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THE HEISENBERG PARAMAGNET

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THE HEISENBERG PARAMAGNET

Approved:

_____
Harold A. Gersch, Chairman

_____
Stephen Spooner

_____
James M. Tanner

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SUMMARY

The Heisenberg paramagnet in one, two, and three dimensions is analyzed by a second order Green's function theory similar to that used by Knapp and ter Haar. This theory which incorporates the exact values for the zero, first, and second moments of the relaxation function as boundary conditions yields results satisfying the rotational symmetry of the paramagnetic region as well as the principle of detailed balance. Predictions obtained for equal time properties in the classical limit are identical with the RPA Green's function theory of Liu as well as the spherical model results of Lax. The quantum limit is analyzed, and present theory predictions for the $1/T$ series coefficients for both internal energy and susceptibility are compared with exact results. The linear chain antiferromagnet is briefly examined near absolute zero.

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CHAPTER I

INTRODUCTION

The phenomenon of paramagnetism occurs only in materials in which
the individual atoms or molecules comprising the substance have a non-
zero magnetic dipole moment. A paramagnet is characterized by the
absence of long range order in the absence of a magnetic field and by a
positive magnetic susceptibility. Although diamagnetic effects are
always present, they can usually be neglected when non-zero atomic
moments are present. In the case of many magnetic substances, a phase
transformation to either the ferromagnetic or antiferromagnetic state
occurs when the temperature is lowered sufficiently. The Heisenberg
model has been used to describe such substances with some success. The
applicability of the Heisenberg model to insulators has been reviewed by
P. W. Anderson[1] and to metals and alloys by A. Arrott[2]. A general
justification of this model will not be attempted here; instead, the
utility of the model will be assumed and its properties investigated. A
brief discussion of how it arose historically will be considered later
in this chapter.

Objective and Scope

The Heisenberg model consists of a large number of spins arranged
on a lattice. These spins may interact both with an external magnetic
field through their magnetic dipole moment and with each other via an
exchange interaction. In insulators for example, this spin is associated

with the localized spins of the electrons in the unfilled shells of the atoms comprising the substance. The Hamiltonian, denoted by H, for the Heisenberg model with nearest neighbor isotropic exchange is given by

$$H = - J \sum_j \sum_d \vec{S}_j \cdot \vec{S}_{j+d} + \mu H_o \sum_j S_j^z \tag{1}$$

where 2J is the exchange constant between neighboring spins $\vec{S}_j$ and $\vec{S}_{j+d}$. The sum over j ranges over all lattice sites, while the sum over d ranges over the set of nearest neighbor displacement vectors only. The interaction of the magnetic moment, $\vec{m}_j = - \mu \vec{S}_j$, at the lattice site j with an external magnetic field, $\vec{H}_o = + H_o \vec{z}$, is reflected in the last term where $\vec{z}$ is a unit vector in the z-direction. The assumption of nearest neighbor isotropic exchange omits the possibility of the spiral structures observed in the rare earth metals, but allows for the possibility of the ferromagnetic state for positive J at low temperatures. The antiferromagnetic state is likewise allowed in the case of negative exchange constant J. The model exhibits the unordered or paramagnetic state at high temperature.

The objective of this dissertation is to describe the thermodynamic behavior of the Heisenberg model with nearest neighbor isotropic exchange and periodic boundary conditions in the limit of zero magnetic field. The dependence on dimensionality, lattice configuration, atomic spin quantum number, and sign of the exchange will be considered.

Survey of Paramagnetism

Some simple calculations related to paramagnetism and the Heisenberg model will now be considered. The simple paramagnet and the Weiss

molecular field give some insight into the behavior of the Heisenberg model. The original justification of the exchange interaction will be presented along with a brief discussion of the effective field theories which result from certain statistical approximations on the form of the Hamiltonian. The limitations of the $1/T$ series expansions for the Heisenberg model will be summarized along with the difficulties encountered with the Green's function approach.

The Simple Paramagnet

Some of the dominant features of paramagnetism at high temperatures may be understood in terms of the simple paramagnet which consists of a large number of particles each with a magnetic dipole moment, $\vec{m}$, interacting with an externally applied magnetic field, $\vec{H}_o$, with an interaction energy, $-\vec{m}\cdot\vec{H}_o$. Classically, the angle between the moment and the field can take on any value, while quantum mechanically the moment is quantized so that only specific projections along the axis of quantization are allowed. In either treatment, the system will be in thermodynamic equilibrium in that state which minimizes the Helmholtz free energy, F, defined by

$$F = U - T S$$

where U is the internal energy, T the temperature, and S is the entropy. There are two opposing effects which determine the thermodynamic state of the system. First, the internal energy is lowest when all moments are aligned with the field. Second, the entropy is largest for random orientations of the moments. If one denotes Boltzmann's constant by k_B, then at temperatures for which the thermal energy, $k_B T$, is much smaller

than the maximum interaction energy of one dipole with the external

field, mH_o, one expects the tendency toward maximum alignment to domi-

nate. In the opposite case, the tendency toward random orientations

should dominate. Therefore the magnetization, $M(H_o,T)$, which is the

average magnetic moment per unit volume, should be a decreasing function

of temperature for fixed values of H_o. This property of the magnetiza-

tion implies that the zero field susceptibility $\tilde{\chi}_o$, defined by

$$\tilde{\chi}_o = \frac{\partial M(H_o,T)}{\partial H_o}\bigg|_{H_o=0}$$

should also be a decreasing function of temperature. Mathematically,

the zero field susceptibility is found to obey the Curie law

$$\tilde{\chi}_o = \frac{C}{T} \tag{2}$$

where C is the Curie constant.

The simple paramagnet represents an incomplete description of

real systems since it fails to account for the interaction between neigh-

boring moments. Nevertheless, the experimental results show that the

Curie law is obeyed at high temperatures by almost all paramagnets.

Deviations from this behavior become important only when the temperature

is sufficiently low so that the interaction energy between neighboring

moments is of the order of the thermal energy, $k_B T$. Kittel[3] demon-

strates by applying the general susceptibility theorem of Kirkwood,

Fröhlich, and Price[4] that the leading term in the 1/T series for the

zero field susceptibility is given by the Curie law independent of the

model assumed so long as diamagnetic effects are neglected. The most
important deviation of the zero field susceptibility from the Curie law
may be understood from the Weiss molecular field model which will now be
considered.

Weiss Molecular Field

The first successful model of ferromagnetism was proposed by
Pierre Weiss[5] in 1907 long before the advent of quantum mechanics. He
assumed that each magnetic moment was acted upon, not only by an exter-
nal magnetic field, but also by an internal field which by hypothesis
was proportional to and in the direction of the average magnetic moment.
The origins of this field, now called the Weiss molecular field,
remained obscure until quantum mechanics was understood. Below a transi-
tion temperature, called the Curie temperature, the substance was ferro-
magnetic exhibiting a spontaneous magnetization which is a finite mag-
netization in the limit of zero applied magnetic field. Above the Curie
temperature the substance was paramagnetic with the zero field suscepti-
bility obeying the Curie-Weiss law,

$$\tilde{\chi}_o = \frac{C}{T - \theta} \tag{3}$$

where θ is the Curie-Weiss temperature.

The Weiss molecular field model in its present day quantum
form[6] can be thought of as a crude statistical approximation on the
Heisenberg model. Equation (1) becomes the more modern version of the
Weiss model Hamiltonian when one of the spin operators in the exchange
interaction is replaced with its average value and when the proportional-
ity between the spin operator and the magnetic moment operator is used.

The original Weiss model results if, in addition, the spin operators are considered as classical angular momentum vectors.

Thus the molecular field gives a rough approximation to the behavior of the Heisenberg model. In particular when J is positive, there is a singularity in the zero field susceptibility that arises as a result of the interaction between neighboring spins. The nature of the singularity is described incorrectly in three dimensions since the inverse susceptibility apparently obeys a $(T-T_c)^{4/3}$ power law in the vicinity of the Curie temperature, T_c, in the three dimensional case.[7] The Weiss molecular field correctly predicts a transition to the ferromagnetic state for temperatures below the Curie temperature, although the expression for the Curie temperature is about 50 percent too large when compared with the expression of Rushbrook and Woods[8] obtained from the 1/T series. In less than three dimensions, the situation is much worse since the Weiss model also predicts a ferromagnetic state at low temperature for the one and two dimensional lattices in disagreement with the proof of Mermin and Wagner[9] which states that the ferromagnetic state cannot exist in one or two dimensions. Perhaps an even more serious deficiency is that there is no mechanism in the Weiss model for short range order. As a result the Weiss model yields a specific heat which is identically zero in the absence of an applied magnetic field throughout the entire paramagnetic region. Thus the Weiss model is fairly good at describing the long range order in the Heisenberg model in three dimensions, but fails completely in describing the short range order aspects of the Heisenberg model.

Heisenberg Exchange Interaction

From a fundamental point of view, the idea that the interaction between neighboring moments arises from magnetic interactions is incorrect. Weiss noted in his 1907 paper that the magnetic dipolar interactions which he initially thought to be responsible for the molecular field were entirely too weak to account for the observations. With the arrival of quantum mechanics, Heisenberg[10] showed that the interactions were quantum mechanical in origin being a direct consequence of the restrictions placed on the wavefunctions by the Pauli exclusion principle when applied to the electronic states of the atoms. More specifically, the electronic wavefunctions must be antisymmetric with respect to the exchange of both the space and spin coordinates of any pair of electrons. Dirac[11] showed for the special case of localized electrons that the symmetry requirement was equivalent within an additive constant to an effective two body potential of the form

$$V_{ij} = -2 J_{ij} \, \vec{S}_i \cdot \vec{S}_j$$

The exchange constant, J_{ij}, is a measure of the spatial overlap of the electrons localized at the lattice sites i and j. For the case of insulators where the electronic wave functions are highly localized, the assumption of only nearest neighbor interactions is probably justified.

Effective Field Theories

An excellent review of the strengths and weaknesses of the effective field theories is contained in the book by Smart.[6] He considers the Weiss molecular field theory, Oguchi,[12] Bethe-Peierls-Weiss,[13-15] and constant coupling approximations and concludes that

the constant coupling approximation is probably the best effective
field theory in the paramagnetic region. The constant coupling approx-
imation gives short range order in the paramagnetic region as well as a
non-linear dependence of the inverse susceptibility on temperature near
the transition temperature. The estimates of the transition temperature
are good to within about twenty percent with two exceptions. There is
no transition predicted for the three dimensional tetrahedral lattice
which is thought to have a Curie transition. In the other case, a Curie
transition is predicted for the two dimensional hexagonal layer lattice
which is impossible by the proof of Mermin and Wagner mentioned earlier.

Smart discusses these effective field theories with both posi-
tive and negative exchange constants. Neel[16] in 1936 pointed out that
an ordered state could exist at low temperatures for negative J. This
state would have antiparallel alignment favored between neighboring
spins. This ordered state seems plausible if one thinks of the spin
operators in (1) as classical vectors. The temperature for which the
transition occurs from the ordered antiferromagnetic state to the
unordered paramagnetic state is known as the Neel temperature.

1/T Series Expansions

The most successful method of analyzing the thermodynamics of the
Heisenberg paramagnet in practice has been the 1/T series expansions of
quantities. Normally, the 1/T series expansions are obtained for the
susceptibility and internal energy from which most other series may be
constructed. One then estimates the Curie temperature by determining
the values of the constants A, T_c, and y in the expression

$$\tilde{\chi}_o^{-1} = A\left(\frac{T-T_c}{T_c}\right)^y$$

which best fit the known terms in the $1/T$ susceptibility series. The determination of the critical temperature depends somewhat on the method used to determine the best fit. Domb and Sykes[7] obtain lower estimates for the Curie temperature than Rushbrooke and Wood[8] using the same data as Rushbrooke and Wood. The estimates are most reliable for the face centered cubic lattice in the infinite spin limit.

Survey of Green's Function Theory

The Heisenberg model has been extensively studied during the last several years using the techniques of double time temperature dependent Green's functions. Formally, the problem of finding the solution for magnetization and time dependent spin-spin correlation functions is reduced to the determination of the solution to an infinite set of coupled first order differential equations. The development of a tractable formalism necessitates a decoupling approximation.

A majority of the decoupling procedures, which have been utilized on the Heisenberg model, have been made at the first stage of the calculation, since further delay introduces an enormous mathematical complexity to the problem. The random phase approximation (RPA) of Bogoliubov and Tyablikov[17-21] has been used extensively in many slightly modified forms. A short and somewhat representative sample of these theories are given by Refs. 17-30.

These first order theories are largely designed to apply to systems in the ordered state, and therefore the failure of the excitation

energies to agree with experiment and the exactly known properties of the Heisenberg model in the paramagnetic region is perhaps understandable. One finds that all these theories with the notable exception of Lines[30] produce excitation energies for which the scaling with temperature is wave vector independent. A further examination of these theories show that all spin wave energies are vanishingly small in the paramagnetic region. Both neutron diffraction[31-35] and Raman[36,37] experiments on magnetic systems reveal that short wavelength excitations remain finite and continue to propagate well into the paramagnetic region. This phenomena is most apparent in one and two dimensional systems.[38-40] Of the literature cited,[17-30] only Lines[30] has a first order Green's function theory for the paramagnetic region that is even qualitatively correct and his approach, which is phenomenological in nature, leaves obscured the underlying basis for the theory.

In Chapter II, both the Green's functions and the corresponding relaxation functions which are pertinent to the Heisenberg model are defined. Some of the spectral relations that are developed in the literature[41,42] and reviewed in Appendices I and II are utilized in constructing the Green's function theory. By using arguments based on the invariance properties of the Heisenberg paramagnet as well as exact moments of the relaxation function, one may conclude that a second order Green's function theory is the best approach because the second order theory incorporates exactly the zero, first, and second moments of the relaxation function as boundary conditions for the Green's function equation insuring non-vanishing excitation energies in the paramagnetic region.

A decoupling of the Green's function equations which is a modification of the procedure used by Knapp and ter Haar[44], and is similar to theories used by Richards[45], and Lo and Halley[46], and Scales and Gersch[43] is examined in Chapter III. The present theory is in fact an extension to all dimensions of the previously published theory of Scales and Gersch.

In Chapter IV, a further approximation is made on the Green's function equations obtained from the truncation used in Chapter III. This approximation is tentatively identified as the classical limit; the proof is deferred to Chapter VI. The equal time properties predicted by the present theory in the absence of a magnetic field in the classical limit are shown to be identical with the predictions of the RPA theory of Liu[21]. It is also found that the thermodynamics reduce to the spherical model results in the classical limit as did the theory reported by Lo and Halley[46].

In Chapter V, quantum effects are examined which were ignored in the classical limit approximation of Chapter IV. In particular, corrections to the Curie and Neel temperatures predicted by the RPA and spherical model by the present theory to order $1/S(S+1)$ are derived. The critical value of the nearest neighbor spin-spin correlation function is also calculated to the same level of approximation. Comparisons of present theory results with $(1/T)$ series results are given in Tables 1 and 2.

In Chapter VI, the $(1/T)$ series expansion for the susceptibility and nearest neighbor correlation function predicted by the present theory is examined and as a by-product the $(1/T)$ series expansions for the

spherical model, the RPA theory, and the RPA theory of Liu are obtained. The present theory is found to give a much more accurate description of the high temperature thermodynamics than either the spherical model or the RPA theory of Liu especially for small spin values as may be seen by an examination of the $(1/T)$ series coefficients tabulated in Appendices III and IV.

In Chapter VII, the predicted solution for the one dimensional antiferromagnet is compared with the experimental data available for $(CD_3)_4NMnCl_3$[39,40], with the predictions of classical theory, and with the predictions of Richards[45]. The present theory is able to explain the excitation spectra observed in this antiferromagnet even though the sublattice magnetization is zero.

CHAPTER II

GREEN'S FUNCTION THEORY

The usual retarded and advanced Green's functions reviewed by Zubarev[41] are defined by

$$G_{\substack{r\\a}}(t) = \langle\langle A(t);B(0)\rangle\rangle_{\substack{r\\a}} = \mp i\theta(\pm t)\langle[A(t),B(0)]\rangle \tag{4}$$

where

$$\theta(t) = 1, \quad t>0; \qquad \theta(t) = 0, \quad t<0 \tag{5}$$

$$[A,B] = AB - BA \tag{6}$$

$$A(t) = \exp(iHt)A(0)\exp(-iHt) \tag{7}$$

$$\langle \cdots \rangle = Z^{-1}\text{Tr}[\exp(-\beta H)\cdots] \tag{8}$$

$$\beta = 1/k_B T \tag{9}$$

$$Z = \text{Tr}[\exp(-\beta H)] \tag{10}$$

and H is the hamiltonian defined by

$$H = -J\Sigma_{j,d} \, \vec{S}_j \cdot \vec{S}_{j+d} \tag{11}$$

where J is the exchange constant in units of energy (Units are chosen so that Planck's constant is equal to 2π.) and where the sum over the spin index j ranges over the positions of all N lattice sites while the sum

over d ranges over the set of nearest neighbor vectors only.

Upon taking the time derivative of (4) and utilizing (6) and (7) in the resulting equation, one finds that both advanced and retarded Green's functions satisfy

$$i\frac{\partial}{\partial t}<<A(t);B(0)>>_{\substack{r\\a}} = <[A,B]>\delta(t)+<<[A,H](t);B(0)>>_{\substack{r\\a}} \qquad (12)$$

The convention that all operators to the left of the semicolon in the Green's function appearing on the right hand side of (12) are to be evaluated at the time t has been used. The function $\delta(t)$ is the Dirac delta function defined by

$$\delta(t) = "\frac{d\theta(t)}{dt}" \qquad (13)$$

One defines the image $\widetilde{A}(\omega)$ of an arbitrary function of the time $A(t)$ under the Fourier transform operator $F(\omega;t)$ via

$$\widetilde{A}(\omega) = F(\omega;t)A(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\ \exp(i\omega t)A(t) \qquad (14)$$

It is convenient to define a relaxation function $R(\omega)$ by

$$R(\omega) = i\omega^{-1}\lim_{\epsilon\to 0+}[F(\omega+i\epsilon;t)G_r(t)-F(\omega-i\epsilon;t)G_a(t)] \qquad (15)$$

The correlation function $<B(0)A(t)>$, which is of ultimate interest, is given by the spectral relation[41]

$$<B(0)A(t)> = F^{-1}(t;\omega)\frac{\omega R(\omega)}{\exp(\beta\omega)-1} \qquad (16)$$

where $F^{-1}(t;\omega)$ is the inverse Fourier transform operator. The spectral

theorem given by (16) is proved in Appendix I.

The relevant Green's functions for the Heisenberg model are given by

$$G_{mn}(j,t) = <<S_j^m(t);S_0^n(0)>>$$ (17)

where m and n are labels which may take on any of the values $+$, $-$, x, y, or z. To each Green's function defined by (17) there corresponds a Green's function defined by

$$G_{mn}(k,t) = F_{k;j}G_{mn}(j,t)$$ (18)

where the Fourier lattice transform operator $F_{k;j}$ is defined by

$$F_{k;j}\cdots = \Sigma_j \exp(ik\cdot j)\cdots$$ (19)

To each Green's function defined by (17) and (18) there corresponds a relaxation function defined by (15). The moments of the relaxation functions, which we denote by $<\omega_k^s>_{mn}$, are defined by

$$<\omega_k^s>_{mn} = \int_{-\infty}^{\infty} \omega^s R_{mn}(k,\omega)d\omega / \int_{-\infty}^{\infty} R_{mn}(k,\omega)d\omega$$ (20)

These moments are related in an important way to the boundary conditions on the Green's functions at time t=0. One finds from (20) that

$$<\omega^s>R(t=0) = \left(i\frac{\partial}{\partial t}\right)^s R(t)_{t=0} = i\left(i\frac{\partial}{\partial t}\right)^{s-1} G_r(t)_{t=0^+}$$ (21)

where R(t) is the inverse Fourier transform of R(ω) defined by (14).

One is now in a position to determine what is wrong with the use

of a first order Green's function truncation in the paramagnetic region. One has that $G_{+-r}(k,t=0^+) = 2i\langle S_0^z \rangle$. Therefore it follows from (21) that

$$\langle \omega_k \rangle_{+-} = 2\langle S_0^z \rangle / R_{+-}(k,t=0) = \langle S_0^z \rangle / \chi_k \qquad (22)$$

where $\frac{1}{2}R_{+-}(k,t=0) = R_{zz}(k,t=0) = \chi_k$ in the paramagnetic region due to the spherical symmetry[42]. It is established in Appendix II that χ_k is the wavelength dependent paramagnetic susceptibility. If one insists that the Green's functions have only one pole corresponding to the magnon energy as is the case in the literature cited[17-30], then the magnon energy must be given by

$$\tilde{E}_k = \langle \omega_k \rangle_{+-} = \langle S_0^z \rangle / \chi_k \qquad (23)$$

as a result of (17). One must in fact solve the Green's function equations in the limit of vanishing magnetic field in order to get a solution since $\langle S_0^z \rangle$ is identically zero when the magnetic field is identically zero.

It is clear, however, that the Green's function for $G_{+-}(k,t)$ must have two poles in the paramagnetic region (to the extent that the concept of elementary excitation is valid) since the operators $F_{k;j}S_j^+$ and $F_{k;j}S_j^-$ in the absence of a magnetic field must by symmetry have equal probability for creating and destroying a magnon. Therefore (22) should be interpreted as a measure of the asymmetry in the location of the poles in the Green's function corresponding to the propagation of a magnon and a magnon hole.

The information contained in the boundary condition for the

second moment of the relaxation function in the paramagnetic region will now be considered. One obtains

$$<\omega_k>_{zz} = 0; \quad <\omega_k^2>_{zz} = 2J(\gamma_0 - \gamma_k)<S_0^x S_d^x + S_0^y S_d^y>/\chi_k \qquad (24)$$

from the relaxation function $R_{zz}(k,t)$. The lattice site d appearing in (24) refers to any one of the nearest neighbor sites of the site 0. The function, γ_k, is defined by

$$\gamma_k = \Sigma_{d'} \; \exp(ik \cdot d') \qquad (25)$$

where the sum over d' ranges over the set of nearest neighbor displacement vectors. Notice that (24) is consistent with a relaxation function given by

$$R_{zz}(k,t) = \chi_k \; \cos(E_k t) \qquad (26)$$

where

$$E_k^2 = <\omega_k^2>_{zz} = 2J(\gamma_0 - \gamma_k)<S_0^x S_d^x + S_0^y S_d^y>/\chi_k \qquad (27)$$

Equation (26) is obtained by assuming that for a given k, the relaxation function contains a pure negative frequency corresponding to the presence of a magnon of energy E_k, and a positive frequency component corresponding to the presence of a magnon hole of energy $-E_k$. The relative amplitude and phase of the two frequency components are fixed by the principle of detailed balance. More explicitly, Marshall and Lowde[42] have shown that for crystals with inversion symmetry, $R_{zz}(k,t)$ must be an even function of t which they show is equivalent to the statement of detailed

balance. Finally (24) determines the energy of the excitations to be given by (27).

It must be emphasized that (26) and (27) are meaningful only to the extent that it is possible to describe the behavior of the Heisenberg paramagnet in terms of elementary excitations. The experimental data[31-40] suggest this assumption is realized most strongly in systems of low dimensionality. In particular, the experimental measurement of the excitations of TMMC (a one dimensional Heisenberg paramagnet with S=5/2 and J=-7.7°K) have revealed the existence of elementary excitations obeying

$$E_k = 6.1 meV |\sin k| \tag{28}$$

over the entire Brillouin zone at $4.4°K$.[40] It will be shown in Chapter VI the present theory is able to explain the excitation spectra given by (28) for TMMC at $4.4°K$.

In the next chapter, a truncation procedure on the Green's function equations at second order will be used to describe the Heisenberg paramagnet. A second order decoupling scheme is chosen because the second moment sum rule for the relaxation function given by (24) is incorporated into the Green's function as a boundary condition. Furthermore, the symmetry of the second order equation of motion for $G_{zz}(j,t)$ guarantees that the condition of detailed balance is satisfied, and this feature is easily retained in the truncation. In fact this theory has a relaxation function given by (26) and excitation energies given by (27). These equations are supplemented by (48)-(52) which define a self consistent scheme for determining the unknown susceptibility and nearest

neighbor correlation function appearing in (26) and (27).

One may justifiably ask why one should use a theory having a relaxation function given by (26) in three dimensions at high temperature when both experimental and theoretical studies indicate that the relaxation function should be Gaussian in ω for large values of k and Lorentzian in ω for small k[42]. The answer is that the dynamics predicted by (26) is certainly unrealistic; however, the static properties are determined by only low order moments $<\omega_k^s>$ of the relaxation function and these are correctly represented in our theory. For example one finds from (16) that

$$F_{k;j}<S_0^z S_j^z>_\beta = \chi_k(1 + c_1\beta<\omega_k>_{zz} + c_2\beta^2<\omega_k^2>_{zz} + \cdots)$$ (29)

Similar remarks hold for the Heisenberg paramagnet at high temperatures in the case of one and two dimensions.

CHAPTER III

DECOUPLING THE EQUATIONS OF MOTION

The Green's function $G_{zz}(j,t)$ is found to satisfy a second order equation,

$$\left(i\frac{\partial}{\partial t}\right)^2 G_{zz}(j,t) = 2J\Sigma_d <S_0^x S_d^x + S_0^y S_d^y> (\delta_{j,0} - \delta_{j+d,0})\delta(t)$$

$$+ 4J^2\Sigma_{d,d'} <<(\vec{S}_j * \vec{S}_{j+d} S_{j+d+d'}^z - \vec{S}_j * \vec{S}_{j+d+d'} S_{j+d}^z)(t); S_0^z(0)>>$$

$$+ 4J^2\Sigma_{d,d'} <<(\vec{S}_{j+d} * \vec{S}_{j+d'} S_j^z - S_{j+d}^z \vec{S}_j * \vec{S}_{j+d'})(t); S_0^z(0)>> \qquad (30)$$

after using (12) two times and simplifying the resulting equation with the aid of the spin angular momentum commutation relations given below. The spin angular momentum commutation relations are

$$[S_j^x, S_j^y] = iS_j^z , \qquad [S_j^y, S_j^z] = iS_j^x , \qquad [S_j^z, S_j^x] = iS_j^y \qquad (31)$$

when the spin operators act on the same lattice site. The spin commutators are always zero between spin operators at different lattice sites. The operation $\vec{S}_{j_1} * \vec{S}_{j_2}$ appearing in (30) is presently to be interpreted as the usual dot product of two vectors. Knapp and ter Haar[44] proceeded to approximate the Green's functions on the right hand side of (30) by

$$<<\vec{S}_{j_1} * \vec{S}_{j_2} S_{j_3}^z (t); S_0^z(0)>> \simeq <\vec{S}_{j_1} * \vec{S}_{j_2}> G_{zz}(j_3, t) \qquad (32)$$

$$\langle\langle S^z_{j_3} \vec{S}_{j_1} * \vec{S}_{j_2}(t); S_0(0)\rangle\rangle \simeq \langle \vec{S}_{j_1} * \vec{S}_{j_2}\rangle G_{zz}(j_3, t) \tag{33}$$

Knapp and ter Haar described this truncation as a natural generalization of the first order RPA decoupling scheme. The reader is referred to their paper for a discussion of the ambiguities that arise in their truncation procedure.

The truncation which will now be considered differs only slightly from that of Knapp and ter Haar. Notice that the Green's functions appearing on the right hand side of (30) which involve only z-component spin operators when summed yield identically zero for all values of j and t. Therefore we interpret the operator $\vec{S}_{j_1} * \vec{S}_{j_2}$ as

$$\vec{S}_{j_1} * \vec{S}_{j_2} = S^x_{j_1} S^x_{j_2} + S^y_{j_1} S^y_{j_2} \tag{34}$$

and (30) is still exact. One can truncate the Green's function equations using (32), (33), and (34).

The reason that (32) and (33) are appropriate when the * product is defined by (34) and are not appropriate when the * product is interpreted as the ordinary dot product will now be examined. For n=x or y (but not z), one has

$$\langle\langle S^n_{j_1} S^n_{j_2} S^z_{j_3}(t); S^z_0(0)\rangle\rangle \simeq \langle S^n_{j_1} S^n_{j_2}\rangle G_{zz}(j_3, t)$$

$$+ \langle S^n_{j_1} S^z_{j_3}\rangle G_{nz}(j_2, t) + \langle S^n_{j_2} S^z_{j_3}\rangle G_{nz}(j_1, t)$$

$$= \langle S^n_{j_1} S^n_{j_2}\rangle G_{zz}(j_3, t) \tag{35}$$

The equality in (35) follows from the fact that both the correlation functions $<S_{j_1}^n S_{j_3}^z>$ and $<S_{j_2}^n S_{j_3}^z>$ are rigorously zero for n=x or y (but not z). This may be seen most easily if the trace is taken in a basis in which the states are eigenstates of the z-component of total spin. Similar arguments apply to (33).

The symmetries of the isotropic Heisenberg model with nearest neighbor interactions, periodic boundary conditions, and the equivalence of nearest neighbor sites will be used to obtain a compact form for the truncated equations of motion contained in (32) and (33). One has

$$<S_{j_1}^x S_{j_2}^x> = <S_{j_1}^y S_{j_2}^y> = <S_{j_1}^z S_{j_2}^z> = <S_{j_1-j_2}^z S_0^z> \qquad (36)$$

and

$$<S_d^z S_0^z> = <S_{d'}^z S_0^z>, \ d \neq d'; \quad \Sigma_{d,d'} <S_{d+d'}^z S_0^z> = \gamma_0 \Sigma_d <S_{d+d_1}^z S_0^z> \qquad (37)$$

where j_1 and j_2 are arbitrary lattice vectors, where d, d', and d_1 are nearest neighbor displacement vectors, and where γ_0 is the number of nearest neighbor displacement vectors.

It is important to retain the fact that (32) and (33) are only approximately true in our truncation since there will be more equations than there are unknowns which can easily lead to a system of equations for which there exists no solution. In anticipation of the problems that will arise, (32) and (33) will be treated as exact when $|j_1-j_2| = |d|$. This leads to

$$\Sigma_{d,d'} <<\vec{S}_j \cdot \vec{S}_{j+d} S_{j+d+d'}^z (t); S_0^z(0)>> = 2f \Sigma_{d,d'} G_{zz}(j+d+d',t) \qquad (38)$$

and

$$\sum_{d,d'} \ll S^z_{j+d} \vec{S}_j * \vec{S}_{j+d'}(t); S^z_0(0) \gg = 2f_{\gamma_0} \sum_d G_{zz}(j+d,t) \tag{39}$$

where

$$f = \ll S^z_0 S^z_{d_1} > \tag{40}$$

However, when $|j_1 - j_2| \neq |d|$ one does not demand a strict equality in (32) and (33) unless $j_1 = j_2$. Instead the approximations

$$\sum_{d,d'} \ll \vec{S}_j * \vec{S}_{j+d+d'}, S^z_{j+d}(t); S^z_0(0) \gg = 2g\gamma_0 \sum_d G_{zz}(j+d,t) \tag{41}$$

and

$$\sum_{d,d'} \ll \vec{S}_{j+d} * \vec{S}_{j+d'}, S^z_j(t); S^z_0(0) \gg = 2g\gamma_0^2 G_{zz}(j,t) \tag{42}$$

where

$$cg = \gamma_0^{-1} \sum_d \ll S^z_0 S^z_{d+d'} > \tag{43}$$

and where c is a constant that may deviate from unity. After combining (38) thru (43) one finds

$$-\frac{\partial^2}{\partial t^2} G_{zz}(j,t) = 4J\delta(t)f\Sigma_d \left(\delta_{j,0} - \delta_{j+d,0}\right)$$

$$+ 8J^2 \Sigma_{j'} G_{zz}(j+j',t) \Sigma_{d,d'} (f\delta_{j',d+d'} - f\delta_{j',d} + g\delta_{j',0} - g\delta_{j',d}) \tag{44}$$

One sees that (44) is a difference equation which is easily solved by use of the Fourier lattice transform defined by (19). The solution is

$$G_{zz}\left(\frac{r}{a}\right)(k,t) = \mp 4\theta(\pm t)Jf(\gamma_0-\gamma_k)\sin(E_k t)/E_k \qquad (45)$$

where

$$E_k^2 = 8J^2(\gamma_0-\gamma_k)(g\gamma_0-f\gamma_k) \qquad (46)$$

The relaxation function is found to be

$$R_{zz}(k,t) = \frac{f \cos(E_k t)}{2J(g\gamma_0-f\gamma_k)} \qquad (47)$$

upon substituting (45) into (15). The wavelength dependent susceptibility χ_k is identified from (47) and (26) as

$$\chi_k = \frac{f}{2J(g\gamma_0-f\gamma_k)} \qquad (48)$$

The susceptibility given by (42) is of the Ornstein-Zernike[47] form. The present theory will be complete once the temperature dependence of the parameters f and g are determined.

Upon substituting the Fourier transform of (47) into (16) one obtains

$$<S_0^z(0)S_j^z(t)> = F_{j;k}^{-1} \frac{\frac{1}{2}\chi_k E_k \cosh(\frac{1}{2}\beta E_k+iE_k t)}{\sinh(\frac{1}{2}\beta E_k)} \qquad (49)$$

for the time dependent spin-spin correlation functions. The parameters f and g are determined from (49) by the self-consistency relations,

$$S(S+1)/3 = <S_0^z(0)S_0^z(0)> = \frac{1}{\beta N} \sum_k \frac{fV(k,T)}{2J(g\gamma_0-f\gamma_k)} \qquad (50)$$

and

$$f = \gamma_0^{-1} \sum_d \langle S_0^z(0) S_d^z(0) \rangle = \frac{1}{\beta N} \sum_k \frac{f\gamma_k V(k,T)}{2J(g\gamma_0 - f\gamma_k)\gamma_0} \tag{51}$$

where

$$V(k,T) = \tfrac{1}{2}\beta E_k \coth(\tfrac{1}{2}\beta E_k) \tag{52}$$

There is an additional self consistency equation that determines the constant c given in (43). It is

$$cg = \gamma_0^{-2} \sum_{d,d'} \langle S_0^z(0) S_{d+d'}^z(0) \rangle = \frac{1}{\beta N} \sum_k \frac{f\gamma_k^2 V(k,T)}{2J(g\gamma_0 - f\gamma_k)\gamma_0^2} \tag{53}$$

The present Green's function theory is now complete. One will find out how well this theory, which is contained in (46)-(52), describes the behavior of the Heisenberg model in the remaining chapters. One can determine qualitatively the behavior of the theory by examining the classical spin limit which is to be considered in the next chapter.

CHAPTER IV

CLASSICAL LIMIT

One may now proceed to recover the classical limit for the equal
time properties of the present theory and show that the thermal prop-
erties of our theory are the same as those predicted by the RPA theory
of Liu[21] as well as the spherical approximation on the Heisenberg
model by Lax[49]. The description of the equal time properties is con-
tained in (46), (50), (51), (52), and the equation

$$<S_0^z(0)S_j^z(0)> = \frac{1}{\beta N} \sum_k \frac{f \exp(-ik \cdot j) \ V(k,T)}{2J(g\gamma_0 - f\gamma_k)}$$ (54)

which may be deduced by substituting (48) into (49) and using the inverse
of the Fourier lattice transform operator defined by (19). In Chapter VI
it will be proved that the classical limit corresponding to this system
of equations is given by (50) and (54) where one uses $V(k,T) = 1$ instead
of the expression given by (52).

The present theory in the classical limit has only one unknown
parameter $h = f/g$. One can also use χ_0 determined from (48) with $k=0$ as
the unknown parameter. The classical limit of (54) is then

$$<S_0^z(0)S_j^z(0)> = \frac{1}{\beta N} \sum_k \frac{\exp(-ik \cdot j)}{\chi_0^{-1} + 2J(\gamma_0 - \gamma_k)}$$ (55)

where the susceptibility χ_0 is determined from

$$S(S+1)/3 = \frac{1}{\beta N} \sum_k \frac{1}{\chi_0^{-1} + 2J(\gamma_0 - \gamma_k)} \tag{56}$$

which is deduced from the classical limit of (50).

In the case of $J = -|J|$ it is more reasonable to express (55) and (56) in terms of the staggered susceptibility χ_s when it can be defined. More precisely, when a lattice is decomposable into two interpenetrating sublattices with the property that nearest neighbors of a point on one sublattice all lie on the other sublattice, then one may define a staggered susceptibility. Then there exists at least one wave vector k_0 such that $\exp(ik_0 \cdot j) = \pm 1$ for all lattice sites j. The lattice points for which $\exp(ik_0 \cdot j) = 1$ are on one sublattice, while the points for which $\exp(ik_0 \cdot j) = -1$ are on the other sublattice. The staggered susceptibility is then determined from (48) by $\chi_s = \chi_{k_0}$. The important wavevectors when $J = -|J|$ are those wavevectors for which $|k - k_0|$ are small. One may define a new wavevector q by

$$q = k - k_0 \tag{57}$$

so that (55) and (56) now become

$$\langle S_0^z(0) S_j^z(0) \rangle = \frac{1}{\beta N} \sum_q \frac{\exp(-i(k_0 + q) \cdot j))}{\chi_s^{-1} + 2|J|(\gamma_0 - \gamma_q)} \tag{58}$$

and

$$S(S+1)/3 = \frac{1}{\beta N} \sum_q \frac{1}{\chi_s^{-1} + 2|J|(\gamma_0 - \gamma_q)} \tag{59}$$

respectively.

The equal time spin-spin correlation functions which one obtains from (55) and (56) are identical with those obtained by Liu[21] when he restored the spherical symmetry to the RPA Green's function theory for the quantum Heisenberg model in the paramagnetic region. It remains an unanswered question why the classical limit for the equal time spin-spin correlations given by (55) and (56) which were calculated by a second order Green's function theory with finite frequencies given by (27) are identical with the equal time spin-spin correlations obtained by Liu from the first order RPA Green's function approximation in which the excitation energies become zero for all wavevectors in the limit of zero magnetic field in accordance with (18). This identity strengthens the parallelism between the present theory and the RPA theory mentioned by Knapp and ter Haar.[44]

About ten years ago, Tahir-Kheli and ter Haar[22] pointed out that their RPA Green's function theory produced the same critical temperatures as the spherical model of Lax[21]. It will now be shown that the equal time spin-spin correlations predicted by the RPA Green's function of Liu are the same as those predicted by the spherical model of Lax. This identity is most easily obtained by a treatment of the Heisenberg model in the spherical approximation paralleling the development leading to Eq. (36) in the paper by Berlin and Kac[49] devoted to the spherical approximation to the Ising model. The transition to the spherical approximation results for the Heisenberg model from the spherical model results of Berlin and Kac requires only a redefinition of the symbols since the new degrees of freedom S_j^x and S_j^y are not dynamically coupled to S_j^z in the spherical approximation. It remains an unanswered

question why the equal time spin-spin correlation functions predicted by the present theory are equivalent to both the spherical model of Lax and the RPA theory of Liu. This identity however gives us an insight into the behavior of our model in one, two, and three dimensions.

The classical limit of the present theory as defined by (55) and (56) predicts a transition from the paramagnetic state to a state of long range order is possible only in three dimensions[49] in agreement with the proof of Mermin and Wagner[50]. For $J>0$, one finds a second order phase transition from the paramagnetic to the ferromagnetic state, spin-spin correlation functions of the Ornstein-Zernike[47] form in the critical region[49], susceptibility obeying a $(T-T_c)^2$ law in the critical region[49] instead of a $(T-T_c)^{4/3}$ law predicted by early $(1/T)$ series methods[51], and the predicted specific heat remains finite at T_c in disagreement with the $(1/T)$ series result[52]. For $J<0$, one must distinguish between two distinct cases. For those lattices for which it is possible to define a staggered susceptibility, one finds a transition from the paramagnetic state to the antiferromagnetic state only in the three dimensional case in agreement with the theorem of Mermin and Wagner[50]. The critical properties are analogous to those for the ferromagnetic transition as in evidenced by the isomorphism that exists between the set of equations, (55) and (56), and the set of equations, (58) and (59). When $J<0$ and χ_s is undefined, one does not generally find a transition even in three dimensions as is evidenced by the face centered cubic lattice with only nearest neighbor interactions.[53] In the case of both positive and negative exchange constants J, one finds that the classical limit is asymptotically exact at high temperatures[32].

In the development that is to follow, one will need the RPA expressions for the Curie and Neel temperature first obtained for arbitrary spin by Tahir-Kheli and ter Haar[22]. The expression for the Curie temperature in the RPA which is to be denoted by $\widetilde{T}_C$ is easily obtained from (56) by setting $\chi_0 = \infty$ while the expression for the Neel temperature in the RPA which is to be denoted by $\widetilde{T}_N$ is easily obtained from (59) by setting $\chi_s = \infty$. Both results may be expressed as

$$\widetilde{T}_C = \widetilde{T}_N = \frac{2|J|S(S+1)}{3k_B} \left(\frac{1}{N} \sum_k \frac{1}{\gamma_0 - \gamma_k} \right)^{-1} \tag{60}$$

It should be recalled that we introduced a parameter c in (43) which may differ from unity if necessary to insure the existence of a solution for f and g. One can show that in the classical limit, c has the unique solution of unity and hence (43) is redundant. The situation is quite different in the quantum case which is now to be considered in the following chapter.

CHAPTER V

QUANTUM RESULTS

The thermodynamics predicted by the present Green's function theory in the quantum case is defined to be the solution to (46), (50), (51), (52), and (54). The solutions to these equations have the same qualitative features as the solution in the classical limit. In particular, one finds that χ_0 and χ_s are decreasing functions of temperature with $\chi_0 = \chi_s = 0$ at infinite temperature and with $\chi_0 = \infty$ at the Curie temperature which implies that $f = g$ due to (48), and with $\chi_s = \infty$ at the Neel temperature which implies that $f = -g$ due to (48). One now finds from (50) that in the quantum limit the Curie temperature which we denote by T_C and the Neel temperature which we denote by T_N are given by

$$T_{\binom{C}{N}} = \frac{2|J|S(S+1)}{3k_B} \left(\frac{1}{N} \sum_k \frac{V(k, T_{\binom{C}{N}})}{\gamma_0 \mp \gamma_k} \right)^{-1} \tag{61}$$

where one choses the minus sign for T_C and the plus sign for T_N in (61). It no longer follows that the Curie and Neel temperatures are equal. The reason for this is that excitation energies appearing in the definition of $V(k,T)$ given by (52) are quite different. In fact one has from (46) that

$$E_{k_{T_C}} = 4Jf^{\frac{1}{2}}(\gamma_0 - \gamma_k), \quad E_{k_{T_N}} = 4|J||f|^{\frac{1}{2}}(\gamma_0^2 - \gamma_k^2)^{\frac{1}{2}} \tag{62}$$

Notice that at T_C, the excitations have the same wavelength dependence as low temperature ferromagnetic magnons, while at T_N the excitations have the same wavelength dependence as low temperature antiferromagnetic spin waves. The fact that both the staggered susceptibility becomes infinite and the excitation energies have a higher periodicity in k-space consistent with a sublattice picture strongly suggests the appearance of antiferromagnetism at lower temperatures although one is unable to explicitly demonstrate this fact since the assumption of a spherically symmetric phase is no longer valid below T_N. Likewise, one can only suggest the existence of the ferromagnetic phase below T_C.

Rushbrooke and Wood[44] have used a (1/T) series expansion for the susceptibility and staggered susceptibility to determine estimates for the Curie and Neel temperature. They find

$$(T_N^{RW} - T_C^{RW})/T_C^{RW} \simeq 0.63/\gamma_0 S(S+1) \tag{63}$$

where T_N^{RW} and T_C^{RW} are their estimates for the Neel and Curie temperatures respectively. One should therefore expect a different expression for the Curie and Neel temperature as is evidenced by (61).

It will now be shown that the Green's function theory in the quantum limit is consistent with the theorem of Mermin and Wagner[50] which states that a phase transition to the ferromagnetic state or antiferromagnetic state at finite temperature is impossible in either one or two dimensions. To do this, observe that $V(k,T)$ as defined in (52) satisfies the inequality, $V(k,T) \geq 1$ for all values of k and T for both positive and negative exchange constant J. This inequality, when used in (61) leads to the results,

$$T_C \leq \tilde{T}_C \; , \qquad T_N \leq \tilde{T}_N \tag{64}$$

which in view of the known values of $\tilde{T}_N$ and $\tilde{T}_C$ implies consistency with the theorem of Mermin and Wagner.

The change in the thermal properties arising due to the quantum effects which were neglected in the classical limit presented in Chapter IV will now be estimated. $V(k,T)$ appearing in (52) may be expanded about $\beta=0$. If one substitutes this expansion into (50) and (51) one obtains

$$2S(S+1)\beta J = 3I(h) + 2\beta^2 J^2 \gamma_0 f + \cdots \tag{65}$$

and

$$2\beta J \gamma_0 f = (\gamma_0 I(h) h^{-1} - 1) - 2\beta^2 J^2 \gamma_0 f/3 + \cdots \tag{66}$$

where $I(h)$ is the lattice sum,

$$I(h) = \frac{1}{N} \sum_k \frac{h}{\gamma_0 - h\gamma_k} \tag{67}$$

and

$$h = f/g \tag{68}$$

A comparison of (50) and (51) with (29) shows that terms to order $\langle \omega_k^2 \rangle_{zz}$ in the expansion given in (65) and (66) have been retained. It should be recalled that the exact zero, first, and second moments of the relaxation function $R_{zz}(k,t)$ have been used as boundary conditions on our Green's function at $t=0$ as is reflected in (21) and (24). Higher moments have not been included in (65) and (66) since these are not correctly given

by the relaxation function as given in (26) which contains only two

frequencies. The contributions from these higher moments to the thermo-

dynamics is small except possibly for $S=\frac{1}{2}$ systems with a small number of

near neighbors for temperatures near the critical temperature in the

three dimensional case. One may rearrange (66) to obtain

$$2\beta J\gamma_0 f = (\gamma_0 I(h)h^{-1}-1)(1+\beta J/3)^{-1} \tag{69}$$

Furthermore, one obtains

$$2S(S+1)\beta J = \frac{3I(h)}{1 - [2S(S+1)]^{-1}(\gamma_0 I(h)h^{-1}-1)(1+\beta J/3)^{-1}} \tag{70}$$

upon substituting (69) into (65). In order to motivate one further

approximation, the expression $(1+\beta J/3)$ which appears in both (69) and

(70) may be written as

$$(1+\beta J/3) = \left(1 + \frac{\widetilde{T}_c I(1)}{6S(S+1)T}\right) \tag{71}$$

with the aid of (60) and (61). Equation (71) indicates that (65) and

(66) when expressed as a series in $(\widetilde{T}_c/T)$ will also be a series in

inverse powers of $S(S+1)$. The same results apply to (69) and (70) which

are derived from (65) and (66). If one now compares (69) and (70) with

the aid of (71), one sees that the denominator of (70) contains higher

terms in inverse powers of $S(S+1)$ than does (69). Therefore one may

make the further approximation of replacing (70) by

$$2S(S+1)\beta J = \frac{3I(h)}{1 - [2S(S+1)]^{-1}(\gamma_0 I(h)h^{-1}-1)} \tag{72}$$

so that (72) reflects the same level of approximation as does (69) in inverse powers of S(S+1).

In the remainder of this thesis, (69) and (72) will be used to describe the high temperature region of the Heisenberg paramagnet. The high temperature region is defined as the entire paramagnetic region for three dimensional paramagnets which undergo either a Curie or Neel transition. For one and two dimensional paramagnets as well as those three dimensional paramagnets which do not undergo a Neel transition when J is negative, the high temperature region is defined to be the temperature range above the Curie-Weiss temperature defined by

$$\theta_{C-W} = 2|J|\gamma_0 S(S+1)/3k_B \qquad (73)$$

A comparison with experiment would require use of analytical expressions for the Watson sums, $I(h)^{(49,50,55-60)}$, to obtain the self-consistency parameters f and h appearing in (69) and (72). However, the primary interest at present is in making a comparison with exactly known properties of the Heisenberg model to test the validity of the statistical approximations used in this thesis. The bulk of the theoretical knowledge related to the Heisenberg paramagnet is contained in the (1/T) series expansion results and results deduced from these series by Pade approximations[51,52,54,61-66]. In the next chapter, the solutions for the specific heat and susceptibility deduced from (69), (71), and (48) will be expressed as a series expansion in powers of (1/T) which may be compared with the exact results.

Before proceeding to the (1/T) series, one may examine the predicted Curie and Neel temperatures as well as values of the nearest

neighbor correlation functions at the critical temperature. The unphysical results obtained by Liu in the RPA for the $S=\frac{1}{2}$ simple cubic paramagnet in which the energy predicted at the critical temperature was lower than the ground state energy disappears when the quantum effects present in (69) and (71) are taken into account.

Using the fact that

$$I(h) = -I(-h) \tag{74}$$

for lattices that are decomposable into two interpenetrating sublattices with the property that nearest neighbor sites always lie on separate sublattices, one finds from (72) with $|h| = 1$ that the Curie and Neel temperature are given by

$$T_C = T_N = \widetilde{T}_C \left(1 - \frac{\gamma_0 I(1)-1}{2S(S+1)} \right) \tag{75}$$

so that the Curie and Neel temperatures are in agreement to order $1/S(S+1)$. Equation (75) is in disagreement with the predictions of Rushbrooke and Wood given in (63). One needs the values of $I(1)$ which are given by

$$I(1) = \begin{matrix} 0.2527 \text{ (sc)} \\ 0.1742 \text{ (bcc)} \\ 0.1122 \text{ (fcc)} \end{matrix} \tag{76}$$

for the simple cubic, body centered cubic, and face centered cubic lattices in order to compare our predictions for the Curie and Neel temperature with the predictions of Rushbrooke and Wood[52-54] which are given

by (63) and

$$T_C^{RW} = 5J(\gamma_0-1)(11S(S+1)-1)/96k_B \qquad (77)$$

Table 1 gives a comparison of present theory predictions for the Curie and Neel temperature with both RPA and (1/T) series predictions. The present theory predictions are uniformly lower than the (1/T) series estimates.

The predictions for the nearest neighbor spin-spin correlation predicted by the present Green's function theory at the critical temperature will now be considered. One obtains

$$\langle \vec{S}_0 \cdot \vec{S}_d \rangle_{\binom{C}{N}}^{GF} = \pm \frac{3k_B T_C(\gamma_0 I(1)-1))}{2|J|\gamma_0(1\pm|J|/3k_B T_C)} \qquad (78)$$

upon substituting (75) into (69) and (74). These values are considerably lower than the RPA values of Liu which are given by

$$\langle \vec{S}_0 \cdot \vec{S}_d \rangle_C^{RPAL} = - \langle \vec{S}_0 \cdot \vec{S}_d \rangle_N^{RPAL} = S(S+1)(1-1/\gamma_0 I(1)) \qquad (79)$$

Present theory values of $\langle \vec{S}_0 \cdot \vec{S}_d \rangle_C$ are much closer to the (1/T) series values of Domb and Sykes[51] than the RPA values of Liu as may be seen by an examination of Table 2.

The power laws in the critical region are the same as for the RPA theory and the spherical model although the numerical values of the coefficients change somewhat as is evidenced by the change in the critical value of the nearest neighbor correlation function calculated above. Since the critical behavior of the spherical model is known to be incorrect, the matter will be pursued no further.

Table 1. Predictions for the Curie and Neel Temperatures. Tabulated Temperatures are Multiples of the Curie-Weiss Temperature, $\theta_{CW} = 2\gamma_0 |J| S(S+1)/3k_B$.

Lattice Method	Curie S=1/2	Neel S=1/2	Curie S=1	Neel S=1	Curie S=5/2	Neel S=5/2
Simple Cubic						
1/T Series[a],[b]	0.629	0.717	0.683	0.719	0.709	0.718
RPA[c]	0.660	0.660	0.660	0.660	0.660	0.660
Present Theory	0.433	0.433	0.575	0.575	0.641	0.641
Body Centered Cubic						
1/T Series[a],[b]	0.661	0.730	0.735	0.764	0.744	0.750
RPA[c]	0.718	0.718	0.718	0.718	0.718	0.718
Present Theory	0.530	0.530	0.647	0.647	0.702	0.702
Face Centered Cubic						
1/T Series[a],[b]	0.692	None	0.752	None	0.780	None
1/T Series[d]	0.679	None	0.747	None	---	None
RPA[c]	0.743	None	0.743	None	0.743	None
Present Theory	0.571	None	0.679	None	0.728	None

(a) Ref. 52

(b) Ref. 54

(c) Ref. 22

(d) Ref. 51

Table 2. Critical Values of the Normalized Nearest Neighbor
Correlation Function $\langle \vec{S}_0 \cdot \vec{S}_d \rangle / S^2$.

Lattice Method	Curie S=1/2	Neel S=1/2	Curie S=1	Neel S=1	Curie S=∞	Neel S=∞
Simple Cubic						
RPA(Liu)[a]	1.02	-1.02	0.68	-0.68	0.34	-0.34
Present Theory	0.53	-0.90	0.55	-0.64	0.34	-0.34
Body Centered Cubic						
RPA(Liu)[a]	0.84	-0.84	0.56	-0.56	0.28	-0.28
Present Theory	0.54	-0.74	0.48	-0.54	0.28	-0.28
Face Centered Cubic						
RPA(Liu)[a]	0.77	None	0.51	None	0.26	None
Present Theory	0.54	None	0.46	None	0.26	None
1/T Series[b]	0.45	None	0.34	None	0.19	None

(a) Ref. 21
(b) Ref. 51

CHAPTER VI

1/T SERIES RESULTS

It is useful to introduce the notation

$$\tilde{J} = 2JS^2 \tag{80}$$

$$K = \tilde{J}/k_B T \tag{81}$$

and

$$X = S(S+1) \tag{82}$$

so that the Hamiltonian given by (11) now becomes

$$H = - \frac{\tilde{J}}{2S^2} \sum_{j,d} \vec{S}_j \cdot \vec{S}_{j+d} \tag{83}$$

It is easier to assess the quantum effects as a function of S with the last form of the Hamiltonian for which the ferromagnetic ground state is independent of S for fixed $\tilde{J}$ and for which the Curie temperature depends only weakly on S for a fixed value of $\tilde{J}$. Equations (69) and (72) become

$$f = \frac{S^2(\gamma_0 I(h)h^{-1}-1)}{K^2(1+vK/6S^2)} \tag{84}$$

and

$$K = \frac{3S^2 X^{-1} I(h)}{1 - \frac{1}{2}v(\gamma_0 I(h)h^{-1}-1)/X} \tag{85}$$

when use is made of (80) thru (82). The variable v which is equal to
unity has been introduced. The reason for the introduction of v is
that if one sets v=0, one recovers the (1/T) series solution for the
classical limit discussed in Chapter IV. One is therefore able to get
(1/T) series expressions for both the spherical model and the RPA model
of Liu as well as the (1/T) series expressions for the quantum limit of
our model.

Notice that (85) gives h as a function of spin and temperature.
So long as $|h| < 1$, one can expand (67) to obtain

$$I(h) = \gamma_0 h^{-1} \sum_{n=0}^{\infty} W_n h^n \tag{86}$$

where

$$W_n = N^{-1} \sum_k (\gamma_k/\gamma_0)^n \tag{87}$$

The lattice sums given in (87) may be interpreted with the aid of (25)
as the probability of returning to the starting point after n random
steps between nearest neighbor spin sites. These values are easily
obtained on a computer and are given in Table 3 for several lattices.
These values are in agreement with the values calculated by Lax[48].

Combining (85), (86), and (87) and inverting the series one
obtains

$$h = \sum_{n=1}^{\infty} A_n (K/S^2)^n \tag{88}$$

where the first four coefficients are given by

Table 3. Probabilities W_n of Returning to Starting Point After n Steps Between Nearest Neighbor Lattice Sites.

Lattice	W_0	W_2	W_3	W_4
Linear	1	1/2	0	3/8
Square	1	1/4	0	9/64
Simple cubic	1	1/6	0	5/72
Face-centered cubic	1	1/12	1/36	5/192
Body-centered cubic	1	1/8	0	27/512

$$A_1 = X\gamma_0/3, \quad A_2 = 0, \quad A_3 = -X^2\gamma_0^2(2X+v)/54, \quad A_4 = X^3\gamma_0 V_3(2X+v)/162 \quad (89)$$

and where V_n is defined by

$$V_n = \gamma_0^n W^n \quad (90)$$

One can now obtain an explicit expression for f as a function of temperature by substituting (88) and (86) into (84). The resulting expression is readily reduced to a (1/T) series in temperature. We write our prediction for the normalized nearest neighbor correlation function as

$$<\vec{S}_0 \cdot \vec{S}_d>^{GF}/S^2 = - \sum_{n=2}^{\infty} B_n^{GF}(v,S) \, S^{-2n} K^{n-1} \quad (91)$$

where one obtains our prediction for the classical Heisenberg model when $v=0$ as well as the series expansion for the RPA theory of Liu[21] and the spherical model of Lax[48], and where one obtains our prediction for the quantum Heisenberg model when $v=1$. The coefficients $B_n^{GF}(v,S)$ are given in Appendix III where they are compared with the exact results[52] $B_n^E(v,S)$.

Upon substituting (68) and (78) into (48) and upon setting $k=0$, one obtains

$$\chi_0 = \frac{S^2 h}{\tilde{J}\gamma_0(1-h)} \quad (92)$$

for the susceptibility. Finally, one obtains after substituting (88) into (92) an expression for the susceptibility as a function of inverse

temperature. The present prediction for the series is expressed as

$$3k_B T \chi_0^{GF}/S(S+1) = \sum_{n=0}^{\infty} D_n^{GF}(v,S) \, S^{-2n} \, K^n \tag{93}$$

where the coefficients $D_n^{GF}(v,S)$ are given in Appendix IV and are compared with the exact coefficients obtained by Brown and Luttinger[67].
Again one obtains predictions for the classical Heisenberg model when $v=0$ and predictions for the quantum Heisenberg model when $v=1$. Equation (93) also gives the exact $1/T$ series for the RPA theory when $v=0$ as well as the exact $1/T$ series for the spherical model of Lax[48] due to the relations established in Chapter IV.

Notice in Appendix III and IV that predicted $(1/T)$ series coefficients for the classical and quantum Heisenberg model are related in precisely the same way as the exact $(1/T)$ series for the classical and quantum Heisenberg models. One observes that the coefficients with subscript n are polynomials in the variable X of degree n in the quantum case, whereas one finds that the coefficients in the classical case contains only the term in the polynomial containing the highest power of the variable X. This rigorous relation is used to establish that by setting $V(k,T)$ in (52) equal to unity, one does indeed obtain the classical limit of the present theory as was tentatively assumed in Chapter IV.

CHAPTER VII

ONE-DIMENSIONAL ANTIFERROMAGNET AT LOW TEMPERATURE

Recently Richards[45] showed that the results of a second order
Green's function theory for a one-dimensional antiferromagnet similar to
the present theory gave good agreement with both Fisher's classical sol-
ution[68] for the inverse correlation length and the static correlation
function and with experimental neutron scattering results for these
quantities in $(CD_3)_4NMnCl_3$ (TMMC) on the temperature interval
$1.1 < T < 40°K$. The spin-spin correlations between nearest and next
nearest neighbor spins in Richard's calculation were taken from the
classical solution, rather than obtaining them from a self-consistent
Green's function theory. This procedure raised the question of whether
the good agreement of the Green's function theory with the classical
solution is in large measure enforced by the utilization of the classi-
cal parameters in that theory. This question has been considered by
Scales and Gersch[43] where it was found that the good agreement with
long range correlation properties found by Richards largely disappears.

The calculation of Scales and Gersch will be reviewed in this
chapter and the theoretical results obtained will be compared with the
experimental results on TMMC as well as competing theoretical results.

In Ref. (43) it was assumed that the constant c appearing in (53)
was unity. Thus the correction for this inconsistency affects only the
values of $<S_0^z S_2^z>$ which were not displayed in Ref. 43. A fully self

consistent treatment is given in this chapter which place the results
obtained by Scales and Gersch on a sounder foundation. It is conveni-
ent to introduce the parameter ℓ defined by

$$\ell = -f/g \tag{94}$$

in order to prevent confusion that might arise between the parameter h
defined by (68) and the parameter h appearing in Ref. (43) which differ
by a factor of (-1). Upon substituting (94) into (46) one obtains

$$E_k^2 = 32J^2 |f| (1-\cos k)(\ell^{-1}+\cos k) \tag{95}$$

for the excitations for the one dimensional antiferromagnet. The
Fourier lattice transform of the equal time spin-spin correlation func-
tion $\langle S_k^z S_{-k}^z \rangle$ which is of interest in quasi-elastic neutron scattering
experiments is given by

$$\langle S_k^z S_{-k}^z \rangle = 4Jf(1 - \cos k)(1 + 2n_k)/E_k \tag{96}$$

as a result of (48) and (48) where the function n_k is defined by

$$n_k = 1/(\exp(\beta E_k)-1) \tag{97}$$

The self consistency parameters f and ℓ are determined by

$$S(S+1)/3 = N^{-1} \sum_k \langle S_k^z S_{-k}^z \rangle \tag{98}$$

and

$$f = N^{-1} \sum_k \langle S_k^z S_{-k}^z \rangle \tag{99}$$

The last two equations are merely a restatement of (50) and (51).

The sums that appear in (98) and (99) which are explicitly independent of n_k are exactly summable in the thermodynamic limit. The self-consistency equations that follow after this summation is performed may be expressed in terms of the remaining lattice sums $L_n(k_i, k_f)$ as

$$L_n(k_i, k_f) = 2N^{-1} \sum_{k_i}^{k_f} A_n(k, \ell) n_k \tag{100}$$

where

$$A_n(k, \ell) = [(1+\ell\cos k)/2]^{-1/2} \sin(k/2) \cos nk \tag{101}$$

The first self-consistency equation is

$$3f/S(S+1) = - MF(\Delta) , \qquad M = \ell^{-1} - 1 \tag{102}$$

where

$$F(\Delta)/2 = D - (D^2 - 1)^{1/2} \tag{103}$$

$$D = 1 + C(1+\Delta)^2 \tag{104}$$

$$C = 3/(\pi^2 S(S+1)) \tag{105}$$

and

$$\Delta = \pi\left(\frac{\ell}{2M}\right)^{1/2} [L_0(0, 2\pi) M/2 + L_1(0, 2\pi)] \tag{106}$$

The second self-consistency equation is given by

$$\log\left[\left(1 + \left(\frac{M}{2}\right)^{1/2}\right)\left(\frac{M}{2} - 1\right)^{-1/2}\right]$$
$$= \pi\ell^{1/2} L_0(0, 2\pi)/2 + (6C|f|/S(S+1))^{1/2} \tag{107}$$

The ground state results are easily obtained after setting $L_n=0$ in (106) and (107). One readily obtains

$$(M/2)^{1/2}\coth^{-1}(M/2^{1/2}) = (4F(0)C)^{-1/2} \tag{108}$$

from the self-consistency equations at $T=0$. Equations (103) and (108) determine $T=0$ values for f and ℓ which are tabulated in Table 4. Present theory values for $f = \langle S_0^z S_1^z \rangle$ are considerably larger than the classical prediction, $f = S(S+1)/3$, and agree fairly well with the exactly known value in the case of $S=\frac{1}{2}$[69] and the rigorous bounds in the case of $S=5/2$[70]. The relation $\langle 0|H|0 \rangle = 6NJf$ between the ground state energy and the correlation function f shows that the ground state energy is quite accurately determined by the present theory.

The ground state results for $S=5/2$ are applicable to TMMC and provide a description of the excitation energies E_k according to (98). The experimental results of inelastic neutron magnetic scattering at $4.4°K$ are known to fit very closely the curve $E_k=6.1$ meV sin k over the entire one-dimensional Brillouin zone[40]. Since $h=0.9986$ at $T=0°K$, the E_k predicted by present theory does not quite go to zero at $k=\pi$ (see (109)). However the percentage deviation of E_k from the value $E_k=4J(2|f|)^{\frac{1}{2}}\sin k$ is only 5% at $k=0.95\pi$ and 1.5% at $k=0.9\pi$.

Richards[45] using classical theory values $f=-S(S+1)/3$ and $\ell=1$ at zero degrees, predicts $E_k=4J(2S(S+1)/3)^{\frac{1}{2}}\sin k$, while Lovesay and Meserve[71] use a theory of the shape of the relaxation function to get $E_k=4J(S(S+1))^{\frac{1}{2}}\sin k$. If one uses the value $J=7.7°K$ obtained from quasi-elastic neutron data[39] in the above expressions for the excitation energies, one obtains the maximum E_k at $k=\pi/2$ to be 5.65 meV

Table 4. Ground State Parameters for the One Dimensional Heisenberg Antiferromagnet.

Spin	ℓ	$3f/S(S+1)$ [a] (Present Theory)	$3f/S(S+1)$ [a] (Exact)
1/2	0.72880	-0.49571	-0.591 [b]
1	0.92935	-0.60214	$-3/4 < 3f/S(S+1) < -1/2$ [c]
5/2	0.99860	-0.76941	$-6/7 < 3f/S(S+1) < -5/7$ [c]

(a) Ground state energy per spin is 6Jf

(b) Ref. 69

(c) Ref. 70

(present theory), 6.41 meV (Richards), and 7.85 meV (Lovesay and Mersrve) compared with 6.1 meV (Hutchings et al).

Equation (98) predicts an energy gap at $k=\pi$,

$$E_g = 8J(|f|(\ell^{-1}-1))^{\frac{1}{2}} \tag{109}$$

which at T=0 is 0.298 meV, and a parabolic dependence of E_k on k for k near π. The energy gap is of course a consequence of ℓ being less than unity. A further implication of ℓ being less than unity is a finite value of the staggered susceptibility at T=0°K since the staggered susceptibility is proportional to $\ell/(1-\ell)$. This in turn implies finite values for both $\varkappa$, the inverse correlation range and $\langle\vec{S}_\pi\cdot\vec{S}_{-\pi}\rangle^{-1}$, contrasted with the zero value predicted by the classical theory for these two quantities.

Numerical calculations[71] on finite spin systems produce E_k spectra with no evidence for such a gap, so we are led to believe its presence represents a flaw in the present theory. It appears that the zero temperature results here correspond to a ground state which is deficient in the long-range spin-spin correlations and concomitant large fluctuations in sub-lattice magnetization about its zero average value since $\ell\neq1$ implies finite staggered susceptibility and finite correlation range.

Solutions for finite temperature are now restricted to low temperatures where the principal contributions to thermal excitations have wavevectors in the neighborhood of k=0 and $k=\pi$. (For TMMC this corresponds to T<25°K.) The lattice sums in (100) involve a phonon-like spectrum on the interval $0 < k < \pi/2$. The sums, $L_n(0,\pi/2)$ become

integrals in the thermodynamic limit, and one finds upon using $E_k \propto k$ and extending the upper limit of integration to infinity that

$$L_n(0,\pi/2) = \frac{\pi(1-\ell)}{6\beta^2 E_G^2} + O(\beta^{-4}) \tag{110}$$

The evaluation of $L_n(\pi/2,\pi)$ is more complicated since its value is very sensitive to the height of the roton-like minimum in the excitation spectrum given by (109). Upper and lower bounds for $L_n(\pi/2,\pi)$ are obtained by the following procedure. At low temperatures (101) indicates $L_0(\pi/2,\pi) \simeq -L_1(\pi/2,\pi)$ so one need only consider $L_0(\pi/2,\pi)$. The excitation spectrum is approximated by $E_k \simeq E_G[1+\ell\cos k)/(1-\ell)]^{1/2}$. Expanding n_k in a geometric series, one obtains

$$L_0(\pi/2,\pi) = \frac{2}{\pi}(2\ell)^{-1/2} \sum_{r=1}^{\infty} \exp(-r\beta E_G) I_r \tag{111}$$

$$I_r = \int_0^{x_0} dx[x(1+x/2)]^{-1/2} \exp(-r\beta E_G x) \tag{112}$$

has $x_0 = -1+(1-\ell)^{-1/2}$ as the upper limit of integration. Substitution of the rigorous bounds, $\exp(-x/4) \le (1+x/2)^{-1/2} \le 1$ into (112) yields

$$I_r = [(r\beta E_G+\eta/4)/\pi]^{-1/2} \exp(-\beta E_G r) \times Erf([x_0(r\beta E_G+\eta/4)]^{1/2}) \tag{113}$$

for some value of η satisfying $0 \le \eta \le 1$. For the case of $S=5/2$, the error function in (113) may be replaced by unity for $T < 25^\circ K$.

After inserting the lattice sums L_0 and L_1 into (106) and (107), upper and lower bounds on f and ℓ are determined by varying the parameter η for fixed T. The quantity $\langle \vec{S}_k \cdot \vec{S}_{-k} \rangle$ in (96) has the Lorentzian form in terms of $\tilde{k} = \pi-k$, $\langle \vec{S}_k \cdot \vec{S}_{-k} \rangle \propto (\tilde{k}^2 + \kappa^2)^{-1}$, defining the inverse correlation

length $\varkappa$ as

$$(\varkappa a)^2 = \frac{2(1-\ell)}{\ell} \left[1 + \frac{n_\pi^2}{1+2n_\pi} \right]^{-1} \tag{114}$$

The inverse correlation length $\varkappa$ depends on the parameter η. Upper and lower bounds for $\varkappa$ at each temperature result by varying η between zero and unity.

Our results, Fisher's classical solution, and Richards result for the inverse correlation length $\varkappa$ are shown in Figure 1. One sees from the figure that the large discrepancy between present theory and the classical solution remains for temperatures up to $25^\circ K$. For temperatures above about $40^\circ K$, a better approximation to present theory is obtained from the high temperature limit which is equivalent to the classical limit $J \to 0$, $S \to \infty$, and $\vartheta = JS(S+1)$ fixed. In this limit the self-consistency equations are easily solved, yielding $\ell = (1+x^2)^{-1/2}$, $3f/S(S+1) = x-h^{-1}$, and $(\varkappa a)^2 = 2(1-\ell)/\ell$ with $x=3/(4\beta\gamma)$. This last expression for $\varkappa$ is shown in Figure 1 as the dotted line. Comparison of $\varkappa$ over an extended temperature range indicates the discrepancy is reduced to about 7% at the Curie-Weiss temperature $\theta=4JS(S+1)\approx 90^\circ K$ for TMMC. Inspection of Figure 2 depicting $\langle \vec{S}_0 \cdot \vec{S}_1 \rangle$ data for $S=1$ shows the improvement of present predictions over the classical results when compared with the computer calculations of Weng[73].

In conclusion, the present theory has been shown to produce an improvement over the classical theory description of local spin behavior, as exemplified by nearest neighbor correlations in the low temperature region for a one-dimensional Heisenberg antiferromagnet. The long
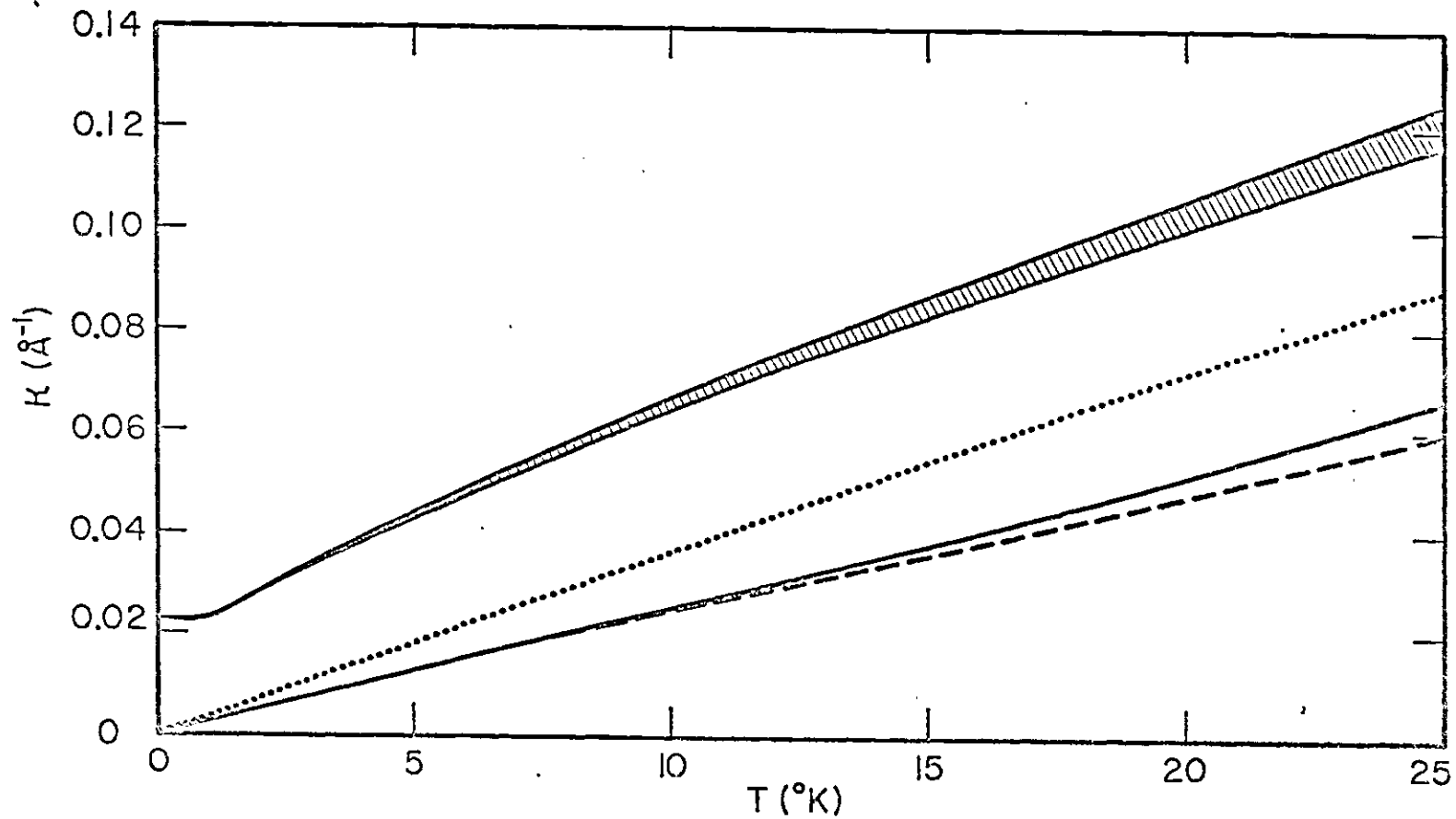
Figure 1. Inverse Correlation range ϰ Versus Temperature for TMMC (S=5/2). Solid line is Fisher's Classical Solution, Dashed Line is Richards' Result, Cross-Sectioned Curve Represents Upper and Lower Bounds of Present Theory, and Dotted Line is Classical Limit of Present Theory.
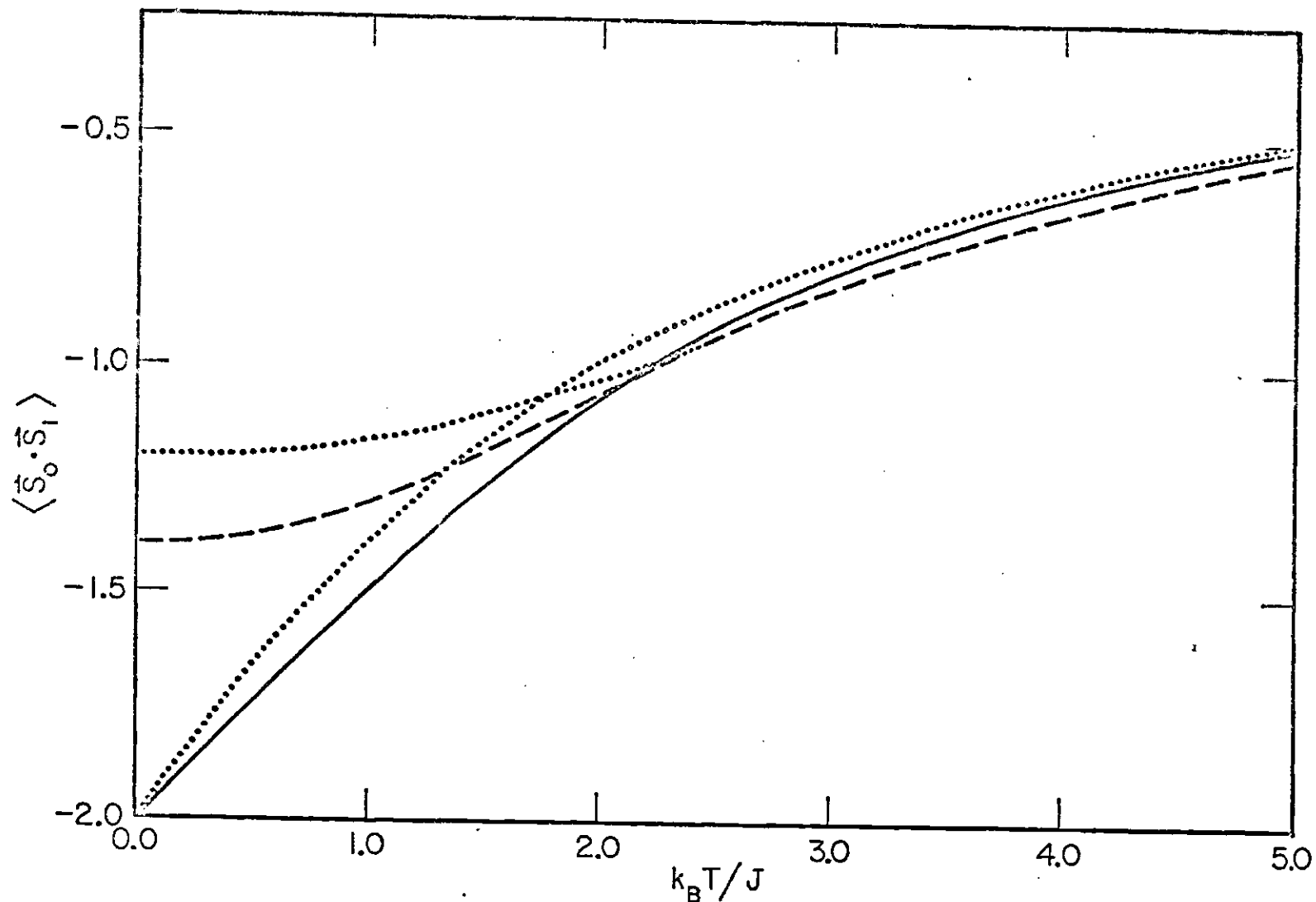
Figure 2. Nearest Neighbor Correlation Function $\langle \vec{S}_0 \cdot \vec{S}_1 \rangle$ Versus Temperature for the Linear Heisenberg Antiferromagnet, S=1. Solid Line is Fisher's Classical Model, Dashed Line is Computer Calculation of Weng. Upper Dotted Line at Low Temperatures is Present Theory, and Lower Dotted Line is Classical Limit of Present Theory.

range spin behavior is, on the other hand, much more accurately given by the classical theory. This unbalanced performance does not seem to us surprising, given that the ground state of this system is characterized by an infinite spin correlation length and concomitant macroscopic fluctuations in sub-lattice magnetization. These characteristics, similar to those present near an ordinary Curie or Neel point of a three-dimensional magnet, are known to receive adequate description via classical theory.

APPENDIX I

The purpose of this appendix is to establish the spectral theorem given by (16) in Chapter II. After substituting the definitions for the Green's functions given by (4) into (15), one finds

$$\omega\ R(\omega)\ =\ F(\omega;t)<[A(t),B(0)]>\tag{115}$$

If one denotes the eigenvalues of the hamiltonian H by E_i and the corresponding eigenfunctions by $|E_i>$, then one finds from (7) that

$$<B(0)A(t)>\ =\ Z^{-1}\ \sum_i\ <E_i|B(0)A(t)|E_i>e^{-\beta E_i}\tag{116}$$

and

$$<A(t)B(0)>\ =\ Z^{-1}\ \sum_j\ <E_j|A(t)B(0)|E_j>\ e^{-\beta E_j}\tag{117}$$

The last two equations become

$$<B(0)A(t)>\ =\ \frac{1}{Z}\ \sum_{ij}<E_i|B(0)|E_j><E_j|A(0)|E_i>\exp(-\beta E_i-i(E_i-E_j)t)\tag{118}$$

and

$$<A(t)B(0)>\ =\ \frac{1}{Z}\ \sum_{ij}<E_i|B(0)|E_j><E_j|A(0)|E_i>\exp(\beta E_j-i(E_i-E_j)t)\tag{119}$$

respectively after the explicit expression for A(t) given by (7) and the completeness property

$$1\ =\ \sum_j\ |E_j><E_j|\tag{120}$$

are used. Upon Fourier transforming (118) and (119) one finds

$$F(\omega; t)<B(0)A(t)> \; = \; e^{-\beta\omega}F(\omega; t)<A(t)B(0)> \tag{121}$$

so that (115) becomes

$$\frac{\omega R(\omega)}{e^{\beta\omega} - 1} = F(\omega; t)<B(0)A(t)> \tag{122}$$

Upon Fourier transforming the last equation, one obtains

$$<B(0)A(t)> \; = \; F^{-1}(t; \omega) \; \frac{\omega R(\omega)}{e^{\beta\omega} - 1} \tag{123}$$

which is the desired result.

APPENDIX II

The purpose of this appendix is to find the linear response of the Heisenberg model to a spatially dependent magnetic field and to show that the susceptibility χ_k to be defined below is identical to $R_{zz}(k, t=0)$.

To the Heisenberg hamiltonian given by (11) one may add a term reflecting the Zeeman interaction of the spins with an applied spatially dependent magnetic field h_k. The Hamiltonian is then

$$\widetilde{H} = H - h_{-k}S_k^Z - h_k S_{-k}^Z \tag{124}$$

where $h_k^* = h_{-k}$ so that the Hamiltonian is Hermetian. The susceptibility χ_k is defined as

$$\chi_k = \frac{1}{N} \frac{\partial}{\partial h_k} \left. \frac{Tr(S_k^Z e^{-\beta\widetilde{H}})}{Tr(e^{-\beta\widetilde{H}})} \right|_{h_k=h_{-k}=0} \tag{125}$$

The evaluation of the derivative in (125) is somewhat tedious because $[H, S_k^Z] \neq 0$ unless $k=0$. Therefore one must expand $e^{-\beta\widetilde{H}}$ in a Taylor's series and take account of the non-commutativity. One finds that

$$N\chi_k = Z^{-1} \sum_{r=1, s=0}^{\infty} \sum^{r-1} Tr(S_k(-\beta H)^{r-s-1}(\beta S_{-k}^Z)(-\beta H)^s/r! - \beta <S_k^Z><S_{-k}^Z> \tag{126}$$

where Z is the partition function in zero field. The last term iz zero in the paramagnetic region since by definition, the paramagnetic region has no long range order.

In the energy eigenstate basis described in Appendix I, the last
equation is found to be

$$N \chi_k = Z^{-1} \sum_{ij} \langle E_i | S_k | E_j \rangle \langle E_j | S_{-k} | E_i \rangle \frac{e^{-\beta E_i} - e^{-\beta E_j}}{E_j - E_i} \tag{127}$$

with the aid of the identity

$$x^r - y^r = (x-y) \sum_{s=0}^{r-1} x^{r-s-1} y^s \tag{128}$$

But (127) is easily shown to be equivalent to

$$N\chi_k = F^{-1}(t{=}0, \omega)(F(\omega; t) \langle S_k^Z(t) S_{-k}^Z(0) \rangle (e^{\beta \omega}-1)/\omega) \tag{129}$$

when compared with the Fourier transform of (119), and when the identifica-
tion $A(t){=}S_k^Z(t)$ and $B(0){=}S_{-k}^Z$ is made. One can use the invariance of the
spin correlation functions to translations to obtain

$$\chi_k = \sum_j e^{ik \cdot j} F^{-1}(t{=}0; \omega)(F(\omega; t) \langle S_j^Z(t) S_0^Z(0) \rangle (e^{\beta \omega}-1)/\omega) \tag{130}$$

Finally (130) is seen to reduce to

$$\chi_k = R_{zz}(k, t{=}0) \tag{131}$$

when compared with (123). This is the desired result.

APPENDIX III

The nearest neighbor spin-spin correlation coefficients $B_n^{GF}(v,S)$ defined by (91) and discussed in Chapter VI are compared below with the exact coefficients denoted by $B_n^{E}(v,S)$ which were deduced from the coefficients of Rushbrooke and Wood[52].

Linear:

$$B_2^{E} = X^2/3, \quad B_3^{E} = 0X^3-vX^2/12, \quad B_4^{E} = X^2(-3X^2-8vX+3v)/135$$

$$B_2^{GF} = X^2/3, \quad B_3^{GF} = 0X^3-vX^2/18, \quad B_4^{GF} = X^2(-5X^2-10vX+1.25v)/135$$

Square:

$$B_2^{E} = X^2/3, \quad B_3^{E} = 0X^3-vX^2/12, \quad B_4^{E} = X^2(7X^2-18vX+3v)/135$$

$$B_2^{GF} = X/3, \quad B_3^{GF} = 0X^3-vX^2/18, \quad B_4^{GF} = X^2(5X^2-20vX+1.25v)/135$$

Simple Cubic:

$$B_2^{E} = X^2/3, \quad B_3^{E} = 0X^3-vX^2/12, \quad B_4^{E} = X^2(17X^2-28vX+3v)/135$$

$$B_2^{GF} = X^2/3, \quad B_3^{GF} = 0X^3-vX^2/18, \quad B_4^{GF} = X^2(15X^2-30vX+1.25v)/135$$

Body Centered Cubic:

$$B_2^{E} = X^2/3, \quad B_3^{E} = 0X^3-vX^2/12, \quad B_4^{E} = X^2(57X^2-38vX+3v)/135$$

$$B_2^{GF} = X^2/3, \quad B_3^{GF} = 0X^3-vX^2/18, \quad B_4^{GF} = X^2(55X^2-40vX+1.25v)/135$$

Face Centered Cubic:

$$B_2^{E} = X^2/3, \quad B_3^{E} = 4X^3/9-vX^2/12, \quad B_4^{E} = X^2(107X^2-78vX+3v)/135$$

$$B_2^{GF} = X^2/3, \quad B_3^{GF} = 4X^3/9-vX^2/18, \quad B_4^{GF} = X^2(105X^2-70vX+1.25v)/135$$

APPENDIX IV

The susceptibility coefficients $D_n^{GF}(v,S)$ defined by (93) and

discussed in Chapter VI are compared with the exact coefficients denoted

by $D_n^E(v,S)$ which were deduced from the coefficients of Brown and

Luttinger[67].

<u>Linear:</u>

$$D_0^E = 1, \quad D_1^E = 2X/3, \quad D_2^E = 2X^2/9 - vX/6$$

$$D_0^{GF} = 1, \quad D_1^{GF} = 2X/3, \quad D_2^{GF} = 2X^2/9 - vX/9$$

<u>Square:</u>

$$D_0^E = 1, \quad D_1^E = 4X/3, \quad D_2^E = 4X^2/3 - vX/3$$

$$D_0^{GF} = 1, \quad D_1^{GF} = 4X/3, \quad D_2^{GF} = 4X^2/3 - 2vX/9$$

<u>Simple Cubic:</u>

$$D_0^E = 1, \quad D_1^E = 2X, \quad D_2^E = 10X^2/3 - vX/2$$

$$D_0^{GF} = 1, \quad D_1^{GF} = 2X, \quad D_2^{GF} = 10X^2/3 - vX/3$$

<u>Body Centered Cubic:</u>

$$D_0^E = 1, \quad D_1^E = 8X/3, \quad D_2^E = 56X^2/9 - 2vX/3$$

$$D_0^{GF} = 1, \quad D_1^{GF} = 8X/3, \quad D_2^{GF} = 56X^2/9 - 4vX/9$$

<u>Face Centered Cubic:</u>

$$D_0^E = 1, \quad D_1^E = 4X, \quad D_2^E = 44X^2/3 - vX$$

$$D_0^{GF} = 1, \quad D_1^{GF} = 4X, \quad D_2^{GF} = 44X^2/3 - 2vX/3$$

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VITA

Sam Allen Scales was born on May 22, 1942 in Shelbyville, Tennessee. He lived at Eagleville, Tennessee until he graduated from Eagleville High School in 1960.

In the fall of 1960, he entered Georgia Institute of Technology where he received his B.S. in Physics with honor in June of 1964 and his M.S. in Physics in June of 1965. He attended the Latin American School of Physics during the Summer of 1966 under the sponsorship of the National Science Foundation. He was selected to be a member of such honor societies as Phi Eta Sigma, Tau Beta Pi, Phi Kappa Phi, and Sigma Pi Sigma.

While at Georgia Tech, he was employed by the Physical Sciences Division of the Georgia Tech Experiment Station during his senior year and his first year of graduate school. Later he taught sophomore physics as a graduate teaching assistant and was employed as a graduate research assistant during portions of his thesis research which was sponsored in part by the National Science Foundation and in part by the National Aeronautics and Space Administration.

On September 3, 1966 he was married to the former Charlotte Marie Swinney. They have one son, Sam Allen Scales, Jr. who was born on their second wedding anniversary.