Exchange-coupled pair model for the random-exchange Heisenberg antiferromagnetic chain

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An approximate model for the $s=\frac{1}{2}$ one-dimensional Heisenberg antiferromagnet with random exchange is presented. A probability for exchange (J) of the form $P(J)=\text{const}\ J^{-\alpha}$, with the constant α in the range $0<\alpha<1$, is considered. The approximation is to decouple alternate spins, which leads to isolated exchange-coupled spin pairs having the same $P(J)$. Explicit results for the magnetization (M), susceptibility (χ), entropy (S), and specific heat (C_H) are given. Several limiting cases are worked out. The low-field (Zeeman energy $<<k_BT$) behavior is $\chi=\text{const}\ T^{-\alpha}$, whereas at intermediate fields (Zeeman energy $>>k_BT$), $M=\text{const}\ H^{1-\alpha}$, and $C_HH=\text{const}\ TH^{-\alpha}$. These results are in agreement with the observed behavior of several tetracyanoquinodimethane (TCNQ) charge-transfer salts with asymmetric donors, such as quinolinium-$(TCNQ)_2$. Comparison with other approximations shows this model to give results almost indistinguishable from the spinless fermion model of Bulaevskii *et al.* and the cluster model of Theodorou and Cohen. It is argued that the work of Alexander, Bernasconi, and Orbach shows that there is a relationship between the density of states and $P(J)$ for the Heisenberg chain, and that they are not the same. This leads to a value of α for the thermodynamic properties which differs from that of $P(J)$ for the fully coupled Heisenberg chain.

I. INTRODUCTION

Recent experimental investigations of the low-temperature magnetic properties of quinolinium-$(TCNQ)_2$ (TCNQ is tetracyanoquinodimethane) have indicated that its magnetic behavior is that of a random-exchange Heisenberg antiferromagnetic chain (REHAC). This was first made apparent by Bulaevskii *et al.*[1] who presented high-field magnetization (M) and low-temperature static magnetic susceptibility (to 0.1 K) measurements. In addition, they introduced a model to explain the results which we shall call the Bulaevskii model. The experimental evidence supporting this interpretation has now been extended to the specific heat[2,3] (to 70 mK) and ESR measurements of the magnetic susceptibility (χ) down to about 10 mK.[4,5] The emphasis of the most revealing experimental work has been the very low-temperature regime, as it is there that the REHAC properties become most prominent.

Recently, important theoretical work on the subject has been published by G. Theodorou and M. H. Cohen.[6–8] Their approach has been to use the Hubbard Hamiltonian with random on-site energy to calculate the spatial dependence of the exchange interaction between sites on which a single electron is localized. They find that the exchange is isotropic (Heisenberg), antiferromagnetic, and that it decreases exponentially at large distances. This result is then combined with a simple statistical model to obtain the probability that a certain value of exchange will occur. Finally they calculate the thermodynamics of the system within the framework of several well-known approximations. Except for numerical approximations and truncation of a perturbation series, their model maintains the connection between the microscopic Hamiltonian and the equivalent REHAC. The main difficulty in comparing their work with experimental results is that they do not obtain a solution of all the relevant thermodynamic quantities for the quantum-mechanical Heisenberg antiferromagnet. Also, certain details of their work are in conflict with properties of disordered one-dimensional systems as calculated by Alexander, Bernasconi, and Orbach.[9–11]

The Bulaevskii model,[1] on the other hand, involves phenomenological assumptions which occlude the connection between the microscopic starting point and the thermodynamics, but permit a complete solution to the thermodynamics which fits the experimental results[1–5] very well.

In this paper, we develop the main results of a third model—the exchange-coupled pair (ECP) model in which all exchange interactions are taken to be antiferromagnetic. It forms a useful framework for describing and understanding many features of the low-temperature magnetic behavior of those segregated-stack TCNQ salts with asymmetric donors which have properties similar to quinolinium-$(TCNQ)_2$. In particular, a complete description of the thermodynamics is easily obtained and, in the

sense evident in what follows, the connection between the microscopic Hamiltonian and the thermodynamics is also maintained. To the best of our knowledge, it is the simplest description of these materials which retains these features. The model is similar in spirit to one involving larger clusters, which has been applied to some types of three-dimensional amorphous magnetic materials.[12] In fact, the systems under consideration here are justly characterized as one-dimensional amorphous antiferromagnets. It should, however, be emphasized that there are two important differences with respect to the three-dimensional case: First, the condition of "frustration" does not occur, and second, as discussed below, the distribution of exchange diverges as $J \to 0$. There is also some similarity to the work of Scott *et al.*,[13] where a distribution of exchange interactions was applied to the classical Heisenberg antiferromagnetic chain. That model is, however, quite different from what is done here as their probability distribution is nonsingular, and rather different physical properties are obtained.

Most of the results in this paper are based on unpublished notes from a course given by one of us (W.G.C.) at the Université Scientifique et Médicale de Grenoble. Brief results of the model are published elsewhere.[5,14]

II. ECP MODEL

It has been argued persuasively by Bulaevskii *et al.*[1] and Theodorou and Cohen[6] that the correct physical description for the materials of interest is the one-dimensional Heisenberg chain with a random, antiferromagnetic exchange interaction between neighboring spins. Thus the physical model we would like to solve is

$$\mathcal{H} = 2\sum_{j=1}^{N'} J_j \vec{S}_j \cdot \vec{S}_{j+1} - g\mu_B H \sum_j S_j^z \ , \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian, j is the site index, J_j is the antiferromagnetic interaction ($J_j \geq 0$) between sites j and $j+1$, $\vec{S}_j$ is the spin operator for the jth site, g is the electron g value, μ_B is the Bohr magneton, H is the externally applied field, and N' is the total number of spins. The discussion will be restricted to $S_j = \frac{1}{2}$. It is assumed that N' is so large that boundary conditions are not important. Alternatively, the ends of the chain can be connected to form a ring. It is assumed that J_j is a random variable whose probability distribution $[P_H(J)]$ for small values of J is given by

$$P_H(J) = A' J^{-(1-c)} \ , \tag{2}$$

where A' and c are constants. The requirements that $P_H(J)$ be integrable and that $\chi \to 0$ as $T \to 0$ (discussed below) limit c to the range $0 < c < 1$.

It is worth commenting here on the origin of the power-law form for $P_H(J)$. Theodorou and Cohen have shown that it follows from two simple conditions.[6,7] The first is that single spins occupy at random equally spaced sites (spacing d) on a line with probability p, as shown schematically on Fig. 1(a). This introduces a distance scale l_1 which is the mean spacing between spins; $l_1 = dp^{-1}$. The second assumption is that the exchange interaction between neighboring spins decreases exponentially with their separation; i.e., $J = \mathcal{J}\exp[-(nd/l_2)]$, where $(n+1)d$ is the pair separation and l_2 is the decay length for J. It is then easily shown that

$$P_H(J) = \frac{pl_2}{d}\mathcal{J}^{-l_2|\ln(1-p)|/d} J^{-[1-l_2|\ln(1-p)|/d]} \ . \tag{3}$$

Comparison with Eq. (2) shows

$$1 - c = 1 - l_2|\ln(1-p)|/d \ , \tag{4}$$

which, in the limit $p \ll 1$, becomes

$$1 - c \simeq 1 - l_2/l_1 \ . \tag{5}$$

Although the above conditions are met in the application of the Hubbard model carried out by Theodorou and Cohen, it is expected that they are much more generally applicable. It has also been pointed out that the above results are one-dimensional. In particular, the divergence in $P_H(J)$ as $J \to 0$, which dominates the low-temperature thermodynamic properties, is lost in two and three dimensions.[8] In these cases the conditions of random site occupation and exponential decay of J with distance lead to $P_H(J) \to 0$ as $J \to 0$ and a completely different ther-

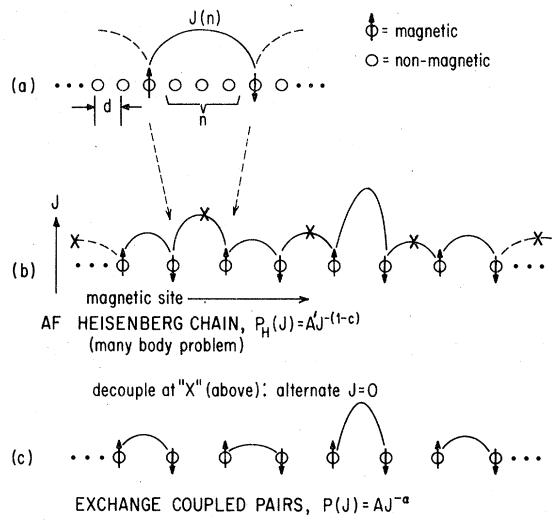

FIG. 1. Pictorial representation of the ECP model. If there is no renormalization of $P(J)$, $P_H(J) = A'J^{-(1-c)} = P(J) = AJ^{-\alpha}$.

modynamic behavior as $T \to 0$.

Unfortunately, there is no exact solution to the thermodynamics of Eqs. (1) and (2). For this reason the ECP model described below is introduced. It would be useful to show that the thermodynamics of the ECP model is a reasonable approximation to that of Eqs. (1) and (2). At this writing, we are aware of arguments which make the correspondence plausible, but which constitute neither a proof of it nor a scheme for evaluating the validity of the approximation. We therefore consider the ECP model as standing alone. Its utility is that it represents rather well and low-temperature thermodynamic properties of quinolinium-$(TCNQ)_2$ and similar materials.

Let us begin our detailed presentation of the ECP model with antiferromagnetic exchange by showing how it is related to the Heisenberg chain. This is shown schematically in Fig. 1. The one-dimensional lattice of sites occupied at random by spins appears in Fig. 1(a). The magnetic sites taken alone constitute a Heisenberg chain with different values of exchange between neighbors [Eq. (1)], as indicated in Fig. 1(b), where the height of each line between adjacent spins represents the magnitude of the exchange interaction between them. The probability $P_H(J)$ is given by Eq. (2). This is the full many-body problem which has not yet been solved. The decoupling procedure used to arrive at the ECP model is simply to set every other value of J to zero, as indicated by the crosses in Fig. 1(b). The remaining problem is a set of independent exchange-coupled pairs with the values of J distributed according to Eq. (2), as indicated in Fig. 1(c). Since the properties of each pair are well known, it is easy to obtain the properties of the ensemble as a superposition of pairs weighted by $P(J)$.

The model just described has a Hamiltonian and probability of couplings given by

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i = \sum_{i=1}^{N} [2J_i \vec{S}_{1i} \cdot \vec{S}_{2i} - h(S_{1i}^z + S_{2i}^z)] \tag{6a}$$

and

$$P(J) = AJ^{-\alpha} \ , \tag{6b}$$

where i indexes each pairs, $\vec{S}_{1i}$ and $\vec{S}_{2i}$ are the spin operators for the first and second spin of the ith pair, $g\mu_B H = h$, and $N = \frac{1}{2}N'$ is the number of pairs. Within the simple picture given here, $P_H(J) = P(J)$, $A' = A$, and $1 - c = \alpha$. However, recent work on diffusion in disordered materials[9–11] indicates that the exponent $1 - c$, which characterizes the distribution of couplings, must be renormalized to the new value of α when the decoupling just described is carried out. This requirement reflects the fact that the exponent behavior of $P_H(J)$ for the Heisenberg chain (physical system) is related to, but not the same as that for its density of states. It is the behavior of the density of states which determines the thermodynamic properties. Since the $P(J)$ of the ECP model is in fact also its density of states, its exponent should be matched to that of the Heisenberg density of states, rather than $P_H(J)$. This point is examined more completely in the latter part of Sec. III. Here, we proceed as if $P_H(J)$ and $P(J)$ are the same.

The states of Eq. (6a) are the well-known singlet-triplet system for each pair. These states are classified by total spin $\vec{S}_i = \vec{S}_{1i} + \vec{S}_{2i}$, $S_i^z = S_{1i}^z + S_{2i}^z$, quantum numbers $S_i = 0, 1$, $\langle S_i^z \rangle = M_i = 0, \pm 1$, and have energy levels given by

$$E_i(S_i M_i) = -hM_i + J_i[S_i(S_i+1) - 2] \ , \tag{7}$$

where a constant has been added to set the energy of the state $|S_i = 1, M_i = 0\rangle$ to zero. The energy levels and quantum numbers for one ECP are shown in the upper right-hand side of Fig. 2. Each pair has the partition function (z)

$$z(h,T,J_i) = 1 + e^{\beta h} + e^{-\beta h} + e^{+2\beta J_i} \tag{8}$$

and free energy (F)

$$F_i(h,T,J_i) = -k_B T \ln[z(h,T,J_i)] \ , \tag{9}$$

where $\beta = (k_B T)^{-1}$.

Since the $P(J)$ of Eq. (6b) is not normalizable, a cutoff is introduced at J_0 to give

$$N = A \int_0^{J_0} J^{-\alpha} dJ \ , \tag{10a}$$

$$A = N(1-\alpha) J_0^{\alpha - 1} \ . \tag{10b}$$

The physical interpretation of J_0 requires some care. The simplest situation is that in which Eq. (6b) represents $P(J)$ for all values of J up to the cutoff

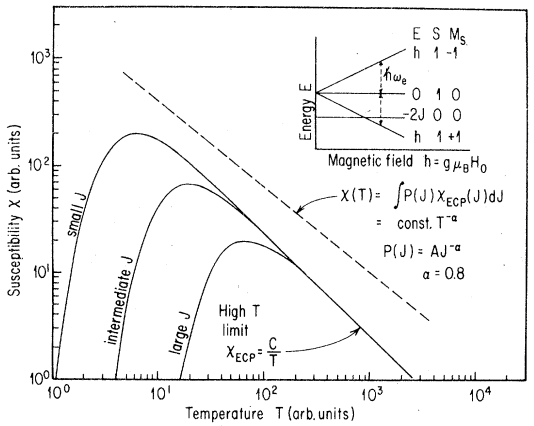

FIG. 2. Energy-level structure and schematic representation of the origin of χ for the ECP model.

J_0, with J_0 being simply the maximum J which occurs between spin pairs. For a J which decreases monotonically with distance between spins, J_0 is then the exchange associated with the minimum distance between unpaired spins. However, the work of Theodorou and Cohen[6] shows that there may be a substantial peak and cutoff of $P(J)$ near the maximum physical value of J. In this case the J_0 introduced above is a parameter used to permit normalization of $P(J)$. It has no direct physical meaning, and greatly exceeds the largest physical J. This is not a serious problem in the treatment given here. As long as k_BT and h are restricted to be less than values of J for which there are substantial deviations from Eq. (6b), those deviations will not be reflected in the thermodynamic properties. With the exception of the high-field magnetization, our presentation will be limited to such cases.

The free energy of the entire system is obtained by summing over each pair

$$F(h,T)=-k_BT\int P(J)\ln[z(h,T,J)]\,dJ \quad . \tag{11a}$$

Within the constraints just discussed, substitution of $P(J)$ from Eq. (6a) gives

$$F(h,T)=-N(1-\alpha)k_BTJ_0^{\alpha-1}\times\int_0^{J_0}J^{-\alpha}\ln[z(h,T,J)]\,dJ \quad . \tag{11b}$$

In most of what follows, several approximations will be used (a) low temperature

$$k_BT \ll J_0 \quad , \tag{12a}$$

(b) low field

$$h \ll k_BT \quad , \tag{12b}$$

(c) intermediate field

$$k_BT \ll h \ll J_0 \quad , \tag{12c}$$

and (d) high field

$$2J_0 \leq h \quad . \tag{12d}$$

Now consider the explicit formulas for the thermodynamic variables. The magnetization (M) is given by

$$M=-\frac{\partial F}{\partial H}=2g\mu_BN(1-\alpha)\left(\frac{k_BT}{2J_0}\right)^{1-\alpha}\times\int_0^{2\beta J_0}\left(\frac{x^{-\alpha}\sinh\beta h}{1+2\cosh\beta h+e^x}\right)dx \quad , \tag{13}$$

where we have introduced the dimensionless variable $x=2\beta J$, and used Eq. (11b). There are two limiting cases of interest. First consider the low-T, low-H approximation [Eqs. (12a) and (12b)], which allows the replacements $\sinh\beta h\simeq\beta h$ and $\cosh\beta h\simeq 1$. Because of the term e^x in the denominator of the integrand, the upper limit of the integral can be extended to ∞. This yields the limiting susceptibility

$$\chi=\frac{g^2\mu_B^2N}{J_0}\left(\frac{2J_0}{k_BT}\right)^{\alpha}f_1(\alpha) \quad , \tag{14}$$

where the function

$$f_n(\alpha)=\int_o^{\infty}\frac{x^{n-\alpha}e^{-x}\,dx}{(1+3e^{-x})^2} \quad , \tag{15}$$

for $n=1,2$ is shown on Fig. 3. To an accuracy of $\pm 3\%$, f_1 is approximated by $f_1=0.445e^{-0.633\alpha}$. It is seen from Eq. (14) that χ diverges as $T^{-\alpha}$.

There is a simple physical picture for this $T^{-\alpha}$ divergence of χ, which is illustrated in Fig. 2. The solid lines show $\chi(T)$ for several different values of J. Each of them has $\chi\propto 1/T$ for $k_BT \gg J$, and drops to zero exponentially in the opposite limit. These are superposed with the weighting factor $P(J)$ to obtain χ for the sytem as a whole. The result rises more slowly than $1/T$ because pairs progressively drop out into their singlet state as k_BT is reduced below J.

The next limits are the intermediate- and high-field cases [Eqs. (12c)] and (12d)], for which $\sinh\beta h\simeq\cosh\beta h\simeq\frac{1}{2}e^{\beta h}$. By using the more general form for F [Eq. (11a)], we obtain

$$M=g\mu_B\int\frac{P(J)\,dJ}{1+e^{\beta(2J-h)}} \quad . \tag{16}$$

Since the denominator of the integrand changes rapidly from 1 to very large values about $2J=h$, to a

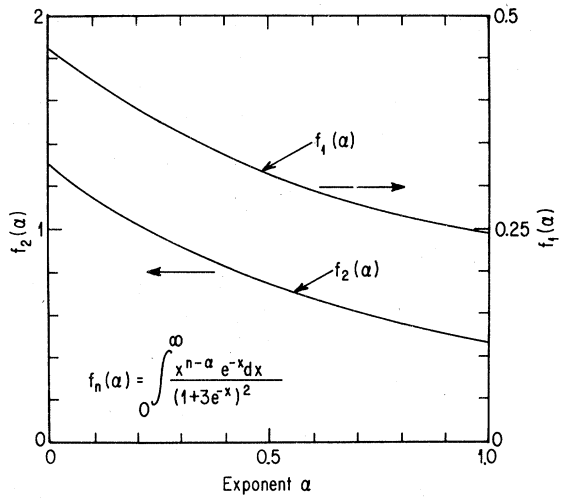

FIG. 3. Functions $f_1(\alpha)$ and $f_2(\alpha)$ as a function of α for the ECP model.

good approximation

$$M = g\mu_B \int_0^{1/2h} P(J)\, dJ = g\mu_B \mathfrak{N}(J \leq \tfrac{1}{2}h) \quad , \quad (17)$$

where $\mathfrak{N}(J \leq \frac{1}{2}h)$ signifies the number of pairs with $J \leq \frac{1}{2}h$. This result is easily interpreted in terms of the energy-level diagram of Fig. 2. As $T \to 0$, each pair will be in its lowest state. For those pairs with $J \leq \frac{1}{2}h$, the lowest state has magnetic moment $g\mu_B$; otherwise, it is zero. Thus, it is seen that the low-temperature magnetization as a function of H provides a very direct probe of $P(J)$, including details of any structure (of width $> k_B T$) or the cutoff at J_0. For the intermediate-field regime [Eq. (12c)], where Eqs. (6b) and (10b) apply,

$$N(J \leq \tfrac{1}{2}h) = N(g\mu_B H/2J_0)^{1-\alpha} \quad , \quad (18)$$

and

$$M = g\mu_B N(g\mu_B H/2J_0)^{1-\alpha} \quad . \quad (19)$$

In this region of H, even though $g\mu_B H >> k_B T$, the magnetization does not saturate, but increases as $H^{1-\alpha}$. Saturation of M is finally reached at the high-field limit (12d), where $M = Ng\mu_B$.

All of our subsequent development will be done in terms of Eq. (6b) for $P(J)$.

The entropy (S) is given by

$$S(H,T) = -\frac{\partial F}{\partial T} = k_B \beta^2 \frac{\partial F}{\partial \beta}$$

$$= k_B \frac{N(1-\alpha)}{J_0^{1-\alpha}} \int_0^{J_0} \frac{dJ}{J^\alpha} \left[\ln(1 + 2\cosh\beta h + e^{2\beta J}) - \frac{2\beta(h\sinh\beta h + Je^{2\beta J})}{1 + 2\cosh\beta h + e^{2\beta J}} \right] \quad . \quad (20)$$

In the very high-T limit $k_B T >> J_0$ and h, $S \to N_0 k_B \ln 4$, as it should. It is easily shown that in the low-T, low- and intermediate-H limits [Eqs. (12a)–(12c)] the integrand of Eq. (20) has dropped to zero rapidly for $J \simeq J_0$, so that the upper limit can be extended to infinity. Substitution of the dimensionless variable $x = 2\beta J$ gives

$$S(H,T) = k_B N(1-\alpha) \left(\frac{k_B T}{2J_0} \right)^{1-\alpha} \int_0^\infty \frac{dx}{x^\alpha} \left[\ln(1 + 2\cosh\beta h + e^x) - \frac{2\beta h \sinh\beta h + xe^x}{1 + 2\cosh\beta h + e^x} \right] \quad . \quad (21)$$

If we take the low-field limit, to order $\beta^2 h^2$ the entropy is (after some integration by parts)

$$S(H,T) = 3Nk_B \left(\frac{k_B T}{2J_0} \right)^{1-\alpha} [f_2(\alpha) - \tfrac{2}{3}\beta^2 h^2 f_1(\alpha)] \quad . \quad (22)$$

The function $f_2(\alpha)$ [Eq. (15)] is graphed on Fig. 2. To an accuracy of $\pm 2.5\%$, $f_2(\alpha)$ is approximated by $f_2(\alpha) = 1.26e^{-1.03\alpha}$. Equation (22) shows that as $h \to 0$, S varies as $T^{1-\alpha}$.

In the intermediate-field case (12c) integration by parts and the substitution $y = x - \beta h$ gives

$$S(H,T) = Nk_B \left(\frac{k_B T}{2J_0} \right)^{1-\alpha} \int_{-\beta h}^\infty (y + \beta h)^{1-\alpha} \left[\frac{y}{(1+e^y)(1+e^{-y})} \right] dy \quad . \quad (23)$$

The part of the integrand in brackets behaves as the derivative of a δ function. Therefore the integral can be evaluated by setting the lower limit to $-\infty$, expanding $(y + \beta h)^{1-\alpha}$ as a power series about $y = 0$, and keeping the first nonzero term

$$S(H,T) = \tfrac{1}{3}\pi^2 Nk_B(1-\alpha) \left(\frac{k_B T}{2J_0} \right) \left(\frac{2J_0}{g\mu_B H} \right)^\alpha \quad , \quad (24)$$

where we have used

$$\int_0^\infty y^2 e^y (1+e^y)^{-2}\, dy = \tfrac{1}{6}\pi \quad .$$

This result shows that S varies as $TH^{-\alpha}$ in the low-T, intermediate-H case. A graph of $S(T)$ for various values of H has been published elsewhere.[5]

From the energy (E)

$$E(H,T) = \frac{-2N(1-\alpha)}{J_0^{1-\alpha}} \int_0^{J_0} \frac{dJ}{J^\alpha} \left[\frac{h\sinh\beta h + Je^{2\beta J}}{1 + 2\cosh\beta h + e^{2\beta J}} \right] \quad , \quad (25)$$

The specific heat at constant H (C_H) is obtained using $C_H = -(k_B T^2)^{-1} \partial E / \partial \beta$

$$C_H(H,T) = \frac{2Nk_B(1-\alpha)}{(k_B T)^2 J_0^{1-\alpha}} \int_0^{J_0} \frac{dJ}{J^\alpha} \left[\frac{h^2 \cosh\beta h + 2J^2 e^{2\beta J} + 2h^2 + (4J^2 + h^2)\cosh\beta h e^{2\beta J} - 4Jh \sinh\beta h e^{2\beta J}}{(1 + 2\cosh\beta h + e^{2\beta J})^2} \right] . \quad (26)$$

The limiting cases for C_H are most easily obtained using $C_H = T(\partial S/\partial T)_H$ and Eqs. (22) and (24). This gives

$$C(0,T) = 3Nk_B(1-\alpha)\left(\frac{k_B T}{2J_0}\right)^{1-\alpha} f_2(\alpha) , \quad (27)$$

for the low-T, $H = 0$ case and

$$C_H(H,T) = \tfrac{1}{3}\pi^2 Nk_B(1-\alpha)\left(\frac{k_B T}{2J_0}\right)\left(\frac{2J_0}{g\mu_B H}\right)^{\alpha} , \quad (28)$$

for the low-T, intermediate-H case. These results show that at zero field C_H varies as $T^{1-\alpha}$, whereas in the intermediate-field regime, it varies as $TH^{-\alpha}$.

III. DISCUSSION

In the first part of this section we discuss the relation of the ECP model to those of the cluster[6] and Bulaevskii models, with special emphasis on those features which can be tested experimentally. Afterwards, several questions regarding the interpretation and validity of the model will be presented.

Of all the cases that have been worked out so far, the limiting temperature and field dependences are identical: for

$$g\mu_B H << k_B T << J_0 ,$$

$$\chi(T) = \text{const } T^{-\alpha} ,$$

$$C_H(0,T) = \text{const } T^{1-\alpha} ,$$

$$S(0,T) = \text{const } T^{1-\alpha} .$$

For

$$J_0 >> g\mu_B H >> k_B T ,$$

$$M(H) = \text{const } H^{1-\alpha} ,$$

$$C_H(H,T) = \text{const } TH^{-\alpha} ,$$

$$S(H,T) = \text{const } TH^{-\alpha} .$$

Thus, in order to test which model best fits experimental results, it is necessary to examine either the intermediate cases or the constants appearing in the limiting cases. In this paper we restrict the discussion to the latter alternative.

The only comparisons presently available for the cluster model are χ, $C_H(0,T)$, and $M(0,H)$. We examine the first two here. Following Theodorou and Cohen,[6] long chains are broken into finite segments (clusters) at points where[15] $2J \leq k_B T$. Clusters with an odd number of spins have the Curie χ of a free spin whereas even-spin clusters are in a singlet ground state. It then follows that for the clusters (subscript "cl"):

$$\chi_{\text{cl}} = \frac{Ng^2\mu_B^2}{8J_0}\left(\frac{2J_0}{k_B T}\right)^{\alpha} \quad (29)$$

and the susceptibility ratio is given by [see Eq. (14)]

$$\frac{\chi_{\text{ECP}}}{\chi_{\text{cl}}} = 8 f_1(\alpha) . \quad (30)$$

For the typical value $\alpha = 0.8$, this ratio is 2.16. The specific heat for the cluster model at $H = 0$ is[6] simply that of a free spin ($k_B \ln 2$) for each cluster with an odd number of spins. This gives

$$C_{\text{cl}}(0,T) = Nk_B(1-\alpha)\ln 2\left(\frac{k_B T}{2J_0}\right)^{1-\alpha} , \quad (31)$$

with the ratio

$$\frac{C_{\text{ECP}}(0,T)}{C_{\text{cl}}(0,T)} = \frac{3f_2(\alpha)}{\ln 2} . \quad (32)$$

For $\alpha = 0.8$, the ratio is 2.47. From this it can be seen that for the same number of spins and $P(J)$, the ECP model has values of χ and C_H about a factor of two larger than the cluster model. In view of the arbitrariness in the relation defining a cluster, $2J = k_B T$, this difference should not be considered significant. Furthermore, an independent measure of the number of spins and $P(J)$ is usually unavailable. In such cases, a comparison of the ratio $\chi_{\text{ECP}} C_{\text{cl}} / \chi_{\text{cl}} C_{\text{ECP}}$ is a more meaningful test of an experimental result. For $\alpha = 0.8$, this ratio is 0.88, which makes it difficult to discriminate experimentally between the two models. Of course, the ECP model can be used for $H \neq 0$, whereas this is difficult for the cluster model.

Now consider the Bulaevskii model[1] (subscript B). The density of states and limiting cases are

$$\rho(\epsilon) = D|\epsilon|^{-\alpha} , \quad (33)$$

with the low-field low-T case [Eqs. (12a) and (12b)] giving

$$\chi_B(T) = 2(1-2^{1+\alpha})\Gamma(1-\alpha)\zeta(-\alpha)\, N'Dg^2\mu_B^2(k_BT)^{-\alpha} \tag{34}$$

and

$$C_B(0,T) = 2(1-2^{\alpha-1})\Gamma(3-\alpha)\zeta(2-\alpha)\, N'Dk_B(k_BT)^{1-\alpha} \tag{35}$$

and the low-T intermediate-H case [Eqs. (12a) and (12c)]

$$M_B(H,0) = (1-\alpha)^{-1} g\mu_B N'D(g\mu_B H)^{1-\alpha} \tag{36}$$

and

$$C_{BH}(T,H) = \tfrac{1}{3}\pi^2 N'Dk_B(k_BT)(g\mu_B H)^{-\alpha}\ , \tag{37}$$

where D is a numerical constant to fit the magnitude, ϵ is the quasiparticle energy, $\Gamma(x)$ is the gamma function, and ζ is the Riemann zeta function.

Because of the adjustable, nonphysical constants in the ECP and Bulaevskii models, it is not possible to compare their magnitudes directly. Instead we examine the ratios of limiting cases within each model. Three such ratios easily related to experimental tests are for the ECP model

$$\frac{\chi H}{M} = 2f_1(\alpha)\left(\frac{g\mu_B H}{k_BT}\right)^{\alpha}\ , \tag{38}$$

$$\frac{C_H(0,T)}{C_H(H,T)} = \frac{9}{\pi^2}f_2(\alpha)\left(\frac{g\mu_B H}{k_BT}\right)^{\alpha}\ , \tag{39}$$

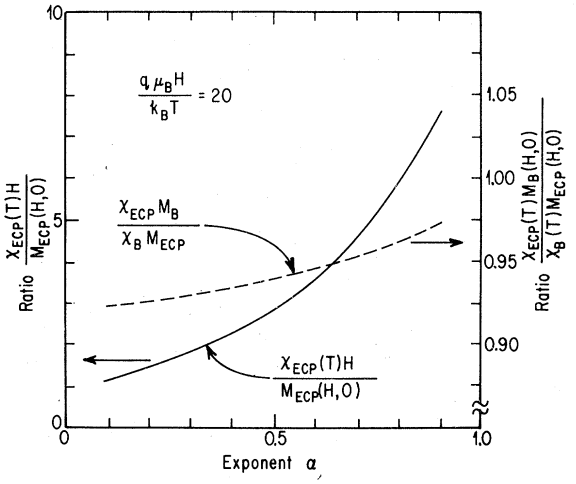

FIG. 4. Ratio $\chi H/M$ for the ECP model as a function of α (solid curve) and its comparison with the Bulaevskii model (dashed curve).

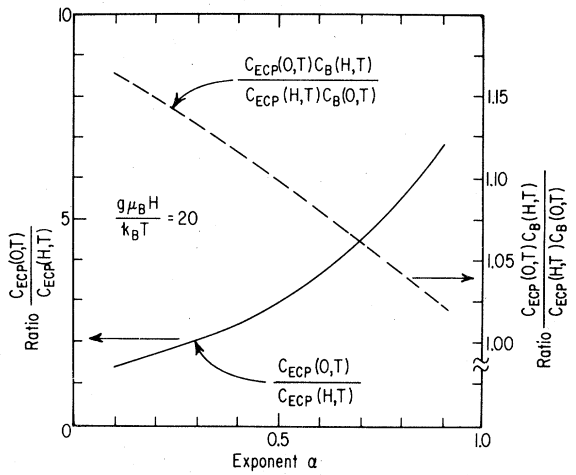

FIG. 5. Ratio $C(0,T)/C(H,T)$ at $g\mu_B H = 20k_BT$ for the ECP model as a function of α (solid curve) and its comparison with the Bulaevskii model (dashed curve).

and

$$\frac{\chi}{C_H(0,T)} = \frac{g^2\mu_B^2}{k_B^2 T}\frac{2f_1(\alpha)}{3(1-\alpha)f_2(\alpha)}\ . \tag{40}$$

The first two of these relate low-field to high-field measurements, and are given as a function of α by the solid curves on Figs. 4 and 5 using $g\mu_B H/k_BT = 20$. These curves permit one to evaluate the corresponding experimental results for all physical values of α. On Fig. 6, the solid line demonstrates the behavior of $k_B^2 T\chi_{ECP}/g^2\mu_B^2 C_{ECP}(0,T)$ as a function of α. This curve establishes a basis for comparing Eq. (40) with experimental results.

For the Bulaevskii model, the same ratios appropri-

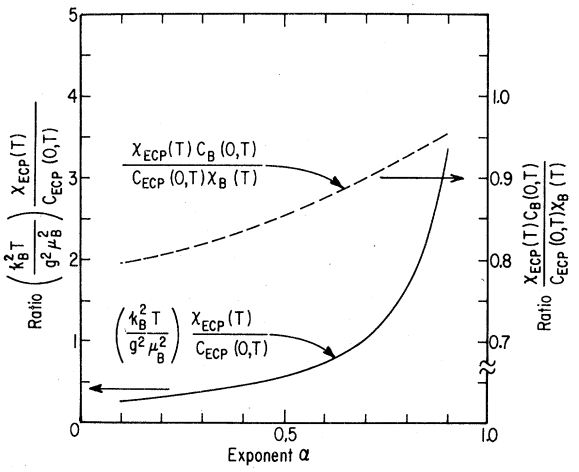

FIG. 6. Ratio $k_B^2 T\chi/g^2\mu_B^2 C(0,T)$ for the ECP model as a function of α (solid curve) and its comparison with the Bulaevskii model (dashed line).

ate for experimental test are

$$\frac{\chi H}{M} = 2(1-2^{1+\alpha})\Gamma(1-\alpha)\zeta(-\alpha)(1-\alpha)\left[\frac{g\mu_B H}{k_B T}\right]^{\alpha} , \tag{41}$$

$$\frac{C_H(0,T)}{C_H(H,T)} = \frac{6(1-2^{\alpha-1})\Gamma(3-\alpha)\zeta(2-\alpha)}{\pi^2}\left[\frac{g\mu_B H}{k_B T}\right]^{\alpha} , \tag{42}$$

and

$$\frac{\chi}{C_H(0,T)} = \left[\frac{1-2^{1+\alpha}}{1-2^{\alpha-1}}\right]\frac{\Gamma(1-\alpha)\zeta(-\alpha)}{\Gamma(3-\alpha)\zeta(2-\alpha)}\left[\frac{g^2\mu_B^2}{k_B^2 T}\right] . \tag{43}$$

Because of the rather complicated nature of these formulas, a simpler comparison of the results of the Bulaevskii and ECP models is obtained using the ratios of Eq. (38)–(41), etc. These ratios are shown by the dashed lines on Figs. 4–6. Their significance is that a value equal to one means there is no distinction between the ratios of intermediate- and low-field limits in the ECP and Bulaevskii models. Examination of these figures shows that all of the ratios are close to one. For $\alpha = 0.8$, which is typical of values observed experimentally, the difference is 8% or less. Hence, an experimental differentiation between the ECP and Bulaevskii models would be rather difficult.

Now we turn to several questions and comments regarding the ECP model. First, it is natural to ask why this simple model can give a good account of the low-temperature static magnetic properties of materials such as quinolinium-$(TCNQ)_2$, which are believed to be described by the many-body Hamiltonian of Eq. (1). The formal answer is that the ECP model has been constructed to have the same structure of energy levels as the real physical system, i.e., the same partition function, free energy, and thermodynamic behavior. It is easy to see why this can be done by an appropriate superposition of exchange-coupled pairs. Reference to the energy-level diagram of Fig. 2 shows that the first excited state in zero field has an energy ϵ above the ground state given by $\epsilon = 2J$. Thus the density of states $N(\epsilon)$ for a superposition of exchange-coupled pairs has the same form as the distribution of couplings $P(J)$. Any experimental result in zero field can then be fitted by an appropriate choice of $P(J)$. Consideration of the properties of antiferromagnets in an applied field rules out the possibility of using triples instead of pairs. In the case of triples, the doublet ground-state splitting in a magnetic field would give a large Curie χ, contrary to the magnetic behavior of the systems under consideration. In fact, examination of the work of Bonner and Fisher[16] on uniform antiferromagnets suggests that one could use even (but not odd) numbered groups of any moderate size as a basis for a superposition model. The choice of pairs is seen as the simplest one. It should also be noted that success of the model in fitting experimental results over a wide range of H[1,2] means that it gives the correct density of states in the presence of a magnetic field as well. This is not surprising as the eigenstates of both the Heisenberg [Eq. (1)] and ECP models can be classified according to the total spin and its z component, and have the same form for the Zeeman splitting in a magnetic field.

From the above it is clear that the $P(J) = AJ^{-\alpha}$ of the ECP model [Eq. (6b)] has the same behavior as its density of states in zero field. But is it the same as the actual distribution of exchange couplings $P_H(J) = A'J^{-(1-c)}$ [Eq. (2)] in the original Heisenberg model? Some insight on this question can be gained on the basis of recent work on one-dimensional diffusion in disordered systems by Alexander, Bernasconi, and Orbach.[9–11] Their work can be easily mapped[10] onto the low-density disordered one-dimensional ferromagnet. Since it is not yet clear whether it also applies to the antiferromagnetic case, the following, in which we use the hypothesis that it does apply, is speculative.

There are several points of contact between their work and the ECP model. They find the low-energy density of states for an arbitrary probability of coupling strengths $\rho(W)$. As an example, they consider the form

$$\rho(W) \propto W^{-\alpha'} , \tag{44}$$

where W is the coupling between nearest neighbors on a chain and α' is an exponent which characterizes the distribution. They demonstrate that disordered behavior is associated with $0 < \alpha' < 1$. For $\alpha' < 0$, a band motion with an averaged value for W $\{W_{\text{eff}}^{-1} = \int [\rho(W)/W]dW\}$ obtains. An exact solution leads to

$$N(\epsilon) \propto \epsilon^{-1/(2-\alpha')} \tag{45}$$

and

$$C_H(0,T) \propto T^{(1-\alpha')/(2-\alpha')} , \tag{46}$$

where ϵ is the energy and $N(\epsilon)$ is the density of states. The important point is that starting from a distribution of couplings $\rho(W)$ they find a density of states $N(\epsilon)$ with a *different* power-law behavior. If we apply these results to the ECP and Heisenberg models, the following correspondences are obtained:

$$C_H \propto T^{(1-\alpha')/(2-\alpha')} \propto T^{1-\alpha}$$

[Eqs. (46) and (27)],

$$N(\epsilon) \propto \epsilon^{-1/(2-\alpha')} \propto P(J \to \epsilon) \propto \epsilon^{-\alpha}$$

[Eqs. (45) and (6b)], and

$$\rho(W) \propto W^{-\alpha'} \propto P_H(J \to W) \propto J^{-(1-c)}$$

[Eqs. (44) and (2)]. Comparison of exponents then

gives

$$\alpha = \frac{1}{2-\alpha'} = \frac{1}{1+c} \quad . \tag{47}$$

One important consequence of this result is that the range of α is modified to $\frac{1}{2} < \alpha < 1$ by the condition on α' and c: $0 < \alpha', c < 1$ (and the assumption that the chain is disordered). But α is the exponent obtained directly in experiments on χ, C_H, etc. Measured values of α reported so far[1,2,4,14,17] fall in the range $0.58 < \alpha < 0.87$, so that there is no evidence to contradict the modified range of α. A second consequence of the distinction between $P_H(J)$ and $P(J)$ is that one must then be careful to relate the microscopic interpretation of $P_H(J)$ presented in Eqs. (3)–(5) to experimental results using Eq. (47). A final consequence is that A' of Eq. (2) may not be the same as A of Eq. (6b). The resolution of this point will not be considered here. As mentioned at the outset, we have just applied results valid for the ferromagnetic case to the antiferromagnetic one. We believe that even if this procedure turns out to be wrong in detail, a renormalization of exponents is still necessary, but perhaps with a correspondence different from that of Eq. (47). More theoretical work is needed on this point.

Before turning to other matters a comment on the discrepancy between the cluster model approach of Theodorou and Cohen[6–8] and the work of Alexander and co-workers[9–11] is appropriate. The disagreement is serious, because both consider the disordered Heisenberg ferromagnet. The difference can be seen, for example, upon comparison of the expressions for the coherence length [Eq. (15) of Ref. 7 versus Eqs. (19) and (21) of Ref. 11] and the distribution of couplings [Eq. (14) of Ref. 7 versus Eq. (11) of Ref. 11]. The reason for the difference is that the clusters of Theodorou and Cohen are constructed as if the distribution of couplings and density of states have the same exponent behavior, whereas the results of Alexander *et al.* indicate they are different.

Another point to consider is the *dynamic* behavior of the REHAC. To date, there is a considerable body of experimental results on quinolinium-$(TCNQ)_2$ in the low-temperature regime. Some examples are: (a) relaxation of protons by electron-spin fluctuations,[18] (b) the electron-spin-resonance linewidth, which is strongly narrowed by exchange,[4,14] and (c) relaxation of the electron Zeeman reservoir to the exchange reservoir and the lattice.[14,19] Can the ECP model be used to explain these results? Certainly not for item (b) as exchange narrowing is a fundamentally many-body phenomenon. Not enough is known at present to properly evaluate the usefulness of the ECP model to the interpretation of the other experiments which reflect the dynamic behavior of the system.

A final question is the relation of static measurements of χ to ESR measurements within the framework of the ECP model. From the energy-level diagram of Fig. 2 it is seen that the ESR transition is simply the $|\Delta M_S| = 1$ transition of the triplet state of each ECP. Isotropy of the exchange interaction leads to a single, narrow line which is independent of the external field orientation (as observed in experiments[4]). The connection between the ESR and static χ is then made using the same arguments previously employed for the ESR of conduction electrons in a metal.[20] The situation for the many-body case [Eq. (1)] is somewhat more complicated, and will be covered in more detail elsewhere.[4]

IV. CONCLUSIONS

We have presented the results of a simple exchange-coupled pair model which is believed to represent the static physical properties of a one-dimensional Heisenberg antiferromagnet with random nearest-neighbor exchange. These results are in agreement with the measured properties of several TCNQ charge-transfer salts with asymmetric donors, such as quinolinium-$(TCNQ)_2$. Explicit formulas are worked out for the magnetization, susceptibility, entropy, and specific heat as a function of temperature and magnetic field. Comparison of these results with two other approximate models of the same physical systems shows that the thermodynamic properties of all three are almost indistinguishable. It is argued that the decoupling procedure used with the ECP model should lead to a renormalization of the exponent which characterizes the distribution of couplings.

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