Z_3 \\
\cdot \\
\cdot \\
Z_{2S}
\end{vmatrix} ,
$$

(5.39)

where $G^i = G^i(k,E)$, and also as,

$$(E\ \underset{\sim}{I} - \underset{\sim}{H}_E) \cdot \underset{\sim}{G}(k,E) = \underset{\sim}{Z}/2\pi, \tag{5.40}$$

where $\underset{\sim}{G}(k,E)$ and $\underset{\sim}{Z}$ are the column vectors as defined for (5.22) except that now $\underset{\sim}{G}$ depends on k as well as E, and $\underset{\sim}{H}_E$ is the matrix containing just the exchange integrals.

We will now show that this system of equations reproduces the results of Tahir-Kheli and ter Haar[4] which was the first successful attempt at using the Tyablikov decoupling of (4.2) to solve the general spin S problem. To find $G^i(k,E)$ from (5.39) one uses the well-known Cramer's Rule. $G^i(k,E)$ is the ratio of two determinants:

$$G^i(k,E) = \det(\underset{\sim}{M}^i)/\det(E\ \underset{\sim}{I} - \underset{\sim}{H}_E), \tag{5.41}$$

where the matrix $\underset{\sim}{M}^i$ is formed from the matrix $E\ \underset{\sim}{I} - \underset{\sim}{H}_E$ by replacing the i th column with the column vector $\underset{\sim}{Z}/2\pi$. Explicitly the matrix $\underset{\sim}{M}^i$ is,

$$\underset{\sim}{M}^{i} = \begin{vmatrix} E-2\bar{S}(J(0)-J(\underset{\sim}{k})) & & & Z_1/2\pi & \\ Z_2 J(\underset{\sim}{k}) & E-2\bar{S}J(0) & & Z_2/2\pi & \\ Z_3 J(\underset{\sim}{k}) & & \cdot & \cdot & \\ \cdot & & & \cdot & \\ \cdot & & & Z_i/2\pi & \\ \cdot & & & \cdot & \\ \cdot & & & \cdot & \\ Z_{2S} J(\underset{\sim}{k}) & & & Z_{2S}/2\pi & \cdot \quad E-2\bar{S}J(0) \end{vmatrix}$$

$$(5.42)$$

The determinant may easily be obtained from (5.42) by expanding in minors about the first column. All the minors of the elements in the first column are zero except for the first and i th elements, as one can readily see by inspection. Then,

$$\det(\underset{\sim}{M}^{i}) = (E-2\bar{S}(J(0)-J(\underset{\sim}{k}))) (Z_i/2\pi) (E-2\bar{S}J(0))^{2S-2}$$

$$+ (-1)^{i+1} Z_i J(k) \times (\text{Minor of the element } Z_i J(\underset{\sim}{k})).$$

$$(5.43)$$

The minor of the element $Z_i J(\underset{\sim}{k})$ turns out to be
$(-1)^i (Z_1/2\pi)(E-2\bar{S}J(0))^{2S-2}$. Hence,

$$\det(\underset{\sim}{M}^{i}) = (E-2\bar{S}(J(0)-J(\underset{\sim}{k}))) (Z_i/2\pi)(E-2\bar{S}J(0))^{2S-2}$$

$$- Z_i J(\underset{\sim}{k})(Z_1/2\pi)(E-2\bar{S}J(0))^{2S-2}.$$

$$(5.44)$$

Since $Z_1 = 2\bar{S}$ this reduces to,

$$\det(\underset{\sim}{M}^{i}) = (Z_i/2\pi)(E-2\bar{S}J(0))^{2S-1}.$$

$$(5.45)$$

From (5.39) we can also quickly obtain,

$$\det(E \underset{\sim}{I} - \underset{\sim E}{H}) = (E-2\bar{S}(J(0)-J(\underset{\sim}{k})))(E-2\bar{S}J(0))^{2S-1}. \quad (5.46)$$

Therefore,

$$G^i(\underset{\sim}{k},E) = \frac{1}{2\pi} \cdot \frac{Z_i}{E-2\bar{S}(J(0)-J(\underset{\sim}{k}))}. \quad (5.47)$$

The wavevector dependent correlation function (5.34) may be gotten from (5.47) by means of the corollary to the Spectral Theorem (3.6),

$$\langle S^-(\underset{\sim}{k})A^i \rangle = \frac{Z_i}{\exp(E(\underset{\sim}{k})/\kappa T)-1}, \quad (5.48)$$

where $E(\underset{\sim}{k})=2\bar{S}(J(0)-J(\underset{\sim}{k}))$. Then using (5.37) the spatially-dependent correlation function becomes,

$$\langle S_h^- A_g^i \rangle = \left(\frac{1}{N}\right)\sum_{\underset{\sim}{k}} \frac{Z_i}{\exp(E(\underset{\sim}{k})/\kappa T)-1} \exp(-i\underset{\sim}{k}\cdot(\underset{\sim g}{R}-\underset{\sim h}{R})). \quad (5.49)$$

For g=h this reduces to,

$$\langle S^- A^i \rangle = Z_i \left(\frac{1}{N}\right) \sum_{\underset{\sim}{k}} 1/(\exp(E(\underset{\sim}{k})/\kappa T)-1). \quad (5.50)$$

If we define,

$$\Phi = \left(\frac{1}{N}\right)\sum_{\underset{\sim}{k}} 1/(\exp(E(\underset{\sim}{k})/\kappa T)-1), \quad (5.51)$$

then (5.50) becomes,

$$\langle S^- A^i \rangle = \langle[A^i,S^-]\rangle\Phi \qquad \text{for } i = 1,2,\ldots,2S. \quad (5.52)$$

As we have mentioned before, both $\langle S^- A^i \rangle$ and $\langle[A^i,S^-]\rangle$ are linear combinations of the moments $\langle(S^z)^n\rangle$ for $n = 0,1,2,\ldots,2S-1$. Hence (5.52) is a set of 2S equations

in the 2S unknown moments. Therefore (5.52) completely
determines the moments. This set of 2S equations is com-
pletely equivalent to the set of 2S equations contained
in equation (3.13) in the paper by Tahir-Kheli and ter Haar.
All that we have done here is to recast their solution
into one that uses the operators $\{A_g^i\}$. Therefore the
decoupling that we have used in (5.28)-(5.30) is completely
equivalent to the RPA as stated in (4.2).

C. The Complete Solution

The matrix equation (5.21) is applicable for a sys-
tem with no exchange, but just an external field and crys-
tal field anisotropy. The matrix equation (5.39) is for a
system which only has exchange coupling between the spins.
The summarized form of each of these equations is,

Crystal field: $\qquad (E\underset{\sim}{I}-\underset{\sim}{H}_{CF})\cdot\underset{\sim}{G} = \underset{\sim}{Z}/2\pi,$ $\qquad\qquad$ (5.53)

Exchange: $\qquad (E\underset{\sim}{I}-\underset{\sim}{H}_{E})\cdot\underset{\sim}{G} = \underset{\sim}{Z}/2\pi.$ $\qquad\qquad$ (5.54)

Then if the system is described by a Hamiltonian
$H = H_{CF} + H_E$, the equations of motion become,

$$(E\underset{\sim}{I}-\underset{\sim}{H}_{CF}-\underset{\sim}{H}_{E})\cdot\underset{\sim}{G} = \underset{\sim}{Z}/2\pi, \qquad\qquad (5.55)$$

or, if we define $\underset{\sim}{H} = \underset{\sim}{H}_{CF} + \underset{\sim}{H}_E$,

$$(E\underset{\sim}{I}-\underset{\sim}{H})\cdot\underset{\sim}{G} = \underset{\sim}{Z}/2\pi. \qquad\qquad (5.56)$$

Writing this out explicitly, we have,

$$
\begin{vmatrix}
E-2\bar{S}(J(0)-J(\underset{\sim}{k})) & -D & & & & \\
Z_2 J(\underset{\sim}{k}) & E-2\bar{S}J(0) & -D & & & \\
Z_3 J(\underset{\sim}{k}) & & E-2\bar{S}J(0) & . & & \\
. & & & & . & \\
. & & & & . & . \\
. & & & & . & -D \\
Z_{2S}J(\underset{\sim}{k})-a_1 D & -a_2 D & -a_3 D & \cdots & -a_{2S-1}D & E-2\bar{S}J(0)
\end{vmatrix}
$$

$$
\times
\begin{vmatrix}
G^1(\underset{\sim}{k},E) \\
G^2(\underset{\sim}{k},E) \\
G^3(\underset{\sim}{k},E) \\
. \\
. \\
. \\
. \\
G_{2S}(\underset{\sim}{k},E)
\end{vmatrix}
= \frac{1}{2\pi}
\begin{vmatrix}
Z_1 \\
Z_2 \\
Z_3 \\
. \\
. \\
. \\
Z_{2S}
\end{vmatrix} .
\tag{5.57}
$$

This set of 2S equations completely determines the moments $<(S^z)^n>$ of the system that includes in its Hamiltonian exchange interactions and crystal field anisotropy. The only approximation that we have had to make is in decoupling the exchange terms via the RPA.

The spectrum of excitations, i.e. the location of the poles of the Green functions is obtained by equating the determinant of the matrix $E\underset{\approx}{I}-\underset{\approx}{H}$ to zero,

$$
\det(E\underset{\approx}{I}-\underset{\approx}{H}) = 0.
\tag{5.58}
$$

Since the determinant is a polynomial of degree 2S in the

variable E, there are 2S possible roots of this equation.
Denoting the roots as $E_m(\underset{\sim}{k})$, we can write,

$$\det(E\underset{\approx}{I}-\underset{\approx}{H}) = \prod_{m=1}^{2S} (E-E_m(\underset{\sim}{k})).$$ (5.59)

As before, the Green functions $G^i(\underset{\sim}{k},E)$ are obtained by divid-
ing (5.59) into the determinant of the matrix which is
formed by replacing the i th column of the matrix
$E\underset{\approx}{I}-\underset{\approx}{H}$ with the column vector $Z/2\pi$. The determinant
of this newly formed matrix is a polynomial of degree 2S-1
in the variable E. Hence a partial fraction expansion will
yield a $G^i(\underset{\sim}{k},E)$ which is a sum of simple poles located
at the points $E_m(\underset{\sim}{k})$ on the real axis in the complex E plane.
Notationally we may write,

$$G^i(\underset{\sim}{k},E) = \frac{1}{2\pi} \sum_{m=1}^{2S} \frac{R_m^i(\underset{\sim}{k})}{E-E_m(\underset{\sim}{k})},$$ (5.60)

where $R_m^i(\underset{\sim}{k})$ is the residue of the m th pole of the i th
Green function. The wavevector dependent correlation func-
tion is then,

$$<S^-(\underset{\sim}{k})A^i> = \sum_{m=1}^{2S} \frac{R_m^i(\underset{\sim}{k})}{\exp(E_m(\underset{\sim}{k})/\kappa T)-1}.$$ (5.61)

Then the spatial correlation function is,

$$<S_h^- A_g^i> = \left(\frac{1}{N}\right)\sum_{\underset{\sim}{k}} \sum_{m=1}^{2S} \frac{R_m^i(\underset{\sim}{k})}{\exp(E_m(\underset{\sim}{k})/\kappa T)-1} \exp(-i\underset{\sim}{k}\cdot(\underset{\sim}{R}_g-\underset{\sim}{R}_h)).$$ (5.62)

and in particular,

$$<S_h^- A_h^i> = \left(\frac{1}{N}\right)\sum_{\underset{\sim}{k}} \sum_{m=1}^{2S} \frac{R_m^i(\underset{\sim}{k})}{\exp(E_m(\underset{\sim}{k})/\kappa T)-1}.$$ (5.63)

This set of 2S equations contains all the necessary

thermodynamic information. Unfortunately, (5.63) cannot be written in any simpler way than it is for a given size spin system. The complete solutions can only be obtained by a high speed computer.

D. The Transition Temperature

The transition temperature is that temperature above which the system is no longer ordered when there is no external magnetic field present. A system which is not ordered has all of its odd moments $\langle (S^z)^{2n+1} \rangle = 0$, since the unordered state is a time reversible state. We may use this fact to obtain T_c, the transition temperature. We cannot, though, merely set the odd moments in (5.63) to zero and expect to obtain a complete set of equations that are useful for solving for T_c. For the particular cases worked out by this author, this process yielded redundant and sometimes trivial equations. The correct procedure for obtaining a complete set of equations, one unknown of which is T_c, is as follows. First define the quantities,

$$\beta_{2n+1} = \lim_{\bar{S} \to 0} (Z_{2n+1}/\bar{S}).$$

(5.64)

Then insert for Z_{2n+1} in (5.63) the quantities $\beta_{2n+1}\bar{S}$, and then expand the functions on the right hand sides of the equations in the variable $\bar{S}$. Comparing the coefficients of the zeroth and first powers of $\bar{S}$ in each equation yields $2S$ independent equations. The $2S$ unknown quantities will then be the quantities Z_i for i even, the

quantities β_i for i odd, and T_c (β_1 is already known to be just the number 2). These equations must also be solved on a high speed computer.

Unfortunately, again, no general expression for T_c has been found for an arbitrary size spin system. Chapter 7 of this thesis will present results for some special cases that have been worked out.

E. A Decoupling Approximation for the
Molecular Field Theory

Suppose we had chosen to make the following decoupling approximation,

$$<<A_g^i S_f^z; S_h^->> = <S_f^z><<A_h^i; S_h^->>\delta_{g,h}, \tag{5.65}$$

$$<<C_g^i S_f^+; S_h^->> = z_i <<S_h^+; S_h^->>\delta_{g,h}, \tag{5.66}$$

instead of the ones we had made in (5.28) and (5.30). The equations of motion would then have been,

$$
\begin{vmatrix}
E-2\bar{S}J(0) & & & & & \\
& E-2\bar{S}J(0) & & & & \\
& & E-2\bar{S}J(0) & & & \\
& & & \cdot & & \\
& & & & \cdot & \\
& & & & & \cdot \\
-a_1 D & -a_2 D & \cdot\,\cdot\,\cdot\,\cdot\,-a_{2S-1}D & & E-2\bar{S}J(0)
\end{vmatrix}
\begin{vmatrix}
G^1(E) \\
G^2(E) \\
G^3(E) \\
\cdot \\
\cdot \\
\cdot \\
G^{2S}(E)
\end{vmatrix}
= \frac{1}{2\pi}
\begin{vmatrix}
z_1 \\
z_2 \\
z_3 \\
\cdot \\
\cdot \\
\cdot \\
z_{2S}
\end{vmatrix},
$$

$$\tag{5.67}$$

where $G^i(E) = <<A_h^i; S_h^->>$. Note that we could have gotten

(5.67) from (5.57) just by setting J(k) = 0. One can

also see that (5.67) could have been obtained from (5.56)

if we chose the Hamiltonian to be the MFT Hamiltonian,

$$H_{MFT} = \sum_i H_i , \qquad (5.68)$$

where H_i is as defined in (2.4). Therefore we are saying

that the decoupling of (5.65) and (5.66) is completely

equivalent to the MFT approximation, which, in turn, is

equivalent to setting J(k) = 0 in (5.57).

The fact that setting J(k)=0 in the RPA equations

of motion yields the MFT results when there is no crystal-

field present (D=0) has been known for some time[15].

Only until now is it known also to hold when D is finite.

None of the elementary theories presented in Chapter 4

gives the MFT result when J(k) is set equal to zero.

The decoupling of (5.65) and (5.66) is certainly

consistent with what we already know about the MFT. This

is a theory which neglects <u>all</u> correlations between spins

at different lattice sites, as indicated by (2.2) where

we have replaced neighboring spin operators by their en-

semble averages, instead of considering their full quantum

mechanical effect.

6. THE MANY-EXCITATION THEORY FOR

AN ANTIFERROMAGNETIC SYSTEM

All of our previous discussion has been concerned
solely with ferromagnetic systems, i.e. systems in which
the aligned spins all point in the same direction. More
frequently though in insulating magnetic salts the spins
are arranged in parallel-antiparallel pairs so that the
net magnetic moment of the crystal is zero. Such a con-
figuration is called antiferromagnetic ordering. The simp-
lest kind of such a system is when the nearest neighbors
of each spin are antiparallel to it. Clearly such a lat-
tice is not translationally invariant, but it is possible
to break the lattice down into translationally invariant
sublattices. We may define a magnetic sublattice as a
Bravais lattice, which contains only spins that point in
the same direction. We can always perform the subdivision
of a lattice into many sublattices, though for complicated
spin structures this may not be an easy thing to do. For
convenience we will only consider a two sublattice model
in this thesis. The extension to a larger number of sub-
lattices is relatively easy to deduce from the two sub-
lattice case.

Anderson and Callen[7] and Lines[8] first solved the

antiferromagnetic problem within the Green function form-
alism. We can use their technique for our problem also.
Following their technique, we will consider two distinct
types of Green functions. The first kind of Green func-
tions will be concerned with correlations between ions
that lie on the same sublattice, the second kind of Green
functions will be concerned only with correlations between
ions that lie on different sublattices. The second kind
of Green functions are not really Green functions at all,
since their equations of motion do not have the inhomo-
geneous term.

We will label the sublattices 1 and 2 respectively.
Sublattice 1 will be the sublattice containing the "up"
spins, and sublattice 2 will contain the "down" spins.
Lattice site index g1 will refer to a point on sublattice
1, and the index g2 will refer to a point on sublat-
tice 2.

Rewriting equation (5.31) for an antiferromagnetic
system yields,

$$
E \langle\langle A_{g1}^i ; S_{h1}^- \rangle\rangle = \delta_{g1,h1} Z_i / 2\pi + 2\sum_{f1} \langle S_{f1}^z \rangle J_{f1,g1} \langle\langle A_{g1}^i ; S_{h1}^- \rangle\rangle
$$

$$
+ 2\sum_{f2} \langle S_{f2}^z \rangle J_{f2,g1} \langle\langle A_{g1}^i ; S_{h1}^- \rangle\rangle
$$

$$
- \sum_{f1} \langle C_{g1}^i \rangle J_{f1,g1} \langle\langle S_{f1}^+ ; S_{h1}^- \rangle\rangle
$$

$$
- \sum_{f2} \langle C_{g1}^i \rangle J_{f2,g1} \langle\langle S_{f2}^+ ; S_{h1}^- \rangle\rangle , \qquad (6.1)
$$

$$E<<A^i_{g2};S^-_{h1}>> = 2\sum_{f1}<S^z_{f1}>J_{f1,g2}<<A^i_{g2};S^-_{h1}>>$$

$$+ 2\sum_{f2}<S^z_{f2}>J_{f2,g2}<<A^i_{g2};S^-_{h1}>>$$

$$- \sum_{f1}<C^i_{g2}>J_{f1,g2}<<S^+_{f1};S^-_{h1}>>$$

$$- \sum_{f2}<C^i_{g2}>J_{f1,g2}<<S^+_{f2};S^-_{h1}>>. \qquad (6.2)$$

We must be more careful now in how we use the ensemble averages $<S^z_f>$ and $<C^i_f>$. Since the direction of the spin alignment is different on each sublattice, these quantities are no longer strictly positive nor are they independent of the index f, as they were before. We shall eliminate some of the confusion by adopting the following convention:

$$<S^z_{f1}> = +\bar{S}, \qquad (6.3)$$

$$<S^z_{f2}> = -\bar{S}, \qquad (6.4)$$

since 1 is the "up" sublattice and 2 is the "down" sublattice. The ensemble averages of the odd powers of S^z must also possess the same property of changing sign from sublattice to sublattice. Recalling that C^i depends only on the odd powers of S^z if i is odd and only on the even powers of S^z if i is even, we adopt the following:

$$<C^i_{f1}> = z_i, \qquad (6.5)$$

$$<C^i_{f2}> = (-1)^i z_i, \qquad (6.6)$$

and therefore the quantities $\bar{S}$ and z_i will then be strictly positive.

By again assuming that the Green functions and the exchange integrals depend only on the difference in their two spatial coordinates, we may perform Fourier transformations as follows:

$$G_1^i(\underset{\sim}{k},E) = \sum_{\underset{\sim gl}{R}-\underset{\sim hl}{R}} \langle\langle A_{gl}^i ; S_{hl}^-\rangle\rangle \exp(i\underset{\sim}{k}\cdot(\underset{\sim gl}{R}-\underset{\sim hl}{R})), \quad (6.7)$$

$$G_2^i(\underset{\sim}{k},E) = \sum_{\underset{\sim g2}{R}-\underset{\sim hl}{R}} \langle\langle A_{g2}^i ; S_{hl}^-\rangle\rangle \exp(i\underset{\sim}{k}\cdot(\underset{\sim g2}{R}-\underset{\sim hl}{R})), \quad (6.8)$$

$$J_{11}(\underset{\sim}{k}) = \sum_{\underset{\sim gl}{R}-\underset{\sim hl}{R}} J_{gl,hl} \exp(-i\underset{\sim}{k}\cdot(\underset{\sim gl}{R}-\underset{\sim hl}{R})), \quad (6.9)$$

$$J_{21}(\underset{\sim}{k}) = \sum_{\underset{\sim g2}{R}-\underset{\sim hl}{R}} J_{g2,hl} \exp(-i\underset{\sim}{k}\cdot(\underset{\sim g2}{R}-\underset{\sim hl}{R})), \quad (6.10)$$

$$J_{12}(\underset{\sim}{k}) = \sum_{\underset{\sim gl}{R}-\underset{\sim h2}{R}} J_{gl,h2} \exp(-i\underset{\sim}{k}\cdot(\underset{\sim gl}{R}-\underset{\sim h2}{R})), \quad (6.11)$$

$$J_{22}(\underset{\sim}{k}) = \sum_{\underset{\sim g2}{R}-\underset{\sim h2}{R}} J_{g2,h2} \exp(-i\underset{\sim}{k}\cdot(\underset{\sim g2}{R}-\underset{\sim h2}{R})), \quad (6.12)$$

$$\langle S_1^-(\underset{\sim}{k})A_1^i\rangle = \sum_{\underset{\sim gl}{R}-\underset{\sim hl}{R}} \langle S_{gl}^- A_{hl}^i\rangle \exp(i\underset{\sim}{k}\cdot(\underset{\sim gl}{R}-\underset{\sim hl}{R})). \quad (6.13)$$

The inverses of these transformations are as follows:

$$\langle\langle A_{gl}^i ; S_{hl}^-\rangle\rangle = \left(\frac{2}{N}\right)\sum_{\underset{\sim}{k}} G_1^i(\underset{\sim}{k},E)\ \exp(-i\underset{\sim}{k}\cdot(\underset{\sim gl}{R}-\underset{\sim hl}{R})), \quad (6.14)$$

$$\langle\langle A_{g2}^i ; S_{hl}^-\rangle\rangle = \left(\frac{2}{N}\right)\sum_{\underset{\sim}{k}} G_2^i(\underset{\sim}{k},E)\ \exp(-i\underset{\sim}{k}\cdot(\underset{\sim g2}{R}-\underset{\sim hl}{R})), \quad (6.15)$$

$$J_{g1,h1} = \left(\frac{2}{N}\sum_{\underset{\sim}{k}} J_{11}(\underset{\sim}{k})\ \exp(i\underset{\sim}{k}\cdot(\underset{\sim}{R}_{g1}-\underset{\sim}{R}_{h1})),\right. \tag{6.16}$$

$$J_{g2,h1} = \frac{2}{N}\sum_{\underset{\sim}{k}} J_{21}(\underset{\sim}{k})\ \exp(i\underset{\sim}{k}\cdot(\underset{\sim}{R}_{g2}-\underset{\sim}{R}_{h1})), \tag{6.17}$$

$$J_{g1,h2} = \frac{2}{N}\sum_{\underset{\sim}{k}} J_{12}(\underset{\sim}{k})\ \exp(i\underset{\sim}{k}\cdot(\underset{\sim}{R}_{g1}-\underset{\sim}{R}_{h2})), \tag{6.18}$$

$$J_{g2,h2} = \frac{2}{N}\sum_{\underset{\sim}{k}} J_{22}(\underset{\sim}{k})\ \exp(i\underset{\sim}{k}\cdot(\underset{\sim}{R}_{g2}-\underset{\sim}{R}_{h2})), \tag{6.19}$$

$$<S_{g1}^{-}A_{h1}^{i}> = \frac{2}{N}\sum_{\underset{\sim}{k}} <S_1^{-}(\underset{\sim}{k})A_1^i>\exp(-i\underset{\sim}{k}\cdot(\underset{\sim}{R}_{g1}-\underset{\sim}{R}_{h1})). \tag{6.20}$$

The sums over $\underset{\sim}{k}$ are to be performed over the first Brillouin zone of the sublattice. The factor $2/N$ corresponds to the fact that there are $N/2$ sites on each sublattice, and hence $N/2$ $\underset{\sim}{k}$ vectors in the first zone.

Using the transformed quantities in (6.7)-(6.12) the equations (6.1) and (6.2) can be written concisely as,

$$EG_1^i(\underset{\sim}{k},E) = z_i/2\pi + 2\bar{S}J_{11}(0)G_1^i(\underset{\sim}{k},E) - 2\bar{S}J_{21}(0)G_1^i(\underset{\sim}{k},E)$$

$$-z_iJ_{11}(\underset{\sim}{k})G_1^1(\underset{\sim}{k},E) - z_iJ_{21}(\underset{\sim}{k})G_2^1(\underset{\sim}{k},E), \tag{6.21}$$

$$EG_2^i(\underset{\sim}{k},E) = 2\bar{S}J_{12}(0)G_2^i(\underset{\sim}{k},E) - 2\bar{S}J_{22}(0)G_2^i(\underset{\sim}{k},E) \tag{6.22}$$

$$- (-1)^i z_i J_{12}(\underset{\sim}{k})G_1^1(\underset{\sim}{k},E) - (-1)^i z_i J_{22}(0)G_2^1(\underset{\sim}{k},E).$$

Since the crystal field anisotropy acts on each spin at each lattice site separately, rather than coupling the spins to each other, it is easy to reintroduce the anisotropy at this point,

$$EG_1^i(\underset{\sim}{k},E) = z_i/2\pi + 2\bar{S}J_{11}(0)G_1^i(\underset{\sim}{k},E) - 2\bar{S}J_{21}(0)G_1^i(\underset{\sim}{k},E)$$

$$-z_iJ_{11}(\underset{\sim}{k})G_1^1(\underset{\sim}{k},E) - z_iJ_{21}(\underset{\sim}{k})G_2^1(\underset{\sim}{k},E)$$

$$-DG_1^{i+1}(\underset{\sim}{k},E), \qquad \text{for } i \leq 2S-1, \qquad (6.23)$$

$$EG_2^i(\underset{\sim}{k},E) = 2\bar{S}J_{12}(0)G_2^i(\underset{\sim}{k},E) - 2\bar{S}J_{22}(0)G_2^i(\underset{\sim}{k},E)$$

$$- (-1)^i z_iJ_{12}(\underset{\sim}{k})G_1^1(\underset{\sim}{k},E) - (-1)^i z_iJ_{22}(\underset{\sim}{k})G_2^1(\underset{\sim}{k},E)$$

$$- DG_2^{i+1}(\underset{\sim}{k},E), \qquad \text{for } i \leq 2S-1, \qquad (6.24)$$

$$EG_1^i(\underset{\sim}{k},E) = z_i/2\pi + 2\bar{S}J_{11}(0)G_1^i(\underset{\sim}{k},E) - 2\bar{S}J_{21}(0)G_1^i(\underset{\sim}{k},E)$$

$$-z_iJ_{11}(\underset{\sim}{k})G_1^1(\underset{\sim}{k},E) - z_iJ_{21}(\underset{\sim}{k})G_2^1(\underset{\sim}{k},E)$$

$$- \sum_{j=1}^{2S-1} Da_jG_1^j(\underset{\sim}{k},E), \qquad (6.25)$$

$$EG_2^i(\underset{\sim}{k},E) = 2\bar{S}J_{12}(0)G_2^i(\underset{\sim}{k},E) - 2\bar{S}J_{22}(0)G_2^i(\underset{\sim}{k},E)$$

$$- (-1)^i z_iJ_{12}(\underset{\sim}{k})G_1^1(\underset{\sim}{k},E) - (-1)^i z_iJ_{22}(\underset{\sim}{k})G_2^1(\underset{\sim}{k},E)$$

$$- \sum_{j=1}^{2S-1} Da_jG_2^j(\underset{\sim}{k},E). \qquad (6.26)$$

This set of equations may be written in block matrix form as,

$$\begin{vmatrix} E\underset{\sim}{I}-\underset{\approx}{H}_{11} & -\underset{\approx}{H}_{21} \\ -\underset{\approx}{H}_{12} & E\underset{\sim}{I}-\underset{\approx}{H}_{22} \end{vmatrix} \begin{vmatrix} \underset{\sim}{G}_1 \\ \underset{\sim}{G}_2 \end{vmatrix} = \frac{1}{2\pi} \begin{vmatrix} \underset{\sim}{z} \\ \underset{\sim}{0} \end{vmatrix}, \qquad (6.27)$$

where the elements are matrices themselves, which are
defined as follows:

$$
E\underset{\sim}{I}-\underset{\sim}{H}_{11} = \begin{vmatrix} E-2\bar{S}(J(0)-J_{11}\underset{\sim}{(k)}) & -D & & & \bigcirc \\ Z_2 J_{11}\underset{\sim}{(k)} & E-2\bar{S}J(0) \cdot & \cdot & & \\ Z_3 J_{11}\underset{\sim}{(k)} & \bigcirc & & \cdot & \cdot \\ \vdots & & & & \cdot \quad -D \\ Z_{2S} J_{11}\underset{\sim}{(k)}-a_1 D & -a_2 D \cdots -a_{2S-1} D & & & E-2\bar{S}J(0) \end{vmatrix}
$$

(6.28)
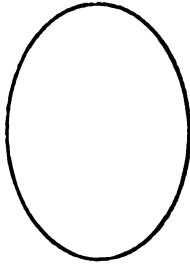
$$
E\underset{\sim}{I}-\underset{\sim}{H}_{22} = \begin{vmatrix} E+2\bar{S}(J(0)-J_{11}\underset{\sim}{(k)}) & -D & & & \bigcirc \\ Z_2 J_{11}\underset{\sim}{(k)} & E+2\bar{S}J(0) \cdot & \cdot & & \\ -Z_3 J_{11}\underset{\sim}{(k)} & \bigcirc & & \cdot & \cdot \\ \vdots & & & & \cdot \quad -D \\ (-1)^{2S} Z_{2S} J_{11}\underset{\sim}{(k)}-a_1 D & -a_2 D \cdots -a_{2S-1} D & & & E+2\bar{S}J(0) \end{vmatrix}
$$

(6.29)

$$
-\underset{\approx}{H}_{21} = \begin{vmatrix} 2\bar{S}J_{21}\underset{\sim}{(k)} \\ Z_1 J_{21}\underset{\sim}{(k)} \\ Z_2 J_{21}\underset{\sim}{(k)} \\ \vdots \\ Z_{2S} J\underset{\sim}{(k)} \end{vmatrix} \bigcirc \quad ,
$$

(6.30)

$$-\underset{\sim}{H}_{12} = \begin{vmatrix} -2\bar{S}J_{12}(\underset{\sim}{k}) \\ Z_2 J_{12}(\underset{\sim}{k}) \\ -Z_3 J_{12}(\underset{\sim}{k}) \\ \vdots \\ (-1)^i Z_{2S} J_{12}(\underset{\sim}{k}) \end{vmatrix} ,$$

$$(6.31)$$

$$\underset{\sim}{G}_1 = \begin{vmatrix} G_1^1(\underset{\sim}{k},E) \\ G_1^2(\underset{\sim}{k},E) \\ G_1^3(\underset{\sim}{k},E) \\ \vdots \\ G_1^{2S}(\underset{\sim}{k},E) \end{vmatrix} , \qquad \underset{\sim}{G}_2 = \begin{vmatrix} G_2^1(\underset{\sim}{k},E) \\ G_2^2(\underset{\sim}{k},E) \\ G_2^3(\underset{\sim}{k},E) \\ \vdots \\ G_2^{2S}(\underset{\sim}{k},E) \end{vmatrix} , \qquad (6.32)$$

$$\underset{\sim}{Z} = \begin{vmatrix} Z_1 \\ Z_2 \\ Z_3 \\ \vdots \\ Z_{2S} \end{vmatrix} , \qquad \underset{\sim}{0} = \begin{vmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{vmatrix} . \qquad (6.33)$$

The quantities $J_{11}(\underset{\sim}{k})$ and $J_{22}(\underset{\sim}{k})$ are equal for a system such as ours which has two completely equivalent sublattices. By the same reasoning, $J_{12}(\underset{\sim}{k})$ and $J_{21}(\underset{\sim}{k})$ must be complex conjugates of each other, and for $\underset{\sim}{k}=0$ they are both real, which implies $J_{12}(0)=J_{21}(0)$. The symbol $J(0)$

here represents either the quantity $J_{11}(0)-J_{21}(0)$ or
$J_{22}(0)-J_{12}(0)$. Note that the matrix $\underset{\approx}{EI}-\underset{\approx}{H}_{11}$ is just the
matrix of (5.57) with $\underset{\sim}{J}(k)$ replaced by $J_{11}(\underset{\sim}{k})$. The matrix
$\underset{\approx}{EI}-\underset{\approx}{H}_{22}$ is the same as $\underset{\approx}{EI}-\underset{\approx}{H}_{11}$ except that the signs before
the quantities Z_i are changed.

Equation (6.27) is really a set of 4S coupled equations
in the 4S Green functions. There are, however, only 2S
unknown thermodynamic quantities, the Z_i, or equivalently
the moments of S^z. All 4S Green functions depend on these
2S quantities, but it is only the Green functions of the
form $G_1^i(\underset{\sim}{k},E)$ which can be related back to these moments
via the Spectral Theorem, and hence they provide a set of 2S
equations which completely determine the moments. The
Green functions $G_2^i(\underset{\sim}{k},E)$ certainly depend on these moments,
but they cannot be used to find these quantities.

The Green functions $G_1^i(\underset{\sim}{k},E)$ can be found by the same
technique that we have used previously. Each of the Green
functions is the ratio of two determinants,

$$G_1^i(\underset{\sim}{k},E) = \det(\underset{\sim}{N}^i)/\det(\underset{\sim}{K}^i), \qquad (6.34)$$

where,

$$\underset{\sim}{K}^i = \begin{vmatrix} \underset{\approx}{EI}-\underset{\approx}{H}_{11} & -\underset{\sim}{H}_{21} \\ -\underset{\sim}{H}_{12} & \underset{\approx}{EI}-\underset{\approx}{H}_{22} \end{vmatrix}. \qquad (6.35)$$

The matrix $\underset{\sim}{K}^i$ is just the coefficient matrix of (6.27), and
the matrix $\underset{\sim}{N}^i$ is formed by replacing the i th column of $\underset{\sim}{K}^i$

with the column vector,

$$\frac{1}{2\pi} \begin{vmatrix} \underset{\sim}{Z} \\ \underset{\sim}{0} \end{vmatrix} \, . \tag{6.36}$$

One can show that the determinant $\det(\underset{\sim}{K}^i)$ is a polynomial in the variable E^2 rather than the variable E. Hence the Green functions $G^i(\underset{\sim}{k},E)$ will have poles that come in positive and negative pairs. Clearly then, $G_1^i(\underset{\sim}{k},E)$ has the form,

$$G_1^i(\underset{\sim}{k},E) = \frac{1}{2\pi} \sum_{m=1}^{2S} \left\{ \frac{R_m^i(\underset{\sim}{k})}{E-E_m(\underset{\sim}{k})} + \frac{T_m^i(\underset{\sim}{k})}{E+E_m(\underset{\sim}{k})} \right\} , \tag{6.37}$$

where the $E_m(\underset{\sim}{k})$ are the 2S possible positive poles, the $R_m^i(\underset{\sim}{k})$ are the residues of the positive poles, and the $T_m^i(\underset{\sim}{k})$ are the residues of the negative poles. Then we have,

$$<S_g^- A_g^i> = \left(\frac{2}{N}\right) \sum_{\underset{\sim}{k}} \sum_{m=1}^{2S} \left\{ \frac{R_m^i(\underset{\sim}{k})}{\exp(E_m(\underset{\sim}{k})/\kappa T)-1} \right.$$

$$\left. + \frac{T_m^i(\underset{\sim}{k})}{\exp(-E_m(\underset{\sim}{k})/\kappa T)-1} \right\} . \tag{6.38}$$

It is the 2S equations of (6.38) that can then be used to determine the 2S moments $<(S^z)^n>$.

We can find the transition temperature for the antiferromagnet in the same way that we found it for the ferromagnet. This method was described in section D of Chapter 5. The transition (or critical) temperature for an antiferromagnet is called the Néel temperature, and is frequently denoted as T_N by other authors, but we will simply continue to use T_c here.

The technique that we have presented here for an antiferromagnetic system which is divisible into two

sublattices is also useful in working with a ferromagnetic system which has two sublattices. The only change we need to make is in the matrix $E\underset{\sim}{I}-\underset{\sim}{H}_{22}$. Recall that for an anti-ferromagnet we had to be careful about the signs of the quantities $<C_g^i>$. For the ferromagnetic case these are all strictly positive. Then for a two sublattice ferro-magnet the equations for the Green functions are as in (6.27) only now the matrix $E\underset{\sim}{I}-\underset{\sim}{H}_{22}$ is the same as the matrix $E\underset{\sim}{I}-\underset{\sim}{H}_{11}$ and $\underset{\sim}{H}_{12}=\underset{\sim}{H}_{21}$, i.e. there are no sign changes in the coefficients of the quantities z_i.

7. THE RESULTS FOR SOME SPECIAL CASES

A. The Spin S=1 Ferromagnet

For S=1 we need only the operators A^1 and A^2, which are S^+ and $S^z S^+ + S^+ S^z$ respectively. Then (5.56) becomes,

$$\begin{bmatrix} E-2\bar{S}(J(0)-J(k)) & -D \\ Z_2 J(k)-D & E-2\bar{S}J(0) \end{bmatrix} \begin{bmatrix} G^1(k,E) \\ G^2(k,E) \end{bmatrix} = \frac{1}{2\pi} \begin{bmatrix} 2\bar{S} \\ Z_2 \end{bmatrix} \quad (7.1)$$

The poles of the Green functions are gotten in the usual way by equating the determinant of the coefficient matrix in (7.1) to zero, and solving for the roots of this equation. The two poles are,

$$E_1(k) = \bar{S}(2J(0)-J(k)) + (D^2-Z_2 DJ(k)+\bar{S}^2 J(k)^2)^{\frac{1}{2}}, \quad (7.2)$$

$$E_2(k) = \bar{S}(2J(0)-J(k)) - (D^2-Z_2 DJ(k)+\bar{S}^2 J(k)^2)^{\frac{1}{2}}. \quad (7.3)$$

Equations (5.63) become,

$$\langle S^- S^+ \rangle = \left(\frac{1}{N}\right) \sum_k \left\{ \frac{R_1^1(k)}{\exp(E_1(k)/\kappa T)-1} \right.$$
$$\left. + \frac{R_2^1(k)}{\exp(E_2(k)/\kappa T)-1} \right\}, \quad (7.4)$$

$$\langle S^-(S^z S^+ + S^+ S^z) \rangle = \left(\frac{1}{N}\right) \sum_k \frac{R_1^2(k)}{\exp(E_1(k)/\kappa T)-1}$$
$$+ \frac{R_2^2(k)}{\exp(E_2(k)/T)-1}. \quad (7.5)$$

where the residues are,

$$R_1^1(\underset{\sim}{k}) = (2\bar{S}E_1(\underset{\sim}{k})-4\bar{S}^2J(0)+Z_2D)/(E_1(\underset{\sim}{k})-E_2(\underset{\sim}{k})), \qquad (7.6)$$

$$R_2^1(\underset{\sim}{k}) = -(2\bar{S}E_2(\underset{\sim}{k})-4\bar{S}^2J(0)+Z_2D)/(E_1(\underset{\sim}{k})-E_2(\underset{\sim}{k})), \qquad (7.7)$$

$$R_1^2(\underset{\sim}{k}) = (Z_2E_1(\underset{\sim}{k})-2\bar{S}Z_2J(0)+2\bar{S}D)/(E_1(\underset{\sim}{k})-E_2(\underset{\sim}{k})), \qquad (7.8)$$

$$R_2^2(\underset{\sim}{k}) = -(Z_2E_2(\underset{\sim}{k})-2\bar{S}Z_2J(0)+2\bar{S}D)/(E_1(\underset{\sim}{k})-E_2(\underset{\sim}{k})). \qquad (7.9)$$

By writing out the angular momentum matrices explicitly one finds that,

$$Z_2 = 6<(S^z)^2> -4, \qquad (7.10)$$

$$<S^-S^+> = (8-\bar{S}-Z_2)/6, \qquad (7.11)$$

$$<S^-(S^zS^++S^+S^z)> = \bar{S}-Z_2/2. \qquad (7.12)$$

Then (7.4) and (7.5) become,

$$(8-6\bar{S}-Z_2)/6 = \left\langle \frac{R_1^1(\underset{\sim}{k})}{\exp(E_1(\underset{\sim}{k})/\kappa T)-1} \right.$$
$$\left. + \frac{R_2^1(\underset{\sim}{k})}{\exp(E_2(\underset{\sim}{k})/\kappa T)-1} \right\rangle_k, \qquad (7.13)$$

$$\bar{S}-Z_2/2 = \left\langle \frac{R_1^2(\underset{\sim}{k})}{\exp(E_1(\underset{\sim}{k})/\kappa T)-1} \right.$$
$$\left. + \frac{R_2^2(\underset{\sim}{k})}{\exp(E_2(\underset{\sim}{k})/\kappa T)-1} \right\rangle_k, \qquad (7.14)$$

where we have used the notation,

$$\langle \quad \rangle_{\underset{\sim}{k}} = \frac{1}{N} \sum_{\underset{\sim}{k}} \qquad (7.15)$$

For any given temperature (7.13) and (7.14) determine

$\bar{S}$ and Z_2 completely in terms of the exchange integrals

J_{fg} and the anisotropy D. Using the technique outlined

in Section D of Chapter 5, the equations that determine

T_c and Z_2 evaluated at $T=T_c$ are as follows,

$$(8 - Z_2)/6 = (Z_2/2) \left\langle \frac{D}{E_o(\underset{\sim}{k})} \coth(E_o(\underset{\sim}{k})/2\kappa T) \right\rangle_{\underset{\sim}{k}}, \qquad (7.16)$$

$$4(Z_2-2)/3Z_2^2 = \left\langle \frac{(J(\underset{\sim}{k})-2J(0)) \exp(E_o(\underset{\sim}{k})/\kappa T_c)}{\kappa T_c (\exp(E_o(\underset{\sim}{k})/\kappa T_c)-1)^2} \right\rangle_{\underset{\sim}{k}}$$

$$- \frac{1}{2} \left\langle \frac{J(\underset{\sim}{k})}{E_o(\underset{\sim}{k})} \coth(E_o(\underset{\sim}{k})/2\kappa T_c) \right\rangle_{\underset{\sim}{k}}, \qquad (7.17)$$

where $E_o(\underset{\sim}{k}) = (D^2-Z_2DJ(\underset{\sim}{k}))^{\frac{1}{2}}$.

Figures 1 and 2 contain plots of $T_c(D)/T_c(0)$ as a

function of D/J a simple cubic (SC) and a body centered

cubic (BCC) lattice respectively. We have assumed that the

exchange J is between nearest neighbors only, hence the

variable $J(0) = zJ$, where z is the number of nearest

neighbors. The Curie temperature T_c is finite for all

possible values of the ratio D/J as it is supposed to be.

At very low anisotropy our results agree very closely with

those of Lines. This is not so surprising since his tech-

nique is certainly the most sophisticated of all the

single excitation theories, and should be reasonably

accurate for small values of D/J. For extremely large

Figure 1. The ratio $T_c(D)/T_c(0)$ versus D/J for a simple cubic spin S=1 ferromagnet. (a) Narath's results. (b) Anderson and Callen's results. (c) Lines's results. (d) The results of this thesis. (e) The molecular field theory results.
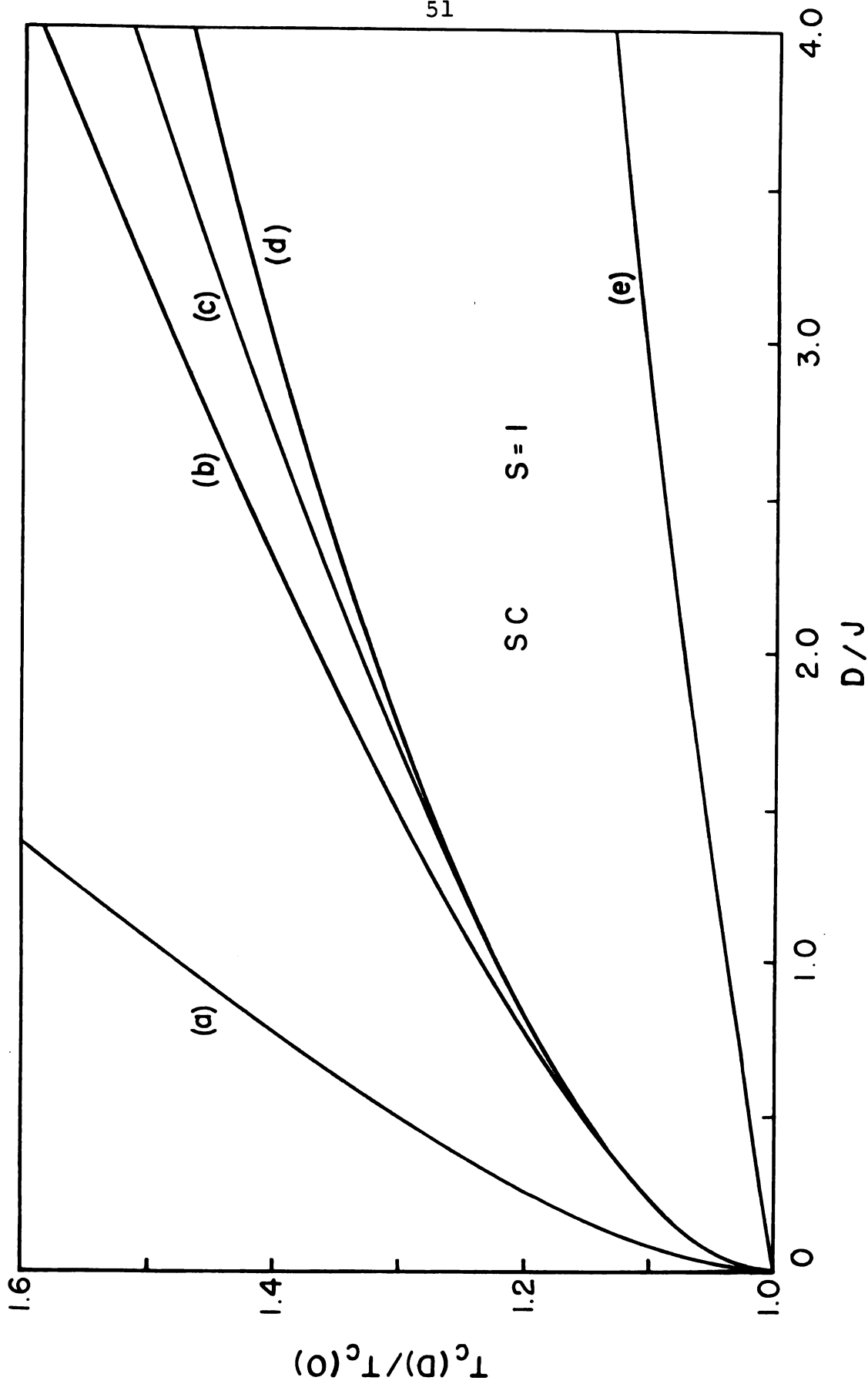
Figure 2. The ratio $T_c(D)/T_c(0)$ versus D/J for a body centered cubic spin S=1 ferromagnet. (a) Narath's results. (b) Anderson and Callen's results. (c) Lines's results. (d) The results of this thesis. (e) The molecular field theory results.
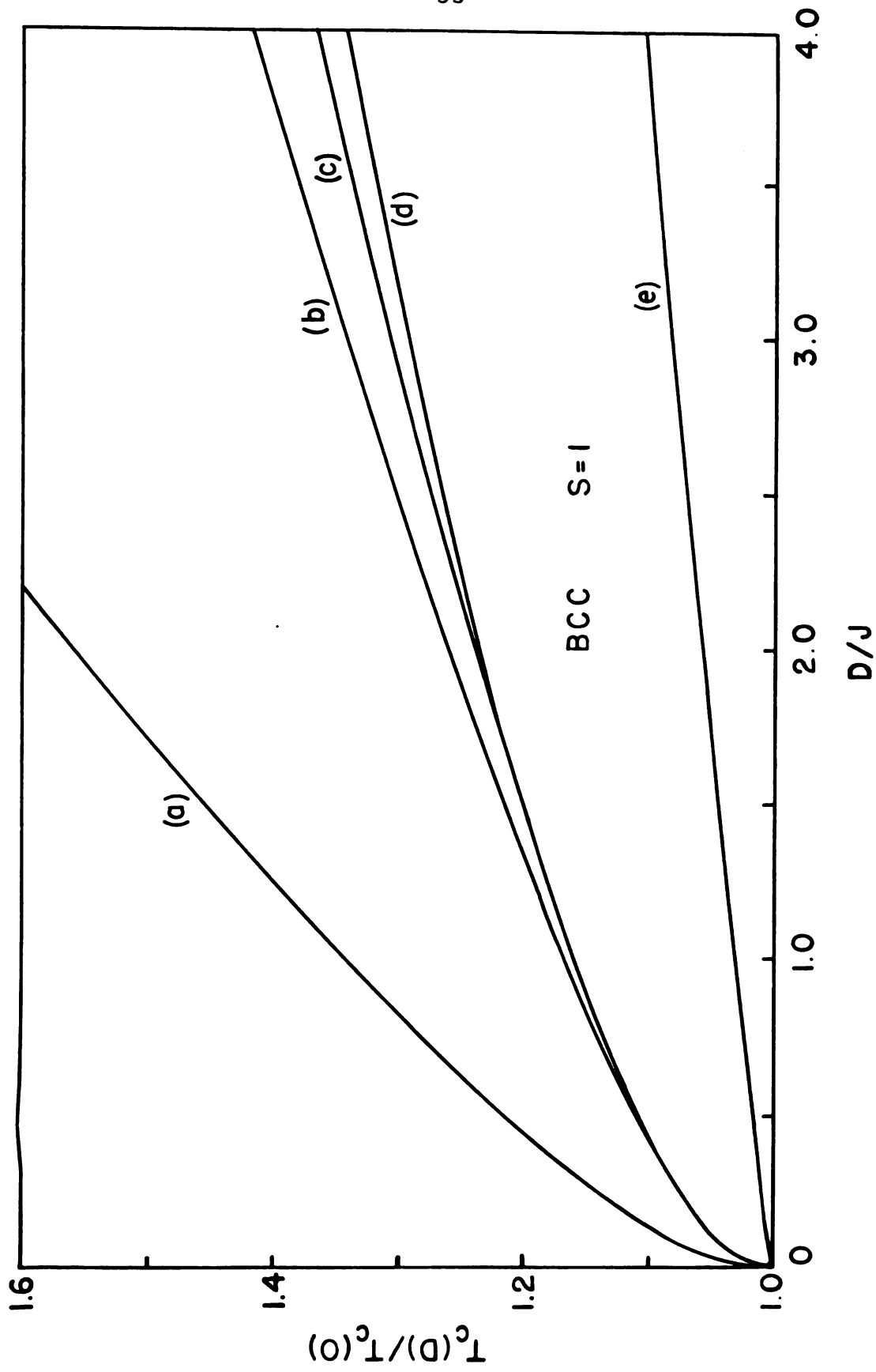
anisotropy, one may expand functions in (7.16) and (7.17)
to obtain $\kappa T_c = 2 \, J(0)$ at $D/J = \infty$. This is the same result
that the MFT gives in the limit $D/J \rightarrow \infty$. Hence for large
values of the anisotropy our RPA results approach the results
of the MFT. For each value of D/J both of our simple cubic
and body centered cubic calculations gave the same value
to Z_2 at $T = T_c$ as did the MFT. Therefore the value of
$<(S^z)^2>$ at $T = T_c$ for a given value of D/J was the same in
each of the three calculations.

Figure 3 contains plots of the sublattice magnetiza-
tion, $\bar{S}$, for a simple cubic lattice as a function of T/T_c
for three different values of D/J. Note that the larger
D/J the "squarer" the curve becomes. This is to be expect-
ed, since the larger D/J the higher one must go in tempera-
ture, i.e. closer to T_c, before the intermediate spins
states, $|S-1>$, $|S-2>,\dots,|-S+1>$, become populated enough
to reduce the ensemble average significantly. Also plot-
ted in Figure 3 is the MFT prediction of $\bar{S}$ as a function
of T/T_c. For all values of T/T_c the MFT curve lies above
our curves. This MFT curve could just as well represent
$D/J = 1.0$, 0.1, or 0.01 since the MFT does not distinguish
between these values within the linewidth we have chosen
for our graph. Hence the Green function calculation pre-
dicts greater changes in $\bar{S}$ versus T/T_c for different D/J
ratios than does the MFT. This is consistent with the
known[14] fact that the MFT underestimates the effect of
the crystal field anisotropy on all the statistical

Figure 3. The sublattice magnetization versus T/T_c for a simple cubic spin S=1 ferromagnet. Curves (a), (b), and (c) are the Green function calculations of this thesis. Curve (d) is the molecular field theory for the same three values of D/J, but in this case the three lines are indistinguishable.
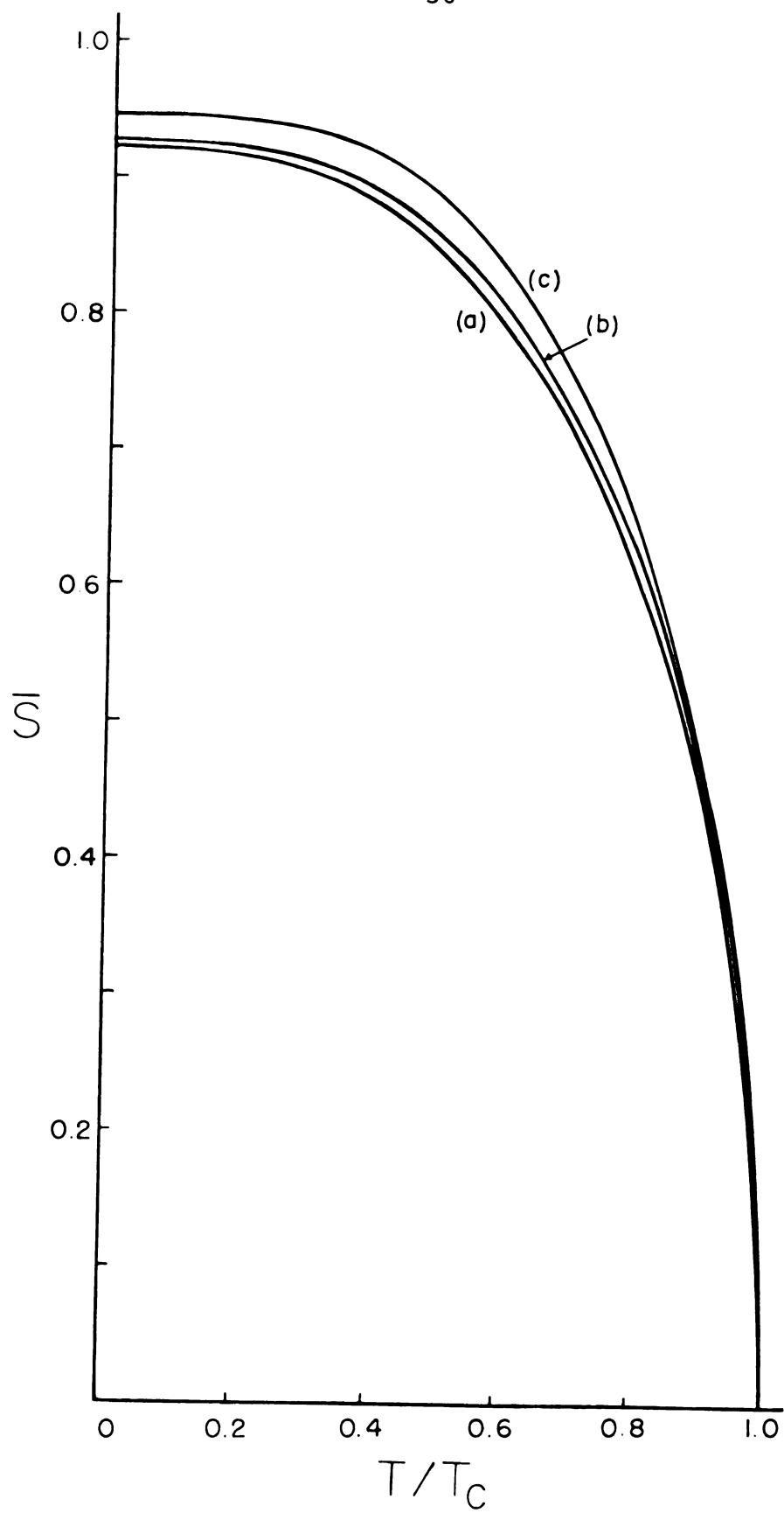
mechanical quantities.

In figure 4 we have plotted $<(S^z)^2>$ versus T/T_c for a simple cubic lattice with $D/J = 1.0$. For $T \lesssim T_c$ the Green function curve lies beneath the MFT curve, but for $T \gtrsim T_c$, the reverse is true. This behavior is typical of all values of D/J. The ensemble average $<(S^z)^2>$ is greater than the isotropic value $S(S+1)/3$ for all values of D/J. Only for $D/J = 0$ will $<(S^z)^2> = S(S+1)/3$.

B. The Spin S=1 Antiferromagnet

For an antiferromagnetic system with S=1 we consider the four Green functions $G_1^1(\underset{\sim}{k},E)$, $G_1^2(\underset{\sim}{k},E)$, $G_2^1(\underset{\sim}{k},E)$, and $G_2^2(\underset{\sim}{k},E)$. Using the formalism presented in Chapter 4, the equations of motion are,

$$
\begin{bmatrix}
E-2\bar{S}(J(0)-J_{11}(\underset{\sim}{k})) & -D & 2\bar{S}J_{21}(\underset{\sim}{k}) & 0 \\
\\
Z_2J_{11}(\underset{\sim}{k})-D & E-2\bar{S}J(0) & Z_2J_{21}(\underset{\sim}{k}) & 0 \\
\\
-2\bar{S}J_{12}(\underset{\sim}{k}) & 0 & E+2\bar{S}(J(0)-J_{11}(\underset{\sim}{k})) & -D \\
\\
Z_2J_{12}(\underset{\sim}{k}) & 0 & Z_2J_{11}(\underset{\sim}{k})-D & E+2\bar{S}J(0)
\end{bmatrix}
$$

$$
\times
\begin{bmatrix}
G_1^1(\underset{\sim}{k},E) \\
\\
G_1^2(\underset{\sim}{k},E) \\
\\
G_2^1(\underset{\sim}{k},E) \\
\\
G_2^1(\underset{\sim}{k},E)
\end{bmatrix}
= \frac{1}{2\pi}
\begin{bmatrix}
2\bar{S} \\
\\
Z_2 \\
\\
0 \\
\\
0
\end{bmatrix}
.
\tag{7.18}
$$

Figure 4. The ensemble average $\langle (S^z)^2 \rangle$ versus T/T_c for a simple cubic spin $S=1$ ferromagnet. (a) The Green function calculation of this thesis for $D/J=1.0$. (b) The molecular field theory prediction for $D/J=1.0$. Note that at $T=T_c$ the curves cross each other.
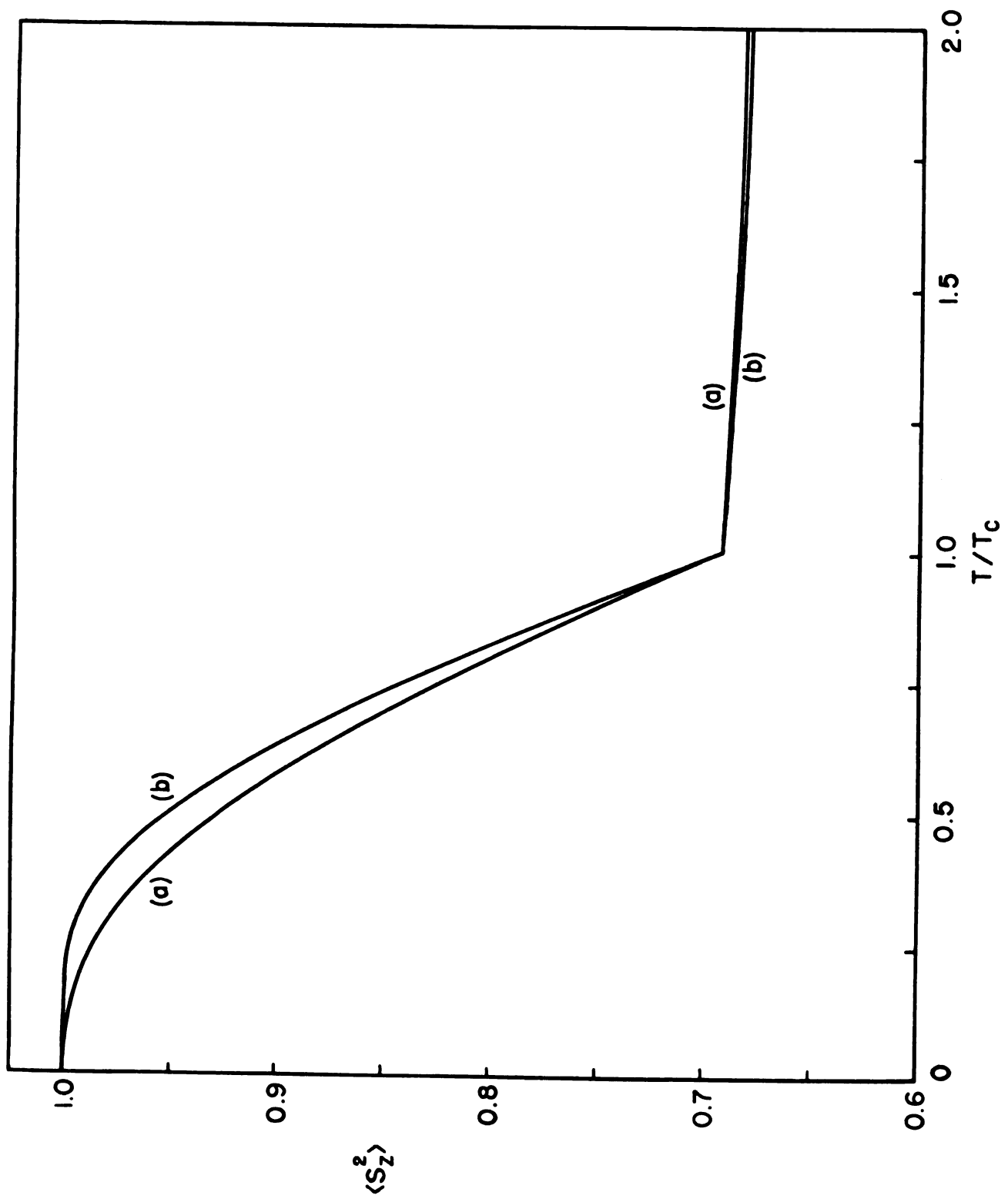
Clearly, there are four simple poles to be associated with each of the Green functions, but as we noted in the previous chapter, they come in positive and negative pairs. The two positive poles are,

$$E_1(k) = +(\alpha_1 + \alpha_2 + (4\alpha_1\alpha_2 + (\alpha_3)^2)^{\frac{1}{2}})^{\frac{1}{2}}, \qquad (7.19)$$

$$E_2(k) = +(\alpha_1 + \alpha_2 - (4\alpha_1\alpha_2 + (\alpha_3)^2)^{\frac{1}{2}})^{\frac{1}{2}}, \qquad (7.20$$

where,

$$\alpha_1 = D^2 - Z_2 D J_{11}(0) + \bar{S}^2 (J_{11}(\underset{\sim}{k}) - J_{12}(\underset{\sim}{k}))(J_{11}(\underset{\sim}{k}) + J_{12}(\underset{\sim}{k})), \qquad (7.21)$$

$$\alpha_2 = \bar{S}^2 (J_{11}(\underset{\sim}{k}) - J_{12}(\underset{\sim}{k}) - 2J(0))(J_{11}(\underset{\sim}{k}) + J_{12}(\underset{\sim}{k}) - 2J(0)), \qquad (7.22)$$

$$\alpha_3 = J_{12}(\underset{\sim}{k})(Z_2 D - 4\bar{S}^2 J(0)). \qquad (7.23)$$

In the above calculation we have assumed that we are working with a lattice which has the property that $J_{12}(\underset{\sim}{k}) = J_{21}(\underset{\sim}{k})$, i.e. the quantity $J_{12}(\underset{\sim}{k})$ is assumed to be real. This is not necessarily so for all lattices.

The form of $G_1^1(\underset{\sim}{k}, E)$ is,

$$G_1^1(\underset{\sim}{k}, E) = \frac{1}{2\pi} \left\{ \frac{R_1^1(\underset{\sim}{k})}{E - E_1(\underset{\sim}{k})} + \frac{T_1^1(\underset{\sim}{k})}{E + E_1(\underset{\sim}{k})} \right.$$
$$\left. + \frac{R_2^1(\underset{\sim}{k})}{E - E_2(\underset{\sim}{k})} + \frac{T_2^1(\underset{\sim}{k})}{E + E_2(\underset{\sim}{k})} \right\}, \qquad (7.24)$$

where we may write the residues in the form,

$$R_1^1(\underset{\sim}{k}) = (E_1^3(\underset{\sim}{k})B_1 + E_1^2(\underset{\sim}{k})B_2(\underset{\sim}{k}) + E_1(\underset{\sim}{k})B_3(\underset{\sim}{k})$$

$$+ B_4(\underset{\sim}{k}))/(2E_1(\underset{\sim}{k})(E_1^2(\underset{\sim}{k}) - E_2^2(\underset{\sim}{k}))), \qquad (7.25)$$

$$R_2^1(\underset{\sim}{k}) = -(E_2^3(\underset{\sim}{k})B_1 + E_2^2(\underset{\sim}{k})B_2(\underset{\sim}{k}) + E_2(\underset{\sim}{k})B_3(\underset{\sim}{k})$$

$$+ B_4(\underset{\sim}{k}))/(2E_2(\underset{\sim}{k})(E_1^2(\underset{\sim}{k}) - E_2^2(\underset{\sim}{k}))), \qquad (7.26)$$

$$T_1^1(\underset{\sim}{k}) = (E_1^3(\underset{\sim}{k})B_1 - E_1^2(\underset{\sim}{k})B_2(\underset{\sim}{k}) + E_1(\underset{\sim}{k})B_3(\underset{\sim}{k})$$

$$+ B_4(\underset{\sim}{k}))/(2E_1(\underset{\sim}{k})(E_1^2(\underset{\sim}{k}) - E_2^2(\underset{\sim}{k}))), \qquad (7.27)$$

$$T_2^1(\underset{\sim}{k}) = -(E_2^3(\underset{\sim}{k})B_1 - E_2^2(\underset{\sim}{k})B_2(\underset{\sim}{k}) + E_2(\underset{\sim}{k})B_3(\underset{\sim}{k})$$

$$+ B_4(\underset{\sim}{k}))/(2E_2(\underset{\sim}{k})(E_1^2(\underset{\sim}{k}) - E_2^2(\underset{\sim}{k}))), \qquad (7.28)$$

where,

$$B_1 = 2\bar{S}, \qquad (7.29)$$

$$B_2(\underset{\sim}{k}) = Z_2D + 4\bar{S}^2(J(0) - J_{11}(\underset{\sim}{k})), \qquad (7.30)$$

$$B_3(\underset{\sim}{k}) = 4\bar{S}Z_2DJ(0) - 16\bar{S}^3J^2(0) - 2\bar{S}D^2, \qquad (7.31)$$

$$B_4(\underset{\sim}{k}) = Z_2^2D^2J_{11}(\underset{\sim}{k}) + 4\bar{S}^2Z_2DJ(0)(J(0) - 2J_{11}(\underset{\sim}{k}))$$

$$- 4\bar{S}^2J(0)D^2 - Z_2D^3 - 16\bar{S}^4J^2(0)(J(0) - J_{11}(\underset{\sim}{k})). \qquad (7.32)$$

Similarly, one has for $G_1^2(\underset{\sim}{k},E)$ the expression,

$$G_1^2(\underset{\sim}{k},E) = \frac{1}{2\pi}\left\{\frac{R_1^2(\underset{\sim}{k})}{E-E_1(\underset{\sim}{k})} + \frac{T_1^2(\underset{\sim}{k})}{E+E_1(\underset{\sim}{k})}\right.$$

$$\left. + \frac{R_2^2(\underset{\sim}{k})}{E-E_2(\underset{\sim}{k})} + \frac{T_2^2(\underset{\sim}{k})}{E+E_2(\underset{\sim}{k})}\right\}, \tag{7.33}$$

where the residues are of the form,

$$R_1^2(\underset{\sim}{k}) = (E_1^3(\underset{\sim}{k})C_1+E_1^2(\underset{\sim}{k})C_2(\underset{\sim}{k})+E_1(\underset{\sim}{k})C_3(\underset{\sim}{k})$$

$$+ C_4(\underset{\sim}{k}))/(2E_1(\underset{\sim}{k})(E_1^2(\underset{\sim}{k})-E_2^2(\underset{\sim}{k}))), \tag{7.34}$$

$$R_2^2(\underset{\sim}{k}) = -(E_2^3(\underset{\sim}{k})C_1+E_2^2(\underset{\sim}{k})C_2(\underset{\sim}{k})+E_2(\underset{\sim}{k})C_3(\underset{\sim}{k})$$

$$+ C_4(\underset{\sim}{k}))/(2E_2(\underset{\sim}{k})(E_1^2(\underset{\sim}{k})-E_2^2(\underset{\sim}{k}))), \tag{7.35}$$

$$T_1^2(\underset{\sim}{k}) = (E_1^3(\underset{\sim}{k})C_1+E_1^2(\underset{\sim}{k})C_2(\underset{\sim}{k})+E_1(\underset{\sim}{k})C_3(\underset{\sim}{k})$$

$$+ C_4(\underset{\sim}{k}))/(2E_1(\underset{\sim}{k})(E_1^2(\underset{\sim}{k})-E_2^2(\underset{\sim}{k}))), \tag{7.36}$$

$$T_2^2(\underset{\sim}{k}) = -(E_2^3(\underset{\sim}{k})C_1+E_2^2(\underset{\sim}{k})C_2(\underset{\sim}{k})+E_2(\underset{\sim}{k})C_3(\underset{\sim}{k})$$

$$+ C_4(\underset{\sim}{k}))/(2E_2(\underset{\sim}{k})(E_1^2(\underset{\sim}{k})-E_2^2(\underset{\sim}{k}))), \tag{7.37}$$

where,

$$C_1 = Z_2, \tag{7.38}$$

$$C_2(\underset{\sim}{k}) = 2\bar{S}D - 2\bar{S}(J(0)-J_{11}(\underset{\sim}{k})), \tag{7.39}$$

$$C_3(\underset{\sim}{k}) = -Z_2D^2+Z_2^2DJ_{11}(\underset{\sim}{k})-4\bar{S}^2(J(0)-J_{11}(\underset{\sim}{k}))(Z_2(J(0)$$

$$+ J_{11}(\underset{\sim}{k}))-D), \tag{7.40}$$

$$C_4(\underset{\sim}{k}) = -2\bar{S}Z_2^2DJ_{11}^2(\underset{\sim}{k}) - 2\bar{S}D^3 + 4\bar{S}Z_2D^2J_{11}(\underset{\sim}{k}) - 2\bar{S}D(J(0)$$

$$-J_{11}(\underset{\sim}{k}))(Z_2J_{11}(\underset{\sim}{k})) + 8\bar{S}^3J(0)(J(0) - J_{11}(\underset{\sim}{k}))(Z_2J(0) - D).$$

$$(7.41)$$

Then using the corollary to the Spectral Theorem, (7.24), (7.33), and (7.10)-(7.12), we have,

$$(8 - \bar{S} - Z_2)/6 = \left\langle \frac{R_1^1(\underset{\sim}{k})}{\exp(E_1(\underset{\sim}{k})/\kappa T) - 1} + \frac{T_1^1(\underset{\sim}{k})}{\exp(-E_1(\underset{\sim}{k})/\kappa T) - 1} \right.$$

$$\left. + \frac{R_2^1(\underset{\sim}{k})}{\exp(E_2(\underset{\sim}{k})/\kappa T) - 1} + \frac{R_2^1(\underset{\sim}{k})}{\exp(-E_2(\underset{\sim}{k})/\kappa T) - 1} \right\rangle_{\underset{\sim}{k}},$$

$$(7.42)$$

$$\bar{S} - Z_2/2 = \left\langle \frac{R_1^2(\underset{\sim}{k})}{\exp(E_1(\underset{\sim}{k})/\kappa T) - 1} + \frac{T_1^2(\underset{\sim}{k})}{\exp(-E_1(\underset{\sim}{k})/\kappa T) - 1} \right.$$

$$\left. + \frac{R_2^2(\underset{\sim}{k})}{\exp(E_2(\underset{\sim}{k})/\kappa T) - 1} + \frac{T_2^2(\underset{\sim}{k})}{\exp(-E_2(\underset{\sim}{k})/\kappa T) - 1} \right\rangle_{\underset{\sim}{k}}.$$

$$(7.43)$$

The above two equations are ones that determine $\bar{S}$ and Z_2 for all temperatures as a function of D and the J_{fg}.

Using the technique outlined in Section D of Chapter 5, we obtain the following two equations which determine the Néel temperature, T_c, and Z_2 evaluated at $T = T_c$,

$$(8 - Z_2)/6 = \left\langle \frac{Z_2D}{2E_o(\underset{\sim}{k})} \coth(E_o(\underset{\sim}{k})/2\kappa T_c) \right.$$

$$\left. + \frac{Z_2D}{2E_{oo}(\underset{\sim}{k})} \coth(E_{oo}(\underset{\sim}{k})/2\kappa T_c) \right\rangle_{\underset{\sim}{k}},$$

$$(7.44)$$

$$8(Z_2-2)/3Z_2^2 = \langle F_1(\underset{\sim}{k})\ coth(E_0(\underset{\sim}{k})/2\kappa T_c)$$

$$+ F_2(\underset{\sim}{k})\ coth(E_{00}(\underset{\sim}{k})/2\kappa T_c)\rangle_{\underset{\sim}{k}},\qquad (7.45)$$

where,

$$F_1(\underset{\sim}{k}) = \frac{(2J(0)-J_{11}(\underset{\sim}{k}))(D^2-Z_2DJ_{11}(\underset{\sim}{k}))+Z_2DJ_{12}(\underset{\sim}{k})(J(0)-J_{11}(\underset{\sim}{k}))}{Z_2DJ_{12}(\underset{\sim}{k})E_0(\underset{\sim}{k})},$$

$$(7.46)$$

$$F_2(\underset{\sim}{k}) = \frac{-(2J(0)-J_{11}(\underset{\sim}{k}))(D^2-Z_2DJ_{11}(\underset{\sim}{k}))-Z_2DJ_{12}(\underset{\sim}{k})(J(0)-J_{11}(\underset{\sim}{k}))}{Z_2DJ_{12}(\underset{\sim}{k})E_{00}(\underset{\sim}{k})},$$

$$(7.47)$$

$$E_0(\underset{\sim}{k}) = (D^2-Z_2D(J_{11}(\underset{\sim}{k})-J_{12}(\underset{\sim}{k})))^{\frac{1}{2}}, \qquad (7.48)$$

$$E_{00}(\underset{\sim}{k}) = (D^2-Z_2D(J_{11}(\underset{\sim}{k})+J_{12}(\underset{\sim}{k})))^{\frac{1}{2}}. \qquad (7.49)$$

Solutions of (7.44) and (7.45) have been obtained for simple cubic and body centered cubic lattices assuming only nearest neighbor exchange. The numerical results obtained for the Néel temperature T_c are equal to the results obtained for the Curie temperature of a ferromagnetic system under the same conditions. A priori there is no reason to expect that the Curie temperature should be equal to the Néel temperature for equivalent systems. For systems which have no crystal field anisotropy, Rushbrook and Wood[16] obtained a larger transition temperature for the antiferromagnet than for the ferromagnet. The RPA, though, does predict rigorously the equivalence

of the transition temperatures in the case of D=0. For our calculation it is not easy to see at first that the temperatures are equal; it is only after the lengthy computer calculations that we find this out. Evidently, the decoupling of (5.28)-(5.30) neglects the fine distinction between antiferromagnetic ordering and ferromagnetic ordering in the region of the phase transition. The ensemble averages $<(S^z)^2>$ also agree with the predictions obtained in the ferromagnetic case for each value of D/J.

Figure 5 shows $\bar{S}$ versus T/T_c for the same three values of D/J as we used in Figure 3, which is the same plot but only for a ferromagnetic system. This curve is quite different than the one for the ferromagnet, especially at low temperatures. The sublattice magnetization, $\bar{S}$, does not reach its full value of unity for any of the D/J ratios, whereas in the ferromagnetic case $\bar{S}=1$ at T=0 for all values of D/J. Our results are consistent with the antiferromagnetic spin wave results[17] in that they both have $\bar{S}$ less than unity, even at T=0. For larger values of D/J the value of $\bar{S}$ at T=0 is larger, and only for D/J = ∞ will $\bar{S}=1$.

The average $<(S^z)^2>$ is plotted in Figure 6, versus T/T_c, and it possesses the same characteristics as the sublattice magnetization curve. For T=0, the average $<(S^z)^2>$ does not approach its ferromagnetic value of unity, but some other value, which is slightly less than unity. The larger D/J is, the larger the T=0 value of

Figure 5. The sublattice magnetization versus T/T_c

for a simple cubic spin S=1 antiferromagnet.

(a) D/J=0.01. (b) D/J=0.1. (c) D/J=1.0.

Figure 6. The ensemble average $\langle (S^z)^2 \rangle$ versus T/T_c for a simple cubic spin $S=1$ antiferromagnet. (a) $D/J = 0.01$. (b) $D/J = 0.1$. (c) $D/J = 1.0$.
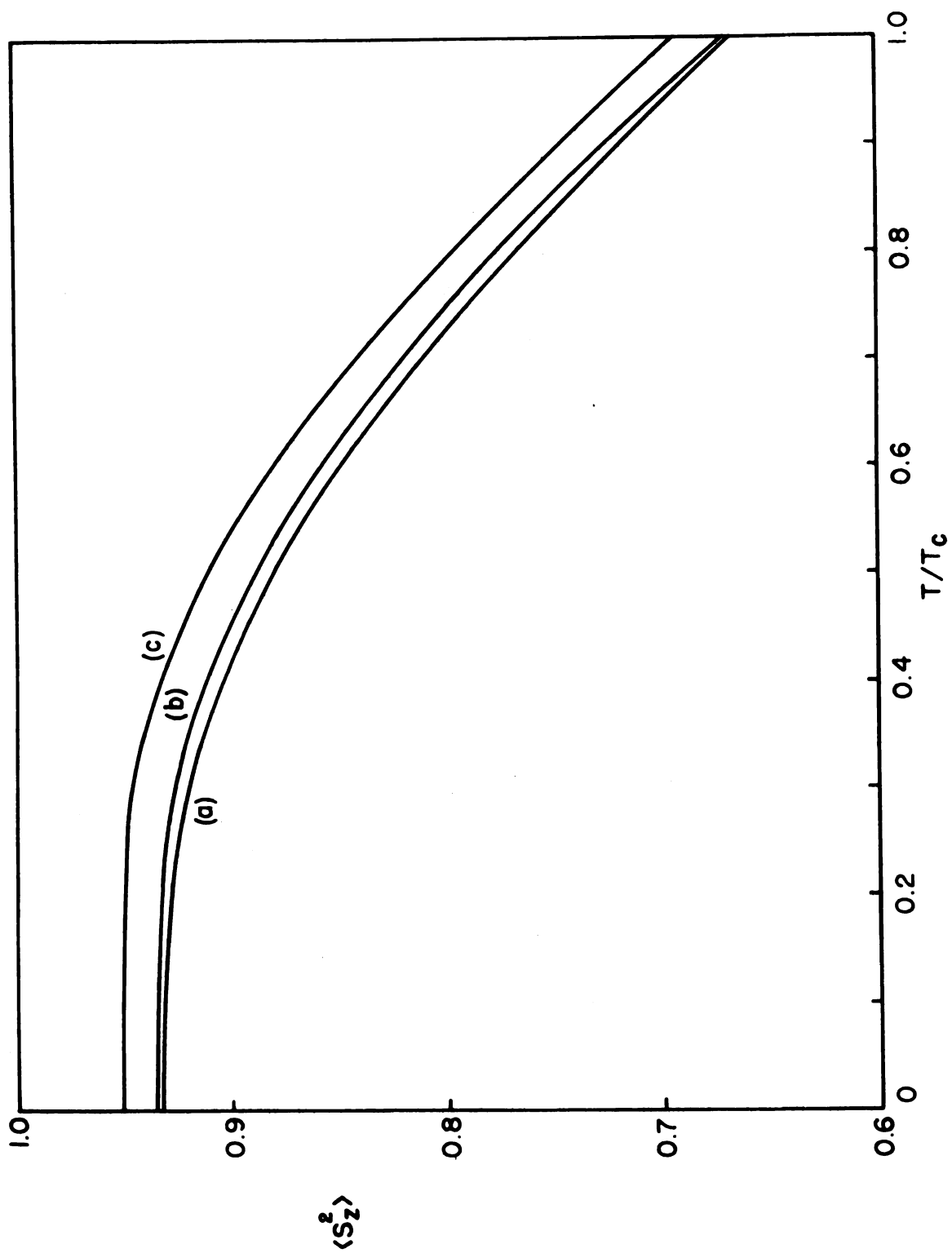
$<(S^z)^2>$. The results for $T \geq T_c$ are the same for the average $<(S^z)^2>$ in the antiferromagnetic case as for the ferromagnetic case which we have plotted in Figure 4.

C. The Spin S=3/2 Ferromagnet

For a spin S=3/2 the equations (5.56) become,

$$\begin{vmatrix} E-2\bar{S}(J(0)-J(\underset{\sim}{k})) & -D & 0 \\ Z_2 J(\underset{\sim}{k}) & E-2\bar{S}J(0) & -D \\ Z_3 J(\underset{\sim}{k}) & -4D & E-2\bar{S}J(0) \end{vmatrix} \begin{vmatrix} G^1(\underset{\sim}{k},E) \\ G^2(\underset{\sim}{k},E) \\ G^3(\underset{\sim}{k},E) \end{vmatrix} = \frac{1}{2\pi} \begin{vmatrix} 2\bar{S} \\ Z_2 \\ Z_3 \end{vmatrix}.$$

$$(7.50)$$

The poles of these Green functions are located at,

$$E_1(\underset{\sim}{k}) = A + 2(B/3)^{\frac{1}{2}} \cos(\Omega/3), \qquad (7.51)$$

$$E_2(\underset{\sim}{k}) = A + 2(B/3)^{\frac{1}{2}} \cos(\Omega/3 + 2\pi/3), \qquad (7.52)$$

$$E_3(\underset{\sim}{k}) = A + 2(B/3)^{\frac{1}{2}} \cos(\Omega/3 + 4\pi/3), \qquad (7.53)$$

where,

$$A = 2\bar{S}(J(0)-J(\underset{\sim}{k})/3), \qquad (7.54)$$

$$B = 4D^2 - Z_2 DJ(\underset{\sim}{k}) + 4\bar{S}^2 J^2(\underset{\sim}{k})/3, \qquad (7.55)$$

$$C = 2Z_2\bar{S}DJ^2(\underset{\sim}{k})/3 + 16\bar{S}D^2 J(\underset{\sim}{k})/3$$

$$- Z_2 D^2 J(\underset{\sim}{k}) - 16\bar{S}^3 J^3(\underset{\sim}{k})/27, \qquad (7.56)$$

$$\cos \Omega = (3C/2B)(3/B)^{\frac{1}{2}}. \qquad (7.57)$$

The residue $R_m^i(\underset{\sim}{k})$ of the m th pole of the i th Green

function is of the form,

$$R_1^i(\underset{\sim}{k}) = (E_3(\underset{\sim}{k})-E_2(\underset{\sim}{k}))(C_1^i E_1^2(\underset{\sim}{k})+C_2^i E_1(\underset{\sim}{k})+C_3^i)/C_4,$$

$$(7.58)$$

$$R_2^i(\underset{\sim}{k}) = (E_1(\underset{\sim}{k})-E_3(\underset{\sim}{k}))(C_1^i E_2^2(\underset{\sim}{k})+C_2^i E_2(\underset{\sim}{k})+C_3^i)/C_4,$$

$$(7.59)$$

$$R_3^i(\underset{\sim}{k}) = (E_2(\underset{\sim}{k})-E_1(\underset{\sim}{k}))(C_1^i E_3^2(\underset{\sim}{k})+C_2^i E_3(\underset{\sim}{k})+C_3^i)/C_4,$$

$$(7.60)$$

where,

$$C_4 = 2B(B)^{\frac{1}{2}} \sin \Omega, \qquad (7.61)$$

$$C_1^1 = 2\bar{S}, \qquad (7.62)$$

$$C_2^1 = -8\bar{S}^2 J(0) + Z_2 D, \qquad (7.63)$$

$$C_3^1 = 2\bar{S}(4\bar{S}^2 J^2(0)-4D^2)-2\bar{S}Z_2 DJ(0)+Z_3 D^2, \qquad (7.64)$$

$$C_1^2 = Z_2, \qquad (7.65)$$

$$C_2^2 = -4\bar{S}Z_2 J(0)+Z_3 D, \qquad (7.66)$$

$$C_3^2 = 4\bar{S}^2 Z_2 J^2(0)-2\bar{S}Z_3 DJ(0), \qquad (7.67)$$

$$C_1^3 = Z_3, \qquad (7.68)$$

$$C_2^3 = 4Z_2 D-4\bar{S}Z_3 J(0), \qquad (7.69)$$

$$C_3^3 = -8\bar{S}Z_2 DJ(0)+4\bar{S}^2 Z_3 J^2(0). \qquad (7.70)$$

Using the technique outlined in section D of Chapter 5 the equations which determine T_c are,

$$T_c = (4 - 2Z_2/3)/<F(\underset{\sim}{k})>_{\underset{\sim}{k}} \, , \tag{7.71}$$

$$6 = 2Z_2 \left\langle \frac{D}{E_o(\underset{\sim}{k})} \coth(E_o(\underset{\sim}{k})/2\kappa T_c) \right\rangle_{\underset{\sim}{k}} + \kappa T_c \left\langle H(\underset{\sim}{k}) \right\rangle_{\underset{\sim}{k}} , \tag{7.72}$$

$$3 - \beta_1/8 = \left\langle M(\underset{\sim}{k}) \coth(E_o(\underset{\sim}{k})/\kappa T_c) \right\rangle_{\underset{\sim}{k}}$$

$$- \left\langle \frac{Z_2 N(\underset{\sim}{k}) \exp(E_o(\underset{\sim}{k})/\kappa T)}{\kappa T_c E_o^2(\underset{\sim}{k})(\exp(E_o(\underset{\sim}{k})/\kappa T)-1)^2)} \right\rangle_{\underset{\sim}{k}}$$

$$- \left\langle (T_c/E_o^2(\underset{\sim}{k}))(Z_2 L(\underset{\sim}{k}) - 4Z_2 J(0) + \beta_1 D \right.$$

$$\left. + (4Z_2 J^2(0) - 2\beta_1 DJ(0))/L(\underset{\sim}{k})) \right\rangle_{\underset{\sim}{k}} , \tag{7.73}$$

where,

$$F(\underset{\sim}{k}) = 4(8-\beta_1)D^2/(2(J(0)-J(\underset{\sim}{k}))(4D^2 - Z_2 DJ(\underset{\sim}{k}))$$

$$- 2Z_2 DJ^2(\underset{\sim}{k}) + \beta_1 D^2 J(\underset{\sim}{k})) , \tag{7.74}$$

$$H(\underset{\sim}{k}) = (4Z_2 D^3 J(\underset{\sim}{k})(8-\beta_1)/E_o^2(\underset{\sim}{k}))(2(J(0)$$

$$- J(\underset{\sim}{k}))(4D^2 - Z_2 DJ(\underset{\sim}{k})) - 2Z_2 DJ^2(\underset{\sim}{k}) + {}_1 D^2 J(\underset{\sim}{k})) , \tag{7.75}$$

$$M(\underset{\sim}{k}) = D(Z_2 J(\underset{\sim}{k}) - 8D)(Z_2 J(\underset{\sim}{k}) - \beta_1 D/2)/(2E_o^3(\underset{\sim}{k})) , \tag{7.76}$$

$$N(\underset{\sim}{k}) = 16D^2 J(0) - 4Z_2 DJ(0)J(\underset{\sim}{k}) + 2Z_2 DJ^2(\underset{\sim}{k}) - \beta_1 D^2 J(\underset{\sim}{k}) , \tag{7.77}$$

$$L(\underset{\sim}{k}) = (2(J(0)-J(\underset{\sim}{k}))(4D^2 - Z_2 DJ(\underset{\sim}{k})) - 2Z_2 DJ^2(\underset{\sim}{k})$$

$$+ \beta_1 D^2 J(\underset{\sim}{k}))/E_o^2(\underset{\sim}{k}) , \tag{7.78}$$

$$E_o(\underset{\sim}{k}) = (4D^2 - Z_2 D J(\underset{\sim}{k}))^{\frac{1}{2}}, \tag{7.79}$$

$$\beta_1 = \underset{\bar{S}\to 0}{\text{Lim}} (Z_3/\bar{S}). \tag{7.80}$$

We have solved these equations numerically for a simple cubic lattice. The results are plotted in Figure 7. As with the spin S=1 ferromagnet, our results closely approximate Lines's results for small anisotropy. For large anisotropy the value of κT_c approaches the value predicted by the MFT which is $9J(0)/2$. The values of Z_2 and β_1 at T_c agree with the MFT values for each value of the ratio D/J, just as they did for the S=1 case.

Figure 7. The ratio $T_c(D)/T_c(0)$ versus D/J for a simple cubic spin S=3/2 ferromagnet. (a) Narath's results. (b) Anderson and Callen's results. (c) Lines's results. (d) The results of this thesis. (e) The molecular field theory results.
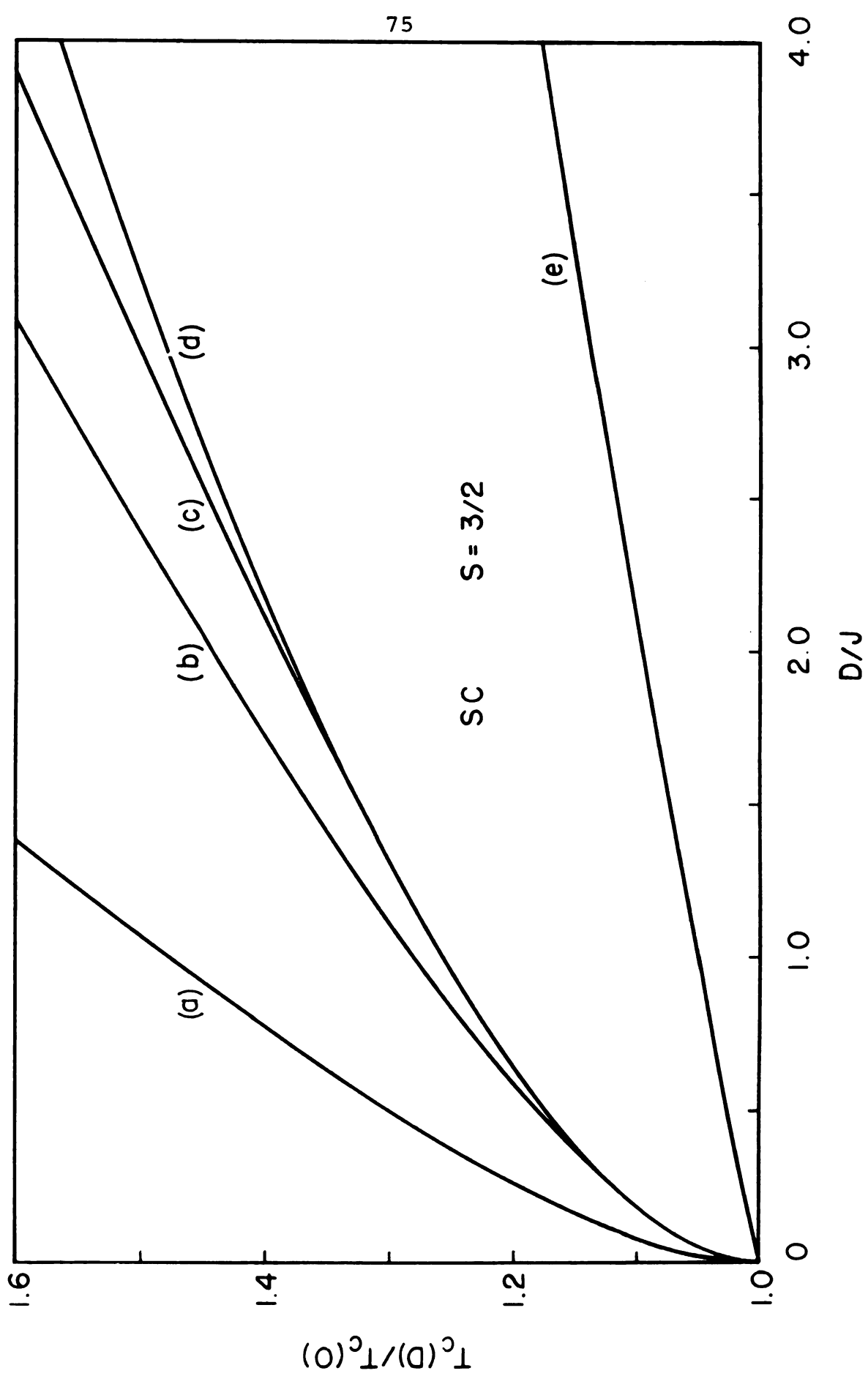
8. SUMMARY AND CONCLUSIONS

We have demonstrated two significant ideas concerning the RPA decoupling of a magnetically ordered system which contains crystal field anisotropy.

First in Chapter 5 we presented a convenient set of spin operators which are appropriate for the solving of a system of non-interacting spins in a crystalline field environment. The inclusion of exchange coupling into the Hamiltonian then introduced higher order Green functions corresponding to the increased complexity of the system. These higher order functions, though, were only higher order _exchange_ Green functions, and not higher order anisotropy Green functions. Hence, unlike previous authors[7,8,13] we never had to approximate any of the anisotropy functions. The problem then was reduced to the decoupling of the exchange Green functions.

Second we found a decoupling approximation which is appropriate for each of the exchange Green functions, and which reproduced completely the results of the usual RPA for $D=0$. Therefore, we have successfully obtained results from a system which contains crystal field anisotropy within the confines of the RPA. We have demonstrated that this technique is valid for any size spin system,

and also for antiferromagnetic as well as ferromagnetic lattices.

The decoupling scheme we have presented here does remarkably well in comparison with the earlier theories on this subject. The transition temperature $T_c(D)$ as a function of the crystal field parameter D is finite for all values of D. Our particular RPA decoupling shows that T_c depends more strongly on D, for low anisotropy, than does the MFT. For anisotropies of the order of the exchange, J, or smaller our results are equivalent to those of Lines. At the transition temperature the moments of S^z as predicted by our RPA calculation and as predicted by the MFT are the same. The temperature dependence of the moments, below T_c, shows a greater variation with changes in D/J than does the MFT prediction. For very large anisotropies our results approach those of the MFT, and at $D/J = \infty$ both theories agree exactly. This is to be contrasted with the earlier single excitation schemes which all predict $T_c = \infty$ at $D/J = \infty$.

In Chapter 7 we presented the numerical solutions for a spin S=1 ferromagnetic, a spin S=1 antiferromagnet, and a spin S=3/2 ferromagnet. At the present time there is no insulating magnetic salt with S=1, or 3/2 for which the parameters D and J are known accurately. Therefore, there is no way to directly check our calculations with experiments. Then, at best, the calculations presented here can only infer one or the other of the parameters

by using the known value of T_c. It is generally not possible to infer these parameters from the sublattice magnetization curves since large changes in D really produce relatively small changes in $\bar{S}(T)$.

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APPENDIX A

APPENDIX A

COMMENTS ON MURAO AND MATSUBARA'S

DECOUPLING APPROXIMATIONS

Murao and Matsubara[18] attempted to solve the spin
S=1 ferromagnet by a technique similar to ours. Their
results, however, are unsatisfactory in a number of import-
ant respects. First, they predict a ratio of $T_c(D)/T_c(0)$
which is smaller than the MFT prediction for each value of
D. Since the MFT is known[14] to underestimate the effect
of the crystal field anisotropy, especially when D is
small, Murao and Matsubara's results are an even further
underestimation. Second, when D is set equal to zero
their results do not reduce to the RPA, but to the MFT.
Both of these defects in their theory resulted from the
particular Green functions they chose to decouple.

For the operators that appear on the left hand side
of the Green function, they chose $S_g^+ = A_g^1$ and A_g^2, just as
we had. In our problem we had fixed the operator on the
right hand side of the Green function to be S_h^-. Murao
and Matsubara chose the adjoints of the operators A_h^1 and
A_h^2 to be inserted on the right hand side of the Green
function. Hence they obtained twice as many equations

of motion as we did because they not only had our set of
equations but also the set of equations with S_h^- replaced
by the adjoint of A_h^2. Two of their four equations
turned out to be equivalent, leaving three independent
equations to be decoupled. But they therefore over-
determined the problem as only two moments were unknown.
Their resolution of this overdeterminancy was to drop
the one equation which they felt, for heuristic reasons,
neglected the important correlations. The remaining
two equations produced the inadequacies mentioned above.

Murao and Matsubara's generation of too many equa-
tions of motion points out an important fact about the
decoupling of Green function equations. Suppose we wish
to approximate a Green function of the form,

$$<< A\ B;\ C >>,\qquad\qquad (A.1)$$

where A, B, and C are spin operators. If A is the only
spin operator with a finite ensemble average, and if
one believes A and B to be relatively uncorrelated,
then one is tempted to try the following,

$$<< A\ B;\ C >> = <A><<B;\ C>>.\qquad\qquad (A.2)$$

The question now is whether this is automatically a
valid thing to do for all possibilities for the operator
C. The point we wish to make here is that (A.2) could
be a very good approximation for some choices of the
operator C, and quite bad for some other choices for C.

Since Murao and Matsubara performed approximations of
the form of (A.2) for <u>two</u> different choices for C, they
had no guarantee that both would be equally valid approx-
imations. Clearly their two choices were mutually con-
flicting, since they did obtain thermodynamic incon-
sistencies.

All of the approximations that we made in (5.28)-
(5.30) are internally consistent with each other since
we have only made the single choice of S_h^- for the oper-
ator C. This fact alone does not insure that we have
decoupled correctly, it only says that we have been con-
sistent. The final justification for the choice $C=S_h^-$
is that it does give physically meaningful results.

APPENDIX B

APPENDIX B

THE WAVEVECTOR SUMS

All of the wavevector sums $\langle \rangle_k$ were performed by
replacing the sum by an integral,

$$\langle \rangle_{\underset{\sim}{k}} = \frac{1}{N} \sum_{\underset{\sim}{k}} \rightarrow \frac{1}{v_{\underset{\sim}{k}}} \underset{\text{1st Zone}}{\int\int\int} dk_x dk_y dk_z, \qquad (B.1)$$

where N is the number of points in the first zone and
$v_{\underset{\sim}{k}}$ is the volume of the first zone. For the antiferro-
magnet, the zone referred to here is the first zone of
the <u>sublattice</u>. The replacement in (B.1) is valid
since N is of the order of Avagadro's Number.

The variable $\underset{\sim}{k}$ appears in all the sums as the argu-
ment of the Fourier transform of the exchange integrals,
$J(\underset{\sim}{k})$, and nowhere else. For a simple cubic lattice with
nearest neighbor exchange only, $J(\underset{\sim}{k})$ is as follows:

$$J(\underset{\sim}{k}) = J(0)(\cos(k_x) + \cos(k_y) + \cos(k_z))/3, \qquad (B.2)$$

where we have chosen the lattice parameter a=1 for con-
venience. For a body centered cubic lattice with nearest
neighbor exchange only, $J(\underset{\sim}{k})$ is,

$$J(\underset{\sim}{k}) = J(0) \cos(k_x) \cos(k_y) \cos(k_z), \qquad (B.3)$$

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where we have chosen the lattice parameter, for this lattice, to be a=2, for convenience. For an antiferromagnet, $J_{12}(k)=J(k)$, and $J_{11}(k) = 0$, since neighbors on the same sublattice are really next nearest neighbors.

The functions defined in (B.2) and (B.3) both have cubic symmetry, that is, they are both invariant under the 48 crystallographic operations of a cube. Since $\underset{\sim}{k}$ appears only in the functions $J(\underset{\sim}{k})$, the integrands themselves are invariant under the 48 operations of the cube. Therefore we need not perform the integrals over the whole zone, but simply over an appropriate 1/48 of it. The boundaries of the regions of integration and the volumes, v_k, of the regions of integration we used are as follows:

Simple Cubic Ferromagnet,

     Boundaries: $k_z = 0$, $k_x=k_y$, $k_y=k_z$, $k_x=\pi$,

     Volume: $v_k = \pi^3/6$,

Simple Cubic Antiferromagnet (sublattice is a face

           centered cubic lattice),

     Boundaries: $k_z=0$, $k_x=k_y$, $k_y=k_z$, $k_x+k_y+k_z=3\pi/2$, $k_x=\pi$,

     Volume: $v_k=\pi^3/12$,

Body Centered Cubic Ferromagnet,

     Boundaries: $k_z=0$, $k_x=k_y$, $k_y=k_z$, $k_x=\pi-k_y$,

     Volume: $v_k=\pi^3/24$,

Body Centered Cubic Antiferromagnet (sublattice is a

     simple cubic lattice),

    Boundaries: $k_z=0$, $k_x=k_y$, $k_y=k_z$, $k_x=\pi/2$,

    Volume: $v_k=\pi^3/48$.

The integrals were performed on a CDC 6500 high speed computer, using Hetherington's[19] integration routine ANCR. This routine determines the integral by fitting the function with appropriate Newton-Cotes[20] quadratures. The particular choice of quadratures depends on the desired error and the variations of the function over the interval of integration. Four place accuracy was generally obtained with approximately a 2000 point mesh, though this figure varied greatly depending on the particular integrand. Calculation time for each integral was of the order of one second.