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Time Correlations of Spin Operators in Finite Linear Magnetic Chains

Fernando Carboni

Technical Report COO-1488-4
under United States Atomic Energy
Commission Contract AT(11-1)1488

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INTRODUCTION

Experimentally a number of substances are known, for example copper tetramine sulfate monohydrate, in which the magnetic ions are arranged in chains with strong exchange interactions within each chain but rather weak interactions between chains. The chains should be almost independent and theoretical values based on a one-dimensional model may be confronted directly with experimental measurements.

With the development of fast digital computers it is feasible to perform exact calculations on finite models of many types of physical systems. Possibilities of exact calculations on finite spin systems depend largely on the number of spins in the system since the order of the matrices to consider increases rapidly with this number. With present day computers, the number of spins that can be handled is rather small. On the linear chain, for example, studies of finite systems have been limited to 11 spins. However, compared with two- and three-dimensional models, the one-dimensional linear chain has the advantage of a low coordination number, i.e., for example, a three-dimensional cubic system of 7 spins includes only nearest neighbors while in a linear chain of 7 spins we are considering neighbors to the third order.

The value of the ground state energy for the infinite

antiferromagnetic chain has been calculated exactly, and calculations of the ground state energy performed on finite chains of N spins show a rapid and regular convergence toward that value. This fact has encouraged the numerical study of other properties for which the $N = \infty$ limits are unknown with the expectation that the results will not be misleading. Various thermodynamic and magnetic properties have been calculated by Bonner and Fisher³ for ferro- and antiferromagnetic chains of two to eleven spins $\frac{1}{2}$ with anisotropic Ising-Heisenberg Hamiltonian. Such calculations require knowledge of the energy level spectrum only.

Accurate values for other properties would be valuable as an aid to judging various approximate theoretical methods which are also applicable to more complex systems. There exists an increasing interest in the calculation of general time correlation functions of spin operators which are basic for the study of certain dynamical properties of solids such as magnetic resonance linewidth and neutron scattering. Very little is known at present about the functional form of correlation functions despite much theoretical effort and the common procedure has been to assume particular and relatively simple expressions to fit the needs.

With this motivation and with the hope of throwing some light on the subject, we have undertaken a numerical study of time correlations of spin operators and resonance

linewidth for finite antiferromagnetic chains of spins $\frac{1}{2}$ coupled by isotropic exchange (Heisenberg) interaction. Since the calculation of correlation functions requires both eigenvalues and eigenvectors of the exchange Hamiltonian, we have diagonalized the matrices for chains of 4 to 11 spins.

The plan of this thesis is as follows: The first part is devoted to present a general method for the diagonalization of the Hamiltonian matrix. In Chap. I, the matrix is reduced to block diagonal form by classifying the states according to the z-component of total spin. The translational invariance of the Hamiltonian is used to obtain further reductions of these blocks by defining a translation operator which leads, in general, to matrices with complex elements. In Chap. II, the translation operator is used to construct a new operator which conveniently splits the blocks into real symmetric matrices. The largest matrices, which are those resulting from the block corresponding to zero z-component of total spin, are reduced further in Chap. III by using the rotational invariance of the Hamiltonian. In Chap. IV, numerical methods to obtain the matrix elements by machine calculations are discussed and the general procedure is reviewed in the last section of the chapter. The second part is devoted to the study of the correlation functions, as functions of the frequency, the temperature and the number of spins. The procedure

used to calculate them and the results are discussed in Chap. V. In Chap. VI we use our correlation functions to compute the frequency dependence of the resonance linewidth for copper tetramine sulfate monohydrate. The results are compared with the values obtained using the gaussian approximation of Kubo and Tomita⁵ and also with recent experimental data. It is found that the frequency dependence of the resonance linewidth predicted by using the exact correlations gives a much better agreement with experiment than the variation predicted on the basis of the gaussian approximation. However, the observed value of the linewidth is about twice as large as the value found in our calculations considering dipolar interactions only. The discrepancy is perhaps due to the effects of hyperfine interaction and anisotropic exchange.

PART I

LINEAR MAGNETIC CHAINS

I. THE TRANSLATION OPERATOR

1. Symmetries and Classification of States

Consider a closed chain of spin $\frac{1}{2}$ atoms coupled by exchange interaction in zero external magnetic field. For a system of N spins, the properties are described by the one-dimensional isotropic exchange Hamiltonian

$$\mathcal{H}_{ex} = -2J \sum_{i=1}^N \vec{S}_i \cdot \vec{S}_{i+1} \quad (1)$$

$$\vec{S}_{i+N} = \vec{S}_i \quad (2)$$

As basic states we may use direct products of "up" and "down" single-spin states. There are 2^N possible states of the system and the problem of calculating the energy levels and eigenfunctions reduces to the diagonalization of the $2^N \times 2^N$ matrix representing the Hamiltonian.

Since the total z-component of spin, $S_z = \sum_{i=1}^N S_i^z$, commutes with $\mathcal{H}_{ex}$, it is convenient to classify our states according to the values of S_z . We call the state with $S_z = -NS$ the state with no spins reversed. If r is the number of spins reversed, there are $\binom{N}{r}$ distinct distributions (states) of r spins reversed. We denote by

$$\varphi_i(N, r), \quad i = 1, 2, 3, \dots, \binom{N}{r} \quad (3)$$

the i th state having N spins of which r are reversed. The original matrix splits into $N + 1$ blocks of order $1, N, \binom{N}{2}, \binom{N}{3}, \dots, \binom{N}{r}, \dots, N, 1$.

Since we are considering closed chains or "rings", the Hamiltonian is invariant under translations. Following Griffiths,¹ we denote the states by chains of plus and minus signs representing the spins "up" and "down" respectively, and introduce the translation operator, T , which translates spins to the left, i.e., for example, for $N = 6$, $r = 3$ and in particular the state $(+ + - + - -)$,

$$T(+ + - + - -) = (+ - + - - +)$$

In general, if we act with this operator N times on a given state, we have

$$T^N \varphi_i(N, r) = \varphi_i(N, r) \quad (4)$$

so that the N eigenvalues of T are the N th roots of unity.

In the example above only the N th power of T leaves the state unchanged, but in some cases, depending upon the given state, other powers of T may also leave a state unchanged. For example, if we consider the state $(+ - + - + -)$, for the same $N = 6$, $r = 3$, we find that the operators T^2 , T^4 and T^6 leave this state unchanged. For a given state, the powers of T having this property are determined by the symmetry properties of the given state under translations. For this reason we first examine the symmetry of the states.

Consider an arbitrary state, $\varphi_i(N, r)$, that we represent as a linear array or chain of r plus signs and $N - r$ minus signs in some order. Let p be the smallest integer for which the operator T^p acting on this state leaves it unchanged.

Then it is necessary that the order of plus and minus signs be such that the chain can be separated (as by partitions) into N/p identical smaller chains of p spins, having exactly the same number of plus and minus signs and in the same order. From these considerations we derive the following conditions:

- 1) p must be an integral divisor of N .
- 2) r must be an integral multiple of N/p or zero.

We classify the states according to the power p defined above and refer to the states as having "symmetry p ". Then, we write $\varphi_j(N, r, p)$ to represent a state of the chain having N spins, r spins reversed, and symmetry p . If $r = 0$ we have $p = 1$.

The following properties are direct consequence of the translational symmetry and conditions (1) and (2).

- a) If $\varphi_j(N, r, p)$ has symmetry p , then, the only powers of T which leave φ_j unchanged are the integral multiples of p , i.e., $T^p, T^{2p}, T^{3p}, \dots, T^{np}$.

Proof. Suppose m is some number between any two multiples of p , i.e.,

$$np < m < (n+1)p.$$

Then we can write $m = np + d$, $d < p$,

$$T^m \varphi_j = T^{np+d} \varphi_j = T^d T^{np} \varphi_j = T^d \varphi_j \neq \varphi_j \quad (5)$$

since $d < p$ and p is the smallest exponent required to leave φ_j unchanged.

b) If N is a prime number, the only possible symmetry is $p = N$ by virtue of condition (1).

c) Given N and r we can form states having different symmetries. The possible values of p for given N and r are all integers p satisfying $1 \leq p \leq N$ and given by

$$p = r' \frac{N}{r}$$

where r' must be an integer such that p is integer.

Consider for example, $N = 12$, $r = 8$. We have

$$p = r' \frac{12}{8} = r' \frac{3}{2}.$$

For $r' = 2, 4, 6$ we get $p = 3, 6, 12$ as only possible symmetries of the states that we can form with $N = 12$ and $r = 8$.

We shall see in the next section that r' is equal to the number of reversed spins in basis of p spins.

2. Number of States of Given Symmetry

If $r = 0$ or $r = N$ there is a single state and it has symmetry 1. If $r \neq 0$ there are a total of $\binom{N}{r}$ states. The number of states of each symmetry consistent with N and r can be calculated as follows. We saw before that a state or chain having symmetry p can be separated by partitions into N/p subchains of p spins each. For example the chain

$$+ - - + - - + - - + - -$$

has symmetry 3 and can be separated into four subchains:

$$| + - - | + - - | + - - | + - - |$$

The number of reversed spins in each subchain is $rp/N = r'$. Any permutation of the r' plus signs and the $p - r'$ minus signs in the subchain evidently will not affect the symmetry of the state (provided the same permutation is done in each subchain). The total number of such permutations is $\binom{p}{r'}$, but this number includes also many states of symmetries less than p that can be formed when we permute the signs. States of symmetry p' less than p can be formed if the following two conditions are satisfied:

- 1) p' is a divisor of p .
- 2) r' is a multiple of p/p' .

The total number of states of symmetry p' is $\binom{p'}{r''}$, where $r'' = r'p'/p$ is the number of spins reversed in basis p' . Then we have

$$\binom{p'}{r''} = \binom{p'}{\frac{rp'}{N}}$$

This process is continued until we get to some $p^{(n)}$ which is the last divisor of p , i.e., a prime number. Note that every divisor of p is also a divisor of N .

If $M(N, r, p)$ is the number of states of N spins, r reversed spins and symmetry p , then we have

$$M(N, r, p) = \binom{p}{\frac{rp}{N}} - \text{sum of states of symmetry } p^{(i)} < p.$$

$$M(N, r, p) = \binom{p}{\frac{rp}{N}} - M(N, r, p') - M(N, r, p'') - \dots - M(N, r, p^{(n)}) \quad (6)$$

where $p', p'', \dots, p$ are the divisors of p less than p .
We define $M(N, r, p) = 0$ if rp/N is not an integer.

Equation (6) is a recursion formula which permits us to classify the states according to their symmetry:

$$Q_i(N, r, p), \quad i = 1, 2, 3, \dots, M(N, r, p). \quad (7)$$

As an example, consider the calculation for a chain of 12 spins with $r = 6$:

$$\text{Total number of states: } \binom{N}{r} = \binom{12}{6} = 924$$

$$\text{Divisors of 12: } 2, 3, 4, 6, 12 \quad (\text{possible values of } p)$$

$$rp/N = 1, \frac{3}{2}, 2, 3, 6$$

$$M(N, r, 2) = \binom{2}{1} = 2$$

$$M(N, r, 3) = 0$$

$$M(N, r, 4) = \binom{4}{2} - 2 = 4 \quad (\text{divisors of 4: } 2)$$

$$M(N, r, 6) = \binom{6}{3} - 2 = 18 \quad (\text{divisors of 6: } 2, 3)$$

$$M(N, r, 12) = \binom{12}{6} - 18 - 4 - 2 = 900 \quad (\text{d. of 12: } 2, 3, 4, 6).$$

The complete calculation for $N = 12$ is shown in table I.

The number $M(N, r, p)$ contains all the states that can be obtained from a given state by the action of the translation operator, T . The number of such states is p . Thus, we must have in $M(N, r, p)$ a certain number of groups of p states each, the members of each group being independent of translation from the members of the other groups, i. e., states belonging to different groups cannot be obtained from one another by translations. For example, we see from

TABLE I

Number of States of Symmetry p for $N = 12$.

$r \backslash p$	1	2	3	4	6	12	sum = $\binom{N}{r}$
0	1						1
1						12	12
2					6	60	66
3				4		216	220
4			3		12	480	495
5						792	792
6		2		4	18	900	924
7						792	792
8			3		12	480	495
9				4		216	220
10					6	60	66
11						12	12
12	1						1

$$\text{Total} = 2^{12} = 4096$$

table I that for $r = 6$, $p = 6$ we have 3 independent groups of 6 states each to give a total of 18 states.

In general, the number of independent groups, $G(N, r, p)$, is given by

$$G(N, r, p) = \frac{M(N, r, p)}{p} \quad (8)$$

We number the groups $1, 2, 3, \dots, G(N, r, p)$ and number the states in each group $0, 1, 2, \dots, p - 1$. Then we can

write the states as

$$\varphi_{\alpha}^i(N, r, p), \quad \begin{array}{l} i = 1, 2, 3, \dots, G(N, r, p) \\ \alpha = 0, 1, 2, \dots, p - 1 \end{array} \quad (9)$$

The superscript i denotes the number of the group. The subscript α denotes the number of translation:

$$\varphi_0^i, \varphi_1^i = T \varphi_0^i, \varphi_2^i = T^2 \varphi_0^i, \dots, \varphi_{\alpha}^i = T^{\alpha} \varphi_0^i \quad (10)$$

3. Eigenfunctions of the Translation Operator

Since the eigenvalues of T are the N roots of unity, we have $T^{-1} = T^{\dagger}$ in a representation in which T is diagonal.

Proof: $T_{ij} = e^{\frac{2\pi i}{N} n_i} \delta_{ij}$, $n_i = 1, 2, \dots, N$ in this representation.

$$\text{Then } (T^{-1})_{ij} = e^{-\frac{2\pi i}{N} n_i} \delta_{ij} = T_{ij}^*$$

Hence $T^{-1} = T^{\dagger}$ in this representation.

But an operator is unitary in one representation, it is unitary in any other representation connected to the original one by a unitary transformation. This is shown by considering

$$T' = S^{-1} T S,$$

where S is a unitary transformation, $S^{-1} = S^{\dagger}$.

Then,

$$T'^{-1} = (S^{-1} T S)^{-1} = S^{-1} T^{-1} S,$$

and

$$T'^{\dagger} = (S^{-1} T S)^{\dagger} = S^{-1} T^{\dagger} S.$$

Now, if $T^{-1} = T^\dagger$ it follows that

$$T^{-1} = T^\dagger, \quad (11)$$

i.e., any operator whose eigenvalues are the roots of unity is unitary. Q.E.D.

A state $\varphi_\alpha^{(N,r,p)}$ shall be denoted φ_α for simplicity. We shall use the former notation only when symmetry considerations are important. We assume that the states φ_α are orthogonal.

Following Griffiths, we denote by t the eigenvalues (Nth roots of 1) of the operator T and introduce the operator

$$F(t) = \frac{1}{N} [1 + t^* T + (t^* T)^2 + \dots + (t^* T)^{N-1}] \quad (12)$$

which is Hermitian and can also be written

$$F(t) = \frac{1}{N} \sum_{n=0}^{N-1} (t^* T)^n \quad (13)$$

Consider the operator $TF(t)$ acting on an arbitrary state φ_α :

$$TF(t) \varphi_\alpha = \frac{1}{N} [T + t^* T^2 + t^{*2} T^3 + \dots + t^{*N-2} T^{N-1} + t^{*N-1} T^N] \varphi_\alpha$$

Multiplying the right hand side by $tt^* = 1$ we have

$$\begin{aligned} TF(t) \varphi_\alpha &= \frac{t}{N} [t^* T + t^{*2} T^2 + \dots + t^{*N-1} T^{N-1} + t^{*N} T^N] \varphi_\alpha \\ &= t \frac{1}{N} [1 + t^* T + (t^* T)^2 + \dots + (t^* T)^{N-1}] \varphi_\alpha \\ &= t F(t) \varphi_\alpha \end{aligned}$$

Therefore, $F(t)$ acting on any state φ_α gives an eigenfunction of T belonging to the eigenvalue t :

$$T [F(t)\varphi_\alpha] = t F(t)\varphi_\alpha \quad (14)$$

Then we can write

$$TF(t) = tF(t), \quad T^n F(t) = t^n F(t) \quad (15)$$

The choice of φ_α remains completely arbitrary but we should note, however, that two eigenfunctions $F(t)\varphi_\alpha$ and $F(t)\varphi_\beta$ are linearly independent only if φ_α and φ_β are independent of translation.

Since $F(t)$ is a function of t also, it is convenient to list some general properties of the roots of unity which will be useful in our problem.

4. Some Properties of the Roots of Unity

A. General Properties

1) The N th roots of unity can be written

$$t_n = e^{i\frac{2\pi}{N}n}, \quad n = 1, 2, 3, \dots, N$$

We call $t_1 = e^{i\frac{2\pi}{N}}$ the first root and $t_N = e^{i2\pi}$ the N th root.

- 2) If t is a root of 1, then t^* is also a root of 1.
- 3) 1 is always one of the roots.
- 4) If N is even, -1 is also a root.
- 5) Every root can be expressed as a power of the first root :

$$t_k = e^{i \frac{2\pi}{N} k} = (t_1)^k \quad (16)$$

6) A positive or negative integral power of any of the roots of 1 reduces to one of the N roots of 1.

7) The product of two distinct roots reduces to one of the N roots :

$$t_n t_m = (t_1)^{n+m} = \text{another root}, \quad (17)$$

by virtue of properties (5) and (6).

B. Symmetry Properties

The roots of unity have some symmetry properties similar to the symmetry properties of the spin states considered before.

8) Suppose t_n is one of the Nth roots of one, then t_n is also a pth root of one if and only if the product pn is a multiple of N.

Proof. Let $t_n = e^{i \frac{2\pi}{N} n}$, then $(t_n)^p = e^{i \frac{2\pi}{N} pn} = 1$ requires $pn = kN$, $k = \text{integer}$.

If we consider only those values of p which are divisors of N, then we can find the root numbers, n, for which $(t_n)^p = 1$ from the equation $n = kN/p$ for some integers k such that $1 \leq n \leq N$.

For example, for $N = 12$, $p = 4$:

$$n = 3k, \quad n = 3, 6, 9, 12$$

$$\text{Then, } (t_3)^4 = (t_6)^4 = (t_9)^4 = (t_{12})^4 = 1.$$

The complete result for $N = 12$, considering all values of p , is shown in table II.

TABLE II

Twelfth roots of unity for which $(t_n)^p = 1$ *

$n \backslash p$	1	2	3	4	6	12
1						x
2					x	x
3				x		x
4			x		x	x
5						x
6		x		x	x	x
7						x
8			x		x	x
9				x		x
10					x	x
11						x
12	x	x	x	x	x	x

* x in table means that $(t_n)^p = 1$

9) if t_i is a p th root of one and $t_i \neq 1$, then

$$\sum_{n=0}^{p-1} (t_i)^n = 1 + t_i + t_i^2 + t_i^3 + \dots + t_i^{p-1} = 0 \quad (18)$$

Proof. Multiply by t_i on both sides of eq.(18),

$$t_i \sum_{n=0}^{p-1} (t_i)^n = t_i + t_i^2 + t_i^3 + \dots + t_i^{p-1} + t_i^p \quad (19)$$

Subtract eq.(19) from eq.(18),

$$(1 - t_i) \sum_{n=0}^{p-1} (t_i)^n = 1 - t_i^p = 0$$

Then we have

$$\sum_{n=0}^{p-1} t_i^n = 0 \quad \text{if } t_i \neq 1.$$

5. Properties of the Operators $F(t)$

The operators $F(t)$ are orthogonal projectors, i.e.,

$$F(t_n) F(t_m) = \begin{cases} F(t_n) & \text{if } t_n = t_m \\ 0 & \text{if } t_n \neq t_m \end{cases} \quad (20)$$

Proof.

$$\begin{aligned} F(t_n) F(t_m) &= \frac{1}{N} \sum_{k=0}^{N-1} (t_n^* T)^k F(t_m) \\ &= \frac{1}{N} \sum_{k=0}^{N-1} (t_n^* t_m) F(t_m) \end{aligned}$$

by eq.(15). But $t_n^* t_m$ is just another root of one by properties (2) and (7), and $\sum_k (t_n^* t_m)^k = 0$ by property (9) unless $t_n^* t_m = 1$ in which case $t_n = t_m$.

We show now a property of $F(t)$ which is not considered in Griffiths' paper : $F(t)$ acting on functions of symmetry p less than N vanishes unless t is an N th root of one which is also a p th root of one.

Proof.

$$\begin{aligned} F(t) \varphi_\alpha(N, r, p) &= \frac{1}{N} \sum_{n=0}^{N-1} (t^* T)^n \varphi_\alpha(N, r, p) \\ &= \frac{1}{N} \left[\sum_{n=0}^{p-1} (t^* T)^n + \sum_{n=p}^{2p-1} (t^* T)^n + \sum_{n=2p}^{3p-1} (t^* T)^n + \dots + \sum_{n=N-p}^{N-1} (t^* T)^n \right] \varphi_\alpha \end{aligned}$$

Renaming the indices we have

$$F(t) \varphi_\alpha(N, r, p) = \frac{1}{N} \left[\sum_{n=0}^{p-1} (t^* T)^n + \sum_{n=0}^{p-1} (t^* T)^{n+p} + \dots + \sum_{n=0}^{p-1} (t^* T)^{n+N-p} \right] \varphi_\alpha$$

$$F(t) \varphi_{\alpha}(N, r, p) = \frac{1}{N} \sum_{n=0}^{p-1} (t^* T)^n \left[1 + (t^* T)^p + (t^* T)^{2p} + (t^* T)^{3p} + \dots + (t^* T)^{N-p} \right] \varphi_{\alpha}.$$

Since φ_{α} has symmetry p , the operators $T^p, T^{2p}, T^{3p}, \dots, T^{N-p}$ leave φ_{α} unchanged (note that $N - p$ is a multiple of p since p divides N). Then we have

$$F(t) \varphi_{\alpha}(N, r, p) = \frac{1}{N} \left[1 + (t^*)^p + (t^*)^{2p} + (t^*)^{3p} + \dots + (t^*)^{N-p} \right] \sum_{n=0}^{p-1} (t^* T)^n \varphi_{\alpha}. \quad (21)$$

Now we can show that the expression in brackets vanishes when $(t^*)^p = 1$. This expression can be written

$$\sum_{n=0}^{\frac{N}{p}-1} (t^*)^{np} = 1 + (t^*)^p + (t^*)^{2p} + \dots + (t^*)^{N-p} \quad (22)$$

Multiplying by $(t^*)^p$ on both sides of (22) we have

$$(t^*)^p \sum_{n=0}^{\frac{N}{p}-1} (t^*)^{np} = (t^*)^p + (t^*)^{2p} + (t^*)^{3p} + \dots + (t^*)^{N-p} + (t^*)^N \quad (23)$$

Subtracting (23) from (22) we get

$$\left[1 - (t^*)^p \right] \sum_{n=0}^{\frac{N}{p}-1} (t^*)^{np} = 1 - (t^*)^N = 0$$

Then we have

$$\sum_{n=0}^{\frac{N}{p}-1} (t^*)^{np} = 0 \quad \text{if } (t^*)^p \neq 1$$

which proves the property.

If $(t^*)^p = 1$, then $\sum_{n=0}^{\frac{N}{p}-1} (t^*)^{np} = \frac{N}{p}$, and

$$F(t) \varphi_{\alpha}(N, r, p) = \frac{1}{p} \sum_{n=0}^{p-1} (t^* T)^n \varphi_{\alpha}(N, r, p) \quad (24)$$

To illustrate the property just discussed we consider

the following example: $N = 4$, $r = 2$. The state $(+ - + -)$ has symmetry $p = 2$. Then for $t = 1$ which is not a square root of 1 we have

$$\begin{aligned} F(i)(+ - + -) &= \frac{1}{4} [1 + iT - T^2 - iT^3] (+ - + -) \\ &= \frac{1}{4} (+ - + -) + i(- + - +) - (+ - + -) - i(- + - +) \\ &= 0 \end{aligned}$$

If we use the eigenfunctions of T to calculate the matrix elements of K_{ex} , the blocks are further reduced into smaller matrices, the size of which can now be calculated by symmetry considerations from tables I and II. We must use only states φ_{α}^i which are independent of translation, say the φ_o^i from each group i of functions.

For example, the block for $N = 12$, $r = 6$, which is 924×924 , is reduced as follows:

The matrices for the roots t_1 , t_5 , t_7 , and t_{11} , do not contain matrix elements from symmetric states ($p < N$) so they contain only $900/12 = 75$ functions φ_o^i independent of translation and we have 4 matrices 75×75 .

For the roots t_2 , t_4 , t_8 , and t_{10} the matrix elements from functions of symmetry 6 do not vanish, then we have $18/6 = 3$ more rows and columns, i.e., 4 matrices 78×78 .

For t_3 and t_9 , $F(t) \varphi_o^i(N, r, p) \neq 0$ for $p = 4$, so we have 2 matrices 76×76 .

For the real roots, t_6 and t_{12} , none of the matrix

elements vanish and we have 2 matrices 80×80 .

The reduction of the matrix using the operator T has the disadvantage that the matrix elements are in general complex, namely, polynomials in t with real coefficients. However, it is possible to make use of the T operator to define new operators which permit a reduction into real symmetric matrices. A discussion of this procedure is the subject of Chap. II.

II. REDUCTION INTO REAL MATRICES

1. Definition of the Operator T

We make use of the translation operator to define a new operator, T , as follows

$$T = T + T^\dagger \quad (25)$$

If φ_α is an arbitrary state, then $T\varphi_\alpha = \varphi_\beta + \varphi_\gamma$, where φ_β has one translation to the left and φ_γ has one translation to the right with respect to φ_α .

T is Hermitian,

$$T^\dagger = T^\dagger + T = T \quad (26)$$

and commutes with $\mathcal{H}_\alpha$, S_z , T and $F(t)$.

Consider now the operator $F(t^*)$ which we derive from equation (12):

$$F(t^*) = \frac{1}{N} [1 + tT + (tT)^2 + \dots + (tT)^{N-1}] \quad (27)$$

Using (27) and proceeding as in the derivation of (14) and (15), we obtain the following relations:

$$TF(t) = tF(t), \quad TF(t^*) = t^*F(t^*) \quad (28a)$$

$$T F(t) = t^*F(t), \quad T F(t^*) = tF(t^*). \quad (28b)$$

2. Eigenvalues and Eigenfunctions of T

Using equations (25) and (28) we have

$$TF(t) = (T + T^*)F(t) = (t + t^*)F(t). \quad (29)$$

Then $F(t)\varphi$ is an eigenfunction of T with eigenvalues $t + t^*$. We can show that the quantities $t + t^* = 2 \cdot \text{Re } t$ are the only possible eigenvalues of T . Suppose Ψ is an eigenfunction (but otherwise arbitrary) of T belonging to some eigenvalue τ . Then,

$$T\Psi = \tau\Psi \quad (30)$$

Acting with some $F(t)$ on both sides of (30) we have

$$F(t)T\Psi = \tau F(t)\Psi$$

$$F(t)(T + T^*)\Psi = \tau F(t)\Psi$$

$$(t + t^*)F(t)\Psi = \tau F(t)\Psi$$

$$[(t + t^*) - \tau]F(t)\Psi = 0$$

for arbitrary Ψ . Then, if $F(t)\Psi \neq 0$, $\tau = t + t^*$.

$F(t^*)\varphi$ is also an eigenfunction of T belonging to the same eigenvalue:

$$TF(t^*)\varphi = (t + t^*)F(t^*)\varphi \quad (31)$$

Therefore, $F(t)\varphi$ and $F(t^*)\varphi$ are two linearly independent (since the $F(t_n)$ are orthogonal projectors) eigenfunctions of T with eigenvalue $t + t^*$. For convenience we choose

the eigenfunctions

$$\frac{1}{2} [F(t)\varphi + F(t^*)\varphi] \quad (32a)$$

and

$$\frac{1}{2i} [F(t)\varphi - F(t^*)\varphi] \quad (32b)$$

and define the operators

$$F_+(t) = \frac{1}{2} [F(t) + F(t^*)] \quad (33a)$$

$$F_-(t) = \frac{1}{2i} [F(t) - F(t^*)] \quad (33b)$$

Then, $F_{\pm}(t)\varphi$ are eigenfunctions of T with eigenvalue $t+t^*$.

The number of distinct eigenvalues $t + t^*$ is $(N + 2)/2$ when N is even, and $(N + 1)/2$ when N is odd. Thus, we limit the roots t_n to be considered to:

Even N : $t_1, t_2, \dots, t_{\frac{N-2}{2}}, t_{\frac{N}{2}} = -1$ and $t_N = 1$.

Odd N : $t_1, t_2, \dots, t_{\frac{N-1}{2}}$ and $t_N = 1$.

3. Properties of the Operators $F_{\pm}(t)$

If t is real, i.e., $t = 1$ or $t = -1$, then $F_+(t) = F(t)$ and $F_-(t) = 0$.

Inverting equations (33) we have

$$F(t) = F_+(t) + iF_-(t) \quad (34a)$$

$$F(t^*) = F_+(t) - iF_-(t) \quad (34b)$$

which will be useful in proceeding sections.

Since $F(t)$ is Hermitian we have, from (33), that $F_+(t)$ is Hermitian and $F_-(t)$ is anti-Hermitian:

$$[F_+(t)]^\dagger = F_+(t) \quad (35a)$$

$$[F_-(t)]^\dagger = -F_-(t) \quad (35b)$$

From the orthogonality of the $F(t)$'s and using the convention above on the roots considered, we can show that all products of the form $F_\pm(t_n) F_\pm(t_m)$ vanish unless t_n is equal to t_m , and in this case we have

$$F_+(t) F_+(t) = \begin{cases} \frac{1}{2}F_+(t), & \text{if } t \text{ is complex} \\ F_+(t) = F(t), & \text{if } t = \pm 1 \end{cases} \quad (36a)$$

$$F_-(t) F_-(t) = \begin{cases} -\frac{1}{2}F_+(t), & \text{if } t \text{ is complex} \\ 0 & \text{if } t = \pm 1 \end{cases} \quad (36b)$$

$$F_-(t) F_-(t) = \begin{cases} \frac{1}{2}F_-(t), & \text{if } t \text{ is complex} \\ 0 & \text{if } t = \pm 1 \end{cases} \quad (36c)$$

Matrix Elements.— With respect to functions $F_\pm(t)\varphi$, the matrix elements of $\mathcal{H}_{ex}$ are real. For $t = \pm 1$ they are certainly real. We examine the case for complex t :

$$\begin{aligned} (F_\pm(t)\varphi, \mathcal{H} F_\pm(t)\varphi') &= (F_\pm^\dagger(t) F_\pm(t)\varphi, \mathcal{H}\varphi') \\ &= \pm (F_\pm(t) F_\pm(t)\varphi, \mathcal{H}\varphi') \\ &= \pm \frac{1}{2} (F_\pm(t)\varphi, \mathcal{H}\varphi') \end{aligned}$$

Now we have

$$\begin{aligned} (F_\pm(t)\varphi, \mathcal{H}\varphi') &= \frac{1}{2} (F(t) + F(t^*)\varphi, \mathcal{H}\varphi') \\ &= \frac{1}{N} \sum_{n=0}^{N-1} \frac{1}{2} (t^{*n} + t^n) (T^n\varphi, \mathcal{H}\varphi') \end{aligned}$$

$$(F_+(t)\varphi, \mathcal{H}\varphi') = \frac{1}{N} \sum_{n=0}^{N-1} (\operatorname{Re} t^n) (T^n \varphi, \mathcal{H}\varphi') \quad (37)$$

which are real since the quantities $(T^n \varphi, \mathcal{H}\varphi')$ are real.

$$\begin{aligned} (F_-(t)\varphi, \mathcal{H}\varphi') &= -\frac{1}{2i} (F(t) - F(t^*)\varphi, \mathcal{H}\varphi') \\ &= -\frac{1}{N} \sum_{n=0}^{N-1} \frac{1}{2i} (t^{*n} - t^n) (T^n \varphi, \mathcal{H}\varphi') \\ &= \frac{1}{N} \sum_{n=0}^{N-1} (\operatorname{Im} t^n) (T^n \varphi, \mathcal{H}\varphi') \end{aligned} \quad (38)$$

which are also real.

The following relations are useful in the actual calculation of matrix elements.

$$F_+(t) T^n = (\operatorname{Re} t^n) F_+(t) - (\operatorname{Im} t^n) F_-(t) \quad (39a)$$

$$F_-(t) T^n = (\operatorname{Re} t^n) F_-(t) + (\operatorname{Im} t^n) F_+(t) \quad (39b)$$

4. Order of the Matrices

The order of the reduced matrices that will result by the use of the T operator can be calculated in the following way. We first note that if for some φ_0^i the function $F(t)\varphi_0^i$ vanishes due to symmetry, then $F(t^*)\varphi_0^i = 0$ also and therefore, $F_{\pm}(t)\varphi_0^i$ vanish identically for exactly the same functions φ as $F(t)$ does (apart from the vanishing of $F_-(t)$ for real t). Then we have $2G(N, r, p)$ functions (independent) for each eigenvalue $t + t^*$ when t is complex and $G(N, r, p)$ functions when t is real, since $F_-(t)$ is equal to zero in this case.

TABLE III

Order of the Matrices for $N = 12, r = 6$

	Eigenvalue						
	t_1+t_{11}	t_2+t_{10}	t_3+t_9	t_4+t_8	t_5+t_7	$2t_6$	$2t_{12}$
No. of $F_+(t)$	75	78	76	78	75	80	80
No. of $F_-(t)$	75	78	76	78	75	0	0
Order	150	156	152	156	150	80	80

The result for $N = 12, r = 6$ is shown in table III. We have, in this case, two matrices of order 150, two of order 156, two of order 80, and one matrix of order 152. Note that the total number of independent functions $F_{\pm}(t)$ is equal to 924, as it was the number of original states corresponding to this block.

5. Normalization of the Eigenfunctions of T

The eigenfunction of T , given by $F_{\pm}(t)\varphi_{\alpha}^i$, are not in general normalized as we shall see in this section. In order to find a complete set of orthonormal eigenfunctions, we assume that the original states, $\varphi_{\alpha}^i(p)$, are orthonormal, i.e.,

$$(\varphi_{\alpha}^i(p), \varphi_{\beta}^j(p')) = \delta_{ij} \delta_{\alpha\beta} \delta_{pp'} \quad (40)$$

and consider the products $(F_{\pm}(t)\varphi_{\alpha}^i(p), F_{\pm}(t)\varphi_{\beta}^j(p'))$:

a) Suppose t is complex. Using (36) we have

$$(F_{+}(t)\varphi_{\alpha}^i(p), F_{+}(t)\varphi_{\beta}^j(p')) = \frac{1}{2} (F_{+}(t)\varphi_{\alpha}^i(p), \varphi_{\beta}^j) \quad (41)$$

since $F(t)$ is Hermitian.

Use of (24) followed by the use of (15) and (40) gives

$$\begin{aligned}
 (F_+(t)\varphi_o^i(p), F_+(t)\varphi_o^j(p')) &= \frac{1}{4p} \sum_{n=0}^{p-1} ([t^{*n} + t^n] T^n \varphi_o^i(p), \varphi_o^j(p')) \\
 &= \frac{1}{4p} \sum_{n=0}^{p-1} (t^{*n} + t^n) (T^n \varphi_o^i(p), \varphi_o^j(p')) \\
 &= \frac{1}{4p} \sum_{n=0}^{p-1} (t^{*n} + t^n) (\varphi_n^i(p), \varphi_o^j(p')) \\
 &= \frac{1}{4p} \sum_{n=0}^{p-1} (t^{*n} + t^n) \delta_{n,0} \delta_{ij} \delta_{pp'} \\
 &= \frac{1}{2p} \delta_{ij} \delta_{pp'}
 \end{aligned} \tag{42}$$

Similarly, we can show that

$$(F_-(t)\varphi_o^i(p), F_-(t)\varphi_o^j(p')) = \frac{1}{2p} \delta_{ij} \delta_{pp'} \tag{43}$$

Now consider

$$\begin{aligned}
 (F_+(t)\varphi_o^i(p), F_-(t)\varphi_o^j(p')) &= -\frac{1}{2} (F_-(t)\varphi_o^i(p), \varphi_o^j(p')) \\
 &= -\frac{1}{4ip} \sum_{n=0}^{p-1} (t^n - t^{*n}) (T^n \varphi_o^i(p), \varphi_o^j(p')) \\
 &= -\frac{1}{4ip} \sum_{n=0}^{p-1} (t^n - t^{*n}) \delta_{n,0} \delta_{ij} \delta_{pp'} \\
 &= 0
 \end{aligned} \tag{44}$$

b) Suppose t is real. Again, using (36), (24), (15) and (40) we have

$$\begin{aligned}
 (F_+(t)\varphi_o^i(p), F_+(t)\varphi_o^j(p')) &= (F(t)\varphi_o^i(p), \varphi_o^j(p')) \\
 &= \frac{1}{p} \sum_{n=0}^{p-1} (t^{*n} T^n \varphi_o^i(p), \varphi_o^j(p')) \\
 &= \frac{1}{p} \sum_{n=0}^{p-1} t^n (\varphi_n^i(p), \varphi_o^j(p'))
 \end{aligned}$$

$$(F_+(t)\varphi_o^i(p), F_+(t)\varphi_o^j(p')) = \frac{1}{p} \delta_{ij} \delta_{pp'} \quad (45)$$

Since $F_-(t) = 0$ when t is real we have

$$(F_-(t)\varphi_o^i(p), F_-(t)\varphi_o^j(p')) = 0 \quad (46)$$

$$(F_+(t)\varphi_o^i(p), F_-(t)\varphi_o^j(p')) = 0. \quad (47)$$

Excluding those functions for which $F(t)\varphi = 0$ (see Sec. 5, Chap. I) and those for which $F_-(t) = 0$ (see Sec. 3, Chap. II), we can write the orthogonality relations, among the remaining functions, in condensed form:

$$(F_\mu(t)\varphi_o^i(p), F_\nu(t)\varphi_o^j(p')) = \begin{cases} \frac{11}{2p} \delta_{\mu\nu} \delta_{ij} \delta_{pp'}, & \text{complex } t \\ \frac{1}{p} \delta_{\mu\nu} \delta_{ij} \delta_{pp'}, & \text{real } t \end{cases} \quad (48)$$

where μ, ν stand for $+$ or $-$. If we define

$$\tau = \begin{cases} 1 & \text{if } t \text{ is complex} \\ 2 & \text{if } t \text{ is real} \end{cases} \quad (49)$$

then, equation (48) can be written

$$(F_\mu(t)\varphi_o^i(p), F_\nu(t)\varphi_o^j(p')) = \frac{\tau}{2p} \delta_{\mu\nu} \delta_{ij} \delta_{pp'} \quad (50)$$

The functions $\sqrt{\frac{2p}{\tau}} F_\mu(t)\varphi_o^i(p)$ thus form a set of orthonormal eigenfunctions of $\mathbb{T}$. We denote this eigenfunctions by

$$\Phi^i(\mu, t, p) = \sqrt{\frac{2p}{\tau}} F_\mu(t)\varphi_o^i(p) \quad (51)$$

6. General Form of the Matrix Elements

In this section we want to derive a general expression for the matrix elements of $\mathcal{K}_{\alpha\alpha}$, which shall be written simply as $\mathcal{K}$, with respect to eigenfunctions of $\mathbb{T}$.

The derivation is simplified if we write eqs. (39a) and (39b) in the form

$$F_{\nu}(t)T^n = (\text{Re } t^n)F_{\nu}(t) - \nu(\text{Im } t^n)F_{-\nu}(t) \quad (52)$$

where we agree to assign to ν the value $+1$ when ν represents the subscript $+$, and the value -1 when ν represents the subscript $-$.

We have to consider first expressions of the form $(\Phi^i(\mu, t, p), T^n \Phi^i(\nu, t, p))$, which with the help of (51) becomes

$$\begin{aligned} (\Phi^i(\mu, t, p), T^n \Phi^i(\nu, t, p)) &= \frac{2p}{\tau} (F_{\mu}(t) \varphi_o^i(p), T^n F_{\nu}(t) \varphi_o^i(p)) \\ &= \frac{2p}{\tau} (F_{\mu}(t) \varphi_o^i(p), F_{\nu}(t) T^n \varphi_o^i(p)) \end{aligned}$$

Now we use (52) and (50) to obtain

$$\begin{aligned} (\Phi^i(\mu, t, p), T^n \Phi^i(\nu, t, p)) &= \frac{2p}{\tau} (F_{\mu}(t) \varphi_o^i(p), [\text{Re } t^n F_{\nu}(t) - \nu \text{Im } t^n F_{-\nu}(t)] \varphi_o^i(p)) \\ &= \frac{2p}{\tau} \left\{ \text{Re } t^n (F_{\mu}(t) \varphi_o^i(p), F_{\nu}(t) \varphi_o^i(p)) - \nu \text{Im } t^n (F_{\mu}(t) \varphi_o^i(p), F_{-\nu}(t) \varphi_o^i(p)) \right\} \\ &= \frac{2p}{\tau} \left\{ (\text{Re } t^n) \frac{\tau}{2p} \delta_{\mu\nu} - \nu (\text{Im } t^n) \frac{\tau}{2p} \delta_{\mu, -\nu} \right\} \\ &= \text{Re } t^n \delta_{\mu\nu} - \nu \text{Im } t^n \delta_{\mu, -\nu} \quad (53) \end{aligned}$$

Consider a general matrix element of $\mathcal{K}$:

$$(\Phi^i(\mu, t, p), \mathcal{H} \Phi^j(\nu, t, p')) = \frac{\sqrt{2p} \sqrt{2p'}}{\tau} (F_\mu(t) \varphi_o^i(p), \mathcal{H} F_\nu(t) \varphi_o^j(p')) \quad (54)$$

Since $\mathcal{H}$ and $F_\nu(t)$ commute, we may act first with $\mathcal{H}$ on $\varphi_o^j(p')$. The matrix element vanishes unless $\mathcal{H} \varphi_o^j(p')$ yields states of the group of $\varphi_o^i(p)$. Suppose $\mathcal{H} \varphi_o^j(p')$ gives a number n_i of states, $\varphi_{\alpha_1}^i(p)$, $\varphi_{\alpha_2}^i(p)$,, $\varphi_{\alpha_{n_i}}^i(p)$, of the group i , then we may write

$$\mathcal{H} \varphi_o^j(p') = \sum_{k=1}^{n_i} a_k \varphi_{\alpha_k}^i(p) + \chi \quad (55)$$

where χ represents all other states which do not contribute to the matrix element, a_k represents the constants in $\mathcal{H}$ and matrix elements of spin operators.

In terms of the translation operator, (55) becomes

$$\mathcal{H} \varphi_o^j(p') = \sum_{k=1}^{n_i} a_k T^{\alpha_k} \varphi_o^i(p) + \chi \quad (56)$$

As an illustration of eq. (56), consider for example a chain with $N = 5$, and suppose

$$\varphi_o^j = + - - + +, \quad \varphi_o^i = - + + - +$$

$$\mathcal{H} = -2J \sum_{i=1}^5 \vec{S}_i \cdot \vec{S}_{i+1}$$

$$= -2J \sum_{i=1}^5 [S_i^z S_{i+1}^z + \frac{1}{2}(S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+)]$$

Then we have

$$\mathcal{H} \varphi_o^j = -2J \left\{ \frac{1}{2}(+ - - + +) + \frac{1}{2}(+ - + - +) + \frac{1}{2}(- + - + +) \right\}$$

$$\mathcal{H} \varphi_o^j = -J T^2 \varphi_o^i - J T^3 \varphi_o^i + \chi$$

Then, $n_i = 2$, $a_1 = a_2 = -J$, $\alpha_1 = 2$, $\alpha_2 = 3$

Substituting eq. (56) into (54) we have

$$\begin{aligned} (\Phi^i(\mu, t, p), \mathcal{H} \Phi^j(\nu, t, p')) &= \frac{\sqrt{2p} \sqrt{2p'}}{\tau} \sum_k a_k (F_\mu(t) \varphi_o^i(p), T^{\alpha_k} F_\nu(t) \varphi_o^j(p')) \\ &= \frac{\sqrt{2p}}{\sqrt{2p'}} \sum_k a_k (\Phi^i(\mu, t, p), T^{\alpha_k} \Phi^j(\nu, t, p)) \\ &= \sqrt{\frac{p}{p'}} \sum_k a_k (\text{Re} t^{\alpha_k} \delta_{\mu\nu} - \nu \text{Im} t^{\alpha_k} \delta_{\mu, -\nu}) \quad (57) \end{aligned}$$

Note that τ cancels out so that in this equation all values of t , real or complex, are treated equally.

III. THE ROTATION OPERATOR

1. Definition of the Operator R

We define a rotation operator, R , which transforms a spin "up" into a spin "down" and viceversa, i.e., for example

$$R(+ - + +) = (- + - -).$$

R commutes with the Hamiltonian and the translation operators T and $\mathbb{T}$.

Let $\bar{\varphi}$ be the state obtained from φ by the action of R , i.e.,

$$R\varphi = \bar{\varphi} \quad (58)$$

Then we have

$$R\bar{\varphi} = \varphi \quad \text{and} \quad R^2\varphi = \varphi \quad (59)$$

Hence, the eigenvalues of R are ± 1 . From the discussion in Sec. 3, Chap. I, it follows that R is unitary and Hermitian:

$$R^\dagger = R^{-1} = R \quad (60)$$

We may choose the eigenfunctions

$$\psi^+ = \frac{1}{\sqrt{2}}(\varphi + \bar{\varphi}) \quad (61a)$$

$$\psi^- = \frac{1}{\sqrt{2}}(\varphi - \bar{\varphi}) \quad (61b)$$

with eigenvalues 1 and -1 respectively.

The operator R does not commute with the total z -component of spin, S_z , unless $S_z = 0$. We may, therefore, use this operator to reduce further those matrices for which $S_z = 0$, i.e., $r = N/2$.

2. Symmetry Properties

The order of the new reduced matrices can be obtained, as before, on the basis of symmetry considerations.

We first note that there are two types of functions among the subset of functions $\varphi(N, r)$ with $r = N/2$:

Type I : Those functions for which $\bar{\varphi} = R\varphi$ is some translation of φ , i.e., $\bar{\varphi}$ is of the form $T^x\varphi$ for some integer x .

Type II: All other functions not having this property.

It suffices to find the number of functions of type I.

Functions of Type I.— Consider an arbitrary chain of an even number of spins. The first x spins of the chain we denote by A and the rest by B , and separate them by a partition:

$$(A \mid B)$$

If the chain resulting from the action of the operator R , whose partitions we denote by $\bar{A}$ and $\bar{B}$ respectively, is supposed to be some translation, T^x , of the original one, we must have the following correspondence

$$(B \mid A) = (\bar{A} \mid \bar{B})$$

The last x spins of B must correspond with the x spins of A . It is then easily verified that every state φ having the property of type I must be of the form

$$\varphi \equiv (A | \bar{A} | A | \dots | \bar{A} | A | \dots | \bar{A} | A | \bar{A}) \quad (62)$$

where A represents some subchain of x spins, $\bar{A} = RA$ and φ is such that $T^x \varphi = \bar{\varphi}$. The number of subchains is even, half of each class and they alternate.

We note that φ must be a symmetric function of symmetry $p = 2x$ and we have

$$\bar{\varphi}(p) = T^{p/2} \varphi \quad (63)$$

Every function of type I is symmetric but not all symmetric functions are of type I.

3. Number of Functions of Type I

Using the "up" and "down" or $+$ and $-$ notation, suppose there are r' plus signs and m' minus signs in A of (63). Then $r' + m' = x$. Every permutation of these signs conserves the properties of type I with respect to the operator R (provided the same permutation is done in every partition). The total number of such permutations is

$$M = \frac{x!}{r'! m'!} = \binom{x}{r'} \quad (64)$$

Now, A has r' minus signs and m' plus signs, so that A and $\bar{A}$ together have x plus signs and x minus signs. Then, we

can form functions of the same symmetry having from $r' = 0$ and $m' = x$ to $r' = x$ and $m' = 0$. The total number of functions of symmetry p (see below) is then

$$M_{\text{tot}} = \sum_{r'=0}^x \binom{x}{r'} = 2^x = 2^{p/2} \quad (65)$$

In M_{tot} we are counting both φ and $\bar{\varphi}$ (which is one translation of φ) and also all other translations of φ . Furthermore, note that in permuting the signs it is possible that states of symmetry less than p be formed. In order to investigate this possibility, we see that for example decompositions of the form

$$| A | \rightarrow | C | \bar{C} |$$

or

$$| A | \bar{A} | \rightarrow | C | \bar{C} | C |$$

are impossible because they do not satisfy the requirement of alternation. It can be shown that the only possible decompositions are of the form

$$| A | \rightarrow | C | \bar{C} | C |$$

of symmetry $2x/3$, and all similar decompositions of symmetries $2x/\ell$, $\ell = 5, 7, 9, \dots$; or decompositions of the form

$$| A | \bar{A} | \rightarrow | C | \bar{C} | C | \bar{C} | C |$$

of symmetry $4x/5$, and all decompositions of symmetries

$4x/\ell$, $\ell = 7, 9, 11, \dots$. Finally, in general, the symmetries, p' , of the functions that could be obtained from a function of symmetry $p = 2x$, are given by

$$p' = \frac{mx}{\ell}, \quad \begin{aligned} m &= 2, 4, 6, \dots \\ \ell &= m + 1, m + 3, m + 5, \dots \end{aligned} \quad (66)$$

The possible values of p' are given by the requirement that p' should be an integral divisor of N .

Since $2^{P/2}$ is the total number of functions including all functions of symmetry p and all possible functions of symmetries p' less than p , we can find now the number of functions of type I and given symmetry, M_p , by the following recursion formula

$$M_p = 2^{P/2} - \text{sum of functions of symmetry } p^{(i)} < p$$

$$M_p = 2^{P/2} - M_{p'} - M_{p''} - \dots \quad (67)$$

where p' , p'' , $\dots$, are values of $p^{(i)} = xm/\ell$ consistent with the requirements: $m = 2, 4, 6, \dots$; $\ell = m + 1, m + 3, \dots$, and $xm/\ell = \text{integral divisor of } N$.

As an example, the calculation for $N = 12$, $r = 6$ is given in table IV.

From eq. (58) and (63) we have that the operator R is equivalent to a translation operator in the subspace spanned by the functions of type I. The eigenfunctions of R , eqs. (61), can be written in this case as

$$\Psi^{\pm}(p) = \frac{1}{\sqrt{2}} (\varphi(p) \pm T^{p/2} \varphi(p)) \quad (68)$$

with eigenvalues ± 1 .

TABLE IV

Functions of Types I and II for $N = 12, r = 6$

p^*	2	4	6	12
No. of fens. of symm. p^*	2	4	18	900
$x = p/2$	1	2	3	6
$2^{p/2}$	2	4	8	64
No. of fens. of type I	2	4	6	60
No. of fens. of type II**	0	0	12	840

*Values taken from table I.

**Obtained by subtraction from the second line.

4. Reduction by the Operator T

We now introduce the operator T which commutes with R . Using the operators $F_+(t)$ and $F_-(t)$ we find that $F_{\pm}(t) \Psi^{\pm}(p)$ are eigenfunctions of T with eigenvalues $t + t^*$. Some of the eigenfunctions of T vanish in the following cases:

- $F_{\pm}(t) \Psi^{\pm}(p)$ vanishes under the same conditions of Sec. 5, Chap. I and Sec. 3, Chap. II, i.e., when $t^p \neq 1$ ($F_{\pm}(t) \Psi^{\pm}(p) = 0$) and when $t = \pm 1$ ($F_-(t) = 0$).
- Additional vanishings for functions of type I:

Consider

$$F_+(t) \Psi^{\pm}(p) = \frac{1}{\sqrt{2}} F_+(t) (\varphi(p) \pm T^{p/2} \varphi(p))$$

$$F_+(t) \Psi^\pm(p) = \frac{1}{\sqrt{2}} F_+(t) (1 \pm T^{p/2}) \varphi(p)$$

Using (39a) we get

$$F_+(t) \Psi^\pm(p) = \frac{1}{\sqrt{2}} [F_+(t) \pm (\operatorname{Re} t^{p/2} F_+(t) - \operatorname{Im} t^{p/2} F_-(p))] \varphi(p)$$

If $t^{p/2}$ is real, i.e., $t^{p/2} = \pm 1$ we have

$$F_+(t) \Psi^\pm(p) = \frac{1}{\sqrt{2}} [F_+(t) \pm t^{p/2} F_+(t)] \varphi(p) \quad (69)$$

Then,

$$F_+(t) \Psi^+(p) = 0, \quad \text{if } t^{p/2} = -1 \quad (70a)$$

$$F_+(t) \Psi^-(p) = 0, \quad \text{if } t^{p/2} = 1 \quad (70b)$$

Now consider

$$\begin{aligned} F_-(t) \Psi^\pm(p) &= \frac{1}{\sqrt{2}} F_-(t) (\varphi(p) \pm T^{p/2} \varphi(p)) \\ &= \frac{1}{\sqrt{2}} [F_-(t) \pm (\operatorname{Re} t^{p/2} F_-(t) + \operatorname{Im} t^{p/2} F_+(t))] \varphi(p) \end{aligned}$$

by using (39b). If $t^{p/2}$ is real we get

$$F_-(t) \Psi^\pm(p) = \frac{1}{\sqrt{2}} [F_-(t) \pm t^{p/2} F_-(t)] \varphi(p) \quad (71)$$

and

$$F_-(t) \Psi^+(p) = 0, \quad \text{if } t^{p/2} = -1 \quad (72a)$$

$$F_-(t) \Psi^-(p) = 0, \quad \text{if } t^{p/2} = 1 \quad (72b)$$

If we denote by $\rho = \pm 1$ the eigenvalues of R , and agree in using ρ also to denote the corresponding superscripts

in $\Psi^\pm$, we can generalize eq. (68) by

$$\Psi^p(p) = \frac{1}{\sqrt{2}} (1 + p T^{p/2}) \varphi(p) \quad (73)$$

and eqs. (70) and (72) by

$$F_\mu(t) \Psi^p(p) = 0 \quad \text{if } t^{p/2} = -p \quad (74)$$

where μ is defined as for eq. (52).

Note that with functions, φ , of type I and given symmetry we can form non-vanishing eigenfunctions of R belonging to only one of the eigenvalues of R , while with functions of type II we can form eigenfunctions belonging to either one of the eigenvalues of R .

5. Order of the Matrices

In order to calculate the size of the reduced matrices that will result by the use of the operators R and T , we proceed as follows. For every eigenvalue of T we have calculated previously a certain number of non-vanishing groups of eigenfunctions independent of translation (see for example table III). Many of these functions are symmetric and may therefore belong to type I. Since we know the total number, M_p , of functions of type I for each p (see table IV), we can find the number of groups (of p functions each) independent of translation by M_p/p . In this way we find the number of independent eigenfunctions of T and R which are of type I. The number of independent eigenfunctions of type II is the difference between the

total number and this number. Since we need two different functions of type II to form an eigenfunction of R , then, the number of independent eigenfunctions Ψ^+ (or Ψ^-) of R is equal to one half the number of functions of type II.

For example, for $N = 12$, $r = 6$ we have 78 independent eigenfunctions of $\mathbb{T}$ (see table III) belonging to the eigenvalue $t_2 + t_{10}$. Among them, there are $60/12 = 5$ eigenfunctions of symmetry 12 and $6/6 = 1$ eigenfunction of symmetry 6 (see table IV) which are of type I. Therefore, we have $78 - 6 = 72$ functions of type II, which implies 36 independent functions Ψ^+ (or Ψ^-) of type II. Furthermore, the 5 functions of type I belong to the eigenvalue $+1$ of R , since $t_2^{12/2} = t_2^6 = 1$, and the one function of symmetry 6 and type I belong to the eigenvalue -1 of R since $t_2^{6/2} = t_2^3 = -1$. Finally, we have $36 - 5 = 41$ functions $F_+ \Psi^+$ and 41 functions $F_- \Psi^+$ for a total of 82 non-vanishing eigenfunctions with eigenvalue $+1$ and $36 - 1 = 37$ functions $F_+ \Psi^-$ and 37 functions $F_- \Psi^-$ for a total of 74 non-vanishing eigenfunctions with eigenvalue -1 . Hence, the original 156×156 matrix corresponding to the eigenvalue $t_2 + t_{10}$ of $\mathbb{T}$ breaks into one 82×82 matrix and one 74×74 matrix.

The complete calculation for the block $N = 12$, $r = 6$ is shown in table V.

TABLE V
Order of the reduced matrices for $N = 12$, $r = 6$

Eigenvalue of	$t_1 + t_{11}$	$t_2 + t_{10}$	$t_3 + t_9$	$t_4 + t_8$	$t_5 + t_7$	$2t_6$				$2t_{12}$						
Symmetry p	12	12	6	12	4	12	6	12	12	6	4	2	12	6	4	2
$p/2$	6	6	3	6	2	6	3	6	6	3	2	1	6	3	2	1
$\frac{p/2}{t_n}$	-1	+1	-1	-1	-1	+1	+1	-1	+1	-1	+1	-1	+1	+1	+1	+1
No. of f. type I	5	5+1=6		5+1=6		5+1=6		5	5+3=8				5+3=8			
No. of f. type II	70	72		70		72		70	72				72			
$\frac{1}{2}$ No. of f. type II	35	36		35		36		35	36				36			
$\rho = 1$																
Vanishing $F_{\pm}$'s	5	1		5+1=6		0		5	1+1=2				0			
No. of f. F_+	35	41		35		42		35	42				44			
No. of f. F_-	35	41		35		42		35	0				0			
Order of matrix	70	82		70		84		70	42				44			
$\rho = -1$																
Vanishing $F_{\pm}$'s	0	5		0		5+1=6		0	5+1=6				8			
No. of f. F_+	40	37		41		36		40	38				36			
No. of f. F_-	40	37		41		36		40	0				0			
Order of matrix	80	74		82		72		80	38				36			

6. General Eigenfunctions of T and R

Using the notation defined for eqs. (73) and (74), the eigenfunctions of T and R can be written

$$F_{\mu}(t) \Psi^{\rho}(p) = \frac{1}{\sqrt{2}} F_{\mu}(t) (1 + \rho R) \varphi(p) \quad (75)$$

We may then construct the operator

$$\mathcal{O}_{\mu}(t, \rho) = \frac{1}{\sqrt{2}} F_{\mu}(t) (1 + \rho R) \quad (76)$$

which gives an eigenfunction of T and R with eigenvalues $t + t^*$ and ρ respectively when acting on any state $\varphi(p)$. Since R is Hermitian and commutes with $F_{\pm}(t)$, then $\mathcal{O}_{+}$ is Hermitian and $\mathcal{O}_{-}$ is anti-Hermitian:

$$\mathcal{O}_{+}^{\dagger} = \mathcal{O}_{+} \quad (77a)$$

$$\mathcal{O}_{-}^{\dagger} = -\mathcal{O}_{-} \quad (77b)$$

Products like $\mathcal{O}_{\pm}(t_1, \rho_1) \mathcal{O}_{\pm}(t_2, \rho_2)$ vanish unless $t_1 = t_2$ and $\rho_1 = \rho_2$.

In order to calculate the matrix elements of $\mathcal{H}$, we have to deal with expressions of the form

$$\mathcal{O}_{\mu}(t, \rho) R^m T^n \varphi(p), \quad \begin{array}{l} m = 0, 1. \\ n = 0, 1, 2, \dots, p-1. \end{array}$$

We first note that

$$\begin{aligned} \mathcal{O}_{\mu}(t, \rho) R &= \frac{1}{\sqrt{2}} F_{\mu}(t) (1 + \rho R) R \\ &= \frac{1}{\sqrt{2}} F_{\mu}(t) (R + \rho) \end{aligned}$$

and since $\beta = \pm 1$ so that $\beta^{-1} = \beta$, this becomes

$$\sigma_{\mu}(t, \beta) R = \beta \sigma_{\mu}(t, \beta) \quad (78)$$

Further, since $\beta^2 = R^2 = 1$, we can generalize (78) to

$$\sigma_{\mu}(t, \beta) R^m = \beta^m \sigma_{\mu}(t, \beta) \quad (79)$$

Then we have from (76)

$$\sigma_{\mu}(t, \beta) R^m T^n = \beta^m \frac{1}{\sqrt{2}} (1 + \beta R) F_{\mu}(t) T^n$$

which by virtue of (52) and (76) gives the result

$$\sigma_{\mu}(t, \beta) R^m T^n = \beta^m [\operatorname{Re} t^n \sigma_{\mu}(t, \beta) - \mu \operatorname{Im} t^n \sigma_{\mu}(t, \beta)] \quad (80)$$

7. Normalization of the Eigenfunctions

Let us first calculate the scalar product

$$(\sigma_{\mu}(t, \beta) \varphi_o^i(p), \sigma_{\nu}(t, \beta) \varphi_o^j(p'))$$

where the states φ_o^i and φ_o^j belong to different translation groups and are also independent of rotation, i.e.,

$$T^n \varphi_o^i \neq \varphi_o^j \quad \text{for all } n,$$

$$R \varphi_o^i \neq \varphi_o^j$$

Using (76) we have

$$(\sigma_{\mu}(t, \beta) \varphi_o^i(p), \sigma_{\nu}(t, \beta) \varphi_o^j(p')) = \frac{1}{2} (F_{\mu}(t)(1 + \beta R) \varphi_o^i(p), F_{\nu}(t)(1 + \beta R) \varphi_o^j(p'))$$

$$\begin{aligned}
(\sigma_\mu(t, \rho) \varphi_o^i(p), \sigma_\nu(t, \rho) \varphi_o^j(p')) &= \frac{1}{2} \left[(F_\mu(t) \varphi_o^i(p), F_\nu(t) \varphi_o^j(p')) \right. \\
&\quad + \rho (F_\mu(t) \varphi_o^i(p), F_\nu(t) R \varphi_o^j(p')) \\
&\quad + \rho (F_\mu(t) R \varphi_o^i(p), F_\nu(t) \varphi_o^j(p')) \\
&\quad \left. + \rho^2 (F_\mu(t) R \varphi_o^i(p), F_\nu(t) R \varphi_o^j(p')) \right] \\
&= (F_\mu(t) \varphi_o^i(p), F_\nu(t) \varphi_o^j(p')) \\
&\quad + \rho (F_\mu(t) R \varphi_o^i(p), F_\nu(t) \varphi_o^j(p')) \quad (81)
\end{aligned}$$

The first term of (81) gives $\frac{1}{2p} \delta_{\mu\nu} \delta_{ij} \delta_{pp'}$ by eq. (50). The second term gives zero for functions of type II since $R \varphi_o^i \neq \varphi_o^j$ and we have

$$(\sigma_\mu(t, \rho) \varphi_o^i(p), \sigma_\nu(t, \rho) \varphi_o^j(p')) = \frac{1}{2p} \delta_{\mu\nu} \delta_{ij} \delta_{pp'}$$

where φ_o^i is of type II.

For functions of type I, $R \equiv T^{p/2}$, and the second term of (81) becomes

$$\begin{aligned}
\rho (F_\mu(t) T^{p/2} \varphi_o^i(p), F_\nu(t) \varphi_o^j(p')) &= \rho \left[\operatorname{Re} t^{p/2} (F_\mu(t) \varphi_o^i(p), F_\nu(t) \varphi_o^j(p')) \right. \\
&\quad \left. - \mu \operatorname{Im} t^{p/2} (F_\mu(t) \varphi_o^i(p), F_\nu(t) \varphi_o^j(p')) \right] \\
&= \rho \operatorname{Re} t^{p/2} \frac{1}{2p} \delta_{\mu\nu} \delta_{ij} \delta_{pp'}
\end{aligned}$$

since in this case $t^{p/2}$ is real because $t^p = 1$ or the product vanishes. Now, if $t^{p/2} = -\rho$, the second term of eq. (81) cancels the first term and the net result is zero. But $t^{p/2} = -\rho$ is the same condition of page 40 for the vanishing of the eigenfunctions, and since the functions for which this happens have been excluded from the matrices, this case is unimportant.

When $t^{p/2} = \rho$, we get

$$(\sigma_\mu(t, \rho) \varphi_o^i(p), \sigma_\nu(t, \rho) \varphi_o^j(p')) = \frac{\tau}{p} \delta_{\mu\nu} \delta_{ij} \delta_{pp'}$$

where φ_o^i is of type I.

We define a number, c , which is equal to 1 for functions of type I and equal to 2 for functions of type II, and denote the functions by $\varphi(p, c)$ according to the type they belong. Then we can generalize with

$$(\sigma_\mu(t, \rho) \varphi_o^i(p, c), \sigma_\nu(t, \rho) \varphi_o^j(p', c')) = \frac{\tau}{cp} \delta_{\mu\nu} \delta_{ij} \delta_{pp'} \quad (82)$$

The functions $\sqrt{\frac{cp}{\tau}} \sigma_\mu(t, \rho) \varphi_o^i(p, c)$ form a set of orthonormal eigenfunctions of T and R . We denote this functions by

$$\Phi^i(\mu, t, \rho, p, c) = \sqrt{\frac{cp}{\tau}} \sigma_\mu(t, \rho) \varphi_o^i(p, c) \quad (83)$$

8. General Form of the Matrix Elements

Consider an arbitrary matrix element of $\mathcal{K}$ with respect to the normalized eigenfunctions (83):

$$\begin{aligned} &(\Phi(\mu, t, \rho, p, c), \mathcal{K} \Phi(\nu, t, \rho, p', c')) \\ &= \frac{\sqrt{cp} \sqrt{c'p'}}{\tau} (\sigma_\mu(t, \rho) \varphi_o^i(p, c), \mathcal{K} \sigma_\nu(t, \rho) \varphi_o^j(p', c')) \\ &= \frac{\sqrt{cp} \sqrt{c'p'}}{\tau} (\sigma_\mu(t, \rho) \varphi_o^i(p, c), \sigma_\nu(t, \rho) \mathcal{K} \varphi_o^j(p', c')) \end{aligned} \quad (84)$$

The matrix element vanishes unless $\mathcal{K}$ acting on φ_o^j gives states of the group of φ_o^i . In general, $\mathcal{K} \varphi_o^j$ gives a sum of states, some of which we suppose are of the group of φ_o^i .

and write them in terms of φ_o^i with the help of the operators T and R as follows

$$\mathcal{H} \varphi_o^j(p', c') = \sum_k a_k R^{m_k} T^{n_k} \varphi_o^i(p, c) + \chi \quad (85)$$

where χ represents all other states which do not contribute to the matrix element; $m = 0, 1$; $n = 0, 1, 2, \dots, p-1$, and a_k represents the constants in $\mathcal{H}$ and matrix elements of spin operators (cf., Sec. 6, Chap. II).

Substituting (85) into (84) and using (80) we have

$$\begin{aligned} & (\Phi^i(\mu, t, \rho, p, c), \mathcal{H} \Phi^j(\nu, t, \rho, p', c')) \\ &= \frac{\sqrt{c\rho} \sqrt{c'\rho'}}{\tau} \sum_k a_k \rho^{m_k} \left[\text{Re} t^{n_k} (\sigma_\mu(t, \rho) \varphi_o^i(p, c), \sigma_\nu(t, \rho) \varphi_o^j(p', c)) \right. \\ & \quad \left. - \nu \text{Im} t^{n_k} (\sigma_\mu(t, \rho) \varphi_o^i(p, c), \sigma_{\bar{\nu}}(t, \rho) \varphi_o^j(p', c)) \right] \end{aligned}$$

Finally, using (82) we obtain

$$\begin{aligned} & (\Phi^i(\mu, t, \rho, p, c), \mathcal{H} \Phi^j(\nu, t, \rho, p', c')) \\ &= \sqrt{\frac{c\rho}{c'\rho'}} \sum_k a_k \rho^{m_k} [\text{Re} t^{n_k} \delta_{\mu\nu} - \nu \text{Im} t^{n_k} \delta_{\mu, \bar{\nu}}] \quad (86) \end{aligned}$$

which is a straightforward generalization of (57).

IV. NUMERICAL CALCULATIONS

1. Introduction

The eigenvalues and eigenvectors for chains from $N = 4$ to $N = 11$ were calculated using the IBM-7040 computer at the Computation Center of The University of Kansas. The eigenvalues were checked against existing calculations.^{2,3}

The matrix elements were calculated by the computer using a numerical notation for the states as explained in this chapter.

Consider the states of a chain having r spins "up" and m spins "down" as a linear array of $r +$ signs and $m -$ signs. Let n_1 be the number of $-$ signs to the left of the first $+$ sign, n_2 the number of $-$ signs between the first and second $+$ signs, n_i the number of $-$ signs between the $(i - 1)$ th and the i th plus signs, and n_{r+1} the number of minus signs to the right of the last $+$ sign in the chain. The set of numbers $(n_1, n_2, n_3, \dots, n_{r+1})$ can be used as a new representation of the given state. For example, the state $(- - + - + + - - + -)$ can be written $(2, 1, 0, 2, 1)$.

The representation defined above has the following two properties:

1) For given N and r , there are $r + 1$ numbers n_i .

2) $\sum_{i=1}^{r+1} n_i = m$.

We now consider the n 's as decimal digits of an integer number of $r + 1$ digits, i.e., we form the number

$$N^r = n_1 \times 10^r + n_2 \times 10^{r-1} + \dots + n_r \times 10 + n_{r+1} \quad (87)$$

The number thus formed can be used of course to represent the given state. In the example above, the given state is represented by the number 21021.

For given N and r , we have then the various states represented by a set of numbers N^r such that, according to property (2), the sum of their digits is constant. From elementary arithmetic, we recall that numbers of this type can be obtained from one another by adding or subtracting multiples of nine.

With respect to property (1), we may say that the set of numbers representing the states have the same number of digits if we conserve and count the zeros to the left of the first non-zero digit. For example the state

$$+ + - - + - = 0021$$

2. Finding the States

The advantage of this method is the fact that the $\binom{N}{r}$ different states having r spins reversed, can be generated in numerical form starting from any given state.

One way of doing this systematically is as follows: Start with the largest number of the set, i.e., the number $m \times 10^r$ which represents the state $(m, 0, 0, \dots, 0)$, and subtract $9 \times 10^{r-1}$ as many times as possible without vio-

lating condition (2), then subtract $9 \times 10^{r-2}$ from the numbers obtained in the first step, then subtract $9 \times 10^{r-3}$ and so on until we subtract 9 as many times as possible without violating condition (2). Each such subtraction gives a new state and the total number of such operations generates the $\binom{N}{r} - 1$ states left.

An example will help to clarify the procedure. Consider a chain with $N = 6$ and $r = 2$. There are $\binom{6}{2} = 15$ states in this case. We start with the state

$$400 \equiv - - - - + +$$

and subtract first 90 and then 9 without violating (2).

The required 15 numbers and operations performed are given below.

				$\xrightarrow{-9}$	
	400				
	310	301			
- 90	220	211	202		
	130	121	112	103	
	040	031	022	013	004

Note that all numbers are different and the sum of their digits is 4.

3. Action of the Operators

The states obtained when the operators of the problem act on any state given in numerical form can be found directly without recurring to the "up" and "down" notation. In order to show the procedure, we shall consider the cor-

$$(k-1 + \sum_{i=1}^{k-1} n_i, k + \sum_{i=1}^{k-1} n_i) \quad k = 2, 3, \dots, r \quad (90)$$

b) With respect to n_1 and n_{r+1} we have

		There is a (- +) pair at	There is a (+ -) pair at
$n_1 \neq 0$	$n_{r+1} \neq 0$	$(n_1, n_1 + 1)$	$(N - n_{r+1}, N - n_{r+1} + 1)$
	$n_{r+1} = 0$	$(n_1, n_1 + 1)$	$(N, 1)$
$n_1 = 0$	$n_{r+1} \neq 0$	$(N, 1)$	$(N - n_{r+1}, N - n_{r+1} + 1)$
	$n_{r+1} = 0$	There are no opposite sign pairs other than stated in (a).	

Rule 3. - The total number of (+ -) or (- +) pairs equals the number of non-zero n's except when n_1 and n_{r+1} are both different from zero in which case the number of pairs equals the number of non-zero n's minus one.

Translation operator. - The action of T on a given state is found by subtracting from N^r the number

$$\overbrace{999 \cdots 9}^{r \text{ nines}} = 10^r - 1$$

For example, $310 \equiv - - - + - +$

$$T(310) = 310 - 99 = 211 \equiv - - - - -$$

The set of all translations of a given state is obtained by subtracting $10^r - 1$ as many times as possible. Each one of these operations gives a new translation state.

When the next subtraction is not possible, we multiply the last number obtained by 10 (this operation gives a new translation state) and repeat the procedure until we get the initial number again. The number of operations performed is equal to the symmetry, p , of the group.

Example.

State	Operation	Equivalence
310	- 99	- - - + - +
211	- 99	- - + - + -
112	- 99	- + - + - -
013	x 10	+ - + - - -
130	- 99	- + - - - +
031	x 10	+ - - - + -
310		

We may see how this occurs by noting first that

$$T(n_1, n_2, \dots, n_{r+1}) \quad (n_1 - 1, n_2, \dots, n_{r+1} + 1), \text{ if } n_1 \neq 0 \quad (91)$$

$$T(0, n_2, \dots, n_{r+1}) \quad (n_2, n_3, \dots, n_{r+1}, 0), \text{ if } n_1 = 0 \quad (92)$$

In the form of eq. (87) we can write

$$(n_1 - 1) \times 10^r + n_2 \times 10^{r-1} + \dots + n_{r+1} = n_1 \times 10^r + n_2 \times 10^{r-1} + \dots + n_{r+1} - (10^r - 1)$$

$$n_2 \times 10^r + n_3 \times 10^{r-1} + \dots + n_{r+1} \times 10 = (n_2 \times 10^{r-1} + n_3 \times 10^{r-2} + \dots + n_{r+1}) \times 10$$

for the two cases given by (91) and (92) respectively. Then, we see that the multiplication by 10 comes when n_1 becomes zero.

Rotation Operator.— The action of R on the state $N^{\circ} = (n_1, n_2, \dots, n_{r+1})$ is described by the formula

$$RN^{\circ} = 10^{n_2+n_3+\dots+n_{r+1}} + 10^{n_3+\dots+n_{r+1}} + \dots + 10^{n_r+n_{r+1}} + 10^{n_{r+1}} \quad (93a)$$

$$= \sum_{\alpha=2}^{r+1} 10^{\sum_{i=\alpha}^{r+1} n_i} \quad (93b)$$

Example.

$$R(+ - - + - +) = R(0210)$$

$$= 10^{2+1+0} + 10^{1+0} + 10^0 = 1011 = - + + - + -$$

Equation (93) can be proved using Fig. 1 and writing below the state RN° in both + and - notation and number notation as shown in Fig. 2.

$$\begin{array}{cccccc}
 \overbrace{n_1} & \overbrace{n_2} & & \overbrace{n_{r-1}} & \overbrace{n_r} & \overbrace{n_{r+1}} \\
 - \dots - & + - \dots - & + - \dots & \dots - + - \dots - & + - \dots - & + - \dots - \\
 \\
 RN^{\circ} \left\{ \begin{array}{cccccc}
 + \dots + & - + \dots + & - + \dots & \dots + - + \dots + & - + \dots + & - + \dots + \\
 0 \dots 0 & 1 0 \dots 0 & 1 0 \dots & \dots 0 1 0 \dots 0 & 1 0 \dots 0 & 1 0 \dots 0
 \end{array} \right. \\
 \underbrace{\hspace{1.5cm}}_{n_1} & \underbrace{\hspace{1.5cm}}_{n_2-1} & & \underbrace{\hspace{1.5cm}}_{n_{r-1}-1} & \underbrace{\hspace{1.5cm}}_{n_r-1} & \underbrace{\hspace{1.5cm}}_{n_{r+1}}
 \end{array}$$

Fig. 2.— Action of the operator R

Equation (93a) follows immediately from the last line of Fig. 2. Note that RN° has $m + 1$ digits, provided we count the n , zeros to the left of the first non-zero digit.

In this work we are interested only in the action of R on states having $r = m = N/2$, and in this case N^r and RN^r have the same number of digits.

Exchange Hamiltonian.— Consider first the operator $\sum_{i=1}^N (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+)$ with condition $S_{i+N}^\pm = S_i^\pm$. The action of this operator on a given state, N^r , is equal to a sum of states of the form: $N^r \pm 9 \times 10^{r-1}$, $N^r \pm 9 \times 10^{r-2}$, ..., $N^r \pm 9$, $10(N^r + 10^{r-1} - 1)$, and $\frac{N^r}{10} + 1 - 10^{r-1}$. This sum consists of only those terms which do not violate condition (2).

Example. Suppose $N^r = 310 \equiv - - - + - +$

The terms which do not violate condition (2) are

$$\begin{aligned} N^r + 9 \times 10^{r-1} &= 310 - 90 = 400 \equiv - - - - + + \\ N^r - 9 \times 10^{r-1} &= 310 - 90 = 220 \equiv - - + - - + \\ N^r - 9 \times 10^{r-2} &= 310 - 9 = 301 \equiv - - - + + - \\ \frac{N^r}{10} + 1 - 10^{r-1} &= 031 + 1 - 10 = 022 \equiv + - - + - - \end{aligned}$$

Therefore, we have

$$\sum_{i=1}^N (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) (310) = (400) + (220) + (301) + (022)$$

To prove the procedure, we consider first the operators $S_i^+ S_{i+1}^-$ and $S_i^- S_{i+1}^+$. Using rule 2 we have

$$S_i^+ S_{i+1}^- (n_1, \dots, n_r) = \begin{cases} (n_1, \dots, n_k - 1, n_{k+1} + 1, \dots, n_r) & \text{if } n_k \neq 0 \text{ and } i = k - 1 + \sum_{\ell=1}^k n_\ell \\ & k = 1, 2, \dots, r \\ (n_2 + 1, n_3, \dots, n_{r+1} - 1, 0) & \text{if } n_1 = 0, n_{r+1} \neq 0 \text{ and } i = N \\ 0 & \text{otherwise} \end{cases}$$

$$S_i^- S_{i+1}^+ (n_1, \dots, n_{r+1}) = \begin{cases} (n_1, \dots, n_{k-1}+1, n_k-1, \dots, n_{r+1}) & \text{if } n_k \neq 0 \text{ and } i = k-1 + \sum_{l=1}^k n_l \\ & k = 2, 3, \dots, r+1 \\ (0, n_1-1, n_2, \dots, n_r+1) & \text{if } n_{r+1} = 0, n_1 \neq 0 \text{ and } i = N \\ 0 & \text{otherwise} \end{cases}$$

Summing over i we obtain the following equations

$$\sum_{i=1}^N S_i^+ S_{i+1}^- (n_1, \dots, n_{r+1}) = \sum_{k=1}^r (1 - \delta_{n_k, 0}) (n_1, \dots, n_{k-1}, n_{k+1}+1, \dots, n_{r+1}) \\ + (1 - \delta_{n_{r+1}, 0}) \delta_{n_1, 0} (n_2+1, n_3, \dots, n_{r+1}-1, 0) \quad (94a)$$

$$\sum_{i=1}^N S_i^- S_{i+1}^+ (n_1, \dots, n_{r+1}) = \sum_{k=1}^{r+1} (1 - \delta_{n_k, 0}) (n_1, \dots, n_{k-1}+1, n_k-1, \dots, n_{r+1}) \\ + (1 - \delta_{n_1, 0}) \delta_{n_{r+1}, 0} (0, n_1-1, n_2, \dots, n_r+1) \quad (94b)$$

Now,

$$N^p = (n_1, n_2, \dots, n_{k-1}, n_k, n_{k+1}, \dots, n_{r+1})$$

$$= n_1 \times 10^r + \dots + n_{k-1} \times 10^{r-k+2} + n_k \times 10^{r-k+1} + n_{k+1} \times 10^{r-k} + \dots + n_{r+1},$$

therefore, the k th state in (94a) is found by subtracting $9 \times 10^{r-k}$ from N^p , since

$$(n_{k-1}+1) \times 10^{r-k+1} + (n_{k+1}-1) \times 10^{r-k} = n_{k-1} \times 10^{r-k+1} + n_{k+1} \times 10^{r-k} - (10-1) \times 10^{r-k}$$

and the k th state in (94b) is found by adding $9 \times 10^{r-k+1}$ to N^p , since

$$(n_{k-1}-1) \times 10^{r-k+2} + (n_k+1) \times 10^{r-k+1} = n_{k-1} \times 10^{r-k+2} + n_k \times 10^{r-k+1} + (10-1) \times 10^{r-k+1}$$

For the last state in (94a) we have that $N^r = n_1 \times 10^{r-1} + n_2 \times 10^{r-2} + \dots + n_{r+1}$, since it exists only if $n_r = 0$. Then,

$$(n_2+1) \times 10^r + n_3 \times 10^{r-1} + \dots + (n_{r+1}-1) \times 10 = 10(N^r + 10^{r-1} - 1)$$

For the last state in (94b), $N^r = n_1 \times 10^r + n_2 \times 10^{r-1} + \dots + n_r \times 10$, since it exists only if $n_{r+1} = 0$. In this case we have that

$$(n_1-1) \times 10^{r-1} + n_2 \times 10^{r-2} + \dots + n_{r+1} = \frac{N^r}{10} + 1 - 10^{r-1}$$

The requirement that $n_k \neq 0$ for the existence of the k th state in eqs. (94) is equivalent to the statement that condition (2) must not be violated when we add or subtract the required quantities.

The action of the operator $\sum_{i=1}^N S_i^z S_{i+1}^z$ with $S_{N+1}^z = S_1^z$ is described by the formula

$$\sum_{i=1}^N S_i^z S_{i+1}^z N^r = \frac{1}{4} [N - 4d_0 + 4(1 - \delta_{n_1,0})(1 - \delta_{n_{r+1},0})] N^r \quad (95)$$

where $N^r = (n_1, n_2, \dots, n_{r+1})$ and d_0 is equal to the number of non-zero n 's in N^r . Equation (95) is a direct consequence of rule 3.

Examples.

$$\sum_{i=1}^N S_i^z S_{i+1}^z (310) = \frac{1}{4} [6 - 4 \times 2] (310) = -\frac{1}{2} (310)$$

$$\sum_{i=1}^N S_i^z S_{i+1}^z (301) = \frac{1}{4} [6 - 4 \times 2 - 4] (301) = \frac{1}{2} (301)$$

4. Limitations of the Method

The chain of largest number of spins that we can treat using this numerical method depends on the maximum number of digits that a particular computer can handle. On the other hand, the application of the method is limited by the fact that none of the n 's can have a value larger than 9. Since the matrix elements with respect to states having $S_z = M$ or $S_z = -M$ are identical, we have to deal only with half the total matrix, i. e., with values $m = N/2$, $r = N/2$. Therefore, the method is limited to a maximum of 18 spins in the chain, which is a larger number than can be handled by present day computers since 18 spins would require diagonalization of matrices of order 4800.

5. Calculation of the Matrix Elements

In this section we review the general procedure for calculating the matrix elements of $\mathcal{H}_{ex}$. For simplicity we use the Hamiltonian

$$\mathcal{H} = -2J \sum_{i=1}^N (\vec{S}_i \cdot \vec{S}_{i+1} - \frac{1}{4}) \quad (96)$$

which was used by Orbach,² and whose eigenvalues are shifted by an amount $NJ/2$ with respect to those of eq. (1). When using (96) the only change occurs in eq. (95) in which the N in the brackets cancels out.

Separation into blocks (Sec. 1, Chap. 1).-- The block for $r = 0$ ($r = N$) has only one eigenvalue (zero) and need not

be considered further. For each block with $r \neq 0$, we start by forming the initial state in numerical form, i.e., the number $m \times 10^r$, from which we derive the $\binom{N}{r}$ states of the r th block by the method of Sec. 2, Chap. IV. (Alternatively, we may use the number $r \times 10^m$ since the numerical notation can also be defined by counting the number of + signs between two - signs).

Separation into groups of translation states and determination of the symmetry of the groups (Sec. 2, Chap. I).-- We pick one state out of the $\binom{N}{r}$ states and calculate the set of translations of that state by the method of Sec. 3, Chap. IV. By counting the operations, this calculation gives us also the value of p (symmetry) for that particular group. Every subsequent state that we pick out from the $\binom{N}{r}$ states must be compared with all those states that we have already classified. If it is equal to one of the classified states then we pick out the next one and so on. When the calculation is finished we have a certain number of groups of functions (independent of translation) and their respective symmetries. These values must check against values calculated as in Sec. 2, Chap. I (see for example table I), and by eq. (8).

From each translation group we may choose of course any of the states to represent φ_0^i (i.e., the zeroth translation of the group), provided this convention is maintained throughout the calculation of the matrix elements.

Finding the digits.-- Since the calculation of the states obtained when the operators of the problem act on a given state, requires, in many cases, the knowledge of the digits of N^0 , i.e., the numbers $n_1, n_2, \dots, n_{r+1}$, the next step is the separation of each number representing a state into its digits. (Zeros to the left of the first non-zero digit must be considered).

Classification into types (Sec. 2, Chap. III).-- If we are dealing with a block of $r = N/2$ (even N), the next step is to classify the states into types as follows: From φ_o^i of the i th group we obtain $\bar{\varphi} = R\varphi_o^i$ by the method of Sec. 3, Chap. IV. $\bar{\varphi}$ is compared first with all other translation states of the i th group. If $\bar{\varphi}$ is equal to one of these translations, then φ_o^i is of type I and we assign $c = 1$ to this group; if $\bar{\varphi}$ is not found among the translations of the i th group, φ_o^i is of type II, we assign $c = 2$ to this group and proceed to find the group to which $\bar{\varphi}$ belongs. The latter group is not considered in the calculation of the matrix elements. When the calculation is finished we have found a certain number of groups of functions (independent of rotation) of type II and a certain number of groups of functions of type I, which must agree with a calculation as in Secs. 3 and 4, Chap. III (see for example tables IV and V).

Matrix Elements.-- For each value of t (see p. 24 for the

values of t to consider) we proceed as follows. With the set of φ_o^i 's and corresponding symmetry numbers p , we first test for vanishings of $F_\mu(t) \varphi_o^i(p)$ according to

$$F_\pm(t) \varphi_o^i(p) = 0, \quad \text{if } t^p \neq 1$$

$$F_-(t) = 0, \quad \text{if } t \text{ is real}$$

If we are dealing with an $r = N/2$ block, the additional test

$$F_\mu(t) \psi^p(p) = 0, \quad \text{if } t^{p/2} = -1$$

for functions of type I, is required.

The vanishing functions are not considered in the matrix elements (if they were considered, they would give just zero rows and columns increasing the order of the matrices).

From equations (57) and (86) we see that the matrices for complex t are real symmetric and of the form

$$\begin{array}{c} \mu = + \\ \mu = - \end{array} \begin{array}{cc} \nu = + & \nu = - \\ \left(\begin{array}{c|c} A & \tilde{B} \\ \hline B & A \end{array} \right) \end{array}$$

where A is a symmetric matrix and $\tilde{B}$ is the transpose of B . It suffices to calculate half the total number of matrix elements, however, the complete calculation takes little extra computer time and provides a good check for the

correctness of the calculations.

To obtain the matrix element $\mathcal{K}_{ij}$ for example (regardless of μ and ν for the moment), we act first with $\mathcal{K}$ on φ_0^j using the method of Sec. 3, Chap. IV, and compare each of the resulting states with all translations of the i th group in order to find the powers of T of eq. (56). If we are dealing with an $r = N/2$ matrix, we have to compare each of the states resulting from $\mathcal{K}\varphi_0^j$ also with the rotated states of the i th group (i.e., with $R\varphi_n^i$) in order to use the form of eq. (85). For given μ and ν , the final numerical value of the matrix element is calculated from eq. (57) or eq. (86) if it is the case.

PART II

TIME CORRELATIONS OF SPIN OPERATORS
AND RESONANCE LINEWIDTH

V. TIME CORRELATIONS OF SPIN OPERATORS

1. Introduction

In this chapter we calculate the Fourier transforms of time correlations of spin operators. We are interested primarily in those correlation functions of two and four spin operators which arise in the usual calculations of the resonance linewidth.^{4,5,6} In general, they are of the form

$$\langle \mathcal{O}_1(\tau) \mathcal{O}_2 \rangle = \frac{\text{tr } \rho \mathcal{O}_1(\tau) \mathcal{O}_2}{\text{tr } \rho} \quad (97)$$

where $\rho = e^{-\beta \mathcal{H}_{ex}}$ is the thermal equilibrium density matrix in zero applied field,

$$\mathcal{O}_1(\tau) = e^{-i\mathcal{H}_{ex}\tau/\hbar} \mathcal{O}_1 e^{i\mathcal{H}_{ex}\tau/\hbar} \quad (98)$$

and $\mathcal{O}_1$ and $\mathcal{O}_2$ are products of spin operators.

A correlation function of this type will sometimes be referred to as "c.f.".

2. Two Spin Correlation Functions

The two spin correlation functions of interest are

$$\langle S_i^z(\tau) S_j^z \rangle, \langle S_i^+(\tau) S_j^- \rangle \text{ and } \langle S_i^-(\tau) S_j^+ \rangle$$

where $S_n^\pm = S_n^x \pm iS_n^y$.

The functions $\langle S_i^+(\tau) S_j^+ \rangle$, $\langle S_i^-(\tau) S_j^- \rangle$ and $\langle S_i^+(\tau) S_j^z \rangle$ are identically zero.

Since $\mathcal{H}_{ex}$, eq. (1), is rotationally invariant, the three non-zero correlation functions are related to one another. In order to show this relations, let R be the quantum mechanical rotation operator (not to be confused with the operator R defined in Chap. III), which commutes with the isotropic exchange Hamiltonian. Since the trace is independent of the coordinates we have

$$\langle \sigma_1(\tau) \sigma_2 \rangle = \frac{\text{tr} \rho \sigma_1(\tau) \sigma_2}{\text{tr} \rho} = \frac{\text{tr} R^\dagger \rho \sigma_1(\tau) \sigma_2 R}{\text{tr} \rho} \quad (99)$$

But $[\mathcal{H}_{ex}, R] = 0$ implies $[\rho, R] = 0$ and

$$\langle \sigma_1(\tau) \sigma_2 \rangle = \frac{\text{tr} \rho R^\dagger \sigma_1(\tau) \sigma_2}{\text{tr} \rho} = \langle R^\dagger \sigma_1(\tau) \sigma_2 R \rangle \quad (100)$$

Let R be defined by its Euler angles φ, θ, ψ , as shown in Fig. 3. The components of angular momentum trans-

Fig. 3.- Euler angles φ, θ, ψ .

form under rotations like the components of ordinary vectors according to the equations

$$\left. \begin{aligned} S_+ &= a^2 S'_+ + 2ab^* S'_z + b^{*2} S'_- \\ S_- &= -b^2 S'_+ + 2a^* b S'_z + a^{*2} S'_- \\ S_z &= -ab S'_+ + (|a|^2 - |b|^2) S'_z - a^* b^* S'_- \end{aligned} \right\} \quad (101)$$

where $a = \cos \frac{\theta}{2} e^{\frac{i}{2}(\psi+\varphi)}$, $b = i \sin \frac{\theta}{2} e^{\frac{i}{2}(\psi-\varphi)}$

Consider a rotation for which $a = 0$ and $|b| = 1$. In this case (101) becomes

$$\left. \begin{aligned} S_+ &\rightarrow -e^{-i(\psi-\varphi)} S_- \\ S_- &\rightarrow -e^{i(\psi-\varphi)} S_+ \\ S_z &\rightarrow -S_z \end{aligned} \right\} \quad (102)$$

and we have

$$\langle S_i^+(\tau) S_j^- \rangle = \langle S_i^-(\tau) S_j^+ \rangle \quad (103)$$

To complete the proof, we make use of the x, y, z components of spin as follows

$$\begin{aligned} \langle S_i^+(\tau) S_j^- \rangle &= \langle (S_i^x(\tau) - iS_i^y(\tau))(S_j^x - iS_j^y) \rangle \\ &= \langle S_i^x(\tau) S_j^x \rangle + \langle S_i^y(\tau) S_j^y \rangle \\ &\quad + i \langle S_i^y(\tau) S_j^x \rangle - i \langle S_i^x(\tau) S_j^y \rangle \end{aligned} \quad (104)$$

We now restrict above rotation to $\psi = 0$, $\varphi = \pi/4$ (the transformation corresponds to a rotation of π about the line $y = x$, in which $x \rightarrow y$, $y \rightarrow x$, $z \rightarrow -z$). Thus we have

$$\langle S_i^y(\tau) S_j^x \rangle \rightarrow \langle S_i^x(\tau) S_j^y \rangle$$

$$\langle S_i^y(\tau) S_j^y \rangle \rightarrow \langle S_i^x(\tau) S_j^x \rangle$$

From eq. (104) we get

$$\langle S_i^+(\tau) S_j^- \rangle = 2 \langle S_i^x(\tau) S_j^x \rangle \quad (105)$$

A simple rotation of $\pi/2$ about the y-axis shows that

$$\langle S_i^x(\tau) S_j^x \rangle = \langle S_i^z(\tau) S_j^z \rangle, \text{ and finally}$$

$$\langle S_i^z(\tau) S_j^z \rangle = \frac{1}{2} \langle S_i^+(\tau) S_j^- \rangle = \frac{1}{2} \langle S_i^-(\tau) S_j^+ \rangle \quad (106)$$

3. Four Spin Correlation Functions

The four spin correlation functions are

$$\begin{aligned} & \langle S_i^z(\tau) S_j^z(\tau) S_k^z S_l^z \rangle \\ & \langle S_i^+(\tau) S_j^-(\tau) S_k^z S_l^z \rangle, \quad \langle S_i^-(\tau) S_j^+(\tau) S_k^z S_l^z \rangle \\ & \langle S_i^z(\tau) S_j^z(\tau) S_k^+ S_l^- \rangle, \quad \langle S_i^z(\tau) S_j^z(\tau) S_k^- S_l^+ \rangle \\ & \langle S_i^+(\tau) S_j^z(\tau) S_k^- S_l^z \rangle, \quad \langle S_i^-(\tau) S_j^z(\tau) S_k^+ S_l^z \rangle \\ & \langle S_i^z(\tau) S_j^+(\tau) S_k^z S_l^- \rangle, \quad \langle S_i^z(\tau) S_j^-(\tau) S_k^z S_l^+ \rangle \\ & \langle S_i^+(\tau) S_j^z(\tau) S_k^z S_l^- \rangle, \quad \langle S_i^-(\tau) S_j^z(\tau) S_k^z S_l^+ \rangle \\ & \langle S_i^z(\tau) S_j^+(\tau) S_k^- S_l^z \rangle, \quad \langle S_i^z(\tau) S_j^-(\tau) S_k^+ S_l^z \rangle \\ & \langle S_i^+(\tau) S_j^-(\tau) S_k^+ S_l^- \rangle, \quad \langle S_i^-(\tau) S_j^+(\tau) S_k^- S_l^+ \rangle \\ & \langle S_i^+(\tau) S_j^-(\tau) S_k^- S_l^+ \rangle, \quad \langle S_i^-(\tau) S_j^+(\tau) S_k^+ S_l^- \rangle \end{aligned} \quad (107)$$

The c.f.'s of all those combinations of spin operators which do not conserve the total z-component of spin, when acting on an arbitrary state, must vanish.

The transformation (102) shows that the two correlation functions appearing in every line of (107) are identical. We can find further relations among these functions by expressing them in terms of S^x , S^y and S^z . For simplicity we neglect the argument (τ) but keep in mind that the first two spin operators are functions of the time. This neglect of τ does not affect the following results since the time-development operator commutes with R .

$$\begin{aligned}\langle S_i^+ S_j^- S_k^+ S_l^+ \rangle &= \langle (S_i^x + iS_i^y)(S_j^x - iS_j^y) S_k^+ S_l^+ \rangle \\ &= \langle S_i^x S_j^x S_k^+ S_l^+ \rangle + \langle S_i^y S_j^y S_k^+ S_l^+ \rangle \\ &\quad + i \langle S_i^y S_j^x S_k^+ S_l^+ \rangle - i \langle S_i^x S_j^y S_k^+ S_l^+ \rangle\end{aligned}$$

As before, the rotation $x \rightarrow y$, $y \rightarrow x$, $z \rightarrow -z$ gives

$$\begin{aligned}\langle S_i^y S_j^y S_k^+ S_l^+ \rangle &\rightarrow \langle S_i^x S_j^x S_k^+ S_l^+ \rangle \\ \langle S_i^x S_j^y S_k^+ S_l^+ \rangle &\rightarrow \langle S_i^y S_j^x S_k^+ S_l^+ \rangle\end{aligned}$$

Then we have

$$\langle S_i^+ S_j^- S_k^+ S_l^+ \rangle = 2 \langle S_i^x S_j^x S_k^+ S_l^+ \rangle \quad (108)$$

In exactly the same manner we show that

$$\langle S_i^+ S_j^- S_k^+ S_l^- \rangle = 2 \langle S_i^z S_j^z S_k^+ S_l^- \rangle \quad (109)$$

Finally, a simple rotation of $\pi/2$ about the y -axis gives

$$\langle S_i^x S_j^x S_k^+ S_l^+ \rangle \rightarrow \langle S_i^z S_j^z S_k^+ S_l^+ \rangle \quad (110)$$

Consequently, we have

$$\begin{aligned}\langle S_i^+ S_j^- S_k^z S_l^z \rangle &= \langle S_i^- S_j^+ S_k^z S_l^z \rangle = \langle S_i^z S_j^z S_k^+ S_l^- \rangle = \langle S_i^z S_j^z S_k^- S_l^+ \rangle \\ &= 2 \langle S_i^x S_j^x S_k^z S_l^z \rangle \quad (111a)\end{aligned}$$

Similarly we obtain

$$\begin{aligned}\langle S_i^+ S_j^z S_k^- S_l^z \rangle &= \langle S_i^- S_j^z S_k^+ S_l^z \rangle = \langle S_i^z S_j^+ S_k^z S_l^- \rangle = \langle S_i^z S_j^- S_k^z S_l^+ \rangle \\ &= 2 \langle S_i^x S_j^z S_k^x S_l^z \rangle \quad (111b)\end{aligned}$$

$$\begin{aligned}\langle S_i^z S_j^+ S_k^- S_l^z \rangle &= \langle S_i^z S_j^- S_k^+ S_l^z \rangle = \langle S_i^+ S_j^z S_k^z S_l^- \rangle = \langle S_i^- S_j^z S_k^z S_l^+ \rangle \\ &= 2 \langle S_i^z S_j^x S_k^x S_l^z \rangle \quad (111c)\end{aligned}$$

and

$$\begin{aligned}\langle S_i^- S_j^+ S_k^- S_l^+ \rangle &= \langle S_i^+ S_j^- S_k^+ S_l^- \rangle = 2 \langle S_i^z S_j^z S_k^z S_l^z \rangle + 2 \langle S_i^x S_j^x S_k^z S_l^z \rangle \\ &\quad + 2 \langle S_i^x S_j^z S_k^z S_l^x \rangle - 2 \langle S_i^x S_j^z S_k^x S_l^z \rangle \quad (112a)\end{aligned}$$

$$\begin{aligned}\langle S_i^- S_j^- S_k^+ S_l^+ \rangle &= \langle S_i^+ S_j^+ S_k^- S_l^- \rangle = 2 \langle S_i^z S_j^z S_k^z S_l^z \rangle + 2 \langle S_i^x S_j^z S_k^x S_l^z \rangle \\ &\quad + 2 \langle S_i^x S_j^z S_k^z S_l^x \rangle - 2 \langle S_i^x S_j^z S_k^z S_l^z \rangle \quad (112b)\end{aligned}$$

$$\begin{aligned}\langle S_i^- S_j^+ S_k^+ S_l^- \rangle &= \langle S_i^+ S_j^- S_k^- S_l^+ \rangle = 2 \langle S_i^z S_j^z S_k^z S_l^z \rangle + 2 \langle S_i^x S_j^z S_k^z S_l^z \rangle \\ &\quad + 2 \langle S_i^x S_j^z S_k^x S_l^z \rangle - 2 \langle S_i^x S_j^z S_k^z S_l^x \rangle \quad (112c)\end{aligned}$$

Using the transformation (101) for the special case $|a| = |b|$, i.e., $\theta = \frac{\pi}{2}$, we find

$$\langle S_i^z S_j^z S_k^z S_l^z \rangle = \frac{1}{8} [\langle S_i^- S_j^- S_k^+ S_l^+ \rangle + \langle S_i^- S_j^+ S_k^+ S_l^- \rangle + \langle S_i^- S_j^+ S_k^- S_l^+ \rangle] \quad (113)$$

Adding eqs. (112a), (112b) and (112c) and comparing

with eq. (113) we get

$$\langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle = \langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle + \langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle + \langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle \quad (114)$$

Substituting (114) into eqs. (112a), (112b) and (112c) we have

$$\langle S_i^- S_j^+ S_k^- S_l^+ \rangle = \langle S_i^+ S_j^- S_k^+ S_l^- \rangle = 4 [\langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle + \langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle] \quad (115a)$$

$$\langle S_i^- S_j^- S_k^+ S_l^+ \rangle = \langle S_i^+ S_j^+ S_k^- S_l^- \rangle = 4 [\langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle + \langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle] \quad (115b)$$

$$\langle S_i^- S_j^+ S_k^+ S_l^- \rangle = \langle S_i^+ S_j^- S_k^- S_l^+ \rangle = 4 [\langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle + \langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle] \quad (115c)$$

Using eqs. (111) we obtain

$$\langle S_i^- S_j^+ S_k^- S_l^+ \rangle = 2 [\langle S_i^- S_j^+ S_k^- S_l^+ \rangle + \langle S_i^+ S_j^- S_k^+ S_l^- \rangle] \quad (116)$$

$$\langle S_i^- S_j^- S_k^+ S_l^+ \rangle = 2 [\langle S_i^- S_j^- S_k^+ S_l^+ \rangle + \langle S_i^+ S_j^+ S_k^- S_l^- \rangle] \quad (117)$$

$$\langle S_i^- S_j^+ S_k^+ S_l^- \rangle = 2 [\langle S_i^- S_j^+ S_k^+ S_l^- \rangle + \langle S_i^+ S_j^- S_k^- S_l^+ \rangle] \quad (118)$$

Equations (111), (112), (113) and (116) to (118) show that it suffices to know only three non-equivalent c.f.'s out of the 19 original functions listed in (107). For example, the functions $\langle S_i^+ S_j^+ S_k^+ S_l^+ \rangle$, $\langle S_i^+ S_j^+ S_k^- S_l^- \rangle$ and $\langle S_i^+ S_j^+ S_k^- S_l^- \rangle$ form a set of non-equivalent c.f.'s from which we can calculate the rest, i.e., any other four spin c.f. can be expressed as a linear combination of these three. The equations also show that if a cyclic permutation of the superscripts is performed on both sides of any of equations (113), (116), (117) and (118), the resulting equation is also true.

4. Correlation Functions for Closed Chains of Spins

In the case of finite chains of N spins, we assume that the value of the subscripts i, j, k, l of the spin operators in the c.f. run from 1 to N . If the chain is closed, the condition $S_{i-N} = S_i$ allows us to define the c.f. for all values of i, j, k, l .

Let S_n^a denote an arbitrary spin operator, i.e., the superscript a stands for $+$, $-$ or z . Then, in general, for any of the c.f.'s we have

$$\begin{aligned} \langle S_i^a S_j^b S_k^c S_l^d \rangle &= \langle S_{i+N}^a S_{j+N}^b S_{k+N}^c S_{l+N}^d \rangle \\ &= \langle S_{i+N}^a S_j^b S_k^c S_l^d \rangle \end{aligned} \quad (119)$$

etc.

That is, we can add N or any multiple of N to some or to all the subscripts without affecting the results.

Negative values of i, j, k, l are allowed if we define

$$S_{-m}^a = S_{N-m}^a, \quad m \neq N \quad (120a)$$

$$S_{-N}^a = S_N^a \quad (120b)$$

but we can avoid them by reducing to positive values (adding multiples of N to the negative subscripts).

We can use the translation operator T , defined in Ch.I, to show a more general property relative to the subscripts of the c.f.'s. For an arbitrary state of the chain, that we denote by $|\alpha\rangle$, we have

$$S_i^a T^n |\alpha\rangle = T^n S_{i+n}^a |\alpha\rangle \quad (121)$$

Since this holds for all $|\alpha\rangle$ we may write

$$S_i^a T^n = T^n S_{i+n}^a \quad n = 1, 2, 3, \dots \quad (122)$$

Multiplying by the Hermitian conjugate of T^n on both sides we get

$$S_{i+n}^a = T^{-n} S_i^a T^n \quad (123)$$

Since T is unitary, eq. (123) corresponds to a unitary transformation which shifts the origin with respect to which we count the spins. Using (123) we have

$$\begin{aligned} \text{tr } \rho S_{i+n}^a S_{j+n}^b S_{k+n}^c S_{l+n}^d &= \text{tr } \rho T^{-n} S_i^a S_j^b S_k^c S_l^d T^n \\ &= \text{tr } T^{-n} \rho S_i^a S_j^b S_k^c S_l^d T^n \\ &= \text{tr } \rho S_i^a S_j^b S_k^c S_l^d \end{aligned} \quad (124)$$

In the last two steps we have used the fact that ρ commutes with T and that unitary transformations conserve the trace. Therefore,

$$\langle S_{i+n}^a S_{j+n}^b S_{k+n}^c S_{l+n}^d \rangle = \langle S_i^a S_j^b S_k^c S_l^d \rangle \quad (125)$$

Equation (125) says that we can add any positive number to all the subscripts without changing the result. Equations similar to (119) and (125) also hold for the two-spin correlation functions.

5. Calculation of the Correlation Functions

Due to the long computation times involved in calculations of this sort and to the limited storage capacity of the computer used, we were unable to calculate correlations for chains larger than 9 spins.

The two-spin correlations, $\langle S_i^z(\tau) S_j^z \rangle$, were computed for all values of j , i.e., $j = i, i + 1, \dots, i + N - 1$. The four spin c.f.'s were computed only for some values of j, k and l . Calculations of the resonance linewidth involve products of spin correlations and dipolar functions of the coordinates of the spins proportional to $1/r^3$, (see Ref. 6). In these calculations the c.f.'s of interest are limited to the case where $i \neq j$ and $k \neq l$. Furthermore, the largest contributions come from terms where i and j are nearest neighbors and k and l are nearest neighbors due to the $1/r_{ij}^3$ and $1/r_{kl}^3$ factors. Consequently, we computed the four spin c.f.'s for $j = i + 1, l = k + 1$ and $k = i, i + 1, \dots, i + N - 1$.

Using eq. (125), we can always assume that the first subscript has the value 1, and summarize the functions of interest as follows:

Two spin correlations: $\langle S_1^z S_j^z \rangle, \quad j = 1, 2, \dots, N$

Four spin correlations: $\langle S_1^a S_2^b S_j^c S_{j+1}^d \rangle, \quad j = 1, 2, \dots, N$

These functions have the following property:

$$\langle S_i^z(-\tau) S_{N-j+2}^z \rangle^* = \langle S_i^z(\tau) S_j^z \rangle \quad (126)$$

$$\langle S_i^a(-\tau) S_2^b(-\tau) S_{N-j+2}^c S_{N-j+3}^d \rangle^* = \langle S_i^a(\tau) S_2^b(\tau) S_j^c S_{j+1}^d \rangle \quad (127)$$

Proof.

$$\begin{aligned} \langle S_i^z(-\tau) S_{N-j+2}^z \rangle^* &= \langle S_i^z S_{N-j+2}^z(\tau) \rangle^* \\ &= \langle S_{N-j+2}^z(\tau) S_i^z \rangle \\ &= \langle S_i^z(\tau) S_j^z \rangle \end{aligned}$$

The last result follows from eq. (125) with $n = j - 1$.

Now consider for example $\langle S_i^+(\tau) S_2^z(\tau) S_j^- S_{j+1}^z \rangle$:

$$\begin{aligned} \langle S_i^+(-\tau) S_2^z(-\tau) S_{N-j+2}^- S_{N-j+3}^z \rangle^* &= \langle S_i^+ S_2^z S_{N-j+2}^-(\tau) S_{N-j+3}^z(\tau) \rangle^* \\ &= \langle S_{N-j+3}^z(\tau) S_{N-j+2}^-(\tau) S^z S^+ \rangle \end{aligned}$$

Adding $j - 1$ to all subscripts according to eq. (125) we have

$$\begin{aligned} \langle S_i^+(-\tau) S_2^z(-\tau) S_{N-j+2}^- S_{N-j+3}^z \rangle^* &= \langle S_2^z(\tau) S_i^+(\tau) S_{j+1}^z S_j^- \rangle \\ &= \langle S_i^+(\tau) S_2^z(\tau) S_j^- S_{j+1}^z \rangle \end{aligned}$$

The last step follows since operators referring to different spins commute.

In the same way, we can prove the property for at least three non-equivalent correlation functions, which proves (127) in general.

Using the above property, all we need to know is $(N+1)/2$

functions when N is odd and $(N+2)/2$ functions when N is even, that is,

$$\begin{aligned} & \langle S_1^z S_j^z \rangle \\ & \langle S_1^a S_2^b S_j^c S_{j+1}^d \rangle \end{aligned} \quad j = 1, 2, \dots, \begin{cases} \frac{N+1}{2} & \text{for odd } N \\ \frac{N+2}{2} & \text{for even } N \end{cases} \quad (128)$$

General Procedure.— Consider an arbitrary correlation function $\langle \sigma_1(\tau) \sigma_2 \rangle$. Let

$$f(\tau) = \langle \sigma_1(\tau) \sigma_2 \rangle \quad (129)$$

and let Ψ_α be the eigenfunctions of $\mathcal{H}_{ex}$. Then we have

$$\begin{aligned} f(\tau) &= \frac{\text{tr } \rho \sigma_1(\tau) \sigma_2}{\text{tr } \rho} = \frac{\sum_\alpha \langle \Psi_\alpha | \rho \sigma_1(\tau) \sigma_2 | \Psi_\alpha \rangle}{\sum_\alpha \langle \Psi_\alpha | \rho | \Psi_\alpha \rangle} \\ &= \frac{\sum_\alpha e^{-\beta E_\alpha} \langle \Psi_\alpha | \sigma_1(\tau) \sigma_2 | \Psi_\alpha \rangle}{\sum_\alpha \langle \Psi_\alpha | \rho | \Psi_\alpha \rangle} \\ &= \frac{1}{Z} \sum_{\alpha\beta} e^{-\beta E_\alpha} \langle \Psi_\alpha | \sigma_1(\tau) | \Psi_\beta \rangle \langle \Psi_\beta | \sigma_2 | \Psi_\alpha \rangle \quad (130) \end{aligned}$$

where $Z = \sum_\alpha e^{-\beta E_\alpha}$ and E_α is the energy eigenvalue corresponding to Ψ_α . Using eq. (98) we have

$$f(\tau) = \frac{1}{Z} \sum_{\alpha\beta} e^{-\beta E_\alpha} \langle \Psi_\alpha | \sigma_1 | \Psi_\beta \rangle \langle \Psi_\beta | \sigma_2 | \Psi_\alpha \rangle e^{i\omega_{\alpha\beta}\tau} \quad (131)$$

where $\omega_{\alpha\beta} = (E_\alpha - E_\beta)/\hbar$.

To calculate the matrix elements in (131) we need the

complete set of eigenvectors of $\mathcal{H}_{ex}$. These eigenvectors are linear combinations of eigenfunctions of $\mathcal{T}$, eq. (51) or of $\mathcal{T}$ and R , eq. (83), if $r = N/2$ for even N . Then we can write

$$\Psi(E_\alpha) = \sum_{k,\mu} C_{k,\mu}(E_\alpha) \Phi^k(\mu, t, p_k) \quad (132a)$$

or

$$\Psi(E_\alpha) = \sum_{k,\mu} C_{k,\mu}(E_\alpha) \Phi^k(\mu, t, \rho, p_k, c_k) \quad \text{if } r = N/2 \quad (132b)$$

where the $C_{k,\mu}(E_\alpha)$ are the components of the eigenvectors, k is the number of the particular component running from 1 to a value equal to one-half the order of the matrix from which the eigenvalue E_α was computed (if t is real, k runs from 1 to a value equal to the order of the matrix). All other symbols in eqs. (132) were defined in Chaps. I to IV.

In eq. (131) we collect all terms having frequencies in the semi-open interval $[\omega_n - \frac{\Delta\omega}{2}, \omega_n + \frac{\Delta\omega}{2})$, where $\Delta\omega$ is any appropriate frequency interval, and define

$$f(\omega_n) = \frac{1}{Z} \sum_{\alpha\beta} e^{-\beta E_\alpha} \langle \Psi_\alpha | \sigma_1 | \Psi_\beta \rangle \langle \Psi_\beta | \sigma_2 | \Psi_\alpha \rangle \delta_{\omega_{\alpha\beta}, \omega} \quad (133)$$

for $\omega \in [\omega_n - \frac{\Delta\omega}{2}, \omega_n + \frac{\Delta\omega}{2})$

The zero frequency interval, $(-\frac{\Delta\omega}{2}, \frac{\Delta\omega}{2})$, is centered about $\omega_0 = 0$ and the n th interval about $\omega_n = n\Delta\omega$ where n may be positive or negative. $f(\omega_n)$ is not a continuous function but is defined only for a discrete set of points and can be represented graphically by a histogram as shown in Fig. 4 for the function $\langle S_i^z(\tau) S_i^z \rangle$ at $T = \infty$.

Fig. 4.- Histogram $f(\omega_n)$ for $\langle S_i^z(\tau) S_i^z \rangle$, $N = 9$, $kT/J = \infty$

Equation (131) can now be approximated by

$$f(\tau) = \sum_{n=-\infty}^{\infty} f(\omega_n) e^{i\omega_n \tau} \quad (134)$$

or simply by

$$f(\tau) = \sum_{\omega=-\infty}^{\infty} f(\omega) e^{i\omega \tau} \quad (135)$$

but with the agreement that we sum over the discrete set of frequencies.

Joining the points at the centers of the intervals by a smooth curve, we construct the continuous function $f(\omega)$ as shown in Fig. 4. If the frequency interval is small, the summation can be approximated by the integral

$$f(\tau) = \frac{1}{\Delta\omega} \int_{-\infty}^{\infty} f(\omega) e^{i\omega \tau} d\omega \quad (136)$$

with ω as a continuous variable.

The frequency interval that we choose to construct the histogram must not be too small as compared with the separation between energy levels because sharp oscillations appear that make it difficult to draw a smooth curve. On the other hand, if the frequency interval is too large, we may lose details relative to the shape of the function.

The effect of using a small frequency interval can be illustrated by considering the curve for the density of states per unit frequency, i.e., the number of pairs of energy levels having frequency, $(E_\alpha - E_\beta)/\hbar$, between ω and $\omega + \Delta\omega$, divided by the frequency interval. Figures 5 and 6 show the density of states, $\rho(\omega)$, for $\Delta\omega = 0.3J/\hbar$

Fig. 5.- Density of states for a chain of nine spins and a frequency interval of $0.3 J/\hbar$

Fig. 6.- Density of states for a chain of nine spins and a frequency interval of $0.6 J/\hbar$

and $\Delta\omega = 0.6J/\hbar$ respectively, corresponding to a chain of nine spins.

Since the approximations given by eqs. (134), (135) and (136) are more accurate the smaller the interval, we want to use the smallest possible frequency interval giving smooth curves. It is rather difficult to find a frequency interval suitable to all chains, since the separation between energy levels is larger for chains of small number of spins. It was found that an interval of $0.8J/\hbar$ is appropriate for chains of more than five spins.

Correlation functions were calculated for values of $kT/J = 0.1, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 5.0, 10.0$ and ∞ . The number of spins in the chain and types of correlation functions considered are given in table VI. We recall from Secs. 2 and 3 of this chapter that the two-spin c.f.'s are all equivalent and that every four-spin c.f. can be expressed as a linear combination of any three non-equivalent ones, hence, the calculated functions provide sufficient information to fill most of the blanks in table VI. In fact, all blanks can be filled except those corresponding to the functions $\langle S_1^+(\tau) S_2^z(\tau) S_j^- S_{j+1}^z \rangle$ and $\langle S_1^z(\tau) S_2^+(\tau) S_j^- S_{j+1}^z \rangle$ for $N = 9$. One reason for not having computed these functions was due to the long computation time (approximately 6 hours) required in this case for each c.f. On the other hand, we shall see in Chap. VI that the c.f.'s of interest in the calculation of the resonance linewidth reduce to the functions $\langle S_1^z(\tau) S_j^z \rangle$ and $\langle S_1^+(\tau) S_2^+(\tau) S_j^- S_{j+1}^- \rangle$.

TABLE VI

Calculated correlation functions

Type of c.f.	N				
	5	6	7	8	9
$\langle S_i^z(\tau) S_j^z \rangle$	x	x	x	x	x
$\langle S_i^+(\tau) S_j^- \rangle$	x		x		
$\langle S_i^z(\tau) S_j^z(\tau) S_j^z S_{j+1}^z \rangle$	x	x	x	x	x
$\langle S_i^+(\tau) S_j^z(\tau) S_j^- S_{j+1}^z \rangle$	x	x	x	x	
$\langle S_i^z(\tau) S_j^+(\tau) S_j^- S_{j+1}^z \rangle$	x	x	x	x	
$\langle S_i^+(\tau) S_j^+(\tau) S_j^- S_{j+1}^- \rangle$	x		x		x

Each type of correlation function was computed separately by special programming and the results were checked against eqs. (106), (113), (116), (117) and (118). Another check is provided by the fact that the value of

$$\sum_{\omega} f(\omega) = \langle S_i^z(0) S_j^z \rangle$$

or

$$\sum_{\omega} f(\omega) = \langle S_i^a(0) S_j^b(0) S_j^c S_{j+1}^d \rangle$$

is known exactly at infinite temperature, and $\langle S_i^z(0) S_j^z \rangle$ at finite temperatures has been calculated by Bonner and Fisher.³ The calculations were performed for values of j

larger than the limits given in eq. (128) in order to have the additional check provided by eqs. (126) and (127).

Figures 7 through 13 illustrate some of the two- and four-spin correlation functions. The curves shown correspond to some particular value of N , but they may be regarded as typical in the sense that we find similar characteristics in the corresponding correlation functions for other values of N . Differences in behavior, which depend on whether N is even or odd, will be discussed in section 6.

A general feature of all two- and four-spin correlation functions is that for $j = 1$ they are always positive and of relatively large magnitude as compared with the magnitudes of the functions for $j > 1$. For infinite temperature, the $j = 1$ correlations are even functions of ω and they have a maximum at $\omega = 0$ which shifts to the negative frequency side as the temperature decreases. The $j > 1$ correlations are also even functions of ω for infinite temperature and they all have an oscillatory behavior as shown in Figs. 7 and 8.

No curves for temperatures lower than 1.2 J/k have been included since the histograms calculated with a frequency interval of 0.8 J/h becomes very irregular for temperatures of that order, making it difficult to obtain reasonable smooth curves, and since practical applications of correlation functions depend mostly on having the appropriate continuous functions to represent them.

$$\langle S_i^z(\tau) S_j^z \rangle$$

$$N = 9$$

$$\Delta\omega = 0.8 \frac{J}{\hbar}$$

Fig. 7.- Two-spin correlation functions $\langle S_1^z(\tau) S_2^z \rangle$ and $\langle S_1^z(\tau) S_3^z \rangle$ for a chain of nine spins at infinite temperature

$$\langle S_i^z(\tau) S_j^z \rangle$$

$$N = 9$$

$$\Delta\omega = 0.8 \frac{J}{\hbar}$$

Fig. 8.- Two-spin correlation functions $\langle S_1^z(\tau) S_4^z \rangle$ and $\langle S_1^z(\tau) S_5^z \rangle$ for a chain of nine spins at infinite temperature

Fig. 9.- Four-spin correlations $\langle S_1^z(\tau) S_2^z(\tau) S_j^z S_{j+1}^z \rangle$ and $\langle S_1^z(\tau) S_2^z(\tau) S_j^z S_{j+2}^z \rangle$ for a chain of eight spins at infinite temperature

Fig. 10.- Four-spin correlations $\langle S_1^+(\tau) S_2^+(\tau) S_j^- S_{j+1}^- \rangle$ and $\langle S_1^+(\tau) S_2^+(\tau) S_j^- S_j^- \rangle$ for a chain of eight spins at infinite temperature

Fig. 11.- Variation of $\langle S_i^z(\tau) S_i^z \rangle$ with temperature

Fig. 12.- Variation of $\langle S_1^z(\tau) S_2^z(\tau) S_1^z S_2^z \rangle$ with temperature

Fig. 13.- Variation of $\langle S_1^+(\tau) S_2^+(\tau) S_1^- S_2^- \rangle$ with temperature

6. Fourier Analysis of the Two-spin Correlation Function

A) Infinite Temperature

We first derive two important equations relative to the Fourier transform of the two-spin correlation function.

Let $f_n(\omega)$ denote the function of frequency corresponding to $\langle S_1^z(\tau) S_n^z \rangle$. From eq. (135) we have

$$f(\tau=0) = \langle S_1^z(0) S_n^z \rangle = \langle S_1^z S_n^z \rangle = \sum_{\omega} f_n(\omega)$$

Since $\langle S_1^z S_1^z \rangle = \frac{1}{4}$ and $\langle S_1^z S_n^z \rangle = 0$ for $n \neq 1$ and infinite temperature, we have

$$\sum_{\omega} f_n(\omega) = \frac{1}{4} \delta_{n,1} \quad (137)$$

Now consider

$$\begin{aligned} \sum_{n=1}^N \langle S_1^z(\tau) S_n^z \rangle &= \sum_{n=1}^N \sum_{\omega} f_n(\omega) e^{i\omega\tau} \\ &= \sum_{\omega} \left(\sum_{n=1}^N f_n(\omega) \right) e^{i\omega\tau} \end{aligned}$$

but

$$\begin{aligned} \sum_{n=1}^N \langle S_1^z(\tau) S_n^z \rangle &= \langle S_1^z \sum_{n=1}^N S_n^z \rangle \\ &= \langle S_1^z S_z \rangle \end{aligned}$$

where S_z is the total z-component of spin which commutes with ρ and $\mathcal{H}_{ex}$, and we have

$$\sum_{n=1}^N \langle S_1^z(\tau) S_n^z \rangle = \langle S_1^z S_z \rangle = \langle S_1^z S_1^z \rangle = \frac{1}{4}$$

Comparing the two equations we must have

$$\sum_{n=1}^N f_n(\omega) = \frac{1}{4} \delta_{\omega,0} \quad (138)$$

Let us now expand the spin operators S_n^z in a Fourier series in the usual way:

$$S_n^z = \frac{1}{\sqrt{N}} \sum_k S_k e^{i\vec{k} \cdot \vec{r}_n} \quad (139)$$

For a one-dimensional linear chain we choose the origin so that $\vec{r}_n = na \vec{l}_a$, where a is the distance between spins and $\vec{l}_a$ is a unit vector along the direction of the chain. With $\vec{k} = k \vec{l}_a$ we have

$$S_n^z = \frac{1}{\sqrt{N}} \sum_q S_q e^{iqn} \quad (140)$$

where $q = ka$. Periodic boundary conditions ($S_{n+N}^z = S_n^z$) require

$$q = \frac{2\pi p}{N}, \quad p = 0, 1, 2, \dots, N-1$$

The inverse of (140) is

$$S_q = \frac{1}{\sqrt{N}} \sum_n S_n^z e^{-iqn} \quad (141)$$

We note for future reference that the connection between the total z-component, S_z , and the $q=0$ Fourier component is simply

$$S_z = \sqrt{N} S_0 \quad (142)$$

and that translational invariance requires

$$\langle S_q(\tau) S_{q'} \rangle = \langle S_q(\tau) S_{-q} \rangle \delta_{q,-q'} \quad (143)$$

Use of (140), (141) and (143) then leads to

$$\langle S_q(\tau) S_{-q} \rangle = \sum_n \langle S_1^z(\tau) S_n^z \rangle e^{-iq(n-1)} \quad (144)$$

$$\langle S_1^z(\tau) S_n^z \rangle = \frac{1}{N} \sum_q \langle S_q(\tau) S_{-q} \rangle e^{iq(n-1)} \quad (145)$$

Let $F_q(\omega)$ be the function of frequency corresponding to $\langle S_q(\tau) S_{-q} \rangle$, i.e., as in eq. (135)

$$\langle S_q(\tau) S_{-q} \rangle = F_q(\tau) = \sum_{\omega} F_q(\omega) e^{i\omega\tau} \quad (146)$$

We can rewrite eqs. (144) and (145) in terms of functions of the frequency:

$$F_q(\omega) = \sum_n f_n(\omega) e^{-iq(n-1)} \quad (147)$$

$$f_n(\omega) = \frac{1}{N} \sum_q F_q(\omega) e^{iq(n-1)} \quad (148)$$

Using eq. (138) we have, from eq. (147),

$$F_0(\omega) = \sum_n f_n(\omega) = \frac{1}{4} \delta_{\omega,0} \quad (149)$$

which agrees with (142) since S_z and S_0 are constants of the motion. Substituting into (148) we obtain

$$f_n(\omega) = \frac{1}{4N} \delta_{\omega,0} + \frac{1}{N} \sum_{q \neq 0} F_q(\omega) e^{iq(n-1)} \quad (150)$$

That the $F_q(\omega)$ are real functions is seen from the symmetry of the exponentials $e^{iq(n-1)}$. Furthermore,

$F_q = F_{-q}$ and, as in the case of $f_n(\omega)$ (see eq. (126)),

we have

$$F_{2\pi - q} = F_q \quad (151)$$

so that we have to consider $(N + 1)/2$ functions when N is odd and $(N + 2)/2$ functions when N is even (cf. Eq.(128)).

Figure 14 shows the correlation functions in terms of Fourier components for a chain of nine spins at infinite temperature. The functions $F_q(\omega)$ for $q \neq 0$ are well behaved functions of ω . For infinite temperature they are even functions and they seem to have zero slope at $\omega = 0$. Equation (150) can be written

$$f_n(\omega) = \frac{1}{4N} \delta_{\omega,0} + g_n(\omega) \quad (152)$$

where

$$g_n(\omega) = \frac{1}{N} \sum_{q \neq 0} F_q(\omega) e^{iq(n-1)} \quad (153)$$

If $g_n(\omega)$ is a well behaved function everywhere, the δ -function in (152) evidently introduces a discontinuity in $f_n(\omega)$ at $\omega = 0$. It seems therefore, that the c.f.'s have a spike or discontinuity at $\omega = 0$ which disappears in the limit $N \rightarrow \infty$. Examination of the graphs of $f_n(\omega)$ show indeed that the curves obtained when we subtract off $1/4N$ from $f_n(0)$ are more or less continuous at $\omega = 0$. However, if we subtract $1/4N$ from $f_n(0)$ for all n , we obtain a new set of functions which violate eq. (138) since the summation would be equal to zero in this case.

Fig. 14.- Two-spin correlation functions in terms of Fourier components of spin operators. The graphs correspond to a chain of nine spins at infinite temperature

Analysis of $f_1(\omega)$.- Figures 15 and 16 show the function $f_1(\omega)$ for chains from $N = 6$ to $N = 9$ in the infinite temperature limit (for $N = 5$ the curve has too many oscillations for the frequency interval considered).

We observe that the point at $\omega = 0$ decreases with N while the $\omega \neq 0$ part of the functions are approximately identical in all cases. If we subtract off the $1/4N$, of eq. (152), from $f_1(0)$ as shown in Figs. 15 and 16, the function can be approximated by a straight line which might well represent this c.f. for a large number of spins.

Analysis of $f_2(\omega)$.- Figures 17 and 18 show the function $f_2(\omega)$ for chains from $N = 6$ to $N = 9$. We observe in this case that the curves are all similar and do not indicate a regular variation with N of the point at $\omega = 0$ as in the case of $f_1(\omega)$. If we subtract $1/4N$ from $f_2(0)$, we obtain values which increase with N , so that for large N probably $f_2(\omega) - \frac{1}{4N} \delta_{\omega,0}$ may look again as one of the original functions without the $1/4N$ subtracted off. In fact, we note that $f_2(0)$ is nearly independent of N in contrast to $f_1(0)$.

Analysis of the functions $f_n(\omega)$, $n > 2$, shows characteristics similar to those of $f_2(\omega)$ but the increase with N of $f_n(0) - 1/4N$ is slower the larger is n .

In view of above discussion and that $|f_1(\omega)| > |f_n(\omega)|$ for $n > 1$, so that $f_1(\omega)$ alone brings in the larger contributions in calculations involving correlation functions,

Fig. 15.- Straight-line approximation to $f_l(\omega) - \frac{1}{4N} \delta_{\omega,0}$ for chains of six and seven spins

Fig. 16.- Straight-line approximation to $f_i(\omega) - \frac{1}{4N} \delta_{\omega,0}$ for chains of eight and nine spins

$$\langle S_1^z(\tau) S_2^z \rangle$$

Fig. 17.- Function $f_2(\omega)$ for chains of six and seven spins. The lower point at $\omega = 0$ corresponds to $f_2(0) = 1/4N$

$$\langle S_1^z(\tau) S_2^z \rangle$$

Fig. 18.- Function $f_2(\omega)$ for chains of eight and nine spins. The lower point at $\omega = 0$ corresponds to $f_2(0) = 1/4N$

it is advisable to correct $f_1(\omega)$ as described above and leave $f_n(\omega)$, $n \geq 2$, unchanged. In this way, the validity of eqs. (137) and (138) would be affected only by an amount of the order of $1/4N$.

B) Finite Temperatures

For finite temperatures, eq. (138) becomes

$$\sum_{n=1}^N f_n(\omega) = \alpha(T) \delta_{\omega,0} \quad (154)$$

where $\alpha(T)$ is a function of the temperature which is related to the static susceptibility since

$$\langle M_x^2 \rangle = \chi kT \quad (155)$$

in the limit $H_0 \rightarrow 0$, and

$$\langle M_x^2 \rangle = \langle M_z^2 \rangle = \gamma^2 \hbar^2 \sum_{m,n} \langle S_m^z S_n^z \rangle = \gamma^2 \hbar^2 N' \sum_n \langle S_i^z S_n^z \rangle \quad (156)$$

where N' is the total number of atoms in the crystal.

Hence,

$$\sum_n \langle S_i^z S_n^z \rangle = \frac{\chi kT}{\gamma^2 \hbar^2 N'} = \alpha(T) \quad (157)$$

and we have $\lim_{T \rightarrow \infty} \alpha(T) = \frac{1}{4}$.

Equation (150) now becomes

$$f_n(\omega) = \frac{\alpha(T)}{N} \delta_{\omega,0} + \frac{1}{N} \sum_{q \neq 0} F_q(\omega) e^{iq(n-1)} \quad (158)$$

and eq. (152) becomes

$$f_n(\omega) = \frac{\alpha(T)}{N} \delta_{\omega,0} + g_n(\omega). \quad (159)$$

Figures 19, 20 and 21 illustrate $f_1(\omega)$ for a chain of nine spins at several temperatures. For low temperatures the curves have been smoothed to reduce the oscillations which appear as the temperature decreases. The smoothing was done by averaging consecutive ordinates according to the following equation:

$$f_a(\omega_{\frac{2n+1}{2}}) = \frac{1}{2} [f(\omega_n) + f(\omega_{n+1})] \quad (160)$$

where $f_a(\omega_i)$ is the first average curve and is defined for intermediate points in the ω axis. Then we repeat the procedure once more so that the second average curve is defined for the same set of ω_n 's as the original function. Note that since $f(\omega) = 0$ for large ω , then the ordinates of the smoothed curves conserve the total sum $\sum_{\omega} f(\omega_n)$. Figure 22 shows the original histogram and the corresponding average curve for $f_1(\omega)$ at $T = 1.6$ J/k in the case of nine spins.

If we assume $g_n(\omega)$ to be a well behaved function of ω , as before, there will be a discontinuity at $\omega = 0$ due to the term $\frac{\alpha(T)}{N} \delta_{\omega,0}$. The point $f_1(0) = \frac{\alpha(T)}{N}$, which is also shown in Figs. 19 to 21, seems to give a good approximation to a continuous curve for temperatures down to $T = 1.6$ J/k.

The behavior of $f_1(\omega)$ at $\omega = 0$ as the temperature decreases is quite different depending on whether N is even or odd. For even N , $f_1(0) \rightarrow 0$ as $T \rightarrow 0$. For odd N , $f_1(0)$

Fig. 19.- $f_i(\omega)$ for $N = 9$ at finite temperatures

Fig. 20.- $f_i(\omega)$ for $N = 9$ at finite temperatures

Fig. 21.- $f_i(\omega)$ for $N=9$ at finite temperatures

Fig. 22.- Typical histogram and corresponding average curve

has little variation with T . This can be shown quite generally by first noting that as $T \rightarrow 0$ only the ground state contributes to the correlation functions and that the zero-frequency contributions to $f_n(\omega)$ come from those terms of eq. (133) containing diagonal matrix elements or matrix elements with respect to degenerate states. Secondly, the chains of even number of spins have a four-fold degenerate ground state with $S_z = \pm \frac{1}{2}$ and complex t (eigenvalue of the translation operator), while the chains of odd number of spins have a none-degenerate ground state with $S_z = 0$ and real t . Therefore, for even N the four-fold degenerate ground state gives non-vanishing contributions to $f_n(0)$, while for odd N the only contribution to $f_n(0)$ coming from the non-degenerate ground state vanishes since in this case evidently

$$\langle \Psi_{g.s.}^{odd} | S_n^z | \Psi_{g.s.}^{odd} \rangle = 0 \quad (161)$$

for all n , which implies $f_n(0) = 0$ for $T = 0$.

VI. RESONANCE LINEWIDTH

1. Introduction

In this chapter we apply the results from previous sections to the calculation of the resonance linewidth, as a function of frequency, of a salt such as $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ which seems to have a linear chain structure as far as magnetic properties is concerned.^{1,3}

The system is described by a total Hamiltonian, $\mathcal{H}$, given by

$$\mathcal{H} = -\gamma \hbar S_z H_0 + \mathcal{H}_{ex} + \mathcal{H}_d \quad (162)$$

the three terms corresponding to, Zeeman, isotropic exchange and dipolar interactions respectively.

If we let

$$\mathcal{H}_0 = -\gamma \hbar S_z H_0 + \mathcal{H}_{ex} \quad (163)$$

and

$$\tilde{\mathcal{H}}_d(\tau) = e^{-i\mathcal{H}_0\tau/\hbar} \mathcal{H}_d e^{i\mathcal{H}_0\tau/\hbar} \quad (164)$$

the full frequency dependence of the resonance linewidth for finite temperatures can be calculated from the following equation:⁶

$$\eta = \frac{1}{8\hbar^2 \langle M_x^2 \rangle} \int_{-\infty}^{\infty} d\tau [\langle q^\dagger(\tau) q \rangle + \langle q(\tau) q^\dagger \rangle] \quad (165)$$

where η is the linewidth in frequency units and

$$g(\tau) = [\tilde{\mathcal{H}}_1(\tau), M_+] \quad (166)$$

$$M_{\pm} = M_x \pm iM_y \quad (167)$$

where M_x , M_y , M_z are the components of the magnetization.

Equation (165) can be written in a more convenient form by noting that $\mathcal{H}_1$ consists of a sum of products of spin operators and may be written as

$$\mathcal{H}_1 = \sum_M G_M \quad (168)$$

where G_M is that part of the dipolar Hamiltonian that induces a change M in total Zeeman quantum number. Then we have

$$\begin{aligned} \tilde{\mathcal{H}}_1(\tau) &= \sum_M e^{i\gamma\hbar S_z H_0 \tau/\hbar} e^{-i\mathcal{H}_{ex}\tau/\hbar} G_M e^{-i\gamma\hbar S_z H_0 \tau/\hbar} e^{i\mathcal{H}_{ex}\tau/\hbar} \\ &= \sum_M e^{iM\omega_0\tau} \hat{G}_M(\tau) \end{aligned} \quad (169)$$

where $\omega_0 = \gamma H_0$ and

$$\hat{G}_M(\tau) = e^{-i\mathcal{H}_{ex}\tau/\hbar} G_M e^{i\mathcal{H}_{ex}\tau/\hbar} \quad (170)$$

From eq. (166) we get

$$g(\tau) = \sum_M e^{iM\omega_0\tau} \hat{g}_M(\tau) \quad (171)$$

with

$$\hat{g}_M(\tau) = [\hat{G}_M(\tau), M_+] \quad (172)$$

If the density matrix is invariant with respect to rotations about the z -axis, then

$$\langle \hat{q}_M(\tau) \hat{q}_{M'}^\dagger \rangle = \langle \hat{q}_M(\tau) \hat{q}_M^\dagger \rangle \delta_{MM'} \quad (173)$$

Equation (173) will be valid if we use the density matrix

$$\rho_0 = e^{-\beta \mathcal{H}_0} / \text{tr} \rho_0 \quad (174)$$

rather than the exact density matrix $\rho = e^{-\beta \mathcal{H}} / \text{tr} \rho$. In doing so, deviations are of the order of $\mathcal{H}_0/kT$ as explained in Ref. 6. Hence, eq. (165) reduces to

$$\eta = \frac{1}{8\hbar^2 \langle M_x^2 \rangle} \int_{-\infty}^{\infty} d\tau \sum_M [e^{iM\omega_0\tau} \langle \hat{q}_M(\tau) \hat{q}_M^\dagger \rangle + e^{-iM\omega_0\tau} \langle \hat{q}_M^\dagger(\tau) \hat{q}_M \rangle] \quad (175)$$

2. Calculation of $\langle \hat{g}_M(\tau) \hat{g}_M^\dagger \rangle$

For simplicity, in the following calculations we neglect the writing of the symbol $\wedge$ on the operators and agree that the time dependence of any operator $\mathcal{O}$ is given by

$$\mathcal{O}(\tau) = e^{-i\mathcal{H}_0\tau/\hbar} \mathcal{O} e^{i\mathcal{H}_0\tau/\hbar} \quad (176)$$

which coincides with previous definition, eq. (98).

We start with the expression for $\mathcal{H}_0$ in the form

$$\mathcal{H}_0 = \frac{1}{2} \sum'_{ij} \left[\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - \frac{3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right] \quad (177)$$

We agree that the prime in a summation will always indicate that the values taken by the indices involved are all different. With $\vec{\mu}_n = \gamma \hbar \vec{S}_n$ we have

$$\mathcal{H}_0 = \frac{\gamma^2 \hbar^2}{2} \sum'_{ij} \left[\frac{\vec{S}_i \cdot \vec{S}_j}{r_{ij}^3} - \frac{3(\vec{S}_i \cdot \vec{r}_{ij})(\vec{S}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right] \quad (178)$$

Let

$$G_M = \sum'_{ij} F_{ij}^{(M)} A_{ij}^{(M)} \quad (179)$$

then we find

$$F_{ij}^{(0)} = -\frac{3}{4} \frac{\gamma^2 \hbar^2}{r_{ij}^3} (3 \cos^2 \theta_{ij} - 1) \quad (180a)$$

$$F_{ij}^{(\pm 1)} = -\frac{3}{4} \frac{\gamma^2 \hbar^2}{r_{ij}^3} \sin \theta_{ij} \cos \theta_{ij} e^{\mp i \phi_{ij}} \quad (180b)$$

$$F_{ij}^{(\pm 2)} = -\frac{3}{8} \frac{\gamma^2 \hbar^2}{r_{ij}^3} \sin^2 \theta_{ij} e^{\mp 2i \phi_{ij}} \quad (180c)$$

$$A_{ij}^{(0)} = S_i^z S_j^z - \frac{1}{3} \vec{S}_i \cdot \vec{S}_j \quad (181a)$$

$$A_{ij}^{(\pm 1)} = S_i^z S_j^{\pm} + S_i^{\pm} S_j^z \quad (181b)$$

$$A_{ij}^{(\pm 2)} = S_i^{\pm} S_j^{\pm} \quad (181c)$$

These quantities obey the following conjugation relations

$$\left. \begin{aligned} [F_{ij}^{(m)}]^* &= F_{ij}^{(-m)} \\ [A_{ij}^{(m)}]^\dagger &= A_{ij}^{(-m)} \end{aligned} \right\} \quad (182)$$

and symmetry relations

$$\left. \begin{aligned} F_{ij}^{(m)} &= F_{ji}^{(m)} \\ A_{ij}^{(m)} &= A_{ji}^{(m)} \end{aligned} \right\} \quad (183)$$

It suffices to calculate the commutator $[G_M, M_+]$ for all values of M since all other commutators can be obtained from them.

$$[G_M, M_+] = \sum_{ij} F_{ij}^{(M)} [A_{ij}^{(M)}, M_+]$$

Substitution of $M_+ = \gamma \hbar S_+ = \gamma \hbar \sum_k S_k^+$ gives

$$[G_M, M_+] = \gamma \hbar \sum_{ij} F_{ij}^{(M)} [A_{ij}^{(M)}, S_i^+ + S_j^+] \quad (184)$$

since spins belonging to different lattice sites commute.
Using the commutation relations for spin operators we find

$$[A_{ij}^{(0)}, S_i^+ + S_j^+] = A_{ij}^{(1)}$$

$$[A_{ij}^{(1)}, S_i^+ + S_j^+] = 2 A_{ij}^{(2)}$$

$$[A_{ij}^{(-1)}, S_i^+ + S_j^+] = -6 A_{ij}^{(0)}$$

$$[A_{ij}^{(2)}, S_i^+ + S_j^+] = 0$$

$$[A_{ij}^{(-2)}, S_i^+ + S_j^+] = -2 A_{ij}^{(-1)}$$

These five equations can be expressed in general by

$$[A_{ij}^{(M)}, S_i^+ + S_j^+] = K_M A_{ij}^{(M')}, \quad M' = M+1 \quad (185)$$

where $K_0 = 1$, $K_1 = 2$, $K_2 = 0$, $K_{-1} = -6$, $K_{-2} = -2$.

Equation (184) now becomes

$$[G_M, M_+] = \gamma \hbar K_M \sum'_{ij} F_{ij}^{(M)} A_{ij}^{(M')} \quad (186)$$

Using (172) we find

$$\langle q_M(\tau) q_M^\dagger \rangle = \gamma^2 \hbar^2 K_M^2 \sum'_{ij} \sum'_{kl} F_{ij}^{(M)} F_{kl}^{(-M)} \langle A_{ij}^{(M)}(\tau) A_{kl}^{(-M')} \rangle \quad (187)$$

$$\langle q_M^\dagger(\tau) q_M \rangle = \gamma^2 \hbar^2 K_M^2 \sum'_{ij} \sum'_{kl} F_{ij}^{(-M)} F_{kl}^{(M)} \langle A_{ij}^{(-M')}(\tau) A_{kl}^{(M')} \rangle \quad (188)$$

Interchange of $i \leftrightarrow k$ and $j \leftrightarrow l$ in (188) gives

$$\langle q_M^\dagger(\tau) q_M \rangle = \gamma^2 \hbar^2 K_M^2 \sum'_{kl} \sum'_{ij} F_{kl}^{(-M)} F_{ij}^{(M)} \langle A_{kl}^{(-M')} A_{ij}^{(M')} \rangle$$

which can be written as

$$\langle q_M^+(\tau) q_M \rangle = \gamma^2 \hbar^2 K_M^2 \sum_j \sum_{kl} F_{ij}^{(M)} F_{kl}^{(-M)} \langle A_{ij}^{(-M')}(-\tau) A_{kl}^{(M')} \rangle^* \quad (189)$$

Using eqs. (113), (116), (117) and (118) we can show the following equivalence of dipolar terms

$$\begin{aligned} \langle A_{ij}^{(1)}(\tau) A_{kl}^{(-1)} \rangle &= \langle A_{ij}^{(-1)}(\tau) A_{kl}^{(1)} \rangle = \langle A_{ij}^{(2)}(\tau) A_{kl}^{(-2)} \rangle \\ &= \langle A_{ij}^{(-2)}(\tau) A_{kl}^{(2)} \rangle = 6 \langle A_{ij}^{(0)}(\tau) A_{kl}^{(0)} \rangle \end{aligned} \quad (190)$$

which allows us to write

$$\langle A_{ij}^{(M')}(\tau) A_{kl}^{(-M')} \rangle = J_{M'} \langle A_{ij}^{(2)}(\tau) A_{kl}^{(-2)} \rangle \quad (191)$$

where $J_0 = 1/6$, $J_{\pm 1} = J_{\pm 2} = 1$.

We now assume that $\hbar \omega_0 / kT \ll 1$ so that thermal averages will be those appropriate to a linear chain in zero applied field and calculate them with the density matrix $\rho_0 = e^{-\beta \mathcal{H}_{ex}} / \text{tr } \rho_0$. We may then use the correlation functions for spin operators calculated in Chap. V, which we introduce here using eq. (181c):

$$\langle A_{ij}^{(2)}(\tau) A_{kl}^{(-2)} \rangle = \langle S_i^+(\tau) S_j^+(\tau) S_k^- S_l^- \rangle \quad (192)$$

Let

$$\langle S_i^+(\tau) S_j^+(\tau) S_k^- S_l^- \rangle = f_{ijkl}(\tau) = \frac{1}{\Delta \omega} \int_{-\infty}^{\infty} f_{ijkl}(\omega) e^{i\omega \tau} d\omega \quad (193)$$

as in eqs. (129) and (136), and consider

$$\begin{aligned} \langle A_{ij}^{(2)}(-\tau) A_{kl}^{(-2)} \rangle^* &= \langle S_i^+(-\tau) S_j^+(-\tau) S_k^- S_l^- \rangle^* \\ &= f_{ijkl}^*(-\tau) = \frac{1}{\Delta \omega} \int_{-\infty}^{\infty} f_{ijkl}(\omega) e^{i\omega \tau} d\omega \end{aligned} \quad (194)$$

Since $f_{ij,kl}(\omega)$ is a real function we have

$$\langle A_{ij}^{(2)}(\tau) A_{kl}^{(-2)} \rangle = \langle A_{ij}^{(2)}(-\tau) A_{kl}^{(-2)} \rangle^* = \frac{1}{\Delta\omega} \int_{-\infty}^{\infty} f_{ij,kl}(\omega) e^{i\omega\tau} d\omega \quad (195)$$

Substituting (195) into (191) and using (187) and (189) we get

$$\begin{aligned} \langle q_M(\tau) q_M^\dagger \rangle &= \langle q_M^\dagger(\tau) q_M \rangle \\ &= \frac{\gamma^2 \hbar^2}{\Delta\omega} K_M^2 J_{M+1} \sum_{ij} \sum_{kl}' F_{ij}^{(M)} F_{kl}^{(-M)} \int_{-\infty}^{\infty} f_{ij,kl}(\omega) e^{i\omega\tau} d\omega \end{aligned} \quad (196)$$

Substituting (196) into (175) and integrating over τ we obtain

$$\begin{aligned} \eta &= \frac{2\pi}{8\hbar^2 \langle M_x^2 \rangle} \frac{\gamma^2 \hbar^2}{\Delta\omega} \sum_M K_M^2 J_{M+1} \sum_{ij} \sum_{kl}' F_{ij}^{(M)} F_{kl}^{(-M)} \\ &\quad \times \int_{-\infty}^{\infty} d\omega f_{ij,kl}(\omega) [\delta(\omega + M\omega_0) + \delta(\omega - M\omega_0)] \end{aligned}$$

and integrating over ω we get

$$\eta = \frac{\pi \gamma^2 \hbar^2}{4\hbar^2 \langle M_x^2 \rangle} \frac{1}{\Delta\omega} \sum_M K_M^2 J_{M+1} \sum_{ij} \sum_{kl}' F_{ij}^{(M)} F_{kl}^{(-M)} [f_{ij,kl}(M\omega_0) + f_{ij,kl}(-M\omega_0)] \quad (197)$$

Let

$$M_{ij,kl}(M\omega_0) = f_{ij,kl}(M\omega_0) + f_{ij,kl}(-M\omega_0) \quad (198)$$

We verify easily that

$$\left. \begin{aligned} M_{ij,kl}(M\omega_0) &= M_{kl,ij}(M\omega_0) \\ M_{ij,kl}(-M\omega_0) &= M_{ij,kl}(M\omega_0) \end{aligned} \right\} \quad (199)$$

Equation (197) can be written in the form

$$\eta(\omega_0) = \frac{\pi \delta^2}{4 \langle M_z^2 \rangle} \frac{1}{\Delta \omega} \sum_{M=0}^2 \gamma_M(\omega_0) \quad (200)$$

that is, $\gamma_M(\omega_0)$ represents the sum of the contributions from the terms in M and $-M$. Substituting the appropriate values for K_M and J_{M+1} , we find

$$\gamma_0(\omega_0) = \gamma_0(0) = \sum_{ij} \sum_{kl} F_{ij}^{(0)} F_{kl}^{(0)} M_{ijkl}^{(0)} \quad (201a)$$

$$\gamma_1(\omega_0) = 10 \sum_{ij} \sum_{kl} F_{ij}^{(1)} F_{kl}^{(-1)} M_{ijkl}^{(1)}(\omega_0) \quad (201b)$$

$$\gamma_2(\omega_0) = 4 \sum_{ij} \sum_{kl} F_{ij}^{(2)} F_{kl}^{(-2)} M_{ijkl}^{(2)}(\omega_0) \quad (201c)$$

3. Reduction of the Sums

In order to evaluate the sums in eqs. (201), for a 3-dimensional solid such as $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$, we consider a set of n independent chains of N spins each. The total exchange Hamiltonian, $\mathcal{H}_{ex}$, is then

$$\mathcal{H}_{ex} = \sum_{\alpha=1}^n \mathcal{H}_{ex}^{\alpha} \quad (202)$$

where $\mathcal{H}_{ex}^{\alpha}$, corresponding to the chain α , is of the form of eq. (1). The $\mathcal{H}_{ex}^{\alpha}$'s commute with one another. Hence, the density matrix is

$$\rho = \frac{e^{-\beta \mathcal{H}_{ex}}}{\text{tr } \rho} = \frac{e^{-\beta \sum_{\alpha=1}^n \mathcal{H}_{ex}^{\alpha}}}{\text{tr } e^{-\beta \sum_{\alpha=1}^n \mathcal{H}_{ex}^{\alpha}}}$$

$$\rho = \frac{\prod_{\alpha=1}^n e^{-\beta \mathcal{H}_{\alpha x}}}{\prod_{\alpha=1}^n \text{tr } e^{-\beta \mathcal{H}_{\alpha x}}} \\ = \prod_{\alpha=1}^n \rho_{\alpha} \quad (203)$$

where

$$\rho_{\alpha} = \frac{e^{-\beta \mathcal{H}_{\alpha x}}}{\text{tr } \rho_{\alpha}} \quad (204)$$

Let $S_{i,\alpha}^a$ be an arbitrary spin operator referring to the i th spin which is on chain α . Then we have

$$S_{i,\alpha}^a(\tau) = e^{-i\mathcal{H}_{\alpha x}\tau/\hbar} S_{i,\alpha}^a e^{i\mathcal{H}_{\alpha x}\tau/\hbar} \\ = e^{-i\sum_{\beta} \mathcal{H}_{\alpha x}^{\beta}\tau/\hbar} S_{i,\alpha}^a e^{i\sum_{\beta} \mathcal{H}_{\alpha x}^{\beta}\tau/\hbar} \\ = e^{-i\mathcal{H}_{\alpha x}^{\alpha}\tau/\hbar} S_{i,\alpha}^a e^{i\mathcal{H}_{\alpha x}^{\alpha}\tau/\hbar} \quad (205)$$

which means that the time dependence of spin operators relative to different chains may be calculated independently in terms of their corresponding $\mathcal{H}_{\alpha x}$.

Now, we are interested in spins at positions i, j, k and l which we assume are found in chains α, β, γ and δ respectively. The density matrix can be written

$$\rho = \rho' \rho_{\alpha} \rho_{\beta} \rho_{\gamma} \rho_{\delta} \quad (206)$$

where ρ' is the product of the density matrices relative to all other chains left.

We see that, for example, if $\alpha \neq \beta$, γ , or δ , then

$$\langle S_i^a(\tau) S_j^b(\tau) S_k^c S_l^d \rangle = \langle S_i^a(\tau) \rangle \langle S_j^b(\tau) S_k^c S_l^d \rangle$$

But

$$\langle S_i^a(\tau) \rangle = \langle S_i^a \rangle = 0$$

since $\langle S_i^z \rangle = \langle S_i^+ \rangle = 0$ in our approximation of neglecting the external field in computation of thermal averages. Thus, a non-zero result is obtained only if in the set (i,j,k,l) each spin belongs to the same chain as at least one other spin. Since we are further interested only in c.f.'s of the type $\langle S_i^+(\tau) S_j^+(\tau) S_k^- S_l^- \rangle$, and $\langle S_i^+ S_j^+ \rangle = 0$ as a consequence of rotational invariance, we are led to consider only the cases illustrated below:

Case I

Case II

Case III

Cases II and III are entirely equivalent as can be shown from the symmetry properties of the F_{ij} 's and the M_{ijkl} 's. Therefore, the summations in eqs. (201) can be written

$$\sum'_{ij} \sum'_{kl} = \sum'_{ij} \sum'_{kl} F_{ij}^{(m)} F_{kl}^{(-m)} M_{ijkl}^{(m)}(\omega_0) + 2 \sum'_{ij} \sum'_{kl} F_{ij}^{(m)} F_{kl}^{(-m)} M_{ijke}^{(m)}(\omega_0) \quad (207)$$

case I case II

Since the evaluation of the summations is entirely different in each case, let us separate $\sum_m(\omega_0)$ into

$$\gamma_M(\omega_0) = \gamma_M^I(\omega_0) + \gamma_M^{II}(\omega_0) \quad (208)$$

corresponding to the first and second term of (207) respectively.

Case I.— We have assumed the external magnetic field parallel to the z-axis. If the chains are also parallel to the z-axis we have $\theta_{mn} = 0$, and

$$F_{nm}^{(0)} = -\frac{3}{2} \frac{\gamma^2 \hbar^2}{r_{nm}^3}, \quad F_{nm}^{(\pm 1)} = F_{nm}^{(\pm 2)} = 0 \quad (209)$$

In order to reduce the sums in (207) we note the following additional properties of the M_{ijkl} 's:

$$M_{ijke} = M_{jlke} = M_{ijek} = M_{jiek} \quad (210)$$

since the spin operators S_i^+ , S_j^+ commute and S_k^- , S_l^- commute.

Substituting (209) into eqs. (201) we have

$$\gamma_0^I = \frac{q}{4} \gamma^4 \hbar^4 \sum'_{ij} \sum'_{ke} \frac{1}{r_{ij}^3 r_{ke}^3} M_{ijke} \quad (211a)$$

case I

$$\gamma_1^I = \gamma_2^I = 0 \quad (211b)$$

Considering only first order terms, i.e., $j = i \pm 1$, and $l = k \pm 1$, we have

$$\gamma_0^I = \frac{q}{4} \frac{\gamma^4 \hbar^4}{c^6} \sum'_{\langle ij \rangle} \sum'_{\langle ke \rangle} M_{ijke} \quad (212)$$

where $\sum'_{\langle ij \rangle}$ means i and j are neighbors, and c is the dis-

tance between spins along the chain.

Now we have, by virtue of (210)

$$\sum'_{\langle ij \rangle} \sum'_{\langle kl \rangle} M_{ijkl} = 4 \sum_{ik} M_{i,i+1,k,k+1} \quad (213)$$

We assume that the sum is independent of the origin i and we have

$$\sum'_{\langle ij \rangle} \sum'_{\langle kl \rangle} M_{ijkl} = 4 N' \sum_k M_{1,2,k,k+1} \quad (214)$$

where N' is the total number of atoms in the crystal. The summation is taken over the N spins in the chain and is expected to converge after a few terms.

Substituting (214) into (212) we have

$$\gamma_o^I = 9 \frac{\gamma^4 \hbar^4}{c^6} N' \sum_k M_{1,2,k,k+1} \quad (215)$$

If the chains are perpendicular to the z -axis and parallel to the x -axis for example, we have $\theta_{nm} = \pi/2$,

$\phi_{nm} = 0, \pi$ and

$$F_{nm}^{(0)} = \frac{3}{4} \frac{\gamma^2 \hbar^2}{r_{nm}^3}, \quad F_{nm}^{(\pm 1)} = 0, \quad F_{nm}^{(\pm 2)} = -\frac{3}{8} \frac{\gamma^2 \hbar^2}{r_{nm}^3} \quad (216)$$

From eqs. (201) we get

$$\gamma_o^I = \frac{9}{4} \frac{\gamma^4 \hbar^4}{c^6} N' \sum_k M_{1,2,k,k+1} \quad (217a)$$

$$\gamma_i^I = 0 \quad (217b)$$

$$\gamma_2^I(\omega_o) = \frac{9}{4} \frac{\gamma^4 \hbar^4}{c^6} N' \sum_k M_{1,2,k,k+1}^{(2\omega_o)} \quad (217c)$$

Case II. - In this case we have

$$\begin{aligned}\langle S_i^+(\tau) S_j^+(\tau) S_k^- S_l^- \rangle &= \langle S_i^+(\tau) S_k^- \rangle \langle S_j^+(\tau) S_l^- \rangle \\ &= 4 \langle S_i^z(\tau) S_k^z \rangle \langle S_j^z(\tau) S_l^z \rangle\end{aligned}\quad (218)$$

As in eq. (135), let

$$f'_{nm}(\tau) = \langle S_n^z(\tau) S_m^z \rangle = \sum_{\omega} f'_{nm}(\omega) e^{i\omega\tau}$$

so that

$$\langle S_i^z(\tau) S_k^z \rangle \langle S_j^z(\tau) S_l^z \rangle = \sum_{\omega} \sum_{\omega'} f'_{ik}(\omega') f'_{jl}(\omega - \omega') e^{i\omega\tau}$$

Then we find that

$$f_{ijkl}^{II}(\omega) = 4 \sum_{\omega'} f'_{ik}(\omega') f'_{jl}(\omega - \omega')$$

It is convenient to define

$$g_{ikjl}(\omega) = \sum_{\omega'} f'_{ik}(\omega') f'_{jl}(\omega - \omega') \quad (219)$$

and

$$\mathcal{M}_{ikjl}^{(M\omega_0)} = g_{ikjl}^{(M\omega_0)} + g_{ikjl}^{(-M\omega_0)} \quad (220)$$

Then $M_{ijkl}^{(M\omega_0)}$ in eq. (207) should be replaced by $4 \mathcal{M}_{ijkl}^{(M\omega_0)}$ and we have

$$2 \sum'_{ij} \sum'_{kl} F_{ij}^{(m)} F_{kl}^{(-m)} M_{ijkl}^{(M\omega_0)} = 8 \sum'_{ij} \sum'_{kl} F_{ij}^{(m)} F_{kl}^{(-m)} \mathcal{M}_{ikjl}^{(M\omega_0)} \quad (221)$$

The summation in (221) can be reduced with the help of some properties of the M_{ijkl} 's. First we observe that eq. (125) implies that we can add any integer number to the subscripts

of $f'_{nm}(\omega)$. Secondly, eq. (126) implies that

$$f'_{i,m}(\omega) = f'_{i,N-m+2}(\omega) \quad (222)$$

Now we can show that

$$f'_{p,p-q}(\omega) = f'_{p,p+q}(\omega) \quad (223)$$

Adding $N - p + 1$ to the subscripts of the left hand side, using (222) and then adding $p - 1$ we have, in that order,

$$f'_{p,p-q} = f'_{i,N-q+1} = f'_{i,q+1} = f'_{p,p+q}$$

which proves (223). Equation (223) shows that the value of m_{ijkl} depends only on the absolute value of the differences: $k - i$ and $l - j$; then

$$\begin{aligned} m_{i,i+m,j,j+n} &= m_{i,i+m,j,j+n} \\ &= m_{i,i+m,l,l+n} = m_{i,i+m,l,l+n} \end{aligned} \quad (224)$$

$$m, n = 0, 1, 2, 3, \dots$$

and we have

$$\begin{aligned} 8 \sum_{ij} \sum_{kl} F_{ij}^{(M)} F_{kl}^{(-M)} m_{ikjl} &= 8 \sum_i \sum_m \sum_n m_{i,i+m,l,l+n} \sum_j F_{ij}^{(M)} F_{i+m,j+n}^{(-M)} \\ &= 8N \sum_m \sum_n m_{i,i+m,l,l+n} \sum_j F_{ij}^{(M)} F_{i+m,j+n}^{(-M)}. \end{aligned} \quad (225)$$

where the meaning of $\sum_j F_{i,j}^{(M)} F_{i+m,j+n}^{(-M)}$ is as follows:

$$\sum_j F_{i,j}^{(M)} F_{i \pm m, j \pm n}^{(-M)} = \sum_j F_{i,j}^{(M)} [F_{i+m, j+n}^{(-M)} + F_{i+m, j-n}^{(-M)} + F_{i-m, j+n}^{(-M)} + F_{i-m, j-n}^{(-M)}], \quad (226a)$$

if $m, n \neq 0$

$$= \sum_j F_{i,j}^{(M)} [F_{i+m, j}^{(-M)} + F_{i-m, j}^{(-M)}], \quad \text{if } m \neq 0, n = 0 \quad (226b)$$

$$= \sum_j F_{i,j}^{(M)} [F_{i, j+n}^{(-M)} + F_{i, j-n}^{(-M)}], \quad \text{if } m = 0, n \neq 0 \quad (226c)$$

$$= \sum_j F_{i,j}^{(M)} F_{i,j}^{(-M)}, \quad \text{if } m, n = 0 \quad (226d)$$

Figure 23 illustrates the lattice points connected by the terms of eqs. (226)

Fig. 23.- Lattice points involved in the lattice sums of equations (226)

Note that the indices $i - m$ and $j - n$, whatever its algebraic value may be, simply label lattice points opposite and symmetric to those labeled by the indices $i + m$ and $j + n$ respectively. If we define

$$L_{nm}^{(M)} = \frac{1}{\delta_{\frac{1}{4}h}} \sum_j F_{ij}^{(M)} F_{i \pm m, j \pm n}^{(-M)} \quad (227)$$

and

$$m'_{mn}(M\omega_0) = m_{l, l+m, l, l+n}^{(M\omega_0)} \quad (228)$$

then we can write

$$8 \sum_{ij} \sum_{kl} F_{ij}^{(M)} F_{kl}^{(-M)} m_{ikjl}^{(M\omega_0)} = 8 \gamma^4 \hbar^4 N' \sum_{mn} m'_{mn}(M\omega_0) L_{nm}^{(M)} \quad (229)$$

4. Summary of Results

Substituting the contributions from cases I and II into eq. (207), we obtain

1) Chains parallel to the z-axis:

$$\gamma_0 = \gamma^4 \hbar^4 N' \left[\frac{9}{c^6} \sum_k M_{l, 2, k, k+l} + 8 \sum_{mn} m'_{mn}(0) L_{nm}^{(0)} \right] \quad (230a)$$

$$\gamma_1(\omega_0) = 80 \gamma^4 \hbar^4 N' \sum_{mn} m'_{mn}(\omega_0) L_{nm}^{(1)} \quad (230b)$$

$$\gamma_2(\omega_0) = 32 \gamma^4 \hbar^4 N' \sum_{mn} m'_{mn}(2\omega_0) L_{nm}^{(2)} \quad (230c)$$

2) Chains parallel to the x-axis:

$$\gamma_0 = \gamma^4 \hbar^4 N' \left[\frac{9}{4c^6} \sum_k M_{l, 2, k, k+l} + 8 \sum_{mn} m'_{mn}(0) L_{nm}^{(0)} \right] \quad (231a)$$

$$\gamma_1(\omega_0) = 80 \gamma^4 \hbar^4 N' \sum_{mn} m'_{mn}(\omega_0) L_{nm}^{(1)} \quad (231b)$$

$$\gamma_2(\omega_0) = \gamma^4 \hbar^4 N' \left[\frac{9}{4c^6} \sum_k M_{l, 2, k, k+l}(2\omega_0) + 32 \sum_{mn} m'_{mn}(2\omega_0) L_{nm}^{(2)} \right] \quad (231c)$$

The denominator of eq. (200) can be easily calculated since

$$\langle M_x^2 \rangle = \langle M_y^2 \rangle = \gamma^2 \hbar^2 \sum_{ij} \langle S_i^z S_j^z \rangle = \gamma^2 \hbar^2 N' \sum_j \langle S_j^z S_j^z \rangle \quad (233)$$

The crystal structure of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ is orthorhombic,⁷ with $a = 7.07$, $b = 12.12$, $c = 10.16$. The distance between copper ions along the c direction, which is believed to be the linear chain axis,^{8,9} is approximately 5.33 Å. The $L_{nm}^{(m)}$ sums were accordingly calculated assuming, for the copper ions, an orthorhombic C lattice with $a = 7.07$, $b = 12.12$, $c = 5.33$, as shown in Fig. 24.

Fig. 24.- Lattice of the Cu ions in copper tetramine sulfate monohydrate

The lattice sums $L_{nm}^{(m)}$ were calculated exact to four significant figures. They are symmetric with respect to n and m , i.e., $L_{nm}^{(m)} = L_{mn}^{(m)}$, and the values are given in table VII for H_0 parallel to c and table VIII for H_0 parallel to a .

TABLE VII*

 $L_{nm}^{(M)} \times 10^5$ in $(\text{\AA})^{-6}$ for H_0 parallel to c

M	n	m					
		0	1	2	3	4	6
0	0	3.3550	0.2245	-1.7820	-1.0470	-0.4655	-0.2142
	1		4.9280	-0.8226	-2.2470	-1.2610	-0.5742
	2			6.2450	0.0103	-1.8900	-1.1020
	3				6.6010	0.1701	-1.8100
	4					6.6820	0.2145
	5						6.7060
1	0	0.4218	0.3080	-0.2389	-0.1984	-0.1147	-0.0666
	1		0.6046	0.1096	-0.3536	-0.2650	-0.1554
	2			0.7288	0.2413	-0.2796	-0.2246
	3				0.8028	0.2818	-0.2564
	4					0.8260	0.2971
	5						0.8365
2	0	0.9419	1.1120	0.4118	0.1478	0.0622	0.0296
	1		2.2960	1.2600	0.4740	0.1773	0.0774
	2			1.9460	1.1420	0.4271	0.1560
	3				1.8990	1.1210	0.4164
	4					1.8880	1.1150
	5						1.8850

$$* L_{nm}^{(M)} = L_{mn}^{(M)}$$

TABLE VIII*

 $L_{nm}^{(M)} \times 10^5$ in $(\text{\AA})^{-6}$ for H_0 parallel to a

M	n	m					
		0	1	2	3	4	5
0	0	4.9540	4.9910	1.4150	0.4155	0.1728	0.0888
	1		11.3200	5.4070	1.5870	0.5043	0.2222
	2			10.0800	5.0800	1.4640	0.4447
	3				9.9570	5.0210	1.4320
	4					9.9250	5.0010
							9.9140
1	0	0.6914	0.7208	0.0913	-0.0232	-0.0249	-0.0173
	1		1.4740	0.6976	0.0664	-0.0405	-0.0369
	2			1.3580	0.7036	0.0794	-0.0317
	3				1.3710	0.7124	0.0852
	4					1.3770	0.7164
	5						1.3800
2	0	0.5413	0.3070	-0.1807	-0.1461	-0.0781	-0.0424
	1		0.9019	0.1609	-0.2588	-0.1885	-0.1031
	2			1.0040	0.2646	-0.2056	-0.1618
	3				1.0580	0.2913	-0.1909
	4					1.0720	0.3003
	5						1.0780

$$* L_{nm}^{(M)} = L_{mn}^{(M)}$$

Since the functions g_{ikjl} , formed by products of two-spin correlations and defined by eq. (219), are the correlation functions of interest in case II, we include the graph of some of them in Figs. 25 to 27. In particular, Fig. 25 shows the effect upon $g_{1,1,1,1}$ of modifying the original two-spin correlations (by subtracting $1/4N$) as discussed in Sec. 6, Chap. V.

Each of the terms appearing in eqs. (230) and (231) have been tabulated separately in tables IX to XV for H_0 parallel to a, and table XVI for H_0 parallel to c.

The resonance linewidth ΔH in magnetic units is given by

$$\Delta H = \frac{\eta}{\delta} \quad (233)$$

The linewidth has been computed using the g factors calculated by paramagnetic resonance¹⁰: $g_a = 2.05$, $g_b = 2.11$, $g_c = 2.18$ (the subscript refers to the crystal axis), and a value of J/k equal to $3.15^\circ K$.

The frequency dependence of the resonance linewidth for copper tetramine sulfate monohydrate is illustrated in Figs. 28 to 30 for H_0 parallel to a, and in Fig. 31 for H_0 parallel to c.

Comparison between our theoretical calculations and recent experimental measurements¹¹ will be discussed in Sec. 5 of this chapter.

TABLE IX

$$\left[\frac{9}{4c^6} \sum_k M_{1,2,k,k+1}(\omega) \right] \times 10^5 \text{ in } (\text{\AA})^{-6} \text{ at infinite temperature}$$

$\frac{\omega \hbar}{J}$	N			
	6	7	8	9
0	2.4944	2.0088	1.8064	1.6272
1.6	0.2173	0.2428	0.3449	0.3942
3.2	0.2950	0.3774	0.2490	0.2678
4.8	0.1267	0.0268	0.0782	0.1184
6.4	0.0000	0.0502	0.0279	0.0208
8.0	0.0000	0.0000	0.0019	0.0001

TABLE X

$$\left[\frac{9}{4c^6} \sum_k M_{1,2,k,k+1}(\omega) \right] \times 10^5 \text{ in } (\text{\AA})^{-6}, \text{ for } N = 9 \text{ at finite temperatures}$$

$\frac{\omega \hbar}{J}$	kT/J				
	1.6	2.0	2.4	5.0	10.0
0	0.7710	0.9024	1.0016	1.3016	1.4592
1.6	0.1220	0.1604	0.1923	0.2943	0.3451
3.2	0.4230	0.3918	0.3696	0.3123	0.2886
4.8	0.1152	0.1245	0.1278	0.1256	0.1218
6.4	0.0992	0.0734	0.0588	0.0322	0.0252
8.0	0.0005	0.0004	0.0003	0.0002	0.0001

TABLE XI

$$[\sum_{nm} m'_{(o)} L_{nm}^{(o)}] \times 10^5 \text{ in } (\text{\AA})^{-6} \text{ for } H_0 \text{ parallel to } a$$

kT/J		N			
		6	7	8	9
1.6	u*	0.0714	0.0632	0.0564	0.0534
	m*	0.0534	0.0473	0.0456	0.0433
2.0	u	0.0949	0.0813	0.0759	0.0702
	m	0.0704	0.0597	0.0602	0.0559
2.4	u	0.1152	0.0978	0.0830	0.0796
	m	0.0843	0.0711	0.0729	0.0636
5.0	u	0.1888	0.1601	0.1552	0.1434
	m	0.1239	0.1149	0.1183	0.1111
10.0	u	0.2328	0.1987	0.1927	0.1793
	m	0.1633	0.1419	0.1455	0.1379
∞	u	0.2824	0.2422	0.2352	0.2202
	m	0.1963	0.1724	0.1761	0.1683

* Top line (u) computed with the unmodified c.f.'s,
lower line (m) computed with the modified c.f.'s.

TABLE XII

$[\sum_{mn} m'_{mn}(\omega) L_{nm}^{(i)}] \times 10^6$ in $(\text{\AA})^{-6}$ for H_0 parallel to a ,
at infinite temperature

$\frac{\omega \hbar}{J}$		N			
		6	7	8	9
0	u*	0.3716	0.3214	0.3092	0.2912
	m*	0.2586	0.2292	0.2312	0.2224
0.8	u	0.0706	0.1002	0.1034	0.1157
	m	0.0470	0.0689	0.0761	0.0894
1.6	u	0.0621	0.0708	0.0718	0.0697
	m	0.0350	0.0540	0.0534	0.0549
2.4	u	0.0440	0.0391	0.0409	0.0387
	m	0.0304	0.0277	0.0319	0.0306
3.2	u	0.0289	0.0226	0.0232	0.0234
	m	0.0222	0.0163	0.0181	0.0187
4.0	u	0.0173	0.0164	0.0154	0.0162
	m	0.0142	0.0141	0.0133	0.0143
4.8	u	0.0096	0.0096	0.0102	0.0102
	m	0.0091	0.0091	0.0099	0.0098
5.6	u	0.0057	0.0063	0.0061	0.0061
	m	0.0057	0.0062	0.0061	0.0060
6.4	u	0.0038	0.0036	0.0034	0.0034
	m	0.0038	0.0036	0.0034	0.0034

* Top line (u) computed with the unmodified c.f's,
lower line (m) computed with the modified c.f's.

TABLE XIII

$[\sum_{mn} m'_{mn}(\omega) L_{nm}^{(2)}] \times 10^6$ in $(\text{\AA})^{-6}$ for H_0 parallel to a ,
at infinite temperature

$\frac{\omega \hbar}{J}$		N			
		6	7	8	9
0	u*	0.1897	0.1715	0.1600	0.1544
	m*	0.1376	0.1263	0.1226	0.1205
0.8	u	0.0653	0.0787	0.0829	0.0873
	m	0.0430	0.0517	0.0598	0.0658
1.6	u	0.0573	0.0609	0.0616	0.0603
	m	0.0302	0.0453	0.0444	0.0462
2.4	u	0.0419	0.0391	0.0400	0.0390
	m	0.0281	0.0266	0.0299	0.0299
3.2	u	0.0293	0.0260	0.0259	0.0262
	m	0.0207	0.0180	0.0195	0.0202
4.0	u	0.0196	0.0186	0.0180	0.0185
	m	0.0154	0.0152	0.0149	0.0158
4.8	u	0.0112	0.0117	0.0125	0.0124
	m	0.0112	0.0109	0.0119	0.0118
5.6	u	0.0076	0.0082	0.0080	0.0079
	m	0.0076	0.0081	0.0079	0.0079
6.4	u	0.0052	0.0049	0.0047	0.0048
	m	0.0052	0.0049	0.0047	0.0048

* Top line (u) computed with the unmodified c.f.'s,
lower line (m) computed with the modified c.f.'s.

TABLE XIV

$[\sum_{mn} m'_{mn}(\omega) L^{(1)}_{nm}] \times 10^6$ in $(\text{\AA})^{-6}$, for $N = 9$, H_0 parallel to a ,
at finite temperatures

$\frac{\omega \hbar}{J}$		kT/J				
		1.6	2.0	2.4	5.0	10.0
0	u*	0.0667	0.0901	0.1033	0.1890	0.2368
	m*	0.0542	0.0720	0.0831	0.1466	0.1823
0.8	u	0.0322	0.0433	0.0498	0.0828	0.0981
	m	0.0266	0.0353	0.0399	0.0651	0.0771
1.6	u	0.0331	0.0395	0.0423	0.0592	0.0652
	m	0.0264	0.0315	0.0335	0.0469	0.0541
2.4	u	0.0245	0.0286	0.0299	0.0367	0.0381
	m	0.0203	0.0236	0.0246	0.0297	0.0305
3.2	u	0.0222	0.0232	0.0228	0.0243	0.0241
	m	0.0184	0.0191	0.0187	0.0197	0.0194
4.0	u	0.0203	0.0202	0.0195	0.0181	0.0171
	m	0.0188	0.0187	0.0179	0.0164	0.0153
4.8	u	0.0188	0.0163	0.0157	0.0126	0.0112
	m	0.0184	0.0159	0.0155	0.0122	0.0109
5.6	u	0.0163	0.0139	0.0122	0.0083	0.0071
	m	0.0162	0.0138	0.0121	0.0083	0.0069
6.4	u	0.0126	0.0099	0.0083	0.0050	0.0040
	m	0.0126	0.0099	0.0083	0.0050	0.0040

* Top line (u) computed with the unmodified c.f.'s, lower line (m) computed with the modified c.f.'s.

TABLE XV

$[\sum_{mn} m'_{mn}(\omega) L_{nm}^{(2)}] \times 10^6$ in $(\text{\AA})^{-6}$, for $N = 9$, H_0 parallel to a ,
at finite temperatures

$\frac{\omega \hbar}{J}$		kT/J				
		1.6	2.0	2.4	5.0	10.0
0	u*	0.0482	0.0596	0.0660	0.1075	0.1298
	m*	0.0413	0.0501	0.0559	0.0863	0.1026
0.8	u	0.0318	0.0404	0.0447	0.0673	0.0774
	m	0.0270	0.0333	0.0362	0.0524	0.0592
1.6	u	0.0343	0.0387	0.0402	0.0529	0.0571
	m	0.0279	0.0309	0.0318	0.0413	0.0442
2.4	u	0.0283	0.0317	0.0325	0.0381	0.0389
	m	0.0237	0.0263	0.0266	0.0302	0.0303
3.2	u	0.0286	0.0285	0.0273	0.0278	0.0272
	m	0.0240	0.0236	0.0223	0.0222	0.0213
4.0	u	0.0259	0.0252	0.0239	0.0218	0.0199
	m	0.0240	0.0231	0.0218	0.0189	0.0173
4.8	u	0.0245	0.0221	0.0202	0.0156	0.0138
	m	0.0240	0.0215	0.0196	0.0150	0.0133
5.6	u	0.0216	0.0183	0.0161	0.0109	0.0092
	m	0.0215	0.0182	0.0160	0.0108	0.0091
6.4	u	0.0168	0.0139	0.0113	0.0069	0.0057
	m	0.0167	0.0139	0.0113	0.0069	0.0057

* Top line (u) computed with unmodified c.f's, lower line (m) computed with the modified c.f's

TABLE XVI

$[\sum_{mn} m'(\omega) L_{nm}^{(M)}] \times 10^6$ in $(\text{\AA})^{-6}$, for $N = 9$, H_0 parallel to c ,
at infinite temperature

$\frac{\omega \hbar}{J}$		M		
		0	1	2
0	u*	0.6512	0.1104	0.4622
	m*	0.5278	0.0859	0.3516
0.8	u	0.4988	0.0725	0.1558
	m	0.3710	0.0541	0.1222
1.6	u	0.3824	0.0504	0.0873
	m	0.2866	0.0387	0.0697
2.4	u	0.2748	0.0322	0.0444
	m	0.2050	0.0251	0.0355
3.2	u	0.1982	0.0209	0.0255
	m	0.1476	0.0167	0.0203
4.0	u	0.1473	0.0138	0.0182
	m	0.1196	0.0125	0.0158
4.8	u	0.1041	0.0087	0.0114
	m	0.0984	0.0085	0.0110
5.6	u	0.0708	0.0051	0.0069
	m	0.0702	0.0051	0.0068
6.4	u	0.0463	0.0027	0.0041
	m	0.0462	0.0027	0.0041

* Top line (u) computed with the unmodified c.f's,
lower line (m) computed with the modified c.f's.

Fig. 25.- $g_{1111}(\omega)$ for $N = 9$ at infinite temperature,
 calculated with the unmodified c.f.'s (solid curve)
 and with the modified c.f.'s (dashed curve)

Fig. 26.- Variation of $g_{1111}(\omega)$ with temperature

Fig. 27.- $g_{1,1,1,2}$, $g_{1,1,1,3}$ and $g_{1,2,1,2}$ for $N = 9$ at infinite temperature

Fig. 28.- Frequency dependence of the resonance linewidth for H_0 parallel to a , calculated with the unmodified c.f.'s (solid curve) and with the modified c.f.'s (dashed curve).

Fig. 29.- Resonance linewidth for chains of N spins at infinite temperature

Fig. 30.- Variation of the linewidth with temperature

Fig. 31.- Frequency dependence of the resonance linewidth for H_0 parallel to c , calculated with the unmodified c.f.'s (solid curve) and with the modified c.f.'s (dashed curve)

Fig. 32.- The calculated frequency dependence of the linewidth for $N = 9$ at infinite temperature (circles) can be approximated by the Lorentzian curve

$$\Delta H = 2.13 + \frac{6500}{\nu^2 + 2350} \quad \text{Gauss}$$

for ν in Gc (solid curve).

We note in Fig. 29 that the values for the linewidth calculated on chains of different number of spins seem to converge rapidly at first, when we compare the curves for $N = 6, 7$ and 8 , but slowly, or no convergence is observed, when we compare the curves for $N = 7, 8$ and 9 . In order to investigate the convergence with N , we have plotted the values of ΔH at zero frequency versus $1/N^2$ in Fig. 33, where we have included also the value for $N = 5$. It is found that the variation is linear with $1/N^2$, but different depending on whether N is even or odd. This situation is very similar to that found by Bonner and Fisher³ for the variation of the antiferromagnetic ground state energy with N in linear chains. Hence, the lack of convergence in Fig. 29 is only apparent and the convergence is understood if we consider each sequence (even or odd N) separately. The probable limiting value for $N = \infty$, estimated by extrapolation of the bisector between the two lines, is 3.55 Gauss for H_0 parallel to a .

Other interesting questions regarding convergence are (1) the convergence of the computed linewidth with increasing correlation range and (2) how this convergence is affected by modification of the basic correlation functions. In order to investigate these points we consider the contribution from case II (spins in different chains) to the linewidth, i.e., that part which depends only on the two-spin correlation functions, and define the following

sequence of functions

$$\sigma_j(\omega) = 10 \sum_{m,n=0}^j m'_{mn}(\omega) L_{nm}^{(1)} + 4 \sum_{m,n=0}^j m'_{mn}(2\omega) L_{nm}^{(2)}$$

$$j = 0, 1, 2, \dots \begin{cases} (N-1)/2 & \text{odd } N \\ N/2 & \text{even } N \end{cases}$$

Fig. 34 shows the convergence of $\sigma_j(\omega)$ with the correlation range j , i.e., the convergence with the number of higher order correlation functions that we take into account. If $j = 0$, only $f_1(\omega)$ (or $\langle S_i^x(\tau) S_i^x \rangle$) is taken into account. Fig. 35 shows the convergence obtained when we use the correlation functions modified as explained in Sec. 6, Chap.V, i.e., $1/4N$ has been subtracted from $f_1(0)$ only. The convergence is essentially unaffected by the modification in this case.

In Fig. 36 we have modified all the correlation functions, i.e., $1/4N$ has been subtracted off from $f_j(0)$ for all values of j . The result is contrary to what one should expect, since we have in this case a diverging effect as we increase the correlation range. This effect is one more reason to believe that the subtraction of $1/4N$, with which we expect to have a better approximation to the correlation functions for large N , is not applicable to correlation functions of order $j \geq 2$.

Fig. 33.- Linewidth at zero frequency versus $1/N^2$.
 Values of ΔH are the calculated with the unmodified
 correlation functions. Probable $N = \infty$ limit
 estimated by dotted line

Fig. 34.- Variation of the contribution from Case II to the linewidth with the correlation range j . Calculation with the unmodified correlation functions

Fig. 35.- Variation of the contribution from Case II to the linewidth with the correlation range j . Calculation with the modified correlation functions ($1/4N$ subtracted off from $f_1(0)$ only)

Fig. 36.- Variation of the contribution from Case II to the linewidth with the correlation range j . Calculation with modification of all correlation functions ($1/4N$ subtracted off from $f_n(0)$ for all n)

5. The Gaussian Approximation

Returning to eq. (175) and collecting the terms having identical exponentials, we can write

$$\eta = \frac{1}{8\hbar^2 \langle M_x^2 \rangle} \sum_M \int_{-\infty}^{\infty} \Gamma_M(\tau) e^{iM\omega_0\tau} d\tau \quad (234)$$

where

$$\Gamma_M(\tau) = \langle q_M(\tau) q_M^\dagger \rangle + \langle q_{-M}^\dagger(\tau) q_{-M} \rangle \quad (235)$$

Taking each term of eq. (234) separately, we define

$$\eta_M = \frac{1}{8\hbar^2 \langle M_x^2 \rangle} \int_{-\infty}^{\infty} \Gamma_M(\tau) e^{iM\omega_0\tau} d\tau \quad (236)$$

as the contribution from Γ_M to the linewidth.

A common procedure in previous work⁵ has been to assume a gaussian behavior for $\Gamma_M(\tau)$,

$$\Gamma_M(\tau) = \Gamma_M(0) e^{-\frac{1}{2} \omega_e^{(M)2} \tau^2} \quad (237)$$

where the "effective exchange frequency" $\omega_e^{(M)}$ is computed from the first two terms of the series

$$\Gamma_M(\tau) = \Gamma_M(0) + \frac{1}{2} \tau^2 \ddot{\Gamma}_M(0) + \dots \quad (238)$$

so that by comparing (237) and (238) we have

$$\omega_e^{(M)} = \left[\frac{\left| \frac{d^2}{d\tau^2} \Gamma_M(\tau) \right|_{\tau=0}}{\Gamma_M(0)} \right]^{1/2} \quad (239)$$

and by using (237) in (236)

$$\eta_M = \frac{\sqrt{2\pi}}{8\hbar^2 \langle M_x^2 \rangle} \frac{\bar{\Gamma}_M(0)}{\omega_e^{(M)}} e^{-M^2 \omega_0^2 / 2 \omega_e^{(M)^2}} \quad (240)$$

In this section we calculate $\omega_e^{(M)}$ and η_M from (239) and (240) in the infinite temperature limit, in order to compare our results of Sec. 4 with those obtained using the gaussian assumption.

Calculation of $\ddot{\bar{\Gamma}}_M(0)$.— Taking the second derivative of $\bar{\Gamma}_M(\tau)$, eq.(235), and using (170) and (172) we get

$$\begin{aligned} \ddot{\bar{\Gamma}}_M(0) = & -\frac{1}{\hbar^2} \langle [\mathcal{H}_{ex}, [\mathcal{H}_{ex}, [G_M, M_+]]] [M_-, G_{-M}] \\ & + [\mathcal{H}_{ex}, [\mathcal{H}_{ex}, [M_-, G_M]]] [G_M, M_+] \rangle \end{aligned}$$

Since the density matrix commutes with $\mathcal{H}_{ex}$ we have

$$\begin{aligned} \ddot{\bar{\Gamma}}_M(0) = & -\frac{1}{\hbar^2} \langle [\mathcal{H}_{ex}, [G_M, M_+]] [[M_-, G_{-M}], \mathcal{H}_{ex}] \\ & + [\mathcal{H}_{ex}, [M_-, G_M]] [[G_M, M_+], \mathcal{H}_{ex}] \rangle \quad (241) \end{aligned}$$

With $\mathcal{H}_{ex}$ in the general form

$$\mathcal{H}_{ex} = - \sum_{mn} J_{mn} \vec{S}_m \cdot \vec{S}_n$$

and using (186) we have

$$[\mathcal{H}_{ex}, [G_M, M_+]] = -\gamma \hbar K_M \sum_{ij} \sum_{mn} J_{mn} F_{ij}^{(M)} [\vec{S}_m \cdot \vec{S}_n, A_{ij}^{(M')}] \quad (242)$$

where we recall $M' = M + 1$ and K_M is defined in (185).

Let

$$\Sigma = \sum'_{ij} \sum'_{mn} J_{mn} F_{ij}^{(M)} [\vec{S}_m \cdot \vec{S}_n, A_{ij}^{(M')}]$$

Since $[\vec{S}_m \cdot \vec{S}_n, A_{ij}^{(M')}] = 0$ unless m or n is equal to i or j we have, summing over n ,

$$\begin{aligned} \Sigma = \sum'_{ij} F_{ij}^{(M)} \sum_m (J_{mi} [\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M')}] + J_{mj} [\vec{S}_m \cdot \vec{S}_j, A_{ij}^{(M')}] \\ + \sum_{n \neq i, j} J_{mn} [\vec{S}_m \cdot \vec{S}_n, A_{ij}^{(M')}]) \end{aligned}$$

Using the fact that $[\vec{S}_i \cdot \vec{S}_j, A_{ij}] = 0$ for spins $\frac{1}{2}$, and summing over m , we obtain

$$\begin{aligned} \Sigma &= \sum'_{ij} F_{ij}^{(M)} \left\{ \sum_{m \neq i, j} J_{mi} [\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M')}] + \sum_{m \neq i, j} J_{mj} [\vec{S}_m \cdot \vec{S}_j, A_{ij}^{(M')}] \right. \\ &\quad \left. + \sum_{n \neq i, j} (J_{ni} [\vec{S}_i \cdot \vec{S}_n, A_{ij}^{(M')}] + J_{jn} [\vec{S}_j \cdot \vec{S}_n, A_{ij}^{(M')}]) \right\} \\ &= 2 \sum'_{ijm} F_{ij}^{(M)} \{ J_{mi} [\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M')}] + J_{mj} [\vec{S}_m \cdot \vec{S}_j, A_{ij}^{(M')}] \} \\ &= 4 \sum'_{ijm} J_{mi} F_{ij}^{(M)} [\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M')}] \end{aligned}$$

Substituting into (242) we have

$$[J_{ex}, [G_m, M_+]] = -4\gamma\hbar K_M \sum'_{ijm} J_{mi} F_{ij}^{(M)} [\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M')}] \quad (243)$$

and (241) becomes

$$\ddot{m}(0) = 16\gamma^2 \sum'_{ijm} \sum'_{kln} J_{mi} J_{nk} F_{ij}^{(M)} F_{kl}^{(-M)} P_{ijmken}^{(M)} \quad (244)$$

where

$$\begin{aligned} P_{ijmken}^{(M)} &= K_M^2 \langle [\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M+1)}] [A_{kl}^{(-M-1)}, \vec{S}_n \cdot \vec{S}_k] \rangle \\ &\quad + K_{-M}^2 \langle [\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M-1)}] [A_{kl}^{(-M+1)}, \vec{S}_n \cdot \vec{S}_k] \rangle \end{aligned} \quad (245)$$

and we have neglected the minus sign in front of (241) since it merely indicates that $\Gamma_M(\tau)$ is concave down.

The required commutators are

$$[\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(0)}] = \frac{1}{6}(S_i^- S_j^+ S_m^z + S_i^z S_j^- S_m^+ + 2 S_i^- S_j^z S_m^+) - h.c. \quad (246a)$$

$$[\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(1)}] = \frac{1}{2}(S_i^- S_j^+ S_m^+ - S_i^+ S_j^+ S_m^- + 2 S_i^+ S_j^z S_m^z - 2 S_i^z S_j^z S_m^+) \quad (246b)$$

$$[\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(2)}] = S_i^+ S_j^+ S_m^z - S_i^z S_j^+ S_m^+ \quad (246c)$$

We particularize to infinite temperature and consider the spins individually quantized. In this case the averages of products of six spin operators break into products of averages of one and two spin operators and we have

$$\left. \begin{aligned} \langle S_i^z \rangle &= 0 \\ \langle S_i^z S_i^z \rangle &= g = \frac{1}{4} \\ \langle S_i^+ S_i^- \rangle &= \langle S_i^- S_i^+ \rangle = f = \frac{1}{2} \end{aligned} \right\} \quad (247)$$

Evaluation of the products of commutators in (245) shows that they are of the form

$$[\vec{S}_m \cdot \vec{S}_i, A_{ij}^{(M)}][A_{kl}^{(-M)}, \vec{S}_n \cdot \vec{S}_k] = Q_M \sum_P q_{\alpha\beta\gamma} \delta_{i\alpha} \delta_{j\beta} \delta_{m\gamma} \quad (248)$$

where P means permutations of $\alpha, \beta, \gamma = k, l, n$ and

$$\left. \begin{aligned} q_{kln} &= -q_{nlk} = 2 \\ q_{nkl} &= -q_{lkn} = -1 \\ q_{lnk} &= -q_{knl} = -1 \end{aligned} \right\} \quad (249)$$

$$Q_0 = \frac{1}{6} f^2 g = \frac{1}{96} \quad (250a)$$

$$Q_{\pm 1} = \frac{1}{4} (f^3 + 4fg^2) = \frac{1}{16} \quad (250b)$$

$$Q_{\pm 2} = f^2 g = \frac{1}{16} \quad (250c)$$

Then we may write (245) as

$$P_{ijmkl n}^{(m)} = R_m \sum_p q_{\alpha\beta\gamma} \delta_{i\alpha} \delta_{j\beta} \delta_{m\gamma} \quad (251)$$

where

$$R_m = K_m^2 Q_{m+1} + K_{-m}^2 Q_{-m+1} \quad (252)$$

Substituting (251) into (244) and summing over i, j, m , we have

$$\ddot{\Gamma}_m^{(0)} = 16\gamma^2 R_m \sum'_{kln} J_{nk} F_{kl}^{(-m)} \sum_p q_{\alpha\beta\gamma} J_{\alpha\gamma} F_{\alpha\beta}^{(m)} \quad (253)$$

Using (249) and summing over P , we have

$$\begin{aligned} \sum_p q_{\alpha\beta\gamma} J_{\alpha\gamma} F_{\alpha\beta}^{(m)} &= 2J_{kn} F_{kl}^{(m)} - 2J_{nk} F_{nl}^{(m)} - J_{nl} F_{nk}^{(m)} + J_{ln} F_{lk}^{(m)} \\ &\quad - J_{lk} F_{ln}^{(m)} + J_{kl} F_{kn}^{(m)} \\ &= 2J_{kn} (F_{kl}^{(m)} - F_{ln}^{(m)}) + J_{ln} (F_{kl}^{(m)} - F_{kn}^{(m)}) + J_{kl} (F_{kn}^{(m)} - F_{ln}^{(m)}) \quad (254) \end{aligned}$$

Therefore, the summation over kln in (253) becomes

$$\begin{aligned} \sum'_{kln} &= \sum'_{kln} J_{kn} F_{kl}^{(-m)} [2J_{kn} (F_{kl}^{(m)} - F_{ln}^{(m)}) + J_{ln} (F_{kl}^{(m)} - F_{kn}^{(m)}) \\ &\quad + J_{kl} (F_{kn}^{(m)} - F_{ln}^{(m)})] \quad (255) \end{aligned}$$

A more familiar form for eq. (255) can be obtained if we add the same expression but with k and n interchanged:

$$\begin{aligned}
\sum'_{kln} &= \frac{1}{2} \sum'_{kln} \left(J_{kn} F_{kl}^{(-m)} [2J_{kn} (F_{kl}^{(m)} - F_{ln}^{(m)}) + J_{ln} (F_{kl}^{(m)} - F_{kn}^{(m)}) + J_{kl} (F_{kn}^{(m)} - F_{ln}^{(m)})] \right. \\
&\quad \left. + J_{nk} F_{nl}^{(-m)} [2J_{nk} (F_{nl}^{(m)} - F_{lk}^{(m)}) + J_{lk} (F_{nl}^{(m)} - F_{nk}^{(m)}) + J_{kl} (F_{nk}^{(m)} - F_{lk}^{(m)})] \right) \\
&= \frac{1}{2} \sum'_{kln} \left(2J_{kn}^2 (F_{kl}^{(-m)} F_{kl}^{(m)} - F_{kl}^{(-m)} F_{ln}^{(m)} - F_{kl}^{(m)} F_{ln}^{(-m)} + F_{ln}^{(-m)} F_{ln}^{(m)}) \right. \\
&\quad \left. + J_{kn} J_{ln} (F_{kl}^{(m)} - F_{kn}^{(m)}) (F_{kl}^{(-m)} - F_{ln}^{(-m)}) + J_{kn} J_{kl} (F_{kn}^{(m)} - F_{ln}^{(m)}) (F_{kl}^{(-m)} - F_{ln}^{(-m)}) \right)
\end{aligned}$$

Interchanging again k and n in the last term we have

$$\begin{aligned}
\sum'_{kln} &= \frac{1}{2} \sum'_{kln} \left\{ 2J_{kn}^2 (|F_{kl}^{(m)}|^2 + 2\text{Re} F_{kl}^{(m)} F_{ln}^{(-m)} + |F_{ln}^{(m)}|^2) \right. \\
&\quad \left. + 2J_{kn} J_{ln} (F_{kl}^{(m)} - F_{kn}^{(m)}) (F_{kl}^{(-m)} - F_{ln}^{(-m)}) \right\} \\
&= \sum'_{kln} \left\{ J_{kn}^2 |F_{kl}^{(m)} - F_{ln}^{(m)}|^2 + J_{kn} J_{ln} (F_{kl}^{(m)} - F_{kn}^{(m)}) (F_{kl}^{(-m)} - F_{ln}^{(-m)}) \right\} \quad (256)
\end{aligned}$$

Finally, substituting (256) into (253) we obtain

$$\begin{aligned}
\ddot{\Gamma}_M(0) &= 16\gamma^2 R_M \sum'_{kln} \left\{ J_{kn}^2 |F_{kl}^{(m)} - F_{ln}^{(m)}|^2 + J_{kn} J_{ln} \right. \\
&\quad \left. \times (F_{kl}^{(m)} - F_{kn}^{(m)}) (F_{kl}^{(-m)} - F_{ln}^{(-m)}) \right\} \quad (257)
\end{aligned}$$

Linear chain.— For a linear chain with nearest neighbor interaction, i.e.,

$$J_{ij} = J \delta_{j, i \pm 1} \quad (258)$$

the summation in (257) contains only the following two cases of interest:

Case A

Case B

Case A.— In this case, the summation in (257) becomes

$$\begin{aligned} \sum'_{k \neq n} = & J^2 \left\{ \sum'_{k \neq l} |F_{k \ell}^{(M)} - F_{\ell, k+1}^{(M)}|^2 + \sum'_{k \neq l} |F_{k \ell}^{(M)} - F_{\ell, k-1}^{(M)}|^2 \right. \\ & \left. + \sum'_{k \neq l} (F_{k \ell}^{(M)} - F_{k, k+1}^{(M)}) (F_{k \ell}^{(M)} - F_{k, k+1}^{(M)}) \delta_{\ell, k+2} + \sum'_{k \neq l} (F_{k \ell}^{(M)} - F_{k, k-1}^{(M)}) (F_{k \ell}^{(M)} - F_{k, k-1}^{(M)}) \delta_{\ell, k-2} \right\} \end{aligned}$$

Summing over l and noting that the F 's are independent of translation, i.e.,

$$F_{i+n, j+n}^{(M)} = F_{ij}^{(M)} \quad (259)$$

we have

$$\begin{aligned} \sum'_{k \neq n} = & J^2 \sum'_{k \neq l} \left\{ |F_{k \ell}^{(M)} - F_{\ell, k+1}^{(M)}|^2 + |F_{k \ell}^{(M)} - F_{\ell, k-1}^{(M)}|^2 \right\} + 4 J^2 N' |F_{12}^{(M)} - F_{13}^{(M)}|^2 \\ = & 4 J^2 N' \sum_{m \geq 2} |F_{1, m}^{(M)} - F_{1, m+1}^{(M)}|^2 + 2 J^2 N' |F_{12}^{(M)} - F_{13}^{(M)}|^2 \quad (260) \end{aligned}$$

For the case under consideration we have

$$F_{1, m}^{(M)} = \frac{1}{(m-1)^3} F_{12}^{(M)} \quad (261)$$

Therefore, (260) becomes

$$\sum'_{k \ell n} = 4 J^2 N' |F_{12}^{(M)}|^2 \left[\frac{149}{128} + \sum_{m \geq 2} \left(\frac{1}{(m-1)^3} - \frac{1}{m^3} \right)^2 \right] \quad (262)$$

Case B.— In this case we have

$$\begin{aligned} \sum'_{k \ell n} &= J^2 \sum_{k \ell} \left\{ |F_{\ell,k}^{(M)} - F_{\ell,k+1}^{(M)}|^2 + |F_{\ell,k}^{(M)} - F_{\ell,k-1}^{(M)}|^2 \right\} \\ &= J^2 N' \left\{ 2 \sum_k F_{1,k}^{(M)} F_{1,k}^{(-M)} + \sum_k F_{1,k+1}^{(M)} F_{1,k+1}^{(-M)} + \sum_k F_{1,k-1}^{(M)} F_{1,k-1}^{(-M)} \right. \\ &\quad \left. - \sum_k [F_{1,k}^{(M)} F_{1,k+1}^{(-M)} + F_{1,k}^{(M)} F_{1,k-1}^{(-M)}] - \sum_k [F_{1,k}^{(-M)} F_{1,k+1}^{(M)} + F_{1,k}^{(-M)} F_{1,k-1}^{(M)}] \right\} \quad (263) \end{aligned}$$

The first three terms of (263) are identified as dipole sums of type $L_{00}^{(M)}$, given by eqs. (226) and (227), and the last two terms of (263) are identified as dipole sums of the type $L_{01}^{(M)}$. Then,

$$\sum'_{k \ell n} = 2 J^2 \gamma^4 \hbar^4 N' (2 L_{00}^{(M)} - L_{01}^{(M)}) \quad (264)$$

Taking the first two terms of the summation in (262) and adding the contributions from cases A and B we have

$$\ddot{\Gamma}_M(0) = 32 J^2 \gamma^6 \hbar^4 R_M N' \left[\frac{149}{64} \left| \frac{F_{12}^{(M)}}{\gamma^2 \hbar^2} \right|^2 + 2 L_{00}^{(M)} - L_{01}^{(M)} \right] \quad (265)$$

Calculation of $\Gamma_M(0)$.— We now proceed to calculate the denominator of (239), $\Gamma_M(0)$. From eqs. (235), (187) and

(188) we have

$$\Gamma_M(0) = \gamma^2 \hbar^2 \sum_{ij}' \sum_{kl}' F_{ij}^{(M)} F_{kl}^{(-M)} [K_M^2 \langle A_{ij}^{(M+1)} A_{kl}^{(-M-1)} \rangle + K_{-M}^2 \langle A_{ij}^{(M-1)} A_{kl}^{(-M+1)} \rangle] \quad (266)$$

Using (191) we get

$$\Gamma_M(0) = \gamma^2 \hbar^2 R'_M \sum_{ij}' \sum_{kl}' F_{ij}^{(M)} F_{kl}^{(-M)} \langle S_i^+ S_j^+ S_k^- S_l^- \rangle \quad (267)$$

where

$$R'_M = K_M^2 J_{M+1} + K_{-M}^2 J_{-M+1} \quad (268)$$

In the summation of eq. (267) the cases of interest are the same cases I and II discussed in Sec. 3. Therefore, we have

$$\Gamma_M(0) = \frac{1}{4} \gamma^2 \hbar^2 R'_M \left\{ 2 \sum_{ij}' \sum_{kl}' F_{ij}^{(M)} F_{kl}^{(-M)} \delta_{ik} \delta_{jl} + 2 \sum_{ij}' \sum_{kl}' F_{ij}^{(M)} F_{kl}^{(-M)} \delta_{ik} \delta_{je} \right\} \quad (269)$$

case I case II

since $\langle S_n^+ S_m^- \rangle = \frac{1}{2} \delta_{nm}$ in either case at infinite temperature. Hence,

$$\Gamma_M(0) = \frac{1}{2} \gamma^2 \hbar^2 R'_M \left\{ \sum_{ij}' |F_{ij}^{(M)}|^2 + \sum_{ij}' |F_{ij}^{(M)}|^2 \right\} \quad (270)$$

case I case II

$$= \frac{1}{2} \gamma^2 \hbar^2 R'_M N' \left\{ \sum_j |F_{1,j}^{(M)}|^2 + \sum_j |F_{1,j}^{(M)}|^2 \right\} \quad (271)$$

case I case II

In case I (all spins in the same chain) we use eq. (261), and in case II we identify the summation as a dipole sum of the type $L_{00}^{(M)}$. Therefore, we have

$$\Gamma_M(0) = \frac{1}{2} \gamma^6 \hbar^6 R'_M N' \left[L_{00}^{(M)} + 2 \left| \frac{F_{12}^{(M)}}{\gamma^2 \hbar^2} \right|^2 \sum_{m \geq 2} \frac{1}{(m-1)^6} \right] \quad (272)$$

Considering only the first term of the summation in (265) we obtain

$$\Gamma_M(0) = \frac{1}{2} \gamma^6 \hbar^6 R'_M N' \left[L_{00}^{(M)} + 2 \left| \frac{F_{12}^{(M)}}{\gamma^2 \hbar^2} \right|^2 \right] \quad (273)$$

Note that in eq. (273) as well as in eq. (265), $F_{12}^{(M)}$ corresponds to two adjacent spins on the same chain.

Summary and results.— The contributions to $\Gamma_M(0)$ and $\ddot{\Gamma}_M(0)$ from the values M and $-M$ are identical, as can be seen from the definition of R_M and R'_M , eqs. (252) and (268) respectively. If we include both contributions in $\Gamma_M(0)$ and $\ddot{\Gamma}_M(0)$, the appropriate values of R_M and R'_M are those given in table XVII.

TABLE XVII

	$M = 0$	$M = 1$	$M = 2$
R_M	1/8	5/4	1/2
R'_M	2	20	8
R_M/R'_M	1/16	1/16	1/16

Substituting (265) and (273) into (239) we have

$$\omega_e^{(M)} = \frac{2J}{\hbar} \left[\frac{\frac{149}{64} \left| \frac{F_{12}^{(M)}}{\gamma^2 \hbar^2} \right|^2 + 2 L_{00}^{(M)} - L_{01}^{(M)}}{2 \left| \frac{F_{12}^{(M)}}{\gamma^2 \hbar^2} \right|^2 + L_{00}^{(M)}} \right]^{1/2} \quad (274)$$

The values of $\omega_e^{(M)}$ and $\Gamma_M(0)$ are shown in tables XVIII

and XIX respectively, for both H_0 parallel to a and H_0 parallel to c.

TABLE XVIII

$\frac{\omega_a^{(M)} \hbar}{J}$ for $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ at infinite temperature

	H_0 parallel to a	H_0 parallel to c
$M = 0$	2.08	2.26
$M = 1$	1.96	2.26
$M = 2$	2.23	1.82

TABLE XIX

$\frac{\bar{\Gamma}_M(0)}{\gamma^6 \hbar^6 N'} \times 10^5$ in $(\text{\AA})^{-6}$ at infinite temperature

	H_0 parallel to a	H_0 parallel to c
$M = 0$	9.85	22.96
$M = 1$	6.91	4.22
$M = 2$	7.06	3.77

From eq. (232), in the case of infinite temperature, we find

$$\langle M_x^2 \rangle = \frac{1}{4} \gamma^2 \hbar^2 N' \quad (275)$$

and using (233), (240) and (275) we obtain the linewidth:

$$\Delta H_M = \frac{\eta_M}{\gamma} = \frac{\sqrt{2\pi}}{2 \gamma^3 \hbar^4 N'} \frac{\bar{\Gamma}_M(0)}{\omega_e^{(M)}} e^{-M^2 \omega_e^2 / 2 \omega_e^{(M)2}} \quad (276)$$

$$\Delta H = \sum_{M=0}^2 \Delta H_M \quad (277)$$

It is interesting to note the following relation between the area under the $\Delta H(\omega)$ curve and $\Gamma_M(0)$: From eq. (234) we have

$$\Delta H(\omega) - \Delta H(\infty) = \frac{1}{8\gamma\hbar^2\langle M_x^2 \rangle} \sum_{M=1}^2 \int_{-\infty}^{\infty} \Gamma_M(\omega) e^{iM\omega\tau} d\tau \quad (278)$$

Integrating over ω on both sides of (278), we obtain

$$\int_{-\infty}^{\infty} [\Delta H(\omega) - \Delta H(\infty)] d\omega = \frac{\pi}{4\gamma\hbar^2\langle M_x^2 \rangle} \sum_{M=1}^2 \frac{1}{M} \Gamma_M(0) \quad (279)$$

Equation (279) can be used to check the calculations of ΔH and $\Gamma_M(0)$.

From (276) and (277), with $J/k = 3.15^\circ\text{K}$ and using the g factors calculated by paramagnetic resonance, we get

$$\Delta H = 0.96 \left[1 + 0.75 e^{-\frac{\omega_0^2}{2\omega_e^{(1)2}}} + 0.67 e^{-\frac{2\omega_0^2}{\omega_e^{(2)2}}} \right] \text{ Gauss} \quad (280)$$

for H_0 parallel to a , and

$$\Delta H = 2.45 \left[1 + 0.18 e^{-\frac{\omega_0^2}{2\omega_e^{(1)2}}} + 0.20 e^{-\frac{2\omega_0^2}{\omega_e^{(2)2}}} \right] \text{ Gauss}$$

for H_0 parallel to c . The frequency dependence of the line-width, for H_0 parallel to a , calculated with the correlation functions for a linear chain of nine spins, is compared in Fig. 33 with the gaussian approximation, eq. (280), and with the experimental results of Rogers¹¹. The curves have been normalized to the maximum point.

Fig. 37.- Frequency dependence of the linewidth: (a) calculated with the exact correlations for $N = 9$, (b) gaussian approximation, and (c) Rogers' experimental points (circles) and fitting curve

The variation predicted using the exact correlations gives a much better agreement with experiment than the variation predicted on the basis of the gaussian approximation. However, the observed value for ΔH of 9 Gauss^{10,11} is about twice as large as the value resulting from our calculations on the linear chain model. The discrepancy is perhaps due to the effects of hyperfine interaction and anisotropic exchange. Assuming that the hyperfine interaction contributes with about 1 Gauss to the linewidth¹², and that an anisotropic exchange of the form $\sum_{\langle ij \rangle} D S_i^z S_j^z$ is present, we estimate that the observed linewidth could be accounted for with $D \approx 0.01$ J, i.e., the anisotropic exchange, if present, is much weaker than the exchange interaction and of approximately the same order of magnitude as the dipolar interaction μ^2/c^3 .

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