Theory of Alternating Antiferromagnetic Heisenberg Linear Chains*

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The exact eigenvalue spectrum and thermodynamic properties of the spin Hamiltonian

$$\mathcal{H}=2\,|\,J\,|\sum_{i=1}^{N/2}(\mathbf{S}_{2i}\cdot\mathbf{S}_{2i-1}+a\mathbf{S}_{2i}\cdot\mathbf{S}_{2i+1})$$

are calculated for short chains of $N=4$, 6, 8, and 10 spins, each of spin $\frac{1}{2}$, for alternation parameter $a=0.2$, 0.4, 0.6, and 0.8, with $\mathbf{S}_{N+1}\equiv\mathbf{S}_1$. The behavior for $N=\infty$ is estimated by extrapolation. Comparison is made with the known results for $a=0$ and 1. The ground-state energy, ground-state short-range order, energy gap, and triplet excitation spectrum are compared with various approximate theories. Zero-temperature infinite-chain magnetization curves are inferred from the finite-chain results. The energy, entropy, specific heat, and magnetic susceptibility for $N=10$ are shown to approximate well the behavior for $N=\infty$ when $kT/|\,J\,|>a$. The magnetic-susceptibility data on the free radical 2,2-bis(*p*-nitrophenyl)-1-picrylhydrazyl are shown to agree well with the theoretical results for an alternating chain with $a\approx0.6$.

I. INTRODUCTION

THE topologically linear chain of nearest-neighbor exchange-coupled spins ($S=\frac{1}{2}$) has been the subject of extensive study. It has been of theoretical interest because it is a relatively simple quantum many-body system which has been found to be susceptible to exact calculation in some instances. It is of experimental interest because of the discovery of crystalline solids, such as $Cu(NH_3)_4SO_4\cdot H_2O$ [1], which clearly exhibit regular antiferromagnetic linear chain behavior.

Most of the theoretical work done to date has concerned the *regular* chain, where the exchange integral coupling any pair of nearest neighbors is taken to be a single constant in the isotropic case, or a set of two constants in the uniaxial anisotropic case. References to work on the regular chain prior to 1964 are well summarized in the paper of Bonner and Fisher.[2] Subsequent papers on the exact solution of the regular-chain problem include (1) calculation of the zero-temperature magnetization curve for arbitrary uniaxial exchange anisotropy,[3,4] and (2) rigorous justification of Bethe's[5] choice of eigenfunctions for representing the ground state,[4] also for the arbitrary uniaxial anisotropic case.

The *alternating* Heisenberg linear chain corresponds to the isotropic Hamiltonian

$$\mathcal{H}(N,a)=-2J\sum_{i=1}^{N/2}(\mathbf{S}_{2i}\cdot\mathbf{S}_{2i-1}+a\mathbf{S}_{2i}\cdot\mathbf{S}_{2i+1}),\quad(1)$$

where J is the exchange integral coupling a spin with its nearest right neighbor and aJ is the exchange integral of a spin with its nearest left neighbor, with $|\,a\,|\leq1$. This paper discusses the completely antiferromagnetic case, where $J<0$ and $a\geq0$, which is thought to characterize the spin arrays found in certain aromatic solid free radicals. A comprehensive list of literature references to studies of magnetic interactions in the radicals (up to September, 1965) is given in the review paper of Nordio, Soos, and McConnell.[6]

Authors who have previously considered the antiferromagnetic alternating chain have used field-theory techniques. They rewrite Eq. (1) in terms of appropriate creation and annihilation operators and then use some approximation scheme to obtain an eigenspectrum. Thus, Lynden-Bell and McConnell[7] calculate the excitation spectrum and susceptibility of the system of noninteracting triplet exciton quasiparticles which result when Eq. (1) is suitably transformed and truncated to a quadratic form in triplet-state creation and annihilation operators. Montgomery[8] does a similar calculation, obtaining an approximate Hamiltonian which is quadratic in terms of boson operators, which he diagonalizes by a canonical transformation. Bulaevskiĭ[9] rewrites Eq. (1) in terms of two sets of fermion operators (corresponding to the two translationally inequivalent adjacent spin sites) and calculates the ground-state and excitation energies of the exact Hamiltonian in the Hartree-Fock (HF) approximation.

Soos[10] does extensive calculations starting from Eq. (1) rewritten in terms of a single set of fermion oper-

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[1] R. B. Griffiths, Phys. Rev. **135**, A659 (1964).
[2] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).
[3] R. B. Griffiths, Phys. Rev. **133**, A768 (1964).
[4] C. N. Yang and C. P. Yang, Phys. Rev. **151**, 258 (1966); **150**, 321 (1966); **147**, 303 (1966).
[5] H. A. Bethe, Z. Physik **71**, 205 (1931).
[6] P. L. Nordio, Z. G. Soos, and H. M. McConnell, Ann. Rev. Phys. Chem. **17**, 237 (1966).
[7] R. M. Lynden-Bell and H. M. McConnell, J. Chem. Phys. **37**, 794 (1962).
[8] C. G. Montgomery, Ph.D. thesis, California Institute of Technology, 1965 (unpublished).
[9] L. N. Bulaevskiĭ, Zh. Eksperim. i Teor. Fiz. **44**, 1008 (1963) [English transl.: Soviet Phys.—JETP **17**, 684 (1963)].
[10] Z. G. Soos, J. Chem. Phys. **43**, 1121 (1965); Phys. Rev. **149**, 330 (1966); Z. G. Soos and R. G. Hughes, J. Chem. Phys. **46**, 253 (1967).

ators. He solves exactly a truncated Hamiltonian, using the pseudospin approach developed by Anderson[11] for superconductivity theory. His theory should improve upon the HF result in the view that he takes into account pair correlations between antiparallel spins which are not explicitly included in the HF calculation.[10] He calculates ground-state energy, minimum energy gap, triplet exciton bandwidth and paramagnetic susceptibility, all as a function of temperature and alternation parameter.[12]

Notable success was achieved by Griffiths[13] and Bonner and Fisher[2] in inferring the physical properties of long *regular* chains ($a=1$) by extrapolating from the behavior calculated for short chains of 2–11 spins. The authors decided to apply the same approach to the *alternating* chain where, for the case $|a|<1$, one might expect properties of finite chains to converge even more rapidly with N to the $N=\infty$ values. The procedure of calculation is given in Sec. II, the results are given and compared with previous calculations mentioned above in Secs. III and IV, and a comparison with experiment is given in Sec. V.

II. METHOD OF CALCULATION

The eigenvalues of Eq. (1) for $N=4$, 6, 8 and 10 and $a=0.2$, 0.4, 0.6 and 0.8 are found by diagonalizing the exact Hamiltonian matrix, written in a suitable representation. The procedure follows closely that used by Griffiths[13] for the regular chain. The chain is closed, i.e., $\mathbf{S}_{N+1}\equiv\mathbf{S}_1$, and N is taken to be even. Since $\mathcal{H}(N,a)$ and

$$S^z=\sum_{i=1}^{N} S_i^z$$

commute, a convenient choice of basis functions are the eigenfunctions of S^z which are direct products of the eigenfunctions of S_i^z. This yields $\mathcal{H}(N,a)$ as a $2^N\times 2^N$ matrix in block form along the diagonal in which the largest block is

$$\binom{N}{N/2}\times\binom{N}{N/2},$$

and each block corresponds to a single S^z. Reduction of the size of the blocks is possible because of the $(N/2)$-fold translational symmetry which results when the chain is closed to form a ring. New basis functions are constructed which are eigenfunctions both of S^z and of the translation operator which transforms spins $1\rightarrow 3$, $2\rightarrow 4$, etc. Each submatrix of $\mathcal{H}(N,a)$ and given S^z, when written in terms of this new basis, is further reduced to a block form along the diagonal in which there are $\frac{1}{2}N$ blocks of approximately equal order. Each of these resulting submatrices is characterized by a given S^z and a given eigenvalue e^{ik} of the translation operator.

Thus, for example, for $N=10$ there are $2^{10}=1024$ eigenstates. By using the simple product eigenstates of S^z as basis functions, the largest submatrix to be diagonalized is

$$\binom{10}{5}\times\binom{10}{5}=252\times 252.$$

When $\mathcal{H}(N,a)$ is written using the eigenfunctions both of S^z and of the translation operator, the size of the largest submatrix is reduced to 52×52. This was the largest matrix we could conveniently diagonalize (considering both significance of the calculation and cost) on the IBM 7094. The complex matrix diagonalization program which we used was written by Jon Petersen of the Service Bureau Corporation and we are most appreciative to him for making it available to us.

The eigenvalues of Eq. (1) for values of N and a considered here range from $-4.5J$ (the ferromagnetic ground state for $N=10$ and $a=0.8$) to $8.31921J$ (the antiferromagnetic ground state for $N=10$ and $a=0.8$). The calculated eigenvalues are exact to within about $\pm 0.00001J$. The eigenvalue spectra obtained were checked against the exact trace relations of Eqs. (2), derived for a closed alternating chain of an even number of spins:

$$\begin{aligned}
&\mathrm{Tr}\mathcal{H}=0,\\
&\mathrm{Tr}\mathcal{H}^2=\tfrac{3}{8}NJ^2 2^N(1+a^2),\\
&\mathrm{Tr}(S^z)^2=\tfrac{1}{4}N2^N,\\
&\mathrm{Tr}\mathcal{H}(S^z)^2=-\tfrac{1}{8}NJ2^N(1+a).
\end{aligned}\qquad (2)$$

For a given N and a, all eigenvalues for any given $|S^z|$ and given eigenvalue of the translation operator are also eigenvalues for each smaller $|S^z|$ and the same eigenvalue of the translation operator. This was a particularly useful check which would reveal sign errors in off-diagonal elements which cannot be detected by the relations (2). Unfortunately, no way was found to use this degeneracy, which is a consequence of $[\mathcal{H},S^2]=0$, to reduce the size of the matrices.[14]

The thermodynamic functions were calculated by direct evaluation of the appropriate partition sums using programs written by the authors for the IBM 1620.

III. GROUND-STATE AND TRIPLET EXCITATIONS

The calculated ground-state energies per spin in units of $|J|$, $\epsilon_0(N,a)$, are given in Table I,[15] along with the estimated infinite-chain values. In order to estimate

[11] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).

[12] The relation between the alternation parameter of Soos and that of this paper is $a=(1-\delta)/(1+\delta)$; also $J_{\mathrm{Soos}}(1+\delta)=-2J$.

[13] R. B. Griffiths, Ph.D. thesis, Stanford University, 1962 (unpublished).

[14] After this work was completed, the authors received a copy of a report of F. Carboni, University of Kansas, 1967 (unpublished), in which he makes use of the operator which rotates all spins by 180° to reduce further the order of the matrices corresponding to $S^z=0$.

[15] Robert Griffiths (private communication).

TABLE I. Ground-state energy per spin, $\epsilon_0(N, a)$.

N	$a=0$	0.2	0.4	0.6	0.8	1.0[a]
4	−0.75000	−0.75826	−0.78589	−0.83589	−0.90826	−1.00000
6	−0.75000	−0.75419	−0.76910	−0.80000	−0.85371	−0.93425
8	−0.75000	−0.75397	−0.76707	−0.79266	−0.83789	−0.91277
10	−0.75000	−0.75395	−0.76677	−0.79082	−0.83192	−0.90309
∞	−0.75000	−0.7539	−0.7667	−0.7899	−0.8246	−0.8859

[a] Values for $a=1.0$, $N=4$, 6, 8 from Orbach, Ref. 17, and for $N=10$ from Griffiths, Ref. 15.

$\epsilon_0(\infty,a)$ it was convenient to use the empirical relation

$$\epsilon_0(N,a)/\epsilon_0(\infty,a)=\exp(C/N^x). \tag{3}$$

The constants C, x, and $\epsilon_0(\infty,a)$ were determined by fitting the relation (3) to the data of Table I at $N=6$, 8, and 10. The results are shown in Fig. 1. The estimated $\epsilon_0(\infty,1)$ of −0.8859 may be compared with the exact value, given by Hulthén,[16] of −0.8863. Notice that Eq. (3) reduces to the form assumed by Bonner and Fisher[2] for the case of $a=1$ when N is large. When a is $\lesssim 0.6$, quite rapid convergence with increasing N is noted so that $\epsilon_0(10,a)$ is within about 0.1% of the estimated $\epsilon_0(\infty,a)$. The value $\epsilon_0(N,0)=-\frac{3}{4}$ is exact.

First-order perturbation theory using $\mathcal{H}(N,0)$ as the unperturbed Hamiltonian yields a zero correction to the ground-state energy for all N. The second-order correction is nonzero for the short chains but was found to be too formidable to calculate for arbitrary N. We infer $\epsilon_0(N,a)=\epsilon_0(N,0)+O(a^2)$. This is in agreement with the curves of Fig. 2.

In Fig. 2 results for the ground-state energy as a function of alternation parameter are compared with three previous approximate calculations of $\epsilon_0(\infty,a)$, viz., the quasiboson calculation of Montgomery,[8] the pseudospin calculation of Soos,[10] and the Hartree-Fock calculation of Bulaevskiĭ.[9] The Hartree-Fock result provides a rigorous upper bound on the antiferromagnetic ground-state energy for the infinite alternating chain, as was pointed out by Griffiths[3] for the corresponding calculation of the infinite regular chain. Bulaevskiĭ's ground-state HF calculation involves finding the smallest diagonal element of Eq. (1) in a particular representation which, in accord with the variation method, yields an upper bound on the ground-state energy. It is plausible, although not rigorously shown, to infer that $\epsilon_0(10,a)$ is a lower bound for the exact $\epsilon_0(\infty,a)$. The extrapolated $\epsilon_0(\infty,a)$ calculated here, the quasiboson result of Montgomery, and the pseudospin result of Soos are within these expected limits.

The short-range order of the alternating chain at absolute zero $\tau(N,a)$ was evaluated by calculating

$$\tau(N,a)=-\frac{4}{N}\sum_{i=1}^{N}\langle S_i^z S_{i+1}^z\rangle \tag{4}$$

in the ground state. The results are shown in Fig. 3. The curve for $N=\infty$ is an extrapolation based on the empirical relation of the same form as Eq. (3), with

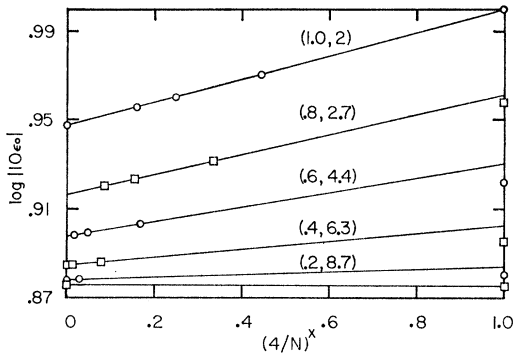

FIG. 1. Logarithm of the ground-state energy per spin *versus* $(4/N)^x$. Values of (a, x) are given next to the corresponding curves. The points for $a=1.0$ are taken from Orbach (Ref. 17) and Griffiths (Ref. 15).

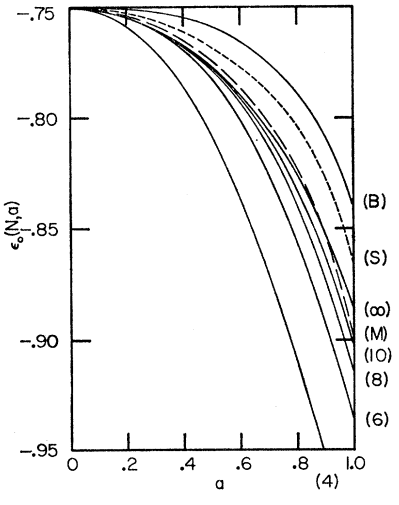

FIG. 2. Ground-state energy per spin as a function of alternation parameter. The number of spins in the chain is given in parentheses next to the corresponding curve. The points for $a=1.0$ are taken from Orbach (Ref. 17). The curve labeled M is the quasiboson result of Montgomery (Ref. 8), the curve labeled S is the pseudospin result of Soos (Ref. 10), and B is the Hartree-Fock result of Bulaevskiĭ (Ref. 9).

[16] L. Hulthén, Arkiv Mat. Astron. Fysik **26A**, No. 11 (1938).

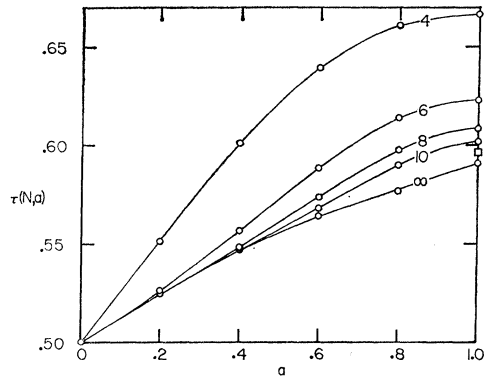

FIG. 3. Ground-state short-range order as a function of alternation parameter for $N=4$, 6, 8, and 10. The value for $N=\infty$ is an estimate as explained in the text. The point □ is the exact value calculated by Orbach (Ref. 17), for $N=\infty$. The points for $a=1.0$ are taken from Bonner and Fisher (Ref. 2).

$\epsilon_0(N,a)/\epsilon_0(\infty,a)$ replaced by $\tau(N,a)/\tau(\infty,a)$. The extrapolated value of $\tau(\infty,1)$ is 0.591, which may be compared with the Soos result of 0.590[8] and the exact result of 0.596,[17] given by Orbach.

When Eq. (4) is evaluated using first-order perturbed wave functions, the lowest-order correction to $\tau(N,0)$ is linear in a. From Fig. 3, the limiting value of $2\tau(\infty,a)=1+a/4+O(a^2)$ may be inferred.

If the alternating chain is placed in an external field H, the Hamiltonian (1) must be augmented by the Zeeman term

$$\mathcal{H}_z=g\beta HS^z, \tag{5}$$

where g is the electron g factor and β is the Bohr magneton. The ground-state magnetization M as a function of H for given N and a, corresponding to $\mathcal{H}+\mathcal{H}_z$, is given in Table II. For a given N and $0<a\leqslant 1$, there are $\frac{1}{2}N$-magnetization steps leading up to the saturation magnetization of $Ng\beta/2$. The minimum field needed to saturate is easily shown to be $2(1+a)\,|J|/g\beta$, independent of N.

TABLE II. Ground-state magnetization.

N	$M/Ng\beta$	$g\beta H/\|J\|$ $a=0.2$	$a=0.4$	$a=0.6$	$a=0.8$
4	$\geqslant 0, <\frac{1}{4}$	0	0	0	0
	$\geqslant\frac{1}{4}, <\frac{1}{2}$	1.83303	1.74356	1.74356	1.83303
	$\geqslant\frac{1}{2}$	2.4	2.8	3.2	3.6
6	$\geqslant 0, <\frac{1}{6}$	0	0	0	0
	$\geqslant\frac{1}{6}, <\frac{1}{3}$	1.77867	1.55081	1.37289	1.30132
	$\geqslant\frac{1}{3}, <\frac{1}{2}$	2.14645	2.36381	2.62711	2.92095
	$\geqslant\frac{1}{2}$	2.4	2.8	3.2	3.6
8	$\geqslant 0, <\frac{1}{8}$	0	0	0	0
	$\geqslant\frac{1}{8}, <\frac{1}{4}$	1.77156	1.50148	1.23427	1.04920
	$\geqslant\frac{1}{4}, <\frac{3}{8}$	1.99408	2.06290	2.20474	2.40619
	$\geqslant\frac{3}{8}, <\frac{1}{2}$	2.26608	2.57221	2.90225	3.24773
	$\geqslant\frac{1}{2}$	2.4	2.8	3.2	3.6
10	$\geqslant 0, <\frac{1}{10}$	0	0	0	0
	$\geqslant\frac{1}{10}, <\frac{1}{5}$	1.77058	1.48770	1.17665	0.91143
	$\geqslant\frac{1}{5}, <\frac{3}{10}$	1.91181	1.87472	1.91587	2.03905
	$\geqslant\frac{3}{10}, <\frac{2}{5}$	2.13890	2.34415	2.59707	2.88327
	$\geqslant\frac{2}{5}, <\frac{1}{2}$	2.31821	2.66115	3.01863	3.38547
	$\geqslant\frac{1}{2}$	2.4	2.8	3.2	3.6

[17] R. L. Orbach, Phys. Rev. 115, 1181 (1959).

Bonner and Fisher[2] estimated the infinite regular chain magnetization by drawing a smooth curve through the midpoints of the magnetization steps for finite N. In Fig. 4 the exact curve of Griffiths[3] for $N=\infty$, $a=1$ is plotted to show the excellent agreement between the midpoints of the steps for $N=10$ (squares) and the limiting result. A smooth-curve estimate of the $a=0.4$ limiting magnetization has been drawn through the midpoints of the $a=0.4$, $N=10$ curve and is also shown in the figure. Similar $N=\infty$ magnetization

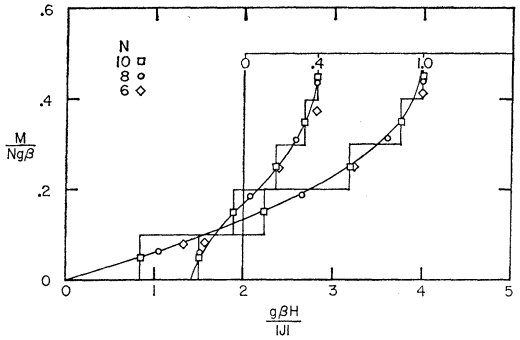

FIG. 4. Ground-state magnetization for $a=0$, 0.4 and 1.0 as a function of magnetic field. The data points are midpoints of the magnetization steps for $N=6$, 8, and 10. The data for $a=1.0$ are from the regular chain eigenvalues calculated by Orbach (Ref. 17) and Griffiths (Ref. 15). The stepped curves are exact results for $N=10$. The smooth curves for $a=0$ and 1.0 are exact results for $N=\infty$, the latter from Griffiths (Ref. 3). The smooth curve for $a=0.4$ is an estimate for $N=\infty$, as explained in the text.

curves may be drawn for other a values. The single step for $a=0$ in Fig. 4 is, of course, exact for all even N.

Estimating the limiting curve for the particular case of $a=0.8$ is most difficult in the vicinity of $g\beta H/|J|\lesssim 1$. It is not clear whether the magnetization for the infinite chain approaches zero for a *nonzero value* of external field, nor can we accurately infer the slope of the magnetization for vanishing M. The results for the extreme a values are known exactly. Thus for $a=0$, M is zero up to a critical field of $H=2\,|J|/g\beta$. For $a=1.0$, Griffiths[3] has inferred and Yang and Yang[4] have verified precisely that there is a zero-field susceptibility at absolute zero of $(dM/dH)/(Ng^2\beta^2/|J|)=1/2\pi^2$. It seems quite unlikely that there is a nonzero susceptibility for $a\lesssim 0.6$, judging from the step midpoint curves for $a=0.2$, 0.4, and 0.6; but no such result can be inferred for $0.8\lesssim a<1.0$. The HF result[9,18] predicts a zero susceptibility for all $0\leqslant a<1$

[18] L. N. Bulaevskiĭ, Zh. Eksperim. i Teor. Fiz. 43, 968, (1962) [English transl.: Soviet Phys.—JETP 16, 685 (1963)].

and a finite susceptibility of $(dM/dH)/(Ng^2\beta^2/|J|) = 1/(2\pi+8)$ for $a=1$. The triplet exciton gas theory[7] and the pseudospin theory[10] both predict a zero susceptibility for $0\leq a\leq 1$.

For the system of isolated pairs, an energy gap exists between the lowest excited (triplet) state and the ground state, while for the infinite regular chain there is no gap.[2] Chains of 4, 6, 8, and 10 spins exhibit a gap, $\Delta(0)$ in units of $|J|$, for all values of the alternation parameter $0\leq a\leq 1$, as is shown in Fig. 5. The various approximate theories of the infinite chain are presented for comparison. It is reasonable to infer that the curve for $N=10$ is an upper limit to the $N=\infty$ value, and hence the HF result is probably the most reliable approximation to the infinite chain result.

Whether or not the gap vanishes for $N=\infty$ and $0<a<1$ is not clear, although disappearance of the gap

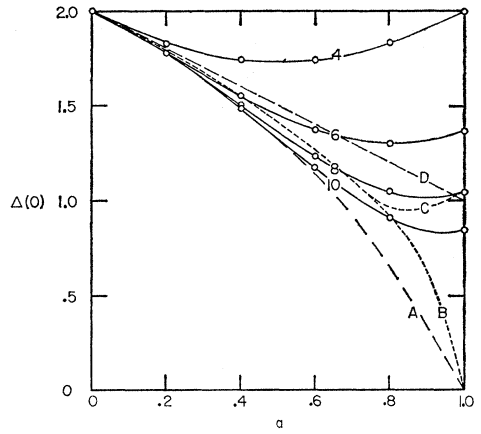

FIG. 5. Alternation energy gap as a function of alternation parameter. Previous calculations plotted for comparison include A, the Hartree-Fock result of Bulaevskiĭ (Ref. 9); B, the quasi-boson calculation of Montgomery (Ref. 8); C, the pseudospin calculation of Soos (Ref. 10); and D, the triplet exciton gas calculation of Lynden-Bell and McConnell (Ref. 7).

for the infinite chain when $a\lesssim 0.6$ appears quite unlikely. For small a, first-order perturbation theory for $N=4$, 6, and 8 yields the result that $\Delta(0)/2=1-a/2+O(a^2)$.

Triplet excitations of Eq. (1) may be discussed in a manner parallel to the spin-wave theory of the regular antiferromagnetic chain given by des Cloizeaux and Pearson.[19] The wave number k is defined via the eigenvalue e^{ik} of the operator which translates each spin in the closed chain to the position of its second-right nearest neighbor. For the boundary condition $\mathbf{S}_{N+1}\equiv\mathbf{S}_1$, the allowed values of e^{ik} for an N-spin chain (N even) are the $N/2$ $N/2$-th roots of unity, with the range of k restricted to $-\pi<k\leq\pi$. The lowest-energy excited states of $\mathcal{H}(N,a)$ for a given k are found to be triplet states for the finite chains investigated and may be identified as the triplet exciton states of McConnell and

[19] J. des Cloizeaux and J. J. Pearson, Phys. Rev. **128**, 2131 (1962).

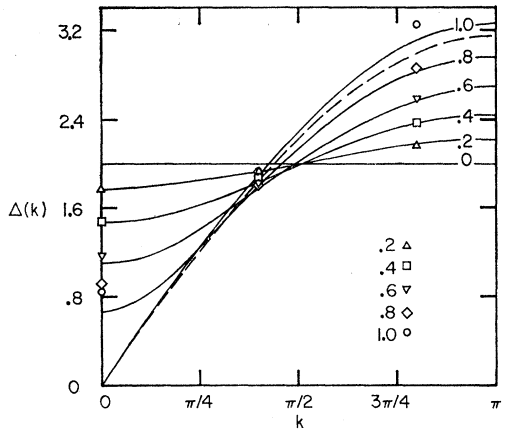

FIG. 6. Triplet exciton spectrum as a function of wave number for $N=10$ and $a=0$, 0.2, 0.4, 0.6, 0.8, and 1.0. The points for $a=1.0$ are from Bonner and Fisher (Ref. 2). The solid curves ($N=\infty$) are from Bulaevskiĭ (Ref. 9). The dashed curve is the exact result for $a=1.0$ and $N=\infty$ of des Cloizeaux and Pearson (Ref. 19). For all the data and curves, $\Delta(k)=\Delta(-k)$.

co-workers.[7,20] When $a=1$ these states make up one-half of the spin-wave states considered by des Cloizeaux and Pearson.

In Fig. 6, the excitation energy of the triplet excitons, $\Delta(k)$ in units of $|J|$, is plotted for $N=10$ and various a values. For comparison, the infinite chain excitation energies of Bulaevskiĭ[9] and the des Cloizeaux and Pearson result[19] for $N=\infty$ and $a=1$ are given. The agreement is best for small a, as might be expected. For small a, the expression of Bulaevskiĭ in our notation reduces to

$$\Delta(k)=2-a\cos k, \tag{6}$$

which is precisely the result of the exciton gas theory[7] and agrees with Montgomery[8] for small a. In Table III, our results for $N=10$ and $a=0.2$ are compared with results of the various approximate theories.

IV. THERMODYNAMIC PROPERTIES

The internal energy, entropy, specific-heat and low-field magnetic susceptibility have been calculated for

TABLE III. Triplet exciton spectrum for $N=10$, $a=0.2$ compared with $N=\infty$, $a=0.2$ results of various approximate calculations.

	$\Delta(0)$	$\Delta(\pm 2\pi/5)$	$\Delta(\pm 4\pi/5)$
$N=10$, exact	1.77058	1.93279	2.17155
$N=\infty$, Bulaevskiĭ[a]	1.770	1.925	2.170
$N=\infty$, Soos[b]	1.787	1.942	2.171
$N=\infty$, Eq. (6)	1.800	1.938	2.162

[a] Reference 9.
[b] Reference 10.

[20] H. Sternlicht and H. M. McConnell, J. Chem. Phys. **35**, 1793 (1961); H. M. McConnell and R. Lynden-Bell, *ibid.* **36**, 2393 (1962).

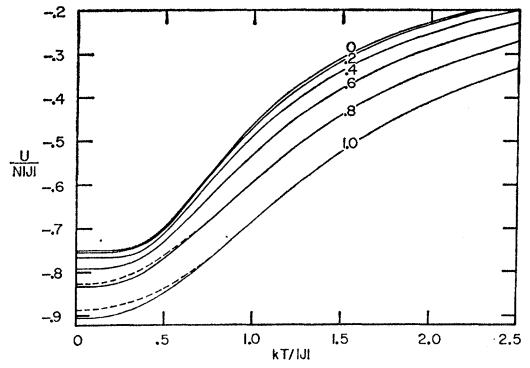

FIG. 7. Internal energy as a function of temperature for the 10-spin chain for the indicated a values of 0, 0.2, 0.4, 0.6, 0.8, and 1.0. The dashed curves are estimates for the ∞-spin chain, as explained in the text. The curves for $a=1.0$ are from Bonner and Fisher (Ref. 2).

$N=4$, 6, 8, and 10 and $a=0.2$, 0.4, 0.6, and 0.8.[21] Where feasible, we have made $N=\infty$ extrapolations. The thermodynamic functions for $a=0$ have been calculated for $N=2$ and these results are readily shown to be exact for all even N. The curves of Bonner and Fisher[2] corresponding to $N=10$ for $a=1.0$ and their $N=\infty$ extrapolations are plotted for comparison. We are indebted to Dr. Bonner for a copy of their numerical results which we used for the plots.

In Fig. 7 the internal energy U for alternating chains of ten spins is plotted *versus* temperature for various a values. The dashed curves at $kT/|J|<0.8$ are an extrapolated estimate of the $N=\infty$ behavior, based on the extrapolation technique already discussed using an equation of the form of Eq. (3). The extrapolated curves for $a=0.2$, 0.4, and 0.6 differ too little from the $N=10$ curves to be shown as separate curves on this graph. The very rapid convergence of the internal energy is evidenced by the fact that the values for $N=8$ and 10 differ by less than 0.5% at all temperatures for $a=0.2$, 0.4, and 0.6, and at $kT/|J|>0.80$ for $a=0.8$. The $N=\infty$ estimates differ from the $N=10$ values by less than 0.5% for all T with a $a=0.2$, 0.4, and 0.6, and at $kT/|J|>0.65$ for $a=0.8$.

The entropy S, plotted in Fig. 8 for $a=0$, 0.8, and 1.0 for 10-spin chains, is a much less sensitive function of alternation parameter than the energy. Also, the convergence with N at a given temperature is less rapid than for U. The agreement of the $N=8$ and 10 curves is to within 0.5% down to $kT/|J|=0$, 0.45, 0.75 and 0.90 for $a=0.2$, 0.4, 0.6, and 0.8, respectively; the $N=10$ and ∞ curves differ by less than 0.5% down to $kT/|J|=0$, 0, 0.65, and 0.80 for the same respective a values.

In Fig. 9, the specific heat in zero magnetic field C_H, for $N=4$, 6, 8, and 10 with $a=0.8$, is plotted along with

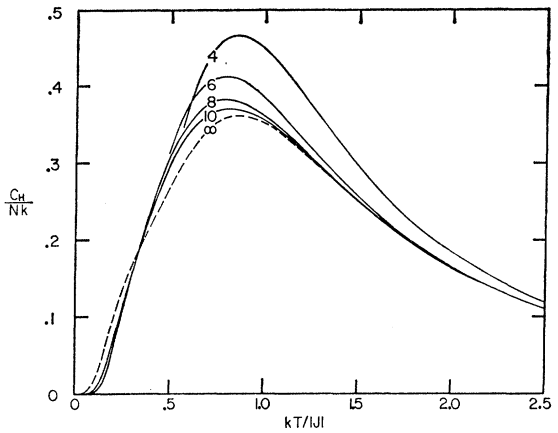

FIG. 9. Specific heat in zero magnetic field for $a=0.8$ and for $N=4$, 6, 8, and 10. The dashed curve is the estimate for $N=\infty$.

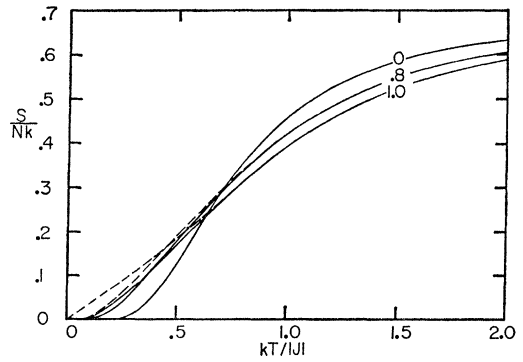

FIG. 8. Entropy as a function of temperature for the 10-spin chain for $a=0$, 0.8, and 1.0. Dashed estimates for $N=\infty$ are given. The curves for $a=1.0$ are from Bonner and Fisher (Ref. 2).

[21] Tables of the thermodynamic properties have been deposited with the ADI Auxiliary Publications Project, c/o Library of Congress, Washington, D.C. 20540. A copy may be obtained by requesting Document No. 9622 and remitting $3.75 for photoprint or $2.00 for microfilm.

an estimate of the $N=\infty$ behavior. The convergence of the specific-heat curves for finite N is relatively poor in the vicinity of the maximum, although certainly more rapid for small a values and high temperatures. The estimate for the $N=\infty$ curve was determined by numerically differentiating the $N=\infty$ estimate of U. This was necessary because the irregular behavior of C_H for small fixed T and increasing N did not admit of an extrapolation function of the form of Eq. (3). The 10-spin-chain specific-heat results for $a=0$, 0.6, and 1.0 are given in Fig. 10, and the inset shows the variation of the value and temperature of the specific-heat maximum with temperature. The curves for $N=8$ and 10 agree to within 0.5% at $kT/|J|>0.15$, 0.15, 0.40, and 1.45 for $a=0.2$, 0.4, 0.6, and 0.8, respectively. The $N=\infty$ estimates are within 0.5% of the $N=10$ values at $kT/|J|>0.6$, 0.6, 0.9, and 1.15 for the same corresponding a values.

For $T\gg|J|/k$, the specific heat may be approximated by the first term in the exact high-temperature

expansion.[22] The result is

$$C_H = \tfrac{3}{8}Nk(1+a^2)(J/kT)^2 \qquad (7)$$

to lowest order in (J/kT), for any even N.

The magnetic susceptibility for $a=0.8$ and $N=4$, 6, 8, and 10 is given in Fig. 11. The $N=\infty$ estimate based on an Eq. (3) extrapolation is also given for $kT/|J|>0.3$. Extrapolation was not attempted for $a=0.8$ below $kT/|J|=0.3$ because of the poor convergence of the finite-chain values as a function of N.

In Fig. 12, the susceptibilities for 10-spin chains with $a=0$, 0.2, 0.4, 0.6, 0.8, and 1.0 are given as solid curves along with the dashed extrapolated $N=\infty$ estimates. The inset shows the variation of the dimensionless Θ/T_m, the ratio of the Weiss constant Θ to the temperature of the maximum susceptibility T_m, as a function of alternation parameter. Also shown in the inset is the dependence of susceptibility maximum χ_m on temperature. The Weiss constant was obtained from the high-temperature expansion for the susceptibility, which is given by

$$\frac{|J|\chi}{Ng^2\beta^2} = \tfrac{1}{4}\left(\frac{|J|}{kT}\right)\left[1-\tfrac{1}{2}(1+a)\left(\frac{|J|}{kT}\right)-\cdots\right]. \qquad (8)$$

Infinite chain estimates are not given because of the good agreement between T_m and χ_m for $N=10$ and the corresponding $N=\infty$ values.

The susceptibilities for 8- and 10-spin chains agree to within 0.5% at $kT/|J|>0.20$, 0.30, 0.75, and 0.95 for $a=0.2$, 0.4, 0.6, and 0.8, respectively. The 10-spin-chain values and ∞-spin-chain estimates differ by less than 0.5% at $kT/|J|>0$, 0, 0.65, and 0.80 for the same corresponding a values. The variation of susceptibility of the infinite alternating chain with temperature for $0<kT/|J|<0.3$ a is very uncertain because of the poor convergence with N of the short-chain values at low temperatures and the uncertainty of the value at $T=0$.

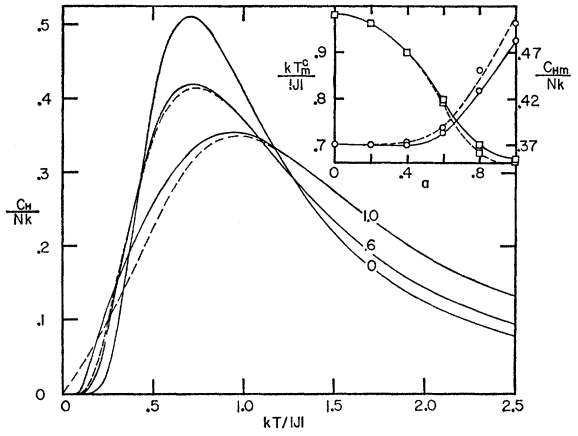

FIG. 10. Specific heat in zero magnetic field for the 10-spin chain for $a=0$, 0.6, and 1.0. The inset shows the temperature of the specific-heat maximum $kT_m^c/|J|$ (circles) and the value of the maximum C_{Hm}/Nk (squares) *versus* alternation parameter for the 10-spin chain. The dashed curves are estimates for $N=\infty$. The data for $a=1.0$ is from Bonner and Fisher (Ref. 2).

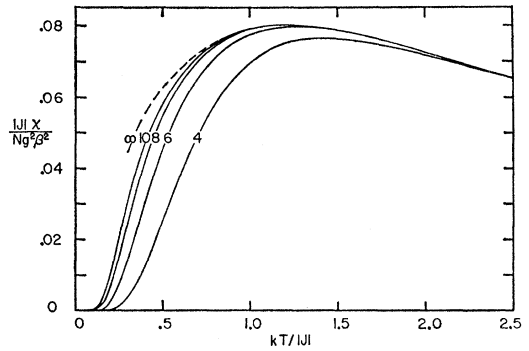

FIG. 11. Susceptibility in low magnetic fields for $a=0.8$ and $N=4$, 6, 8, and 10. The dashed estimate for $N=\infty$ is given down to $kT/|J|=0.3$.

The two previously published susceptibility calculations for Eq. (1) may be compared with our results. The triplet exciton gas[7] yields the correct susceptibility in the limit of vanishing a, but for $a\neq 0$ in the region $kT/|J|\gtrsim a$, where a meaningful comparison can be made with our $N=10$ result, there is only rough qualitative agreement. Similarly, poor quantitative agreement with the pseudospin calculation[10] is noted, even in the $a=0$ limit. These two calculations involve approximations which should be best at $T\ll|J|/k$ and so this lack of agreement is perhaps not surprising. Rough qualitative agreement is found since all three results are increasing functions of a at low temperature,

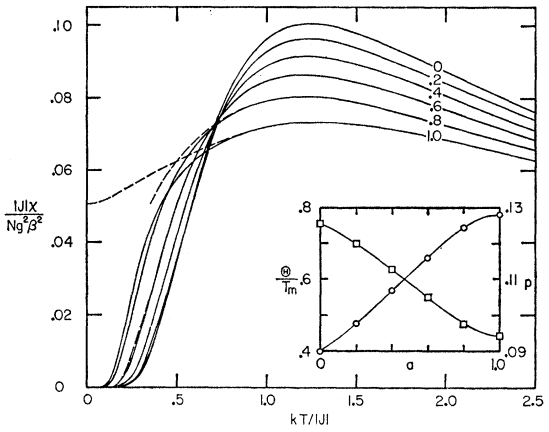

FIG. 12. Susceptibility in low magnetic fields for the 10-spin chain for $a=0$, 0.2, 0.4, 0.6, 0.8, and 1.0. Dashed estimates for $N=\infty$ are given. The inset shows the Weiss constant divided by the temperature of the susceptibility maximum Θ/T_m (circles) and the product of maximum susceptibility times the corresponding temperature, $p=\chi_m kT_m/Ng^2\beta^2$ (squares), versus alternation parameter for the 10-spin chain. The data for $a=1.0$ is from Bonner and Fisher (Ref. 2).

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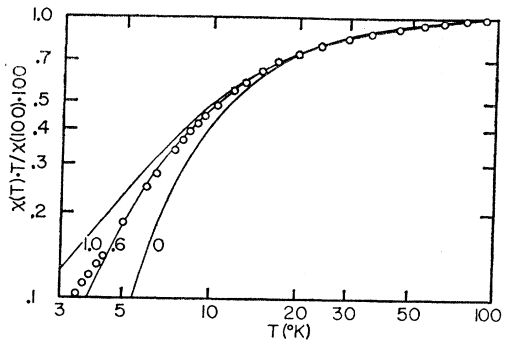

FIG. 13. Relative susceptibility-temperature product *versus* temperature of the solid free radical $D(NO_2)_2$·.The circles are experimental data from Duffy and Strandburg (Ref. 26). The curves are theoretical fits corresponding to the indicated a values of 0, 0.6, and 1.0.

decreasing functions of a at high temperature, and pass through a single maximum at $T\approx|J|/k$.

It is interesting to compare our results for the isotropic alternating chain with the results of Bonner and Fisher[2] for the anisotropic regular chain. The anisotropic regular chain may be characterized by the Hamiltonian

$$\mathcal{G}(N,\gamma)=-2J\sum_{i=1}^{N}[\gamma\mathbf{S}_i\cdot\mathbf{S}_{i+1}+(1-\gamma)S_i^zS^z_{i+1}], \quad (9)$$

where, clearly, $\mathcal{G}(N,1)\equiv\mathcal{H}(N,1)$. The completely anisotropic Ising limit is characterized by $\gamma=0$ and the isotropic Heisenberg limit by $\gamma=1$.

With one exception, the qualitative features of the thermodynamic functions considered here for $\mathcal{H}(N,a)$ are quite similar to the corresponding functions for $\mathcal{G}(N,\gamma)$, where the variation of a or γ does not substantially change these features. The exception is the perpendicular susceptibility, which is discussed below.

The qualitative behavior of C_H as a function of a is quite similar to the behavior of the specific heat of the anisotropic chain (9) as a function of γ. Either stronger alternation or increased anisotropy shifts the specific-heat maximum to lower temperatures, increasing its maximum value and reducing the high temperature "tail".

The anisotropic regular chain exhibits a parallel susceptibility which has the same qualitative dependence on γ as do the curves of Fig. 10 on a, and for $\gamma\neq1$ the parallel susceptibility is zero[2] at $T=0$. The perpendicular susceptibility of the anisotropic chain[23] is nonzero at $T=0$ for all $0\leqslant\gamma\leqslant1$, and is always equal to or greater than the corresponding parallel value, approaching a nonzero value for all γ as $T\to0$. In our case, as previously pointed out, it is unclear whether or not χ at $T=0$ is zero for $N=\infty$ and $0\leqslant a<1$.

[23] Jill Bonner (private communication).

V. COMPARISON WITH EXPERIMENT

Strongly alternating antiferromagnetic spin chains account rather well for the magnetic behavior of the ionic free-radical solids triethylammonium$(TCNQ)_2$ [24] and Würster's blue perchlorate (below its 189°K transition temperature).[6,25] Corroborating crystal-structure studies support these interpretations. Regular (or very weakly alternating) antiferromagnetic chains account well for the magnetic susceptibility of the singly nitrated DPPH radical solid (2-phenyl-2-*p*-nitrophenyl-1-picrylhydrazyl.).[26] Attempts by the authors to fit susceptibility data of various free radicals to an alternating-chain susceptibility of intermediate alternation ($a\approx0.5$) have met with success only in one case, that of doubly nitrated DPPH [2,2-bis(*p*-nitrophenyl)-1-picrylhydrazyl].

In Fig. 13, the relative susceptibility-temperature data (circles) of Duffy and Strandburg[26] for doubly-nitrated DPPH [$D(NO_2)_2$·] are given along with the theoretical curves for $a=0$, 0.6, and 1.0. The theoretical curves have been arbitrarily fitted to the experimental data at 20°K. The "best fit" $a=0.6$ curve corresponds to $J/k=-7.7$°K. For an absolute fit one requires 94.2% spins which, within the quoted experimental error, agrees with the experimental 93% found from the Curie-Weiss law observed at high temperatures. The low temperature rise in χ below 3°K is attributed to paramagnetic impurities.[26] This alternating chain interpretation should be regarded as tentative until supplemental measurements, such as detailed crystal-structure determinations, are made.

Note added in proof. As kindly pointed out to us by Dr. Zoltán Soos, the data (Ref. 26) on the free radical *N*-picryl-9-aminocarbazyl also fit rather well to a linear-chain susceptibility of intermediate alternation ($a\approx0.4$, $J/k=-58$°K).

ACKNOWLEDGMENTS

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