Magnetization Curve at Zero Temperature for the Antiferromagnetic Heisenberg Linear Chain*

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The highest and lowest energies as a function of the total spin are computed for the class of "unbound" states in the Bethe formalism for the linear chain of spin-$\frac{1}{2}$ atoms with a Heisenberg exchange interaction between nearest neighbors. The lowest energies are used to compute the magnetization curve for the infinite antiferromagnetic chain in the limit of zero temperature. At zero temperature and in zero field, the magnetic susceptibility has the value 0.050661 $g^2\mu^2/J$, where μ is the Bohr magneton, g the electron g factor, and the interaction between neighboring spins is of the form $2JS_1 \cdot S_2$.

I. INTRODUCTION

THE properties of antiferromagnetic insulators are often discussed on the basis of the Heisenberg model of exchange between neighboring atoms. Calculations for two and three dimensions invariably proceed by means of approximations whose validity is difficult to judge. Hence, there is some interest in examining the one-dimensional case, for which a certain amount of progress has been made toward an exact solution.

Bethe[1] showed that the eigenvalue problem for a chain of N spin-$\frac{1}{2}$ atoms with Hamiltonian

$$\mathcal{3C}=2J \sum_{i=1}^{N} S_i \cdot S_{i+1}, \qquad (1)$$

$$S_{N+1} \equiv S_1,$$

where S_i is the spin operator for the ith atom and J the "exchange integral," could be reduced to that of solving a set of coupled transcendental algebraic equations. Using this procedure, Hulthén[2] calculated the exact ground-state energy for an infinite antiferromagnetic $(J>0)$ chain; and des Cloizeaux and Pearson[3] have recently obtained the energies of the lowest lying excitations or "spin waves."

The class C[4] of "unbound" states in the Bethe formalism is of particular interest for the antiferromagnetic chain, since it contains the ground state and the des Cloizeaux and Pearson spin waves. In this paper we compute (in Sec. III) the minimum and maximum energies of states in class C with a given total spin S, as a function of S. There is good reason to believe that the states of minimum energy in class C are also the lowest of all levels (for a given S) in the antiferromagnetic chain. Assuming this to be the case, we calculate (in Sec. IV) the magnetization as a function of magnetic field at zero temperature.

Section II contains a summary of the Bethe formalism for the eigenvalue problem. A proof of the existence of real solutions to the Bethe equations for states in class C is found in Appendix A. The derivation of Hulthén's integral equation, upon which the work in Sec. III B, C, and D depends, is summarized in Sec. III A.

The results of our computations do not agree with those of Ledinegg and Urban.[5] The reason for this discrepancy is discussed in Appendix B.

II. THE BETHE EQUATIONS

Let E_F and E_{AF} be the largest and smallest eigenvalues of the Hamiltonian (1) with $J>0$, corresponding to the ferro- and antiferromagnetic ground states, respectively:

$$E_F=\frac{1}{2}NJ,$$
$$E_{AF}=NJ(\frac{1}{2}-2\ln2). \qquad (2)$$

The second equation[2] holds in the limit $N \to \infty$. For a state with energy E, define the normalized energies[6]

$$\epsilon=\frac{1}{2}(E_F-E)/JN,$$
$$\eta=\frac{1}{2}(E-E_{AF})/JN=\ln2-\epsilon. \qquad (3)$$

With "up" and "down" defined with respect to the positive z axis, let $\Psi(n_1,n_2, \ldots n_r)$ be a state for which the spins $n_1, n_2, \ldots, n_r$ are down and all other spins are up. Any eigenstate of (1) with z component of spin equal to $\frac{1}{2}N-r$ may be written as a linear combination of such states:

$$\Psi=\sum a(n_1,n_2, \ldots,n_r)\Psi(n_1,n_2, \ldots,n_r), \qquad (4)$$

with summation over all sets of r (distinct) indices n_j.

The eigenfunctions discussed by Bethe[1] are of the form

$$a(n_1,\cdots,n_r)=\sum_{P=1}^{r!} \exp i\left(\sum_{j=1}^{r} k_{Pj}n_j+\frac{1}{2}\sum_{j<l} \phi_{PjPl}\right), \qquad (5)$$

where the summation extends over all permutations of the integers $1, 2, \ldots, r$, and Pj is the image of j under

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[1] H. Bethe, Z. Physik **71**, 205 (1931).
[2] L. Hulthén, Arkiv Mat. Astron. Fysik **26A**, No. 11, (1938).
[3] J. des Cloizeaux and J. J. Pearson, Phys. Rev. **128**, 2131 (1962).
[4] This notation comes from Ref. 3 and is explained in detail in Sec. II.

[5] E. Ledinegg and P. Urban, Acta Phys. Austriaca **6**, 257 (1953).
[6] Our definition of ϵ is smaller than that given in Refs. 1, 2, and 3 by a factor of N^{-1}.

the Pth permutation. The "wave vectors" k_j (real or complex) satisfy the equations

$$Nk_j = 2\pi\lambda_j + \sum_{l(\neq j)} \phi_{jl} \qquad j=1,2,\cdots,r, \qquad (6)$$

where the λ's are integers between 0 and $N-1$, and the ϕ's are defined by

$$\cot\tfrac{1}{2}\phi_{jl} = \tfrac{1}{2}(\cot\tfrac{1}{2}k_j - \cot\tfrac{1}{2}k_l), \qquad (7)$$
$$-\pi \leq \phi_{jl} \leq \pi.$$

The energy of the state (5) is equal to

$$\epsilon = N^{-1} \sum_{j=1}^{r} (1-\cos k_j). \qquad (8)$$

The order of the λ's associated with a state (5) through Eq. (6) is unimportant. Furthermore, a state with some λ's equal to zero has the same energy and total spin as the corresponding state in which the zero λ's have been eliminated.[2] Hence, without loss of generality we may assume that

$$0 < \lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_r < N. \qquad (9)$$

By "class C" we denote either the sets $\{\lambda_j\}$ satisfying, in addition to (9), the restriction

$$\lambda_{j+1} \geq \lambda_j + 2, \qquad (10)$$

or the eigenstates (5) corresponding to these sets. The importance of class C comes from the following properties.

1. For each set $\{\lambda_j\}$ in class C there is a solution to (6) for which all the k_j are real and no two are equal. [When two k's are equal, the state (5) vanishes identically.]

2. For a given total spin S, the state with the lowest energy ($J>0$) belongs to class C.

Appendix A contains a rigorous proof of the first property, together with a general discussion of the behavior of the solutions $\{k_j\}$ of (6) as a function of the sets $\{\lambda_j\}$. The second property has not yet been proved, but it is very plausible on the basis of arguments by Bethe[1] and Orbach,[7] and calculations on finite chains by des Cloizeaux and Pearson,[3] and the author.[8]

For an antiferromagnetic chain, the energy of a state is lowest when ϵ [see (3)] is largest, and vice versa. Now by Eq. (8), ϵ is largest, for a given r, when the k_j cluster near the center of the interval $[0,2\pi]$. This may be expected, according to plausible arguments in Appendix A, when the λ_j cluster near the center of $[0,N]$, subject to the constraint (10). Hence, for a given total spin $S=\tfrac{1}{2}N-r$, the state of minimum energy in class C should correspond to

$$\lambda_1 = \tfrac{1}{2}N - r + 1, \quad \lambda_2 = \lambda_1 + 2, \quad \lambda_3 = \lambda_2 + 2, \ldots,$$
$$\lambda_r = \tfrac{1}{2}N + r - 1. \qquad (11)$$

[7] R. Orbach, Phys. Rev. **112**, 309 (1958).
[8] R. B. Griffiths (unpublished).

By a similar argument, the state of maximum energy in class C should correspond to

$$\lambda_1 = 1, \quad \lambda_2 = 3, \ldots, \quad \lambda_{r/2} = r-1,$$
$$\lambda_{r/2+1} = N-(r-1), \quad \lambda_{r/2+2} = N-(r-3), \ldots,$$
$$\lambda_r = N-1. \qquad (12)$$

For $S=0$ there is only one state in class C, the antiferromagnetic ground state,

$$\lambda_1 = 1, \quad \lambda_2 = 3, \quad \lambda_3 = 5, \ldots, \quad \lambda_{N/2} = N-1. \qquad (13)$$

We have tacitly assumed in writing (11), (12), and (13) that N and r are even; minor modifications are required if one or the other is odd.

There also exist solutions of (6) for which two or more of the k_j are not real but complex. For the case $r=2$, Bethe[1] showed that complex k values result in a state (5) for which $|a(n_1,n_2)|^2$ decreases exponentially as $|n_2-n_1|$ increases, and thus has the form of two spin waves interacting to form a bound state. We shall, for convenience, refer to any state for which some of the k_j are complex as a "bound" state, and to states for which all k_j are real as "unbound" states. Some of the unbound states are not contained in class C, though Bethe's discussion indicates that these are relatively few in number as N becomes infinite.

III. THE HULTHÉN INTEGRAL EQUATION

A. The Antiferromagnetic Ground State

In the limit of large N it is reasonable to replace (6), (7), (8) for the set λ_j given by (13) by the equations

$$k(x) = 2\pi x + \tfrac{1}{2}\int_0^1 \phi(x,y)dy, \qquad (14)$$

$$\cot\tfrac{1}{2}\phi(x,y) = \tfrac{1}{2}[\cot\tfrac{1}{2}k(x) - \cot\tfrac{1}{2}k(y)], \qquad (15)$$
$$-\pi \leq \phi \leq \pi,$$

$$\epsilon_0 = \tfrac{1}{2}\int_0^1 [1-\cos k(x)]dx, \qquad (16)$$

where λ_j has been replaced by Nx and k_j by $k(x)$.

By differentiating both sides of (14) with respect to x, Hulthén[2] obtained an integral equation linear in the function dx/dk:

$$1 = \pi\frac{dx}{dk} + \csc^2(\tfrac{1}{2}k)\int_0^{2\pi} \frac{(dx/dk')dk'}{4+(\cot\tfrac{1}{2}k - \cot\tfrac{1}{2}k')^2}, \qquad (17)$$

which, by means of the substitution

$$\xi = \cot\tfrac{1}{2}k,$$
$$f_0(\xi) = -dx/d\xi, \qquad (18)$$

may be rewritten in the form

$$f_0(\xi) = g_0(\xi) - \int_{-\infty}^{\infty} K(\xi-\eta) f_0(\eta) d\eta, \qquad (19)$$

where

$$g_0(\xi) = (2/\pi)(1+\xi^2)^{-1}, \qquad (20)$$

$$K(\xi-\eta) = (2/\pi)[4+(\xi-\eta)^2]^{-1}, \qquad (21)$$

and further,

$$\epsilon_0 = \tfrac{1}{2}\pi \int_{-\infty}^{\infty} f_0(\xi) g_0(\xi) d\xi. \qquad (22)$$

For our purposes it is convenient to write Hulthén's solution of Eq. (19) in the form

$$f_0(\xi) = g_0(\xi) - \int_{-\infty}^{\infty} R(\xi-\eta) g_0(\eta) d\eta \qquad (23a)$$

$$= \tfrac{1}{2}\operatorname{sech}\tfrac{1}{2}\pi\xi, \qquad (23b)$$

$$\epsilon_0 = \ln 2, \qquad (24)$$

where the resolvent kernel $R(x)$ may be written as an infinite sum,

$$R(x) = \pi^{-1} \sum_{n=1}^{\infty} 2n(-1)^{n+1}(4n^2+x^2)^{-1}, \qquad (25)$$

or as an integral,

$$R(x) = (4\pi)^{-1} \int_{-\infty}^{\infty} [1+(y+x)^2]^{-1} \operatorname{sech}(\tfrac{1}{2}\pi y) dy, \qquad (26)$$

and satisfies the equation

$$\int_{-\infty}^{\infty} K(\xi-\eta) R(\eta-\zeta) d\eta = K(\xi-\zeta) - R(\xi-\zeta). \qquad (27)$$

B. States of Minimum Energy

For the sets of integers given by (11), the Hulthén equations (14) and (16) must be replaced by

$$k(x) = 2\pi x + \tfrac{1}{2} \int_{(1/2)-\rho}^{(1/2)+\rho} \phi(x,y) dy, \qquad (28)$$

$$\epsilon = \tfrac{1}{2} \int_{(1/2)-\rho}^{(1/2)+\rho} [1-\cos k(x)] dx, \qquad (29)$$

where ρ is determined by the condition

$$\tfrac{1}{2}N - S = r = N\rho. \qquad (30)$$

Also, define σ by

$$\sigma = S/N = \tfrac{1}{2} - \rho. \qquad (31)$$

Equation (28) may be transformed by the same procedure previously applied to (14); we shall denote

$-dx/d\xi$ by $f(\xi)$[9]:

$$f(\xi) = g_0(\xi) - \int_{-\alpha}^{\alpha} K(\xi-\eta) f(\eta) d\eta, \qquad (32)$$

$$\epsilon = \tfrac{1}{2}\pi \int_{-\alpha}^{\alpha} f(\xi) g_0(\xi) d\xi, \qquad (33)$$

with limits of integration determined by the requirement

$$\rho = \tfrac{1}{2} \int_{(1/2)-\rho}^{(1/2)+\rho} dx = \tfrac{1}{2} \int_{-\alpha}^{\alpha} f(\xi) d\xi. \qquad (34)$$

In Eqs. (32)–(34), only the values of $f(\xi)$ for $|\xi| \leq \alpha$ are employed, although (32) also *defines* $f(\xi)$ for $|\xi| > \alpha$. Multiply the right- and left-hand sides of (32) by $R(\zeta-\xi)$ and integrate with respect to ξ from $-\infty$ to $+\infty$. By interchanging the order of integration on the right-hand side, and using (27), (23a), (32), and the fact that $f(\xi) = f(-\xi)$ and $R(x) = R(-x)$, one obtains the equation

$$f(\xi) = f_0(\xi) + \int_{\alpha}^{\infty} [R(\xi-\eta)+R(\xi+\eta)] f(\eta) d\eta. \qquad (32a)$$

Similarly, in place of (33) and (34) one has

$$\eta = \epsilon_0 - \epsilon = \pi \int_{\alpha}^{\infty} f_0(\xi) f(\xi) d\xi, \qquad (33a)$$

$$\sigma = \tfrac{1}{2} - \rho = \tfrac{1}{2} \int_{\alpha}^{\infty} f(\xi) d\xi. \qquad (34a)$$

[Multiply both sides of (32a) by $g_0(\xi)$ and integrate from $-\infty$ to $+\infty$. Upon interchanging the order of integration, and using (22), (23a), and (33), one obtains (33a). To obtain (34a), integrate both sides of (32) from $-\infty$ to $+\infty$.]

The asymptotic behavior of η and σ for large values of α determines the magnetic susceptibility in small magnetic fields at zero temperature, and hence we shall examine it in some detail using Eqs. (32a)–(34a). For large α, it is clearly an excellent approximation to replace $f_0(\xi)$ [see (23b)] by $\exp(-\tfrac{1}{2}\pi\xi)$ in (32a) and (33a), since only values of f_0 for $\xi \geq \alpha$ are required. Even for $\alpha = 3$, the fractional error is less than 10^{-4}. By use of this approximation and the function

$$p(\xi) = e^{\pi\alpha/2} f(\xi+\alpha), \qquad (35)$$

Eqs. (32a)–(34a) may be rewritten in the form

$$\mathrm{p}(x) = e^{-\pi x/2} + \int_{0}^{\infty} [R(x-y)+R(x+y+2\alpha)] \mathrm{p}(y) dy, \qquad (36)$$

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[9] L. Hulthén (Ref. 2) obtained Eq. (32), but did not attempt to solve it.

$$\eta = b(\alpha)e^{-\pi\alpha}, \tag{37}$$

$$\sigma = a(\alpha)e^{-\pi\alpha/2}, \tag{38}$$

where

$$a(\alpha) = \frac{1}{2}\int_0^\infty \mathrm{p}(x)dx, \tag{39}$$

$$b(\alpha) = \pi\int_0^\infty e^{(-1/2)\pi x}\mathrm{p}(x)dx. \tag{40}$$

Since the kernel $R(x)$ decreases as x^{-2} for large x, it is reasonable to suppose that the function $p(x)$ is determined primarily by the first kernel in the integrand in (36) when α is large. One can, in fact, show (we shall not give the proof here) that as α becomes infinite,[10]

$$a(\alpha) = a_0[1 + (2\pi\alpha)^{-1}] + O(\ln\alpha/\alpha^2),$$
$$b(\alpha) = b_0 + O(\alpha^{-2}), \tag{41}$$

$$da(\alpha)/d\alpha = O(\alpha^{-2}),$$
$$db(\alpha)/d\alpha = O(\alpha^{-2}), \tag{42}$$

where a_0 and b_0 are obtained from (39) and (40) when $p(x)$ is replaced by $q(x)$, the solution to the equation

$$q(x) = e^{(-1/2)\pi x} + \int_0^\infty R(x-y)q(y)dy. \tag{43}$$

Equation (43) has been solved numerically[11] using a computer program with several internal checks. We believe the results,

$$a_0 = 0.48394,$$
$$b_0 = 1.15573 \tag{44}$$

are correct to five decimal places. Combining (37), (38), (41), and (44), we have, for large α or for small σ,

$$\eta = \{4.9348[1 - (\pi\alpha)^{-1}] + O(\ln\alpha/\alpha^2)\}\sigma^2, \tag{45a}$$

$$= 4.9348\left(1 + \frac{1}{2\ln\sigma}\right)\sigma^2 + O\left[\frac{\sigma^2\ln(|\ln\sigma|)}{(\ln\sigma)^2}\right]. \tag{45b}$$

It is clear that η is not an analytic function of σ at $\sigma = 0$. The constant 4.9348 agrees with $\pi^2/2$ to five significant figures, and there are certain plausible (though far from rigorous) arguments based on the spin-wave spectrum of des Cloizeaux and Pearson[3] which suggest that the value should be $\pi^2/2$ exactly.

The asymptotic behavior given by (37), (38), and (41) is in agreement with numerical calculations of η and σ for finite α (discussed below in part D), but in

disagreement with results published by Ledinegg and Urban,[5] which we believe to be in error. For further discussion, see Appendix B.

C. States of Maximum Energy

For a given total spin S, the states of maximum energy in class C are associated with sets of integers of the form (12). The integral equations in the limit $N \to \infty$ are obtained in close analogy to the results in part B, so we shall omit details. Corresponding to Eqs. (32)–(34) one has

$$f(\xi) = g_0(\xi) - \int_\alpha^\infty [K(\xi-\eta) + K(\xi+\eta)]f(\eta)d\eta, \tag{46}$$

$$\epsilon = \pi\int_\alpha^\infty f(\xi)g_0(\xi)d\xi, \tag{47}$$

$$\rho = \int_\alpha^\infty f(\xi)d\xi, \tag{48}$$

and, corresponding to Eqs. (32a)–(34a),

$$f(\xi) = f_0(\xi) + \int_{-\alpha}^\alpha R(\xi-\eta)f(\eta)d\eta, \tag{46a}$$

$$\eta = \pi\int_0^\alpha f_0(\xi)f(\xi)d\xi, \tag{47a}$$

$$\sigma = \frac{1}{2}\int_0^\alpha f(\xi)d\xi. \tag{48a}$$

When α or σ is small we have

$$\eta \sim \pi\sigma, \tag{49}$$

whereas when α is large, and therefore ρ is small

$$\epsilon \sim \frac{2}{3}\pi^2\rho^3. \tag{50}$$

The results (49) and (50) have been confirmed by numerical computations.

It must be emphasized that the energy is a maximum *only* for states in class C. In general, for a given value of S, there will be states not belonging to class C with energies both less than and greater than the maximum for class C.

D. Numerical Solutions of the Integral Equations

The integral equations (32) and (46a) were approximated by a set of 41 coupled linear algebraic equations which were solved using a Control Data Corporation 1604 digital computer. The results are shown in Fig. 1 where the normalized energies ϵ and η [see (3)] are plotted as a function of $\sigma = S/N$, where S is the total spin of the state, and $\rho = \frac{1}{2} - \sigma$.

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[10] Capital O stands for "of the order of" in the sense used by E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, Cambridge, England, 1927), 4th ed., p. 11.

[11] The actual computations were carried out, purely as a matter of convenience, on an integral equation equivalent to (43), but which used the kernel K instead of R.
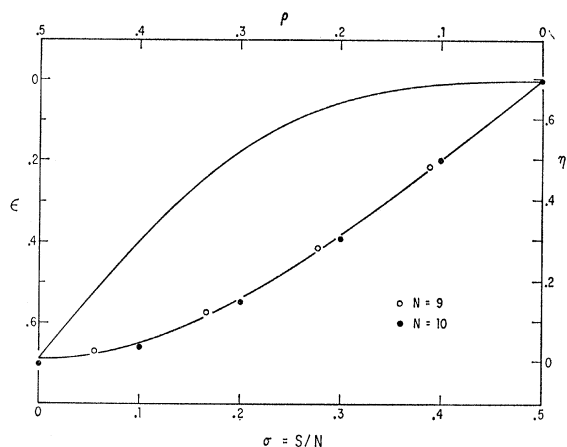
FIG. 1. Highest and lowest energies for states in class C as a function of the total spin S. The circles represent the lowest energies for finite chains containing 9 and 10 atoms.

Table I contains values of σ and η for the lower curve in Fig. 1. If the arguments alluded to in Sec. II are correct, these energies, for a given σ, should not only be the lowest in class C, but also the lowest for all states in the antiferromagnetic chain. Fortunately, there are some independent checks on this property.

TABLE I. The minimum energy η of levels in class C for various values of $\sigma = S/N$. At zero temperature, σ is proportional to the magnetization and $2d\eta/d\sigma$ is proportional to the applied magnetic field.

σ	η	$2\dfrac{d\eta}{d\sigma}$	σ	η	$2\dfrac{d\eta}{d\sigma}$
0.000000	0.00000000	0.00000	0.17822	0.12262	2.529
0.001280	0.00000759	0.02362	0.19293	0.14177	2.677
0.002407	0.00002668	0.04412	0.2088	0.16357	2.828
0.004531	0.00009387	0.08235	0.2258	0.18829	2.977
0.006218	0.00017608	0.11245	0.2441	0.2162	3.125
0.008538	0.0003303	0.15349	0.2636	0.2475	3.268
0.011728	0.0006198	0.2094	0.2845	0.2823	3.405
0.016117	0.0011630	0.2855	0.2955	0.3012	3.470
0.02216	0.002182	0.3887	0.3068	0.3209	3.533
0.02600	0.002989	0.4534	0.3184	0.3417	3.593
0.03050	0.004095	0.5285	0.3304	0.3634	3.650
0.03579	0.005607	0.6156	0.3428	0.3861	3.703
0.04200	0.007678	0.7166	0.3554	0.4097	3.753
0.04931	0.010509	0.8333	0.3685	0.4343	3.798
0.05789	0.014377	0.9677	0.3818	0.4598	3.840
0.06799	0.019654	1.1220	0.3955	0.4862	3.877
0.07986	0.02684	1.2980	0.4095	0.5135	3.909
0.09382	0.03659	1.4975	0.4239	0.5416	3.937
0.11020	0.04979	1.7214	0.4385	0.5706	3.960
0.11943	0.05802	1.8425	0.4535	0.6002	3.977
0.12943	0.06754	1.9695	0.4687	0.6306	3.990
0.14025	0.07855	2.102	0.4842	0.6616	3.997
0.15194	0.09125	2.240	0.5000	0.6931	4.000
0.16458	0.10586	2.383			

Energies for finite chains containing $N = 2, 3, 4, \ldots,$ 10 atoms have been computed directly from the Hamiltonian (1).[8,12,13] The lowest energies as a function

[12] R. Orbach, Phys. Rev. 115, 1181 (1959).
[13] J. C. Bonner and M. E. Fisher (to be published).

of S lie above the lower curve in Fig. 1 for $N = 3, 5, 7,$ and 9, and below the curve for $N = 2, 4, 6, 8,$ and 10. Points for $N = 9, 10$ are shown in Fig. 1 (open and solid circles, respectively) and lie quite close to the computed curve, which should represent the limit as N becomes infinite.

A strict upper bound on the minimum energy curve is provided by the work of Bulaevskii.[14] At zero temperature he, in effect, finds, in a particular representation, the lowest diagonal element of the Hamiltonian (1) in a subspace containing all states with a given z component of total spin. Of course, the lowest diagonal element must be larger than the lowest eigenvalue. The energy so obtained is, in our notation,

$$\eta_B = \sigma^2 - \pi^{-1} \cos\pi\sigma - (\pi^{-1} \cos\pi\sigma)^2 + \ln 2 - \tfrac{1}{4}. \quad (51)$$

A strict lower bound on the minimum energy curve may be obtained if we write the Hamiltonian (1) as

$$\mathcal{3C} = \mathcal{3C}_0 + \mathcal{3C}_1, \quad (52)$$

where

$$\mathcal{3C}_0 = 2J \sum_{i=1}^{N} (S_i{}^x S_{i+1}{}^x + S_i{}^y S_{i+1}{}^y), \quad (53)$$

$$\mathcal{3C}_1 = 2J \sum_{i=1}^{N} S_i{}^z S_{i+1}{}^z, \quad (54)$$

and the superscripts denote the x, y, and z components of the spin operators. The Hamiltonian (53) has been solved exactly[15] and the minimum energy obtained as a function of the z component of total spin. Of course (54) is just the Ising Hamiltonian. The sum of the minimum energies for these two Hamiltonians,

$$\eta_C = |\sigma| - \pi^{-1} \cos\pi\sigma + \ln 2 - \tfrac{1}{2}, \quad (55)$$

is a lower bound on the minimum energy for (1), since the lowest eigenvalue of the sum of two Hermitian matrices is larger than the sum of the lowest eigenvalues of the summands.[16]

We therefore expect that

$$\eta_C(\sigma) \leq \eta(\sigma) \leq \eta_B(\sigma), \quad (56)$$

and, indeed, the values of η in Table I lie within the specified bounds. For instance, at $\sigma = 0.3554$ we have

$$\eta_B = 0.4103,$$

$$\eta = 0.4097,$$

$$\eta_C = 0.4089.$$

For larger values of σ the bounds are even closer together, since $\eta_B - \eta_C$ goes to zero as $(\tfrac{1}{2} - \sigma)^4$ as σ

[14] L. N. Bulaevskii, Zh. Eksperim. i Teor. Fiz. 43, 968 (1962) [translation: Soviet Phys.—JETP 16, 685 (1963)].
[15] E. Lieb, T. Schultz, and D. Mattis, Ann. Phys. (N. Y.) 16, 407 (1961); S. Katsura, Phys. Rev. 127, 1508 (1962); see also Ref. 14.
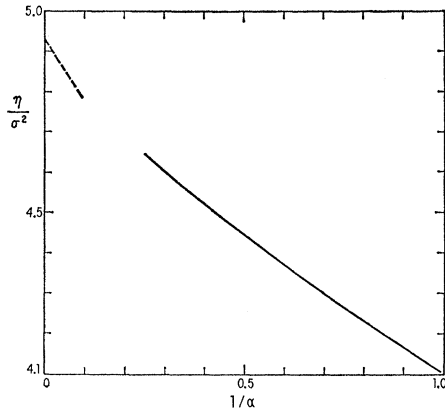[16] Pointed out, for example, by P. W. Anderson, Phys. Rev. 83, 1260 (1951).

FIG. 2. The ratio η/σ^2 for the states of minimum energy in class C as a function of $1/\alpha$. The dashed line at the left side gives the asymptotic behavior as α^{-1} goes to zero.

approaches $\frac{1}{2}$. These bounds are not of much value when σ is small.

The numerical calculations also confirm the asymptotic behavior of η and σ for large α given by Eqs. (37)–(42). In Fig. 2 the ratio

$$b(\alpha)/a(\alpha)^2 = \eta/\sigma^2$$

is plotted as a function of $1/\alpha$. Results for $\alpha > 4$ were not very accurate and have not been included in the graph. But there is no reason to doubt that the curve approaches the asymptotic limit, shown by a dotted line, smoothly as α^{-1} approaches zero.

IV. MAGNETIC MOMENT AND SUSCEPTIBILITY AT ZERO TEMPERATURE

Let there be a magnetic field H along the positive z axis. The Zeeman energy

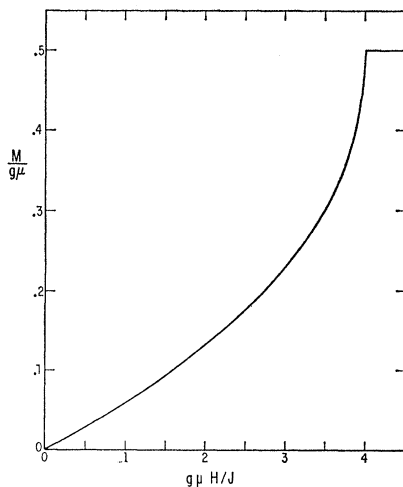$$\mathcal{3C}_z = g\mu H \sum_{i=1}^{N} S_i^z \qquad (57)$$

FIG. 3. The magnetization as a function of magnetic field for the antiferromagnetic chain at zero temperature.

commutes with the exchange energy (1). Here μ is the Bohr magneton, g the electron g factor, and S_i^z the z component of the ith spin. The lowest level of the chain with a given total spin S will have an energy

$$E_M(S) = E(S) - g\mu H S, \qquad (58)$$

where $E(S)$ is the lowest energy in the absence of a magnetic field,

$$E(S) = 2NJ\eta(S/N) + E_{AF}. \qquad (59)$$

By $\eta(S/N) = \eta(\sigma)$ we mean the function corresponding to the lower curve in Fig. 1 and the values in Table I.

Let $S_0 = N\sigma_0$ be the value of S for which $E_M(S)$ is a minimum. It is determined by setting the derivative with respect to S of the right-hand side of (58) equal to zero, with the result
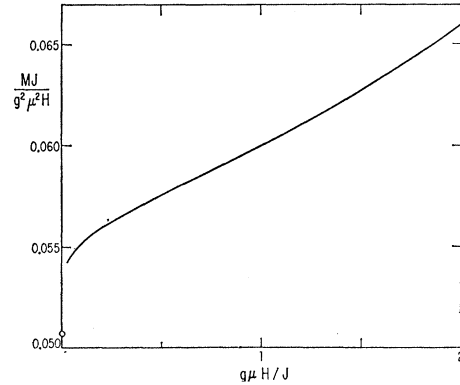
$$g\mu H/J = 2\eta'(\sigma_0). \qquad (60)$$

FIG. 4. The ratio of magnetization to magnetic field as a function of the field, at zero temperature. The circle at the left side [obtained from Eq. (62)] shows the ratio in the limit as H goes to zero.

Here $\eta'(\sigma)$ stands for $d\eta/d\sigma$; this quantity is tabulated as a function of σ in Table I. At zero temperature, the free energy of the chain F is equal to $E_M(S_0)$, and the average magnetization per spin, M, is given by

$$M = -N^{-1}dF/dH = g\mu\sigma_0. \qquad (61)$$

Figure 3 shows M as a function of H. As H goes to zero, the ratio M/H approaches a limiting value,[17] the zero field susceptibility:

$$\chi = 0.050661 g^2\mu^2/J. \qquad (62)$$

The numerical constant in (62), $a_0^2/4b_0$, is equal to $(2\pi^2)^{-1}$ to five significant figures. [See the remark following (45b).]

The ratio M/H as a function of H is shown in Fig. 4. A peculiar feature of this curve is that it approaches the limiting value at $H=0$ with infinite slope [as may be

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[17] The reader may verify this using (37), (38), (41), and (42) to evaluate $d\eta/d\sigma$ for large values of α.

verified by means of (41) and (42)], a result of the fact that $\eta(\sigma)$ is not an analytic function near $\sigma=0$.

V. CONCLUSION

The principal results of the present paper are found in Fig. 1 (and Table I) which shows the upper and lower limits of the energies of states in class C as a function of the total spin of the state, in the limit $N \to \infty$. From the lower limit we have computed the magnetization as a function of field in the limit of zero temperature.

The magnetization curve is exact in the sense that we have made no approximations in treating the Hamiltonian (1) other than the neglect of terms which vanish (or are expected to vanish) as N becomes infinite relative to the terms retained. Nevertheless, certain hypotheses which enter into the Bethe formalism and our use thereof are, at present, supported by plausible arguments rather than rigorous proof. Perhaps we may say that the energies and magnetization curve computed above are "exact" in the same sense that Hulthén's value for the ground-state energy or the des Cloizeaux and Pearson spin-wave spectrum are "exact."

The problem of determining the magnetization and other thermodynamic quantities at low (nonzero) temperatures for the antiferromagnetic chain remains unsolved. (At high temperatures, the numerical results obtained for finite chains are probably adequate for most purposes.[8,13]) Unfortunately, if this problem is to be attacked within the framework of the Bethe formalism, it appears necessary to calculate energies for states outside class C, a rather difficult task since the k_j are in general complex.

ACKNOWLEDGMENTS

APPENDIX A. EXISTENCE OF SOLUTIONS OF EQUATION (6) FOR STATES IN CLASS C

It is convenient to regard (6) as a nonlinear transformation of the vector $(k_1, k_2, \ldots, k_r)$ into another vector with components

$$k_j' = 2\pi N^{-1}\lambda_j + N^{-1} \sum_{l(\neq j)} \phi(k_j, k_l), \qquad \text{(A1)}$$

where for ϕ_{jl} we have written $\phi(k_j, k_l)$. A solution to (6) is a fixed point of the transformation (A1). If we attempted to solve (A1) by iteration, a sensible starting value for the k_j would be $2\pi N^{-1}\lambda_j$, which lies within the interval $(0,2\pi)$. The function $\phi(k_j, k_l)$ is positive for $k_l > k_j$ and negative for $k_j > k_l$ if k_j and k_l are real and

fall in the interval $(0,2\pi)$. Hence the second term on the right side of (A1) represents an "attractive force" between pairs of wave vectors, whereas the term $2\pi N^{-1}\lambda_j$ tends to "anchor" k_j near its starting position.

When the starting values of k_j and k_{j+1} are too close together, successive iteration may result in a "collision": $k_{j+1} = k_j$. But a solution to (6) for which two k's coincide is trivial: The corresponding wave function (5) vanishes identically. A possible remedy in this situation is to make k_j and k_{j+1} complex. However, condition (10) for states in class C ensures that the initial values of the k_j are far enough apart to make "collisions" impossible, and hence one may expect a solution to (6) for which all the k's are real. We shall now make these intuitive notions more precise.

Let V be the real r-dimensional space of vectors of the form $(k_1, k_2, \ldots, k_r)$ and let K be the subset of those vectors whose components satisfy the inequalities

$$k_1 \geq 2\pi N^{-1}, \quad k_r \leq 2\pi(1-N^{-1}),$$
$$k_{j+1} - k_j \geq 2\pi N^{-1}, \quad j=1, 2, \ldots, r-1. \qquad \text{(A2)}$$

The function $\phi(k_j, k_l)$ [see (7)] is, in absolute value, less than or equal to π. It is continuous for all k_j, k_l in the interval $(0,2\pi)$ except at the points $k_j = k_l$. Thus, the transformation (A1) is continuous on the set K. The inequality

$$k_{j+1}' - k_j' \geq 2\pi N^{-1}(\lambda_{j+1} - \lambda_j) - 2N^{-1}\phi(k_j, k_{j+1}) \qquad \text{(A3)}$$

is a consequence of the fact that the function $\phi(k_j, k_l)$ in either the region $k_j < k_l$ or the region $k_j > k_l$ is monotone increasing in k_j and decreasing in k_l.

The λ_j for states in class C satisfy the inequalities (9) and (10). This, together with the inequality (A3) and the properties of ϕ mentioned above, implies that the k_j' satisfy the inequalities (A2). In other words, the transformation (A1) carries the set K into itself. The set K is closed, convex, and bounded; and, since the transformation (A1) is continuous on K, there must exist at least one fixed point by Brouwer's theorem.[18] We have not been able to show that the solution is unique.

APPENDIX B. THE LEDINEGG-URBAN CALCULATION

For convenience, we enclose equation numbers from the paper by Ledinegg and Urban[5] in square brackets, and transcribe the equations in our notation. They obtain the following asymptotic behavior for σ and η as a function of α for large α using Eqs. (32)–(34):

$$\sigma \sim 0.518 e^{(-1/2)\pi\alpha}, \qquad \text{[38d]}$$

$$\eta \sim 0.398 e^{(-1/2)\pi\alpha}/\alpha^2. \qquad \text{[37]}$$

The result [38d] agrees with our calculations—see (38), (41), and (44)—except for the numerical constant.

[18] G. T. Whyburn, *Analytic Topology*, American Mathematical Society Colloquium Publications, Vol. XXVIII (American Mathematical Society, New York, 1942), p. 243.

However, [37] is in disagreement with (37) and (41); in particular, the exponent in the former is half that in the latter. The numerical solutions to Eqs. (32)–(34) support (37) and (41) rather than [37].

Ledinegg and Urban obtain their asymptotic estimate as follows. The function $f(\xi)$ in (32) (their Eq. [23]) is set equal to

$$f(\xi) = f_0(\xi) + \phi(\xi), \qquad [24a]$$

where $f_0(\xi)$ is the solution of (19) given by (23). They assume that

$$|\phi(\xi)|/f_0(\xi) \ll 1, \qquad [24c]$$

stating that this inequality will be justified through an explicit calculation of the function ϕ. The justification for [24c] is contained in their Eq. [33a] which indicates that [24c] is correct, but *only* for $|\xi| < \alpha$. But they have already used [24c] for $|\xi|$ *greater than* α in order to deduce an approximate integral equation for ϕ, [26b]. Thus their treatment is not internally consistent.

On the basis of our results it may be shown that $f(\xi)$ decreases as ξ^{-2} for large ξ; on the other hand, $f_0(\xi)$ decreases exponentially. Hence, in fact, [24c] does not hold for $\xi > \alpha$, and the integral equation [26b] is not correct.

Zero-Field Spin Absorption in Paramagnetic Salts*

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The spin absorption spectrum in the absence of a static magnetic field has been observed in several paramagnetic salts at liquid-helium temperatures. The absorptive component of the complex susceptibility χ'' was measured as a continuous function of frequency over the range 130–4000 Mc/sec by observing the influence of powdered samples on the transmission of a tunable coaxial resonant cavity. Exchange narrowing in qualitative agreement with the theory of Wright was observed in cupric salts. Moments of the shape functions obtained by expressing the results in terms of an empirical, fitted function yield, on the basis of the theories of Wright and Caspers, values of the exchange constant A of 3.3 and 3.7 for the cupric potassium and cupric ammonium Tutton salts, respectively. The cupric salt experimental curves are lower and broader than the curves proposed by Locher and Gorter. The absorption band in chromic potassium alum has a "flat-topped" appearance, and a width approximately three times the dipolar relaxation frequency ν_0. No temperature dependence of the shape functions was observed.

I. INTRODUCTION

SPIN absorption refers to the absorption of energy from an oscillating magnetic field by a system of mutually interacting magnetic spins which occurs whenever the frequency of oscillation is sufficiently high to compete with the relaxation processes tending to maintain the internal statistical equilibrium of the system. Two classes of spin systems have been investigated: assemblies of atoms having nuclear magnetic dipole moments and crystalline compounds containing magnetic ions. The nuclear magnetic case, for which the spin absorption frequencies are of the order 10^4 cps, has been discussed by Anderson.[1] Magnetic ions in concentrated magnetic salts have spin absorption frequencies of the order 10^9 cps, and have been the subject of a large number of investigations,[2–7] including experiments reported in the present paper.

In paramagnetic salts, for the case of small or zero static magnetic fields, and at frequencies much higher than the reciprocal of the spin-lattice relaxation time ($\tau_L^{-1} < 10^8$ cps at liquid-helium temperatures), the absorption of energy from the oscillating field is a manifestation of the spin-spin relaxation processes. Even a weak spin-lattice interaction is sufficient to maintain the spin system in good thermal contact with the lattice, but slight departures from equilibrium completely internal to the spin system give rise to a quadrature component of the magnetization χ''. The resulting spin absorption, proportional to χ'', may be thought of as arising from transitions among energy levels each of which corresponds to a stationary state of the crystal as a whole. The frequency dependence of χ'' is expressed in the form

$$\chi'' = \tfrac{1}{2}\pi[\nu f(\nu)/kT], \qquad (1)$$

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[1] A. G. Anderson, Phys. Rev. 125, 1517 (1962).

[2] For a review of early work, see C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, New York, 1947); C. J. Gorter, *Progress in Low Temperature Physics* (Interscience Publishers, Inc., New York, 1957), Vol. II, p. 267.

[3] L. J. Smits, H. E. Derksen, J. C. Verstelle, and C. J. Gorter, Physica 22, 773 (1956).

[4] J. C. Verstelle, G. W. J. Drewes, and C. J. Gorter, Physica 24, 632 (1958).

[5] H. Hadders, P. R. Locher, and C. J. Gorter, Physica 24, 839 (1958).

[6] P. R. Locher and C. J. Gorter, Physica 27, 997 (1961).

[7] P. R. Locher and C. J. Gorter, Physica 28, 797 (1962); P. R. Locher, thesis, Leiden, 1962 (unpublished),