I. THEORY OF THE LINEAR HEISENBERG ANTIFERROMAGNET

II. PHONON EFFECTS IN TRIPLET EXCITON THEORY

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To My Mother

And to the Memory

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ABSTRACT

PART I

In the Heisenberg model, the hamiltonian describing a linear array of tightly-bound electrons that are exchange-coupled to their neighbors is

$$\mathcal{H} = \sum_{j=1}^{N/2} \left\{ J(1+\delta)\vec{S}_{2j} \cdot \vec{S}_{2j+1} + J(1-\delta)\vec{S}_{2j} \cdot \vec{S}_{2j-1} - \frac{J}{2} \right\}$$

where $-1 \leq \delta \leq 1$ is the alternation parameter, $\vec{S}_j$ is the electron spin on the jth site, and $J > 0$ (antiferromagnetic coupling). The solutions of the one-dimensional antiferromagnet are studied by transforming to pseudo-spin operators similar to those used by Anderson in superconductivity theory. In a self-consistent molecular-field approximation, the ground state energy, the excitation spectrum, and the coherence between antiparallel spins are found for arbitrary δ and temperature. At $0°K$, the solutions agree with or improve upon previous calculations of the properties of the regular ($\delta = 0$) or the alternating ($\delta \neq 0$) antiferromagnet. For $T > 0$, good agreement is found with the experimental paramagnetic susceptibilities of organic crystals whose spin properties may be represented by a regular or an alternating antiferromagnet. The temperature dependence of the excitation energies agrees with the observed behavior of the singlet-triplet energy gap in triplet

exciton systems. The high temperature and weak alternation extension of triplet exciton theory is presented.

PART II

Certain organic crystals consist of linear chains of antiferromagnetically-coupled, tightly-bound electrons; their EPR (electron paramagnetic resonance) properties are discussed in terms of triplet excitons. We consider a deformable lattice and investigate the influence of phonons on triplet excitons. For low exciton density (i.e., at low temperature) the excitons, on account of the phonons, are localized and diffusional; they resemble chargeless polarons in the strong-coupling limit. A general expression for the rate, and its temperature dependence, of an exciton process in a phonon bath at thermal equilibrium is found. In particular, we obtain the diffusion constant for exciton motion, the activation energy for diffusion, and the rates of exciton creation and annihilation; we estimate these parameters for Wurster's blue perchlorate. Even at $0°K$, diffusional excitons are mobile enough to account for the absence of hyperfine structure in the EPR spectra. Modifications, due to the phonons, of the parameters of the effective exciton hamiltonian are obtained and a spin-independent, phonon-coupled repulsion between excitons is rederived.

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I. THEORY OF THE LINEAR HEISENBERG ANTIFERROMAGNET.

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Abstract

We consider a linear array of tightly-bound electrons
that are exchange-coupled to their neighbors. The hamiltonian,
in the Heisenberg model, is

$$\mathcal{H} = \sum_{j=1}^{N/2} \left\{ J(1+\delta)\vec{S}_{2j} \cdot \vec{S}_{2j+1} + J(1-\delta)\vec{S}_{2j} \cdot \vec{S}_{2j-1} - \frac{J}{2} \right\},$$

where δ is the alternation parameter and the exchange integral J
is positive, corresponding to antiferromagnetic coupling. We
investigate the solutions for the one-dimensional antiferromagnet,
for any $/\delta/\leq 1$, by transforming the hamiltonian first to Fermi
creation and annihilation operators and then to pseudo-spin
operators similar to the ones used by Anderson in connection with
superconductivity. We thus take into account the coherence
between antiparallel electrons in a self-consistent manner. We
exploit the similarity between the linear antiferromagnet and
superconductivity theory to obtain the ground-state energy and the
excitation spectrum for arbitrary δ and temperature. We thus
obtain a complete thermodynamic description. In particular, we
calculate the paramagnetic susceptibility and compare it with
experiment.

At $0°K$, the solutions we present agree with or improve
upon previous calculations, for either the regular ($\delta = 0$) or the

alternating ($\delta \neq 0$) antiferromagnet, of the ground-state energy, the excitation spectrum, and the short-range order. Using the finite temperature extension of the theory, we find good agreement between the calculated and the experimental paramagnetic susceptibilities of organic crystals whose structures, so far as spin properties are concerned, may be approximated by either the regular or the alternating antiferromagnet. The temperature dependence of the excitation energies, a many-body effect describing the decrease of coherence between antiparallel electrons with increasing temperature, agrees with the observed behavior of the singlet-triplet energy gap in paramagnetic exciton systems. Thus we obtain the extension of exciton theory to arbitrary temperature and alternation. The electron pairs forming triplet excitations are, for any alternation, increasingly separated at high temperatures, where, as expected, the electrons behave like a paramagnetic gas.

I. Introduction

We consider a system of N electrons, each tightly localized on a fixed site. The N sites, which may be either atoms or molecules, form a one-dimensional array; they are numbered consecutively from 1 to N, and they form a ring, so that site N+1 is the same as site 1. We consider the exchange interactions between neighboring electrons. The hamiltonian for the spin system is

$$ H = \sum_{j=1}^{N} J_{j,j+1} \left\{ \vec{S}_j \cdot \vec{S}_{j+1} - \frac{1}{4} \right\} . \qquad \text{I.1}$$

Here $\vec{S}_j = \frac{1}{2}$ is the spin associated with the electron on the jth site. $J_{j,j+1}$ is the exchange integral for the electrons on sites j and j+1. In the case of antiferromagnetic coupling, to which we restrict the discussion, the exchange integrals are positive. For the particular case of alternating exchange integrals, the hamiltonian is

$$ H = \sum_{j=1}^{N/2} \left\{ J(1+\delta) \vec{S}_{2j} \cdot \vec{S}_{2j+1} + J(1-\delta) \vec{S}_{2j} \cdot \vec{S}_{2j-1} - \frac{J}{2} \right\}, \qquad \text{I.2}$$

where $-1 \leq \delta \leq 1$ and δ is the "alternation" parameter. Equation I.2 is the hamiltonian for the one-dimensional alternating Heisenberg antiferromagnet. The purpose of this paper is to investigate its solutions.

The regular ($\delta = 0$) Heisenberg antiferromagnet has been investigated many times, and some of its properties have been found exactly. The treatments fall into two classes. The first

class is based on the formalism invented by Bethe (1), in one of the first discussions of the linear antiferromagnet. The second class is based on the reduction of the hamiltonian to Fermi operators (2-5). There are a number of difficulties associated with both methods, and it is not difficult to find contradictory statements about the properties of the regular antiferromagnet in the literature. The discrepancies, for the most part, hinge on whether or not there is a gap in the excitation spectrum. We shall have to adopt a definite point of view in this matter in order to discuss the properties of the regular antiferromagnet at finite temperatures. Although we shall not be able to make rigorous statements, we shall present at least a partial reconciliation.

Bethe's formalism gives, in several instances, exact results in the limit of an infinite ($N \rightarrow \infty$) system. Thus Hulthén found the ground-state energy of the regular antiferromagnet (6), and Des Cloizeaux and Pearson found a class of elementary triplet excitations and no energy gap (7). Griffiths extended their results to excitations of higher multiplicity and attempted to find the properties of the regular antiferromagnet at finite temperatures (8,9). In Bethe's formalism, there are two classes of solutions. For the case of antiferromagnetic coupling, the lowest energy state for a fixed total S_z always falls into the class which is mathematically tractable (1,8). Griffiths assumed that he need consider only this class of solutions, which include the ground state and the excitations found by Des Cloizeaux and

Pearson, to construct the partition function. He then showed that in fact the finite-temperature properties of the regular antiferromagnet seem to depend entirely on the other class of solutions (9).

In order to obtain, at least approximately, properties of the regular antiferromagnet for which the Bethe formalism was entirely unsuited, Anderson (10) and Marshall (11,12) extended spin-wave theory, which is entirely adequate for the case of ferromagnetic coupling ($J < 0$), to antiferromagnetic coupling ($J > 0$). Their formalisms, in terms of Bose operators, gave unexpectedly good results for the case of spin-$\frac{1}{2}$ particles, where drastic assumptions had to be made. Several authors then reduced the hamiltonian for the regular antiferromagnet to Fermi operators (2-5). Once end effects had been considered in detail (13), the hamiltonian could be expressed exactly in terms of Fermi operators. Approximations had to be introduced, however, because the hamiltonian could not be diagonalized. Several attempts to obtain solutions have been reported (5,13-16). These treatments yield approximate ground-state energies only. But they give an excitation spectrum. Since the problem has been reduced to that of an interacting system of fermions, it is straightforward to calculate the thermal properties of the spin system by using statistical mechanics.

The method we present falls into the second class. We express the hamiltonian, both for the regular and the alternating antiferromagnet, in terms of Fermi operators. We then introduce

a pseudo-spin formalism very similar to the one used by Anderson in connection with superconductivity (17). The hamiltonian, for the special case of antiferromagnetic coupling, is solved in a self-consistent molecular-field approximation, for arbitrary alternation and temperature.

The pseudo-spin formalism makes it possible to take into account the coherence between antiparallel electrons. That such coherence is important is evident from the simple example of two electrons on two sites. The ground state singlet function, $\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$ has lower energy than either of the product functions $\alpha_1\beta_2$ or $\beta_1\alpha_2$, in which each electron has fixed S_z on each site. Marshall (11) recognized that exchange between electrons with antiparallel spins is intrinsically more complicated than exchange between electrons with parallel spins, but did not incorporate this into his approximate treatment. We generalize the coherence between antiparallel spins to the case of many electrons. The solutions we obtain are therefore consistently better than is possible with just a Hartree-Fock molecular-field approximation (5,18,19).

We obtain solutions for arbitrary δ and temperature. In the limit of $0°K$ and $\delta = 0$, that is, for the regular antiferromagnet at absolute zero, we reproduce the results obtained by Ruijgrok and Rodriguez (14) by a variational calculation. We then find, using second-order perturbation theory, the ground-state energy to within 0.1% of the exact value. In the other limit, for strong alternation ($\delta = \pm 1$), we have non-interacting systems of

two electrons on two sites. The ground-state energy is then given exactly by the pseudo-spin formalism.

Organic molecular crystals have been of considerable experimental and theoretical interest recently (20). Many of these crystals, as far as their spin properties are concerned, are believed to be composed of essentially non-interacting chains (21). The components of the chains are ions or free radicals, on each of which there is a tightly-bound unpaired electron. If we consider the molecular integrals J to be parameters to be determined experimentally, the hamiltonian for the tightly-bound unpaired electrons is just that of the one-dimensional alternating antiferromagnet. Crystals corresponding to both of the extreme cases δ = 0 and δ = 1 have been postulated (22,23), as well as crystals corresponding to intermediate cases (24, 25).

The most successful theory of the spin properties of these organic crystals is due to Lynden-Bell and McConnell (24). The model we present reduces, for low temperatures and large alternation, to their treatment. We also obtain the temperature range in which it is a good approximation to assume, as they did, that exciton-exciton interactions are negligible. We obtain the paramagnetic contribution to the magnetic susceptibility of organic crystals exhibiting exciton behavior. Our results agree with experiment both in the case of the regular and the strongly alternating antiferromagnet. We also find the decrease in the singlet-triplet energy gap with increasing temperature that has been observed experimentally for strongly alternating systems (33).

In section II, we transform the hamiltonian of the Heisenberg antiferromagnet several times and finally express it, for arbitrary alternation, in terms of pseudo-spin operators. In section III, we present the self-consistent solution for the alternating antiferromagnet at $0°K$. In section IV, we extend the discussion to finite temperatures and find an expression for the magnetic susceptibility. Results are presented in section V. The results are compared with previous theories and with experiment in section VI.

II. Transformations of the Hamiltonian

The alternating antiferromagnet has translational symmetry.
The wave number k is therefore a good quantum number. In addition,
for any δ, the hamiltonian is isotropic. The total spin and the z-
component of the total spin are therefore good quantum numbers.
Finally, except for the arbitrary labelling of the sites, the
hamiltonian is invariant under $\delta \to -\delta$. We therefore consider only
$0 \le \delta \le 1$.

We first express the hamiltonian for the alternating anti-
ferromagnet in terms of Pauli operators. We define $P_j^+ \equiv S_j^+$; as
usual, $S_j^+ = S_j^x + iS_j^y$; x, y, z form an arbitrary cartesian coordinate
system. Then $P_j = S_j^-$ and, for spin $\frac{1}{2}$, $S_j^z = -\frac{1}{2} + P_j^+ P_j$. It is easy
to verify that any combination of P_j^+, P_j commutes for different
sites. For the same site,

$$[P_j^+, P_j^+]_- = [P_j, P_j]_- = 0 \ , \ [P_j^+, P_j]_+ = 0, \qquad \text{II.1}$$

where $[\ ,\ ]_-$ and $[,]_+$ denote the commutator and the anticommutator,
respectively. The hamiltonian in terms of the Pauli operators is

$$\mathcal{H} = \sum_j \{ -JP_j^+ P_j + \tfrac{1}{2}J(P_j^+ P_{j+1} + P_{j+1}^+ P_j) + \tfrac{1}{2}J\delta(-1)^j($$
$$P_j^+ P_{j+1} + P_{j+1}^+ P_j) + J(1 + \delta(-1)^j) P_j^+ P_j P_{j+1}^+ P_{j+1} \}. \qquad \text{II.2}$$

The sums are from j = 1 to j = N. We may interpret P_j^+, P_j as
creation and annihilation operators. P_j^+ creates a unit of z-com-
ponent of spin and P_j annihilates a unit of z-component of spin
on the site j. We choose to work with the complete set of states

in which the z-component of spin is given on each site. The
vacuum state is defined to be the state in which $S_z = -\frac{1}{2}$ on all
the sites. A "particle" in state j then means that site j has
$S_z = +\frac{1}{2}$.

We next transform to Fermi operators. The creation and
annihilation operators f_n^+, f_n create and annihilate, respectively,
a unit of z-component of spin on site n,

$$f_n^+ \equiv (-1)^{\sigma_n} P_n^+$$
$$f_n = (-1)^{\sigma_n} P_n \, , \qquad \text{II.3}$$

where

$$\sigma_n \equiv \sum_{j=1}^{n-1} P_j^+ P_j = \sum_{j=1}^{n-1} f_n^+ f_n \, . \qquad \text{II.4}$$

The anticommutation relations are

$$[f_n^+ , f_{n'}^+]_+ = [f_n, f_{n'}]_+ = 0 \, , \quad [f_n^+ , f_{n'}]_+ = \delta_{nn'} \, . \quad \text{II.5}$$

The operators σ_n, which appear as exponents, in general make the
transformation useless. However, when an operator contains at
most interactions between sites which may be labelled by consecu-
tive integers, the factors $(-1)^{\sigma_n}$ all become unity. The hamil-
tonian operator for the alternating antiferromagnet has this
property. Writing S_z and S^2 in terms of Pauli operators, we see
that only the former involves at most interactions between con-
secutively labelled sites:

$$S_z = \sum_j S_j^z = -\tfrac{1}{2}N + \sum_j P_j^+ P_j \,,$$

$$S^2 = S_z(S_z - 1) + S^+ S^- = S_z(S_z - 1) + \sum_{jj'} P_j^+ P_{j'} \,. \qquad \text{II.6}$$

Our inability to find a simple expression for S^2 in terms of Fermi operators will make it difficult to classify our final states by the total spin angular momentum. As discussed by Marshall (11), the ground state is a singlet for antiferromagnetic coupling. There are then $\tfrac{1}{2}N$ particles; S_z vanishes. The expectation value of S^2 is negligible (11), of order N rather than N^2, for any state with $\tfrac{1}{2}N$ sites with $S_z = \tfrac{1}{2}$ and $\tfrac{1}{2}N$ sites with $S_z = -\tfrac{1}{2}$, as is also evident from II.6. We use a linear combination of states with vanishing total S_z to construct an approximate ground state, with $< S^2 >/N^2 \lesssim 1/N$. The apparent loss of the quantum number S is the biggest disadvantage of the transformation to Fermi operators. Nevertheless, using other results, we may associate a fixed S with any state.

End effects, that is, the interactions between sites N and 1, may be included exactly (13,26). We use the notation of reference 26 and summarize the conclusions. For simplicity, we always take N to be even, so that the ground state is a singlet. We define the total number operator σ,

$$\sigma = \sum_{j=1}^{N} f_n^+ f_n \qquad \text{II.7}$$

As shown in references 13 and 26, we must specify whether the expectation value of σ is even or odd in the ground state. The parity α is defined to be 1, 2 for σ odd, even. Since $\sigma = S_z + \frac{1}{2}N$, σ (and hence α) is a good quantum number; we may work in the subspace with fixed energy and parity.

The exact hamiltonian for the alternating antiferromagnet, in terms of fermion operators, is

$$H^{(\alpha)} = \sum_{n=1}^{N} -J f_n^\dagger f_n + \sum_{n=1}^{N-1} \tfrac{1}{2} J (1 + \delta(-1)^n)(f_n^\dagger f_{n+1} + f_{n+1}^\dagger f_n)$$

$$-(-1)^\alpha \tfrac{1}{2} J (1 + \delta(-1)^N)(f_N^\dagger f_1 + f_1^\dagger f_N) + \sum_{n=1}^{N} J(1 + \delta(-1)^n) f_n^\dagger f_n f_{n+1}^\dagger f_{n+1}. \qquad \text{II.8}$$

Even solutions of $H^{(2)}$ and odd solutions of $H^{(1)}$ are solutions of the hamiltonian.

The translational invariance of the antiferromagnet may be used to further reduce the hamiltonian to more nearly diagonal form. The operators $a_k^\dagger$, a_k create and annihilate, respectively, a unit of z component of spin in a state with momentum $\hbar k$.

$$a_k^\dagger \equiv \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikn} f_n^\dagger$$

$$a_k = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{-ikn} f_n . \qquad \text{II.9}$$

The usual anticommutation relations for Fermi operators are obeyed:

$$[a_k^\dagger, a_{k'}^\dagger]_+ = [a_k, a_{k'}]_+ = 0, \qquad [a_k^\dagger, a_{k'}]_+ = \delta_{kk'}. \qquad \text{II.10}$$

The inverse relations are

$$f_n^+ = \frac{1}{\sqrt{N}} \sum_k e^{-ikn} a_k^+$$

$$f_n = \frac{1}{\sqrt{N}} \sum_k e^{ikn} a_k \, .$$

II.11

The values of k depend on the parity. As shown in reference 26, they may be found from the condition

$$e^{ikN} = -(-1)^\alpha \, .$$

II.12

Since N is even by hypothesis, there are two cases:

$$\alpha = 1 \qquad k = 0, \pm \frac{2\pi}{N}, \pm \frac{4\pi}{N}, \ldots, \pm \frac{(N-2)\pi}{N}, +\pi,$$

$$\alpha = 2 \qquad k = \pm \frac{\pi}{N}, \pm \frac{3\pi}{N}, \ldots, \pm \frac{(N-1)\pi}{N} \, .$$

II.13

The transformed hamiltonian is

$$H^{(\alpha)} = -\sum_k^\alpha J \left\{ (1-\cos k) a_k^+ a_k + \frac{\delta}{2} (a_{k+\pi}^+ a_k e^{-ik} + a_k^+ a_{k+\pi} e^{ik}) \right\}$$

$$+ \sum_{\substack{k_1 k_2 k_3 k_4 \\ k_1 + k_2 = k_3 + k_4}}^\alpha \frac{J}{N} e^{i(k_3 - k_2)} a_{k_1}^+ a_{k_2}^+ a_{k_3} a_{k_4} + \sum_{\substack{k_1 k_2 k_3 k_4 \\ k_1 + k_2 = k_3 + k_4 + \pi}}^\alpha \frac{J\delta}{N} e^{i(k_3 - k_2)} a_{k_1}^+ a_{k_2}^+ a_{k_3} a_{k_4} \, .$$

II.14

" $\sum_k^\alpha$ " denotes that the sum runs over the values of k appropriate to the parity α.

The quadratic part of the hamiltonian is diagonal only for the regular (δ = 0) antiferromagnet. For δ > 0, the lattice has $\frac{1}{2}$N equivalent pairs of sites, rather than N equivalent sites. Thus a linear combination of the operators in equation II.9 is required to diagonalize the quadratic part of the hamiltonian.

The excitation spectrum breaks up into two branches, separated by an energy gap, as in the familiar case of lattice vibrations. Before we finish the diagonalization of the quadratic terms, we examine several c-number terms in the interaction (the quartic) part of the hamiltonian. We pick out the terms that have non-vanishing expectation values in the ground state for the best zeroth-order functions.

The excitation density ρ is, by definition,

$$\rho \equiv \frac{\sigma}{N} = \frac{1}{N} \sum_n f_n^+ f_n = \sum_k^\alpha a_k^+ a_k .$$ II.15

Since $S_z = N(\rho - \frac{1}{2})$ and S_z commutes with the hamiltonian, ρ is a good quantum number. We choose, therefore, a representation in which ρ and $H^{(\alpha)}$ are simultaneously diagonal. The parity is then also diagonal, since $\alpha = 1, 2$ for σ odd, even. The term $k_2 = k_3$ in the first quartic term of II.14 involves only ρ; it is the Hartree term,

$$\sum_{kk'}^\alpha \frac{J}{N} a_k^+ a_k a_{k'}^+ a_{k'} = JN\rho^2 .$$ II.16

The exchange term is the term $k_1 = k_3$ in the first quartic term of II.14,

$$\sum_{\substack{kk' \\ k \neq k'}}^\alpha \frac{J}{N} \cos(k-k') a_{k'}^+ a_k^+ a_{k'} a_k = -\sum_{\substack{kk' \\ k \neq k'}}^\alpha \frac{J}{N} \left\{ \cos k \cos k' a_k^+ a_k a_{k'}^+ a_{k'} + \sin k \sin k' a_k^+ a_k a_{k'}^+ a_{k'} \right\} .$$ II.17

As usual, the exchange, or the Fock, term has the opposite sign from the direct, or the Hartree, term. The antiferromagnet has symmetry in k and -k; that is, clockwise and counterclockwise motion are equivalent except for direction. The ground-state expectation value of the second term in II.17 therefore vanishes. We define the c-number β

$$\beta \equiv - \frac{2}{N} \left\langle \sum_k^{\alpha} \cos k \, a_k^+ a_k \right\rangle . \qquad\qquad \text{II.18}$$

The ground-state expectation value is understood. The expectation value of the exchange term is $-1/4NJ\beta^2$. Since we have not omitted a value of k in the definition of β, this result is correct to order $1/N$. The expectation value of $a_k^+ a_k$, the number operator, is in general temperature-dependent. β is therefore a function of temperature. The direct and the exchange terms are the only terms in the quartic part of the hamiltonian that include only the number operators. ρ and β thus correspond to the terms kept in a Hartree-Fock calculation.

We have yet to consider the coherence between electrons with antiparallel spins. It is evident from II.14 that, for $\delta >$ 0, electrons with unlike S_z, in states k and k + π, are to be paired. Self-consistency then requires that we treat as c-numbers all terms in the quartic part of the hamiltonian which involve the operators $a_k^+ a_{k+\pi}$. We shall see that, even for the regular ($\delta = 0$) antiferromagnet, there is such pairing, at least at low temperatures. In other words, the ground-state expectation values of the

operators $a_k^+ a_{k+\pi}$ do not vanish, at low temperatures, for any alternation. These operators, as well as the number operators, must be included in a self-consistent treatment.

It is straightforward, but slightly tedious, to pick out the terms in $a_k^+ a_{k+\pi}$ in the quartic part of the hamiltonian. We obtain, using II.15,

$$H^{(\alpha)} = - NJ\rho(1-\rho) + H_{red}^{(\alpha)} + V^{(\alpha)},$$ II.19

where

$$H_{red}^{(\alpha)} = J \sum_k^\alpha \left\{ \cos k \, a_k^+ a_k - \delta i \sin k \, a_k^+ a_{k+\pi} \right\}$$

$$- \frac{J}{N} \sum_{\substack{kk' \\ k \neq k'}}^\alpha \left\{ \cos k \cos k' \, a_k^+ a_k a_{k'}^+ a_{k'} + \right.$$ II.20

$$(1 + \sin k \sin k') a_{k+\pi}^+ a_k \, a_{k'}^+ a_{k'+\pi} + 2\delta i \cos k \sin k' \, a_k^+ a_k a_{k'}^+ a_{k'+\pi}$$

$$\left. + \sin k \sin k' \, a_k^+ a_k a_{k'}^+ a_{k'} + \cos k \cos k' \, a_{k+\pi}^+ a_k a_{k'}^+ a_{k'+\pi} \right\}$$

and

$$V^{(\alpha)} = \frac{J}{N} \sum_{\substack{k_1 k_2 k_3 k_4 \\ k_1 + k_2 = k_3 + k_4 \\ k_2 \neq k_3, k_4 ; \; k_2 \neq k_3+\pi, k_4+\pi}}^\alpha e^{i(k_3 - k_2)} a_{k_1}^+ a_{k_2}^+ a_{k_3} a_{k_4} + \frac{J\delta}{N} \sum_{\substack{k_1 k_2 k_3 k_4 \\ k_1 + k_2 = k_3 + k_4 + \pi \\ k_1 \neq k_3, k_4, k_3+\pi, k_4+\pi}}^\alpha e^{i(k_3 - k_2)} a_{k_1}^+ a_{k_2}^+ a_{k_3} a_{k_4}.$$ II.21

No approximations of any kind have been made thus far. The hamiltonian II.19 is exactly equivalent to the hamiltonian I.2 for the alternating antiferromagnet, provided that we take the even solution of $H^{(2)}$ and the odd solutions of $H^{(1)}$. The reduced

hamiltonian, equation II.20, is formally very similar to the reduced hamiltonian solved in the B.C.S. theory of superconductivity (27).

We define two c-numbers associated with the operators $a_k^+ a_{k+\pi}$:

$$\Delta \equiv \frac{2}{N} \left\langle \sum_k^\alpha a_k^+ a_{k+\pi} \right\rangle \qquad \qquad \text{II.22}$$

$$\xi \equiv \frac{2}{N} \left\langle \sum_k^\alpha i \sin k \, a_k^+ a_{k+\pi} \right\rangle. \qquad \qquad \text{II.23}$$

Since all the k values are included in the definitions of Δ and ξ, the reduced hamiltonian in terms of Δ, ξ, and β is correct to order $1/N$. Δ and ξ are, like β, temperature-dependent. We shall see that Δ represents, roughly, the coherence between antiparallel electrons in the case of the regular or the weakly alternating antiferromagnet, while ξ represents, roughly, the coherence for a strongly alternating lattice. The last two terms in II.20 both have vanishing expectation values in the ground state. We have already shown that the expectation value of the first term vanishes. We show that the expectation value of the second vanishes after we transform to pseudo-spin operators.

We wish to obtain self-consistent solutions for $H_{red}^{(\alpha)}$, β, Δ, and ξ. In general, this is no easy task, as is suggested, for instance, by the complexities of spin-wave theory, for ferromagnetic coupling, in the case of an arbitrary number of reversed spins. For antiferromagnetic coupling, it is known that the ground

state is a singlet for even N (11). There are $\frac{1}{2}N$ reversed spins,
so that $\rho = \frac{1}{2}$. For $\rho = \frac{1}{2}$, in the limit of large N, it is possible
to solve $\mathcal{H}_{red}^{(\alpha)}$ exactly. It is essential that we have J > 0, so
that we shall be concerned only with antiferromagnetic coupling.
Also, since we must have ρ very nearly equal to $\frac{1}{2}$, we consider
only the case of no applied external magnetic field. It is
straightforward to generalize to the case of a weak, constant,
external magnetic field.

Each fermion is a filled state of II.20 and represents a
spin with $S_z = \frac{1}{2}$, while each empty state represents a spin with
$S_z = -\frac{1}{2}$. For $\rho = \frac{1}{2}$, or $\frac{1}{2}N$ fermions, the ground state is the
state in which the states $-\pi < k < -\frac{1}{2}\pi$ and $\frac{1}{2}\pi < k < \pi$ are full.
We have already chosen the zero of energy for $\mathcal{H}_{red}^{(\alpha)}$ at the Fermi
level when $\rho = \frac{1}{2}$. We now restrict the discussion to a subspace
of the total set of k states. We consider the subspace in which
the states k and $k + \pi$ have, for all k, unlike S_z. It is easy to
show that the ground state in the Hartree-Fock approximation lies
in this subspace. We call this state the unrotated Fermi state,
for reasons which will become evident later. The exact ground
state of $\mathcal{H}_{red}^{(\alpha)}$ also lies in this subspace.

We now define pseudo-spin operators analogous to the ones
introduced by Anderson in connection with superconductivity (17).
There are, for both $\alpha = 1$ and $\alpha = 2$, $\frac{1}{2}N$ states $-\frac{1}{2}\pi < k < \frac{1}{2}\pi$. We
use these k-values to label the pair states k, $k + \pi$. Each pair
state is considered to have pseudo-spin $S_z = \frac{1}{2}$ if the states
(k, $k + \pi$) are (empty, full) and pseudo-spin $S_z = -\frac{1}{2}$ if the states

(k, k + π) are (full, empty). Thus, for instance, in the unrotated Fermi state, all the pseudo-spins have $S_z = +\frac{1}{2}$. If the pair state k, k + π has pseudo-spin $S_z = +\frac{1}{2}$ and we operate with $a_k^+ a_{k+\pi}$, we obtain pseudo-spin $S_z = -\frac{1}{2}$; if the pair state has pseudo-spin $S_z = -\frac{1}{2}$, the operator $a_k^+ a_{k+\pi}$ annihilates the state. Therefore $a_k^+ a_{k+\pi}$ behaves like a lowering operator for pseudo-spins. It is easy to verify that, in the subspace spanned by k, k + π with unlike z-components of real spin, for $-\frac{1}{2}\pi < k < \frac{1}{2}\pi$,

$$\sigma_k^3 = -(a_k^+ a_k - a_{k+\pi}^+ a_{k+\pi})$$
$$\tfrac{1}{2}\sigma_k^+ = a_{k+\pi}^+ a_k$$
$$\tfrac{1}{2}\sigma_k^- = a_k^+ a_{k+\pi} ,$$

II.24

where the σ's are the well-known Pauli spin operators. As usual, $\sigma_k^+ = \sigma_k^x + i\sigma_k^y$ and $\sigma_k^- = \sigma_k^x - i\sigma_k^y$. The Pauli operators also obey the usual commutation relations,

$$[\sigma_k^i, \sigma_{k'}^j]_- = 2i\sigma_k^l \delta_{kk'} , \quad \text{i,j,l cyclic.} \qquad \text{II.25}$$

The expressions for $H_{red}^{(\alpha)}$, β, Δ, and ξ all have simple forms in terms of the pseudo-spin operators:

$$\beta = \frac{2}{N} \left\langle \sum_k^\alpha \cos k \, \sigma_k^3 \right\rangle \qquad \text{II.26a}$$

$$\Delta = \frac{2}{N} \left\langle \sum_k^\alpha \sigma_k^x \right\rangle \qquad \text{II.26b}$$

$$\xi = \frac{2}{N} \left\langle \sum_k^\alpha \sin k \, \sigma_k^y \right\rangle \qquad \text{II.26c}$$

$$H_{red}^{(\alpha)} = -\sum_k^\alpha J \left\{ \left(1 + \frac{1}{N} \sum_{\substack{k' \\ k' \neq k}}^\alpha \cos k' \sigma_{k'}^3 \right) \cos k \sigma_k^3 + \delta \sin k \sigma_k^y \right\}$$

$$-\frac{J}{N} \sum_{\substack{kk' \\ k \neq k'}}^\alpha \left\{ \sigma_k^x \sigma_{k'}^x + \sin k \sin k' \sigma_k^y \sigma_{k'}^y + 2\delta \cos k \sin k' \sigma_k^3 \sigma_{k'}^y \right\} \qquad \text{II.26d}$$

In equations II.26a-d, the range of k is from $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$, running over the values specified in II.13. We show now that the last term in II.20 has vanishing ground-state expectation value. Since $\sigma_k^y = i(a_k^+ a_{k+\pi} - a_{k+\pi}^+ a_k)$,

$$-\frac{J}{N} \sum_{\substack{kk' \\ k \neq k'}}^\alpha \cos k \cos k' a_{k+\pi}^+ a_k a_{k'}^+ a_{k'+\pi} = -\frac{J}{N} \sum_{\substack{kk' \\ k \neq k'}}^\alpha \cos k \cos k' \sigma_k^y \sigma_{k'}^y , \qquad \text{II.27}$$

where, in the first term, the range of k,k' is from $-\pi$ to π and, in the second, from $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$. Since σ_k^y is odd under time reversal, the expectation value of $\frac{1}{N} \sum_k^\alpha \cos k \sigma_k^y$ vanishes in the ground state.

We summarize briefly the development in this section. We rewrote the hamiltonian (equation I.2) for the one-dimensional alternating antiferromagnet in terms of (a) Pauli operators, (b) Fermi operators in position space, and (c) Fermi operators in momentum space. We obtained the exact expressions II.19-21. We then used the good quantum numbers at our disposal, defined c-numbers, and, for the special case $\rho = \frac{1}{2}$, rewrote a part of the hamiltonian in terms of pseudo-spin operators (equations II.26a-d). We now ignore $V^{(\alpha)}$ in II.19) and solve the remaining part of the hamiltonian exactly in the limit $N \to \infty$.

III. Solution of $H_{red}^{(\alpha)}$ at Absolute Zero

We seek the $T = 0°K$ solution to equations II.26a-d. Instead of finding explicitly the Bogoliubov canonical transformation (29) that diagonalizes $H_{red}^{(\alpha)}$, we use the equivalent, and for our purposes more convenient, formalism of Anderson (17). $H_{red}^{(\alpha)}$ may be written in terms of a pseudo-field $\vec{B}_k$

$$H_{red}^{(\alpha)} = - \sum_k^{\alpha} \vec{B}_k \cdot \vec{\sigma}_k \qquad \text{III.1}$$

The components of the pseudo-field $\vec{B}_k$ are obtained by differentiating II.26d with respect to σ_k^z, σ_k^y, and σ_k^x, respectively,

$$B_k^3 = J(\jmath + \delta\xi)\cos k \qquad \text{III.2a}$$

$$B_k^4 = J(\delta\jmath + \xi)\sin k \qquad \text{III.2b}$$

$$B_k^x = J\Delta, \qquad \text{III.2c}$$

where $\jmath = 1 + \beta$. The pseudo-field components depend explicitly on the parity, since $\jmath$, ξ, and Δ depend on α. Each pseudo-spin is to be quantized parallel to the average field it sees. The molecular field is treated as a classical vector (30). It turns out that for large δ, Δ vanishes. We therefore consider separately the two cases $\Delta^2 > 0$ and $\Delta^2 = 0$.

For case (a), $\Delta^2 > 0$ and $0 \leq \delta \leq \delta_o$, where $\delta_o = 0.11905$ is the largest δ for which $\Delta > 0$. It is evident from figure 1 that:
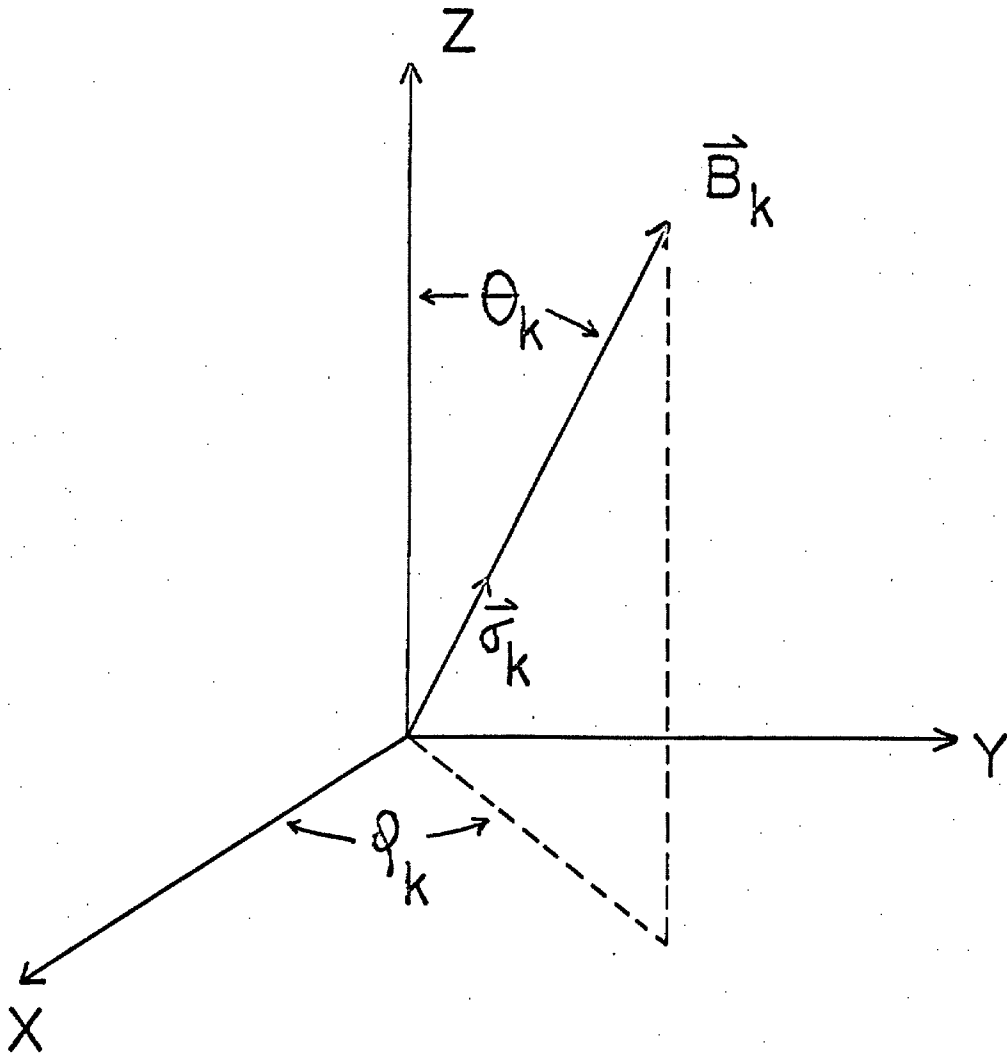
Fig. 1. Method of solving $\mathcal{H}_{red}^{(\alpha)}$. The pseudo-spins are quantized along the molecular field.

$$\tan \varphi_k = \frac{B_k^y}{B_k^x} = \frac{(\delta_\delta + \xi)}{\Delta} = \frac{\sigma_k^y}{\sigma_k^x} \qquad \text{III.3}$$

and that

$$\tan \Theta_k = \frac{B_k^\perp}{B_k^\delta} = \frac{\left((B_k^x)^2 + (B_k^y)^2\right)^{\frac{1}{2}}}{B_k^\delta} = \frac{\sigma_k^\perp}{\sigma_k^\delta} . \qquad \text{III.4}$$

In the ground state, the pseudo-spins are along the molecular field. Since $\sigma_k^z = \cos \Theta_k$, $\sigma_k^y = \sin \Theta_k \sin \varphi_k$, and $\sigma_k^x = \sin \Theta_k \cos \varphi_k$, we obtain from II.26a-c, II.3-4

$$\beta = \delta - 1 = \frac{2}{N} \frac{(\delta + \delta\xi)q}{\sqrt{(1-\delta^2)(\delta^2 - \xi^2)}} \sum_{k=-\frac{\pi}{2}}^{\frac{\pi}{2}k} \frac{\cos^2 k}{\sqrt{1-q^2\sin^2 k}} , \qquad \text{III.5a}$$

$$1 = \frac{2}{N} \frac{q}{\sqrt{(1-\delta^2)(\delta^2 - \xi^2)}} \sum_k^\alpha \frac{1}{\sqrt{1-q^2\sin^2 k}} , \qquad \text{III.5b}$$

$$\xi = \frac{2}{N} \frac{(\xi + \delta_\delta)q}{\sqrt{(1-\delta^2)(\delta^2 - \xi^2)}} \sum_k^\alpha \frac{\sin^2 k}{\sqrt{1-q^2\sin^2 k}} , \qquad \text{III.5c}$$

where, for $\Delta^2 > 0$,

$$q^2 = \frac{(1-\delta^2)(\delta^2 - \xi^2)}{\Delta^2 + (\delta + \delta\xi)^2} < 1. \qquad \text{III.6}$$

In the limit of an infinite system ($N \to \infty$), the sums may be replaced by integrals. δ, Δ, and ξ are then exact, and they no longer depend on the parity. III.5a-c, III.6 then reduce to a

set of three coupled integral equations,

$$\frac{2}{\pi\sqrt{(1-\delta^2)(\gamma^2-\xi^2)}} = \frac{1}{q\,K(q)}\,,$$
III.7a

$$\xi = \frac{(\xi+\delta\gamma)}{q^2 K(q)}\,D(q)\,,$$
III.7b

$$\beta = \gamma-1 = \frac{(\gamma+\delta\xi)}{q\,K(q)}\left\{q K(q) - \frac{D(q)}{q}\right\}.$$
III.7c

Here $K(q)$ and $E(q)$ are the complete elliptic integrals of the first and second kind (31), respectively, and $D(q) = K(q) - E(q)$. ξ and γ are eliminated. The resulting self-consistency, or master, equation is

$$\frac{q\pi}{2} = D(q)\left\{1 + \delta^2\left[\left(\frac{\pi q}{2(q^2 K(q)-D(q))}\right)^2 - 1\right]\right\}^{\frac{1}{2}}.$$
III.8

After solving III.8 for q, we have the full solution, since

$$\gamma = \frac{q^2 K(q)}{D(q)(1-\delta^2)}\,,$$
III.9a

$$\xi = \frac{\delta\gamma\,D(q)}{q^2 K(q)-D(q)}\,,$$
III.9b

$$\Delta = \left\{\frac{(1-\delta^2)(\gamma^2-\xi^2)}{q^2} - (\gamma+\delta\xi)^2\right\}^{\frac{1}{2}}.$$
III.9c

The contribution of the term in ρ, $-1/4NJ$, in II.19 is included in all the energy results we give. The ground-state energy is,

from II.26d, III.9a-c,

$$E^{(a)}/JN = -\frac{1}{4}K^2(q)\left\{\frac{4}{\pi^2} + \frac{\delta^2}{(1-\delta^2)}\frac{q^4}{(q^2K(q)-D(q))^2}\right\}$$

$$= -\frac{1}{4}\left\{\gamma^2 + \Delta^2 + \xi^2 + 2\gamma\delta\xi\right\}. \qquad \text{III.10}$$

For the special case $\delta = 0$, the master equation and the ground-state energy are identical with the results obtained by Ruijgrok and Rodriguez via a variational calculation (14). It is evident from III.9b that $\xi = 0$ if $\delta = 0$; then $B_k^y = 0$ for all k. The pseudo-field lies entirely in the xz plane for the regular anti-ferromagnet, which is therefore characterized by one non-vanishing coherence parameter, Δ.

We consider next case (b), where $\Delta^2 = 0$. As shown in figure 2, the maximum value of δ for non-vanishing Δ is a decreasing function of temperature. Thus there exist ranges of δ in which we have two solutions; for instance, the range $0 \leq \delta \leq \delta_0$ at $0°K$. For an infinite system, we need consider only the solution corresponding to case (a) when there is a choice. Since the energy per site is slightly lower for case (a) than for case (b), the difference in the total energies becomes infinite as $N \to \infty$.

When $\Delta^2 = 0$, the coherence between antiparallel spins is due entirely to the alternation δ (ξ vanishes for $\delta = 0$). The pseudo-field is then entirely in the yz plane (cf. fig. 1), so that the only undetermined angle is Θ_k. Using the same argument as in case (a), we find
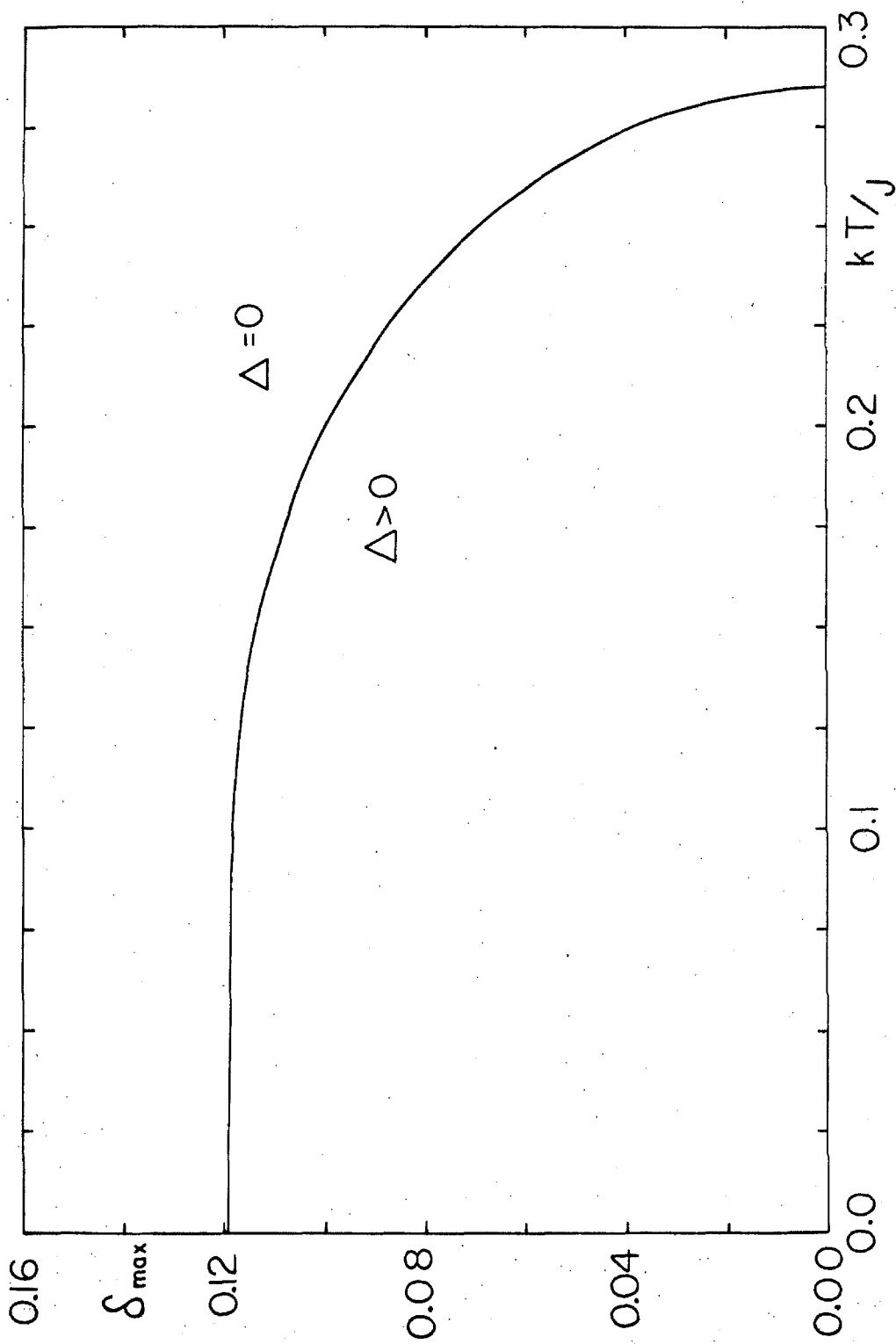
Fig. 2. The temperature dependence of δ_m, the largest δ for which $\Delta > 0$.

$$\tan \theta_k = \frac{B_k^y}{B_k^z} = \gamma \tan k = \frac{\sigma_k^y}{\sigma_k^z} \qquad \text{III.11}$$

where

$$\nu = \frac{\delta \gamma + \xi}{\gamma + \delta \xi} \qquad \text{III.12}$$

and $0 \le \gamma \le 1$. For the ground state, since $\sigma_k^z = \cos \theta_k$ and $\sigma_k^y = \sin \theta_k$, we have

$$\xi = \frac{2}{N} \sqrt{1-q^2} \sum_k^\alpha \frac{\sin^2 k}{\sqrt{1-q^2 \sin^2 k}}, \qquad \text{III.13a}$$

$$\beta = \gamma - 1 = \frac{2}{N} \sum_k^\alpha \frac{\cos^2 k}{\sqrt{1-q^2 \sin^2 k}}, \qquad \text{III.13b}$$

where $q^2 = 1 - \gamma^2$ and the sums are over the range $-\frac{1}{2}\pi < k < \frac{1}{2}\pi$. In the limit of an infinite system, the sums become integrals, and the master equation is

$$q^2 \left(\frac{\pi}{2} + K(q) \right) - D(q) = D(q) \frac{\sqrt{1-q^2}(1 - \delta \sqrt{1-q^2})}{\sqrt{1-q^2} - \delta}. \qquad \text{III.14}$$

The c-numbers ξ and γ are

$$\xi = \frac{2}{\pi} \frac{\sqrt{1-q^2}}{q^2} D(q), \qquad \text{III.15a}$$

$$\beta = \gamma - 1 = \frac{2}{\pi} \left(K(q) - \frac{D(q)}{q^2} \right). \qquad \text{III.15b}$$

The ground-state energy per site is

$$E^{(b)}/JN = -\frac{1}{4}\{\gamma^2 + \xi^2 + 2\delta\xi_\gamma\}. \qquad \text{III.16}$$

For both cases (a) and (b), the solution is equivalent to a Bogoliubov canonical transformation. We now obtain a B.C.S.-Bogoliubov-type ground-state function by means of a pseudo-spin rotation (30). The characteristic feature of the ground state is the coherence between filled and empty states (17,27,29). For the alternating antiferromagnet, the coherence is between electrons with unlike real S_z.

In the singlet ground state of the simple system of two electrons on two sites, $\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$, the z-component of spin for each electron has vanishing expectation value for each site. The product functions $\alpha_1\beta_2$ and $\beta_1\alpha_2$, on the other hand, give expectation values of $+\frac{1}{2}$ or $-\frac{1}{2}$ for the z-component of the spin of either electron on either site. The generalization to the case of many electrons on many sites is that the expectation value of S_k^z in the ground state is not just $\pm\frac{1}{2}$, but may assume intermediate values. The ground-state wave function for the states k, $k + \pi$, expressed in terms of spin functions, is $u_k\alpha_k\beta_{k+\pi} - v_k\beta_k\alpha_{k+\pi}$; however, u_k and v_k are in general not $1/\sqrt{2}$, although $/u_k/^2 + /v_k/^2$ is always equal to unity. The transformation back to spin operators is obtained by considering the states to be labelled in the order k_1, $k_1 + \pi$, k_2, $k_2 + \pi$, $\ldots k_{\frac{1}{2}N}$, $k_{\frac{1}{2}N} + \pi$, where $-\frac{1}{2}\pi < k_i < \frac{1}{2}\pi$ for all i and the order of the k_i's is arbitrary. The Fermi operators a_k^+, a_k are transformed back to spin

operators: $P_k^+ = (-1)^{\sigma_k} a_k^+$, $P_k = (-1)^{\sigma_k} a_k$, where σ_k is the partial

occupation number, defined by analogy with equation II.4. In the

subspace of different S_z for the states k, $k + \pi$, we always have

a phase factor -1 between the two states ($\alpha_k \beta_{k+\pi}$ and $\beta_k \alpha_{k+\pi}$) with

unlike S_z which may be constructed for the states k, $k + \pi$. By

constructing the ground-state wave function entirely out of such

components, we take maximum advantage of the coherence.

The unrotated Fermi state is

$$| \Phi_F^{(\alpha)} \rangle \; = \; \prod_{k=-\frac{\pi}{2}}^{\frac{\pi}{2}} {}^\alpha \; a_{k+\pi}^+ \; |0\rangle \, , \qquad\qquad \text{III.17}$$

where $/0 >$ is the vacuum state, in which all electrons have real

$S_z = -\frac{1}{2}$, and the $\frac{1}{2}N$ values of k in the product are those allowed

by II.13. The vacuum state is even. The operators a_k^+, a_k change

the number of fermions by one (or annihilate the state) and there-

fore change the parity of the state (26). Hence the unrotated

Fermi state is even ($\alpha = 2$) if $\frac{1}{2}N$ is even or odd ($\alpha = 1$) if $\frac{1}{2}N$ is

odd. In the former case, the ground state has an even number of

fermions, while in the latter an odd number. In terms of the

pseudo-spins, the unrotated Fermi state is the state in which all

the pseudo-spins have $S_z = \frac{1}{2}$. We have rotated the pseudo-spins in

both cases (a) and (b) so that they lie along the molecular field.

The ground-state function of $\mathcal{H}_{red}^{(\alpha)}$ is the state in which all the

pseudo-spins have $S_{z'} = \frac{1}{2}$, where z' is along the molecular field.

In general, we rotate through the angles ϕ_k and θ_k. The rotation

operator, in Messiah's notation (32), for ϕ_k, θ_k as defined in

figure 1, is

$$R(-\phi_k, \theta_k, 0) = e^{\frac{i}{2}\phi_k \sigma_k^3} e^{-\frac{i}{2}\theta_k \sigma_k^y}.$$

III.18

The ground state function for $\mathcal{H}_{red}^{(\alpha)}$ is, therefore,

$$|\Phi_o^{(\alpha)}\rangle = \prod_{k=-\frac{\pi}{2}}^{\frac{\pi}{2}\alpha} e^{\frac{i}{2}\phi_k \sigma_k^3} e^{-\frac{i}{2}\theta_k \sigma_k^y} |\Phi_F^{(\alpha)}\rangle,$$

III.19

where the values of k are those allowed by II.13. Using the properties of the spin operators and the relation $\sigma_k^+ |\Phi_F^{(\alpha)}\rangle = 0$, the ground state is

$$|\Phi_o^{(\alpha)}\rangle = \prod_k^{\alpha} \{\cos\tfrac{1}{2}\phi_k + (a_{k+\pi}^+ a_{k+\pi} - a_k^+ a_k)i\sin\tfrac{1}{2}\phi_k\} \times$$

$$\{\cos\tfrac{1}{2}\theta_k + \sin\theta_k\, a_k^+ a_{k+\pi}\} |\Phi_F^{(\alpha)}\rangle.$$

III.20

The parity of the ground state is the same as the parity of the unrotated Fermi state, since the two states differ from each other only by a rotation.

The lowest excited states of $\mathcal{H}_{red}^{(\alpha)}$ have one more or one fewer fermion than the ground state. They therefore have parity opposite to that of the ground state. The states with one more or one fewer fermion are degenerate. Their excitation energies are expected to be equal to the magnitude of the molecular field they see:

case (a) $\varepsilon_k^{(a)} \equiv |B_k| = J\sqrt{\Delta^2 + (\gamma + \delta\xi)^2}\sqrt{1 - q^2\sin^2 k}$, III.21a

case (b) $\varepsilon_k^{(b)} \equiv |B_k| = J(\gamma + \delta\xi)\sqrt{1 - q^2\sin^2 k}$. III.21b

We note that, because the parity has changed, the sums in III.5a-c and III.13a,b are over entirely different k-values for the excited states than for the ground state. In order to obtain excitation energies, the energy per site must be calculated to order 1/N, rather than just to order 1. The calculation to order 1/N is given in appendix I, for the special case of the regular ($\delta = 0$) antiferromagnet. As expected, the excitation energy III.21a is found. We therefore assume, as is usual in superconductivity theory (17), that III.21a,b represent the excitation energies in general. This assumption undoes the exact treatment of the end effects and is reasonable in the limit $N \to \infty$.

As a simple example, we consider the regular antiferromagnet. Since $\xi = 0$, $\phi_k = 0$ for all k. The ground state is, from III.20,

$$| \Phi_0^R \rangle = \prod_k^\alpha (\cos \tfrac{1}{2}\theta_k + \sin \tfrac{1}{2}\theta_k \, a_k^\dagger a_{k+\pi}) | \Phi_F \rangle. \qquad \text{III.22}$$

The u-v canonical transformation that diagonalizes $\mathcal{H}_{red}^{(\alpha)}$ is, for $\delta = 0$,

$$\eta_k^\dagger \equiv u_k a_k^\dagger + v_k a_{k+\pi}^\dagger$$

$$\eta_k = u_k a_k + v_k a_{k+\pi} , \qquad \text{III.23}$$

where $u_k = \cos\tfrac{1}{2}\theta_k = \frac{1}{\sqrt{2}}(1 + \frac{\jmath \cos k}{\sqrt{\Delta^2 + \jmath^2 \cos^2 k}})^{1/2}$, $v_k = \sin\tfrac{1}{2}\theta_k = \frac{1}{\sqrt{2}}(1 - \frac{\jmath \cos k}{\sqrt{\Delta^2 + \jmath^2 \cos^2 k}})^{1/2}$, $\theta_{k+\pi} = -\theta_k$, and $\eta_k^\dagger$, η_k are Fermi creation and annihilation operators. The variational calculation of Ruijgrok and Rodriguez (14) reduces to this transformation.

$\mathcal{H}_{red}^{(\alpha)}$ becomes

$$\mathcal{H}_{red}^{(\alpha)} - \frac{1}{4}NJ = -NJ\mathcal{E} + \sum_{k=-\frac{\pi}{2}}^{\frac{\pi}{2}\alpha} \varepsilon_k \left(\eta_k^+\eta_k + \eta_{k+\pi}\eta_{k+\pi}^+\right), \quad \text{III.24}$$

where $\mathcal{E} = \frac{K(q)}{\pi^2}$, $q = 0.9505389$, and $\varepsilon_k = J\sqrt{\Delta^2 + \gamma^2\cos^2 k}$.
These results may be obtained by setting $\delta = \xi = 0$ in case (a).
In the ground state, the states $-\pi < k < -\frac{1}{2}\pi$ and $\frac{1}{2}\pi < k < \pi$ are
filled. III.24 thus represents particles and holes with identical
excitation energies, as shown in figure 3. They are the elemen-
tary excitations of $\mathcal{H}_{red}^{(\alpha)}$ for the special case $\delta = 0$.

An equation like III.24 may be written for the alternat-
ing antiferromagnet. For case (a), we replace $\mathcal{E}$ by $E^{(a)}$ and ε_k by
$\varepsilon_k^{(a)}$ (III.10 and III.21a, respectively); for case (b), we replace
$\mathcal{E}$ by $E^{(b)}$ and ε_k by $\varepsilon_k^{(b)}$ (III.16 and III.21b, respectively). The
coefficient u_k and v_k of the fermion operators η_k^+, η_k are
functions of the alternation. The elementary excitations are
again particles and holes with identical dispersion relations.
At $0°K$, there is an energy gap in the spectrum of $\mathcal{H}_{red}^{(\alpha)}$ for any
δ. The excitation spectrum for arbitrary δ may be represented by
figure 3. For $\delta > 0$, there is an energy gap at any temperature,
as expected from the lower symmetry of the alternating antiferro-
magnet; figure 3 thus represents the excitations of $\mathcal{H}_{red}^{(\alpha)}$ for
$\delta > 0$ at any temperature.

The commutation relations

$$\left[S_3, \eta_k^+\right]_- = \eta_k^+ \quad, \quad \left[S_3, \eta_k\right]_- = -\eta_k \quad (-\tfrac{\pi}{2}<k<\tfrac{\pi}{2}) \quad \text{III.25}$$
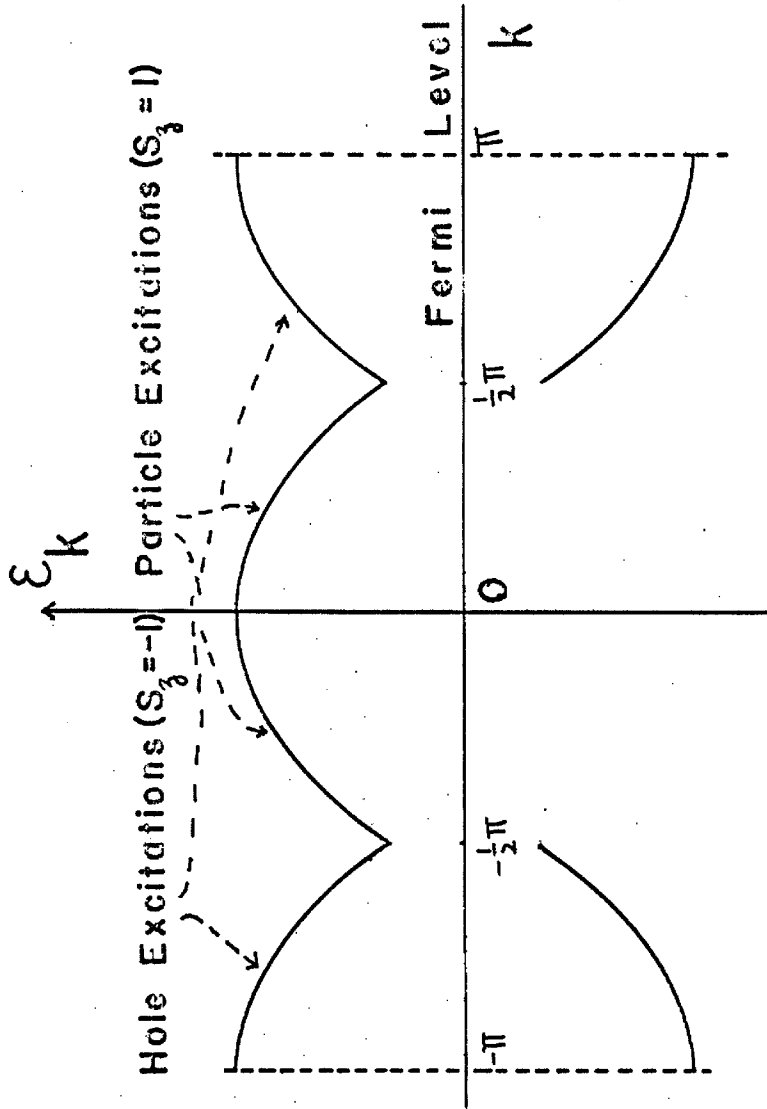
Fig. 3. Schematic excitation spectrum for the regular antiferromagnet at low temperature or for the alternating antiferromagnet at any temperature.

are valid for arbitrary values of u_k, v_k in III.23. We construct the arbitrary state $/X >$, $-\frac{1}{2}\pi < k_i < \frac{1}{2}\pi$,

$$|\chi\rangle = \eta_{k_1}^+ \eta_{k_2}^+ \cdots \eta_{k_n}^+ \eta_{k_{n+1}\pm\pi} \cdots \eta_{k_{n+m}\pm\pi} |\Phi_o^{(\alpha)}\rangle \qquad \text{III.26}$$

which has n particles and m holes. We now suppose that $/\Phi_o^{(\alpha)}>$ is the <u>exact</u> ground state function of the entire hamiltonian. For antiferromagnetic coupling, the ground state has vanishing real S_z. Using III.25 repeatedly, we have, in units of $\hbar$,

$$S_z |\chi\rangle = (n-m)|\chi\rangle . \qquad \text{III.27}$$

We may therefore associate a positive unit of z component of spin with particles and a negative unit of z component of spin with holes. This result is independent of the coefficients u_k, v_k (or, equivalently, of the angles ϕ_k, θ_k that describe the pseudo-spin rotation). It therefore holds for any alternation $0 \leq \delta \leq 1$.

We see above some of the differences between the exact and the reduced hamiltonian. Neither S_z nor S^2 commute with $\mathcal{H}_{red}^{(\alpha)}$, although the expectation value of S_z vanishes and that of S^2 is negligible in the ground state of $\mathcal{H}_{red}^{(\alpha)}$. S_z is related to the number operator: $S_z = N(\rho - \frac{1}{2})$. As in the theory of superconductivity, we have had to relax the condition that the number operator be a good quantum number. We only specify its expectation value.

IV. <u>Extension to Finite Temperatures</u>

The solution of a hamiltonian like $H_{red}^{(\alpha)}$ at finite temperatures has become a standard technique (30). We use again Anderson's pseudo-spin method. In effect, we are solving for the Gibbs free energy of the many-body system. We immediately exclude the trivial case $\delta = 1$, the case of non-interacting pairs of electrons on two sites, since then we do not have, even for $N \rightarrow \infty$, a macroscopic system. For $0 \leq \delta < 1$, in the sense of an ensemble average, the magnitude of the pseudo-spins is (17,30)

$$\langle \sigma_k \rangle = \tanh \frac{|B_k|}{kT} \qquad \qquad \text{IV.1}$$

where k is Boltzmann's constant and $/B_k/$ is the magnitude of the molecular field (cf. IIIa-c). In order to take into account all the excitations possible, and not just those in the subspace of unlike real S_z for states k, k + π, we replace T by 2T. The reason is that we double the number of excitations, and hence the entropy, since the excitations of $H_{red}^{(\alpha)}$ are non-interacting. Doubling the excitations amounts to replacing T by 2T in the free energy (30).

We may use these results from superconductivity theory, in spite of the fact that when we introduce states with total S_z different from zero, we change the term $-NJ\rho(1 - \rho)$ in the hamiltonian II.19. In the case of no applied magnetic field, antiferromagnetic coupling, and large N, the probable deviations from $\rho = \frac{1}{2}$ are of order $1/\sqrt{N}$. The deviations of $-NJ\rho(1 - \rho)$ from

-1/4 NJ are therefore of order 1/N, or of the same order as the errors we have neglected in the solution of $\mathcal{H}_{red}^{(\alpha)}$.

We set $\mu_k = |B_k|/2kT$. The finite-temperature forms of β, Δ, ξ are obtained by substituting IV.1 (with T replaced by 2T) in II.26a-c:

$$\beta(T) = \frac{2}{N} \sum_k^\alpha \cos k \cos \theta_k \tanh \mu_k , \qquad \text{IV.2a}$$

$$\Delta(T) = \frac{2}{N} \sum_k^\alpha \sin \theta_k \cos \varphi_k \tanh \mu_k , \qquad \text{IV.2b}$$

$$\xi(T) = \frac{2}{N} \sum_k^\alpha \sin k \sin \theta_k \sin \varphi_k \tanh \mu_k . \qquad \text{IV.2c}$$

The values of k are from $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$. We also define the integrals $K(q,\mu)$, $E(q,\mu)$ which reduce to the complete elliptic integrals of the first and second kind, respectively, in the limit $\mu \to \infty$ (that is, $T = 0°K$),

$$K(q,\mu) \equiv \frac{2}{\pi} \int_0^{\frac{\pi}{2}} d\theta \; \frac{\tanh(\mu\sqrt{1-q^2\sin^2\theta})}{\sqrt{1-q^2\sin^2\theta}} \qquad \text{IV.3a}$$

$$E(q,\mu) \equiv \frac{2}{\pi} \int_0^{\frac{\pi}{2}} d\theta \sqrt{1-q^2\sin^2\theta} \; \tanh(\mu\sqrt{1-q^2\sin^2\theta}). \qquad \text{IV.3b}$$

As before, $D(q,\mu) = K(q,\mu) - E(q,\mu)$.

The development is exactly as in the 0°K case. The pseudo-spins are quantized along $\vec{B}_k$, and the molecular field is treated as a classical vector. We again distinguish between case (a),

$\Delta^2(T) > 0$, and case (b), $\Delta^2(T) = 0$. For $\Delta^2(T) > 0$, we substitute $\beta(T)$, $\Delta(T)$, $\xi(T)$, $K(q,\mu)$, and $E(q,\mu)$ for β, Δ, ξ, $K(q)$, and $E(q)$, respectively, where

$$\mu^{(a)} = \frac{J}{2kT}\left\{ \Delta^2(T) + (\}(T) + \delta \xi(T))^2 \right\}^{\frac{1}{2}} \qquad \text{IV.4}$$

After taking the limit $N \to \infty$, we obtain the master equation for case (a)

$$\frac{\pi q}{2} = D(q,\mu)\left\{ 1 + \delta^2\left[\left(\frac{\pi q}{2(q^2 K(q,\mu) - D(q,\mu))} \right)^2 - 1 \right] \right\}^{\frac{1}{2}} \qquad \text{IV.5}$$

The temperature-dependent value of q is

$$q^2 = \frac{(1-\delta^2)(\}^2(T) - \xi^2(T))}{\Delta^2(T) + (\}(T) + \delta \xi(T))^2} < 1. \qquad \text{IV.6}$$

The expressions for $\beta(T)$, $\xi(T)$, $\Delta(T)$, and $E^{(a)}(T)/JN$ are given by III.9a-c, and III.10, respectively, with $K(q)$, $D(q)$ replaced by $K(q,\mu)$, $D(q,\mu)$.

For case (b), the expression for μ is

$$\mu^{(b)} = \frac{J}{2kT}(\}(T) + \delta \xi(T)). \qquad \text{IV.7}$$

In the limit $N \to \infty$, we obtain the master equation

$$q^2\left(\frac{\pi}{2} + K(q,\mu) \right) - D(q,\mu) = D(q,\mu)\left\{ \frac{\sqrt{1-q^2}(1 - \delta\sqrt{1-q^2})}{\sqrt{1-q^2} - \delta} \right\}. \qquad \text{IV.8}$$

where the temperature-dependent value of q is

$$q^2 = \frac{(1-\delta^2)(\gamma^2(T) - \xi^2(T))}{(\gamma(T) + \delta\xi(T))^2} .$$

IV.9

$\beta(T)$, $\xi(T)$, and $E^{(b)}(T)/JN$ are given by III.15a, b, and III.16, respectively, with $K(q)$, $D(q)$ replaced by $K(q,\mu)$, $D(q,\mu)$. Whenever possible, we choose the solution corresponding to case (a), as in the previous section.

The ground state, III.20, is changed only in that ϕ_k, θ_k (or, equivalently, u_k, v_k) are temperature dependent. The parity of the ground state and of the excited states remains unchanged. There are again $\frac{1}{2}N$ excitations (particles) with real $S_z = 1$ and $\frac{1}{2}N$ excitations (holes) with real $S_z = -1$. The particles and holes have the same spectrum (cf. fig. 3). However, the excitation energies are temperature dependent,

case (a) $\quad \varepsilon_k^{(a)} = |B_k| = J\sqrt{\Delta^2(T) + (\gamma(T) + \delta\xi(T))^2}\sqrt{1 - q^2(T)\sin^2 k}$, IV.10a

case (b) $\quad \varepsilon_k^{(b)} = |B_k| = J(\gamma(T) + \delta\xi(T))\sqrt{1 - q^2(T)\sin^2 k}$. IV.10b

$\Delta(\delta, T)$ decreases with increasing T and vanishes at a critical temperature $T_c(\delta)$. The regions in which $\Delta(\delta, T) > 0$ and $\Delta(\delta, T) = 0$ are shown in figure 2. The regular antiferromagnet has the highest critical temperature, determined from

$$\beta(T_c) = \gamma(T_c) - 1 = \frac{2}{\pi}\int_0^{\frac{\pi}{2}} d\theta \cos\theta \tanh\left(\frac{J\gamma(T_c)}{2kT_c}\cos\theta\right)$$

IV.11a

$$1 \;=\; \frac{2}{\pi} \int_0^{\frac{\pi}{2}} d\theta \;\frac{1}{\cos\theta}\; \tanh\!\left(\frac{J\delta(T_c)}{2kT_c}\cos\theta\right). \qquad\qquad \text{IV.11b}$$

The value of $T_c(0)$ is, in units of J/k, 0.2848. For $T > T_c(0)$, the excitation spectrum of the regular antiferromagnet has no energy gap. The equations then reduce to the Hartree-Fock equations for the regular antiferromagnet (5,18). $\Delta(\delta,T)$ thus represents a coherence that occurs only at low temperatures, where, since the coherence results in an energy gap, it profoundly influences the properties of the regular antiferromagnet. $\Delta(\delta,T)$ is therefore very reminiscent of the energy gap in superconductivity theory.

The weakly alternating antiferromagnet ($0 \leq \delta \leq \delta_0$) exhibits a second-order transition at $T = T_c$, where Δ vanishes. There exist general arguments forbidding transitions of any order in one-dimensional systems (41,42). The transition is therefore spurious. We have another indication that the solutions of $\mathcal{H}_{red}^{(\alpha)}$ are approximate. In particular, the introduction of a molecular field, an infinite-range interaction in k-space, makes transitions possible. Slightly below the transition temperature, we have two self-consistent solutions, corresponding to cases (a) and (b), with very nearly the same energies per site. The interaction $V^{(\alpha)}$, although perhaps usually negligibly small, may then become important. The fact that, quite rigorously, the transition at $T = T_c$ is not first-order, even in the molecular-field approximation, is

encouraging. By contrast, in superconductivity theory, a first-order change is ruled out experimentally; it is therefore <u>assumed</u> that the phonons remain unchanged during the transition. Since it is a three-dimensional system, a second-order transition is allowed and, in fact, observed.

The approximate solutions we present for the weakly alternating antiferromagnet agree, through the first derivatives of the free energy, with the analytic properties of the true free energy. For stronger alternation ($\delta > \delta_0$), there is no problem, since then Δ vanishes identically at all temperatures. Except near T_c, it should be a good approximation to neglect $V^{(\alpha)}$. In the following, we shall not need the temperature derivatives of the free energy; we use only the excitation spectrum.

We conclude this section by finding an expression for the magnetic susceptibility. The ground state of the regular antiferromagnet (N even) is known to be a singlet; both S and S_z are good quantum numbers. The class of elementary excitations found by Des Cloizeaux and Pearson for the regular antiferromagnet are triplets (7), a result that is expected from any isotropic system of spins whose ground state is a singlet. The ground state is a singlet and S, S_z are good quantum numbers for the alternating antiferromagnet also. The N electrons may be classified as $\frac{1}{2}N$ sets of two electrons, with each set having a singlet and three triplet states. We have found $\frac{1}{2}N$ excitations with $S_z = 1$ and $\frac{1}{2}N$ excitations with $S_z = -1$; the excitations are degenerate in pairs. We identify these excitations as two components of triplet states.

It turns out that the $S_z = 0$ components of the assumed triplets have excitation energies that are exactly twice the excitation energies of the $S_z = \pm 1$ components. Since we have lost the classification of states by S and have truncated the hamiltonian, it is not surprising that we have artificially introduced an energy gap between states that are in fact degenerate. We assume that the excitations of the alternating antiferromagnet are triplets, with excitation energies IV.10a,b. We also assume, for reasons we discuss in section VI, that there are negligibly few, if any, low-lying collective excitations.

The susceptibility of independent triplets has been found in connection with the theory of paramagnetic excitons (24). The derivation is straightforward if it is recalled that the triplets resemble fermions and that only one of the three states of the triplet may be occupied at any time. In the limit $N \to \infty$, the magnetic susceptibility per site of the alternating antiferromagnet is

$$\text{case (a)} \quad \chi^{(a)} = \frac{4}{3} g_e^2 \beta_e^2 \frac{1}{kT} \int_0^{\frac{\pi}{2}} \frac{d\theta}{\pi} \cdot \frac{1}{1 + \frac{1}{3} \exp\left\{ \varepsilon^{(a)}(\theta)/kT \right\}} , \qquad \text{IV.12a}$$

$$\text{case (b)} \quad \chi^{(b)} = \frac{4}{3} g_e^2 \beta_e^2 \frac{1}{kT} \int_0^{\frac{\pi}{2}} \frac{d\theta}{\pi} \frac{1}{1 + \frac{1}{3} \exp\left\{ \varepsilon^{(b)}(\theta)/kT \right\}} , \qquad \text{IV.12b}$$

where g_e is the electronic g factor, β_e is the Bohr magneton, and the excitation energies are given by IV.10a,b.

V. Numerical Results

The numerical results we present in this section are the exact solutions of $\mathcal{H}_{\text{red}}^{(\alpha)} - (1/4)JN$ in the limit $N \to \infty$; that is, they are the exact solutions of $\mathcal{H}^{(\alpha)} - V^{(\alpha)}$ for $\rho = \frac{1}{2}$. The master equations IV.5 and IV.8 are solved for q, for fixed values of μ and δ, with the aid of an IBM 7090 computer. λ, ξ, Δ, and E/JN are then obtained, for case (a), from equations III.9a-c and III.10 and, for case (b), from equations III.15a-b, and III.16, where $K(q,\mu)$ and $D(q,\mu)$ have been substituted for $K(q)$ and $D(q)$. These parameters are obtained as functions of the reduced temperature kT/J. From IV.10a-b, we obtain the energy gap, $\epsilon_{\frac{\pi}{2}}$, and the band width, $\epsilon_0 - \epsilon_{\frac{\pi}{2}}$, for the single excitations corresponding to cases (a) and (b), respectively. The magnetic susceptibility per site is given by IV.12a-b. Whenever we have a choice, we choose the solution corresponding to case (a). We have found the parameters that describe the 21 antiferromagnets $\delta = 0.00, 0.05, 0.10, \ldots, 0.95$, and 0.99 in the temperature range $0 \le kT/J < 2.2$. The tables may be found in appendix III. The results are, for the most part, accurate to at least five significant figures.

We consider first the behavior of the two coherence parameters Δ and ξ. The behavior of $\Delta(\delta,T)$ is summarized in figures 2 and 4. For $\delta \ge \delta_0 = 0.11905$, Δ vanishes even at $0°K$; The highest reduced temperature for non-vanishing Δ occurs for the regular antiferromagnet at kT/J = 0.2848. The behavior of ξ as a function of kT/J is shown in figure 5 for $\delta = 0.00, 0.05, 0.10,$

Fig. 4. The temperature dependence of the coherence parameter Δ for fixed values of δ.
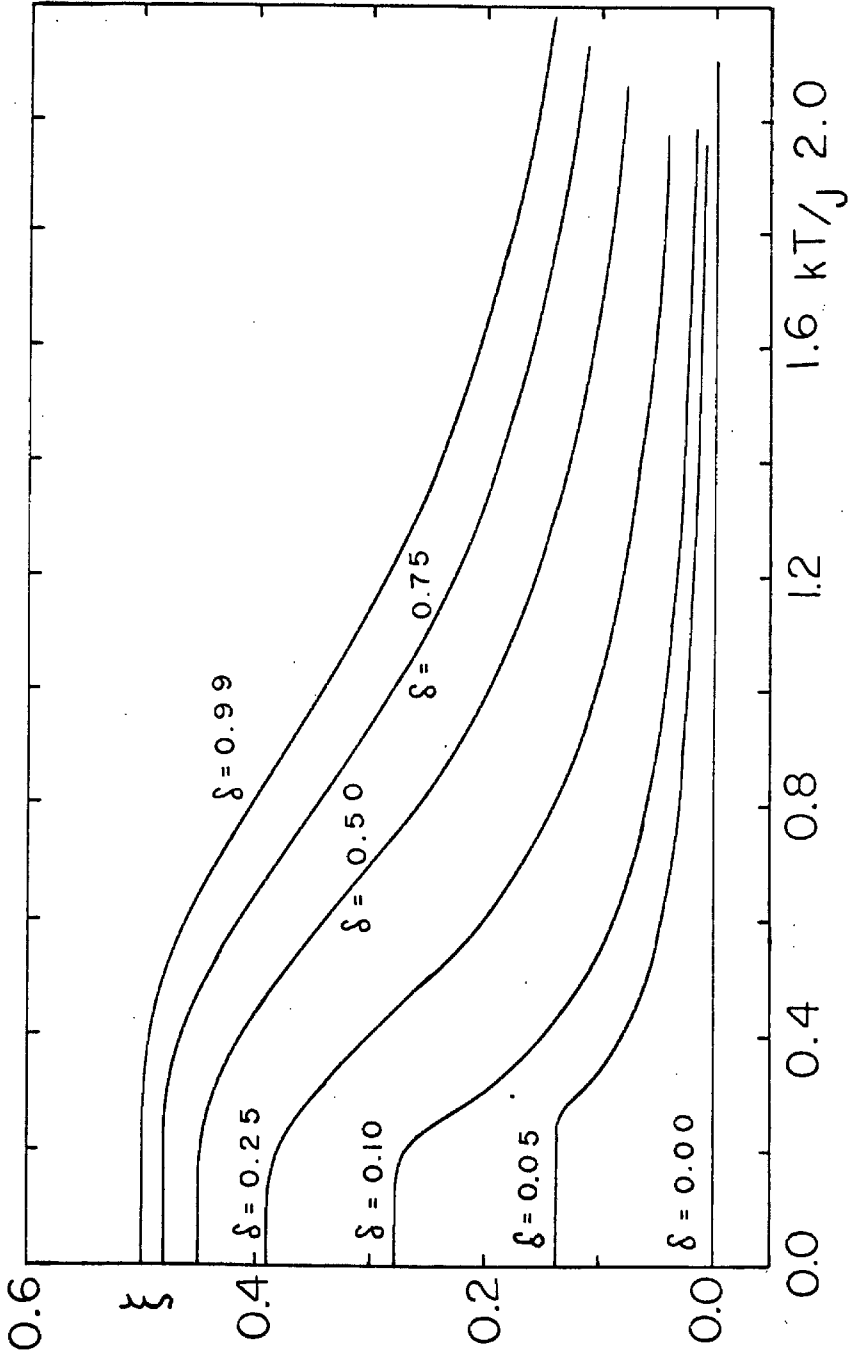
Fig. 5. The temperature dependence of the coherence parameter ξ for fixed values of δ.

0.25, 0.50, 0.75, and 0.99. The maximum value of ξ is $\frac{1}{2}$, which occurs for the completely alternating ($\delta = 1$) antiferromagnet. In the limit of infinite temperature, ξ goes to zero asymptotically, a result we expect for any coherence effect.

β, or $\gamma - 1$, is shown in figure 6 as a function of kT/J for $\delta = 0.00$, 0.10, 0.25, 0.50, 0.75, and 0.99. β represents the tendency of excitations to remain in the low-energy states of a band. It is also the parameter that expresses the exchange term II.17 and is therefore found in any Hartree-Fock treatment. The energy gap in the Hartree-Fock approximation ($\Delta = \xi = 0$) is, from IV.10a-b, $J(1 + \beta)\delta$. (When setting $\Delta = \xi = 0$, the master equation must be solved again; thus β will not be the same in the Hartree-Fock solution as in the solutions we present.) The energy gap $J(1 + \beta)\delta$ is largely due to the alternation of the exchange integrals. It depends on the coherence between electrons with unlike S_z only to the extent that β is slightly larger when the coherence is included. The presence of this intrinsic energy gap, which goes asymptotically to $J\delta$ as $T \to \infty$, stabilizes the spin system at low temperatures. Thus the parameters describing strongly alternating antiferromagnets (cf. figs. 5-10) all remain at their absolute zero values up to higher reduced temperatures than the parameters describing weakly alternating antiferromagnets.

The ground-state energy per site is shown as a function of kT/J in figure 7 for $\delta = 0.00$, 0.10, 0.25, 0.50, 0.95, and 0.99. The asymptotic value, for any alternation, is $-1/4$ as $T \to \infty$; $-1/4$ is just the constant term in the hamiltonian I.2 of the
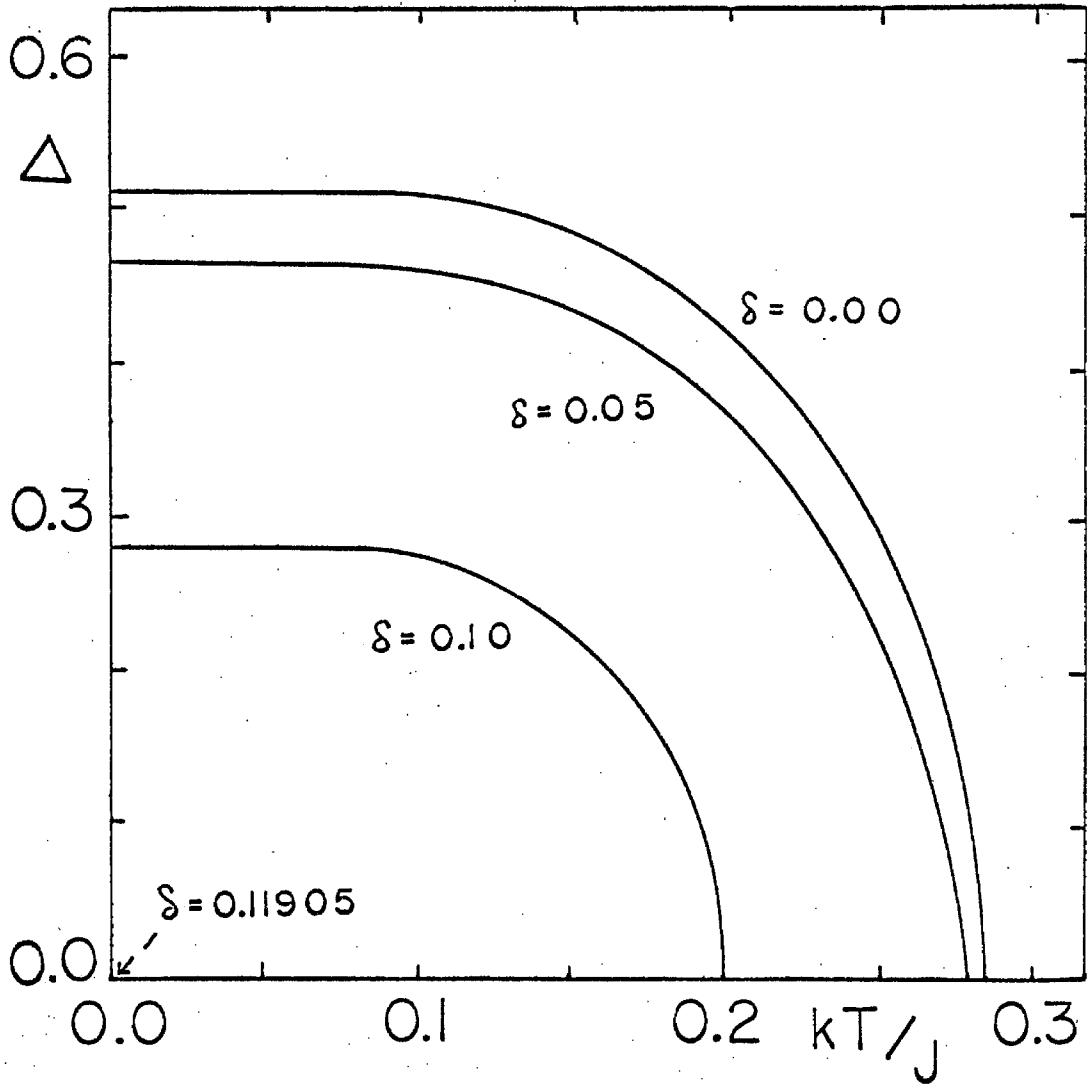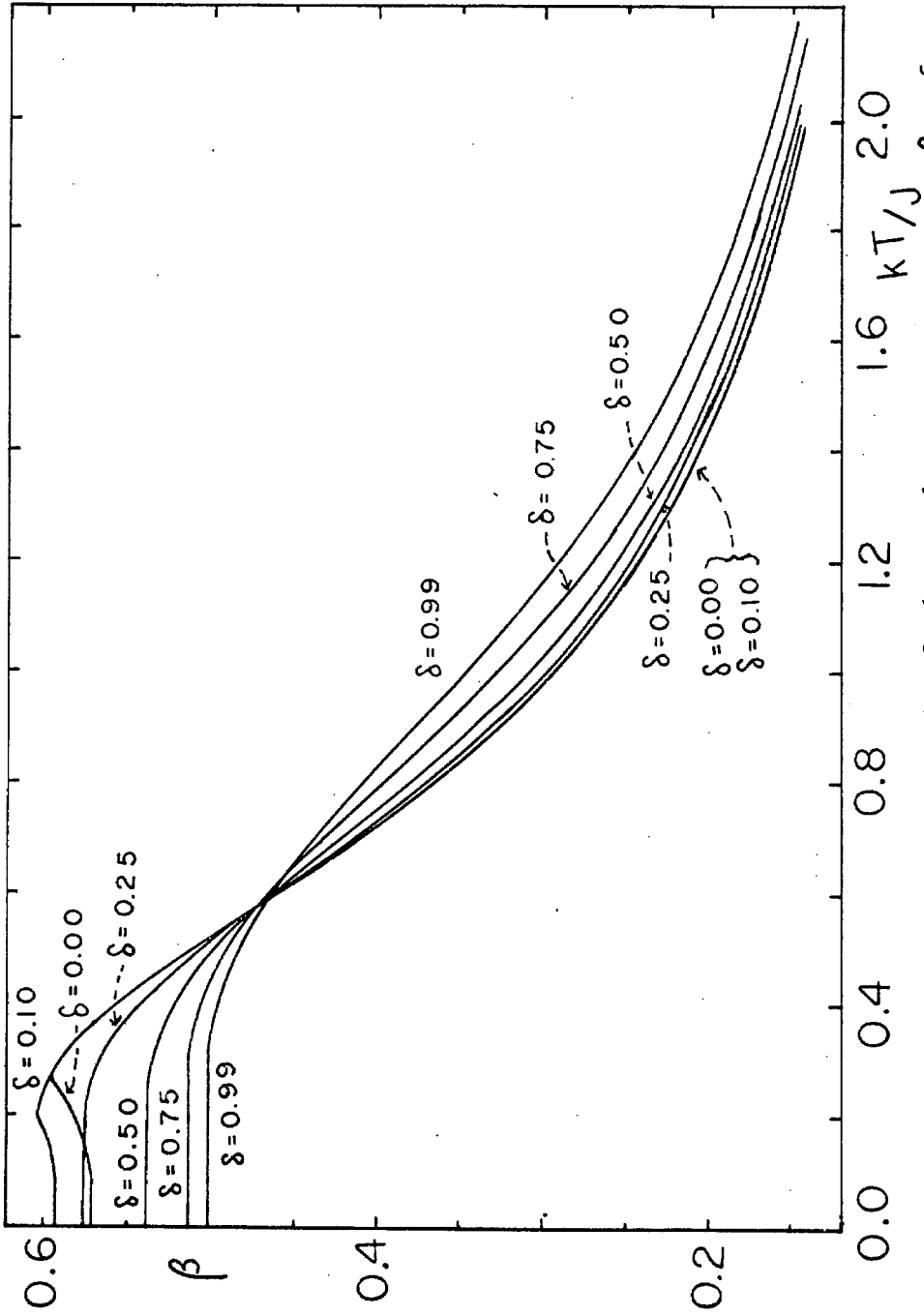
Fig. 6. The temperature dependence of the exchange parameter β for fixed values of δ.
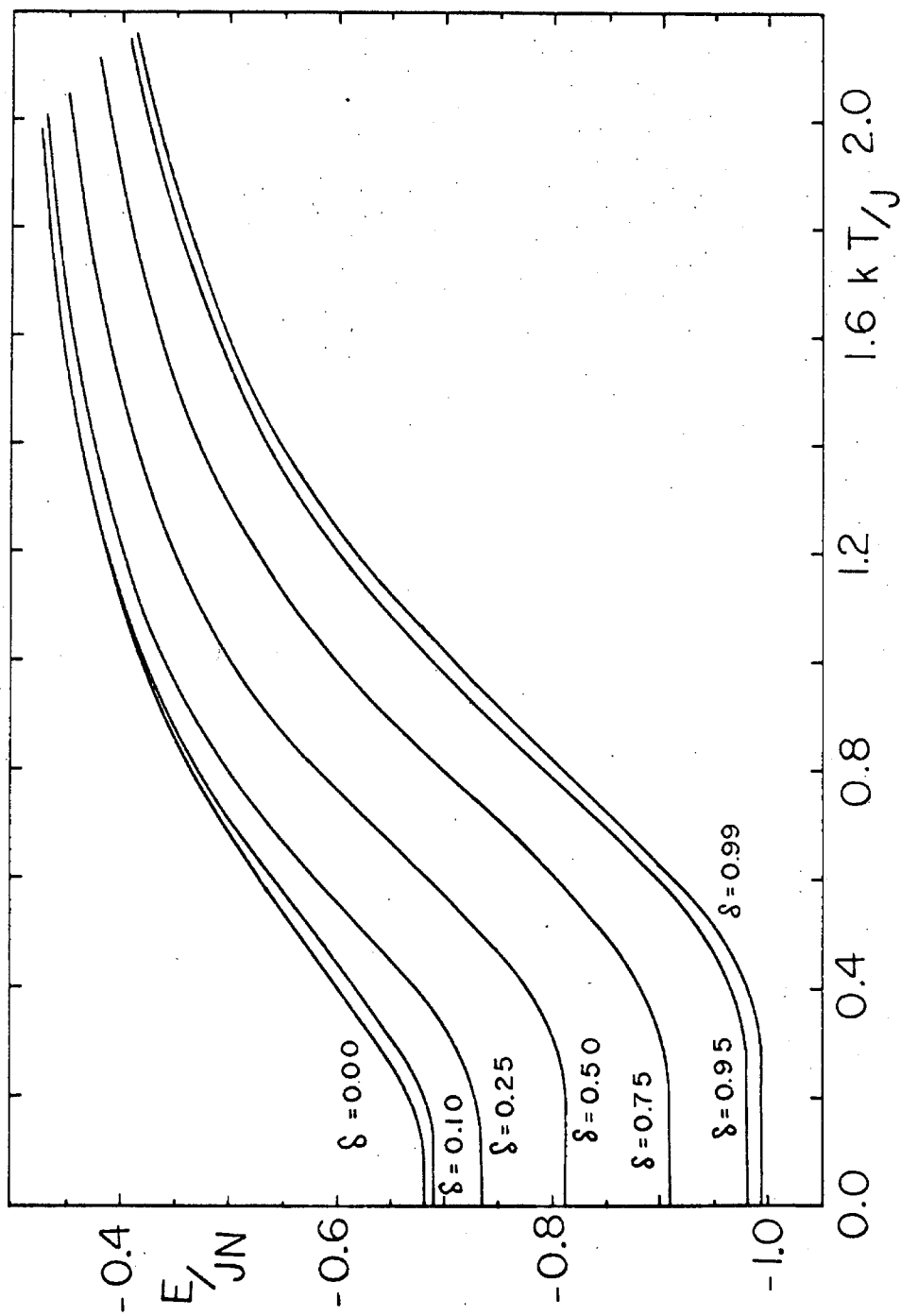
Fig. 7. The temperature dependence of the ground-state energy per site for fixed values of δ.

spin system, so that, as expected, the high temperature contribution of the terms $\vec{S}_j \cdot \vec{S}_{j+1}$ vanishes. Except for small δ ($\delta < 0.2$), the ground state energy is essentially linear in δ, as is evident from III.16 and figures 5 and 6.

The minimum energy gap, $\epsilon_{\frac{\pi}{2}}$, and the bandwidth, $\epsilon_o - \epsilon_{\frac{\pi}{2}}$, are shown in figures 8 and 9 as functions of kT/J. At low temperatures and for small δ, the energy gap is almost constant, due to Δ. The bandwidth is reduced by the energy gap; it is smaller than in the Hartree-Fock approximation. The asymptotic value of the energy gap, Jδ, is also shown in figure 9. The energy gap decreases by a factor of two between low and high temperatures for $\delta = 0.99$ and by more than a factor of two for smaller alternations. The bandwidth remains approximately constant as a function of temperature, especially for large δ. In effect, raising the temperature lowers the entire band but does not, to a first approximation, change the bandwidth. The low-temperature behavior of the antiferromagnet is determined by the energy gap. For the same J, the energy gap at $0°K$ may be as small as $\Delta J = 0.51313J$ for the regular antiferromagnet or as large as 2J for the completely alternating ($\delta = 1$) antiferromagnet.

The magnetic susceptibility as a function of kT/J is shown in figure 10, for $\delta = 0.00, 0.10, 0.25, 0.50, 0.75,$ and 0.99. The low-temperature behavior is an exponential divided by T, as is expected for a collection of non-interacting triplets. This ideal behavior persists as long as the energy gap remains at its $0°K$ value; then, since the energy gap decreases, the susceptibility
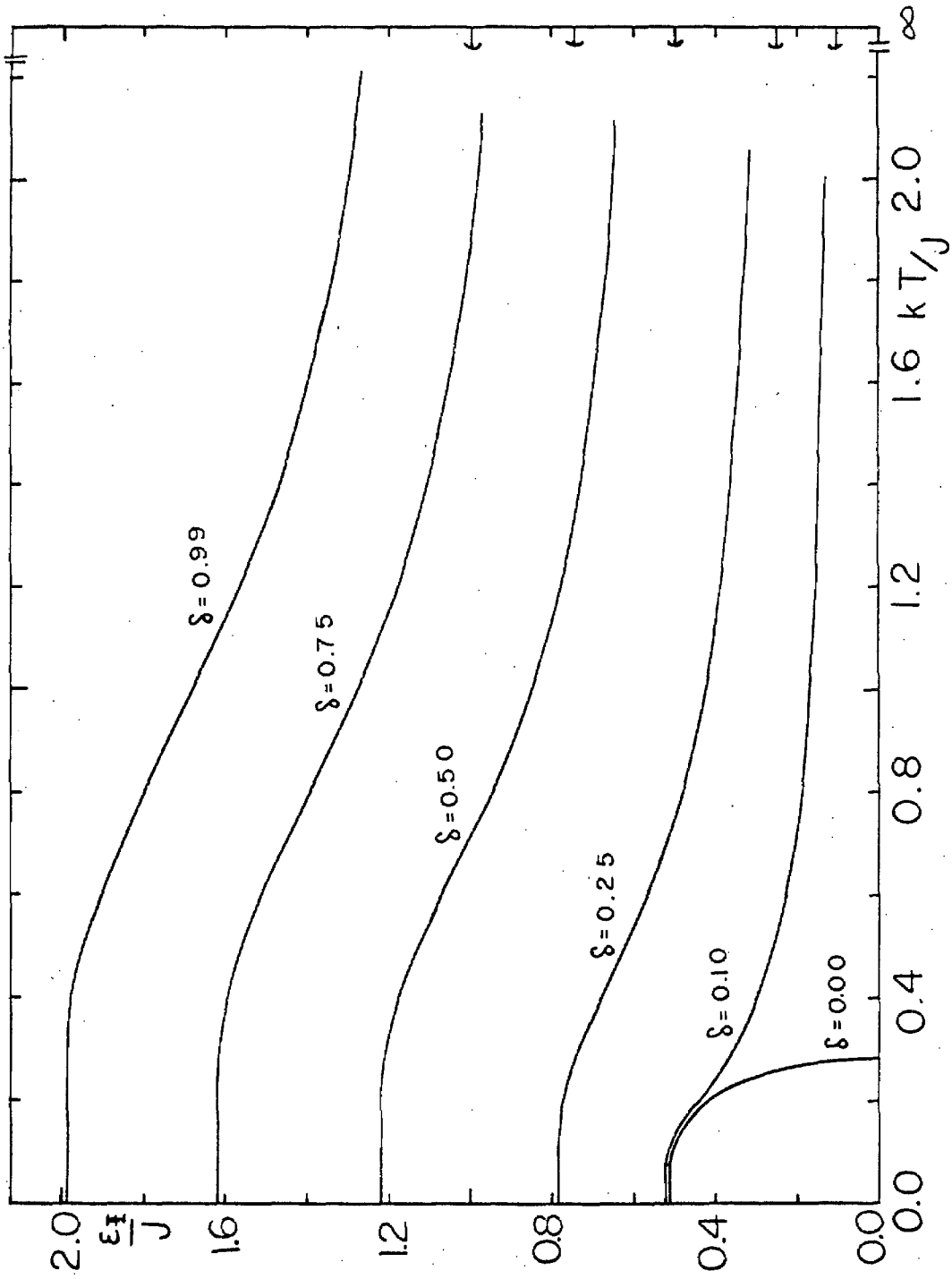
Fig. 8. The temperature dependence of the minimum energy gap of $\mathcal{H}_{red}^{(\infty)}$ for fixed values of δ.
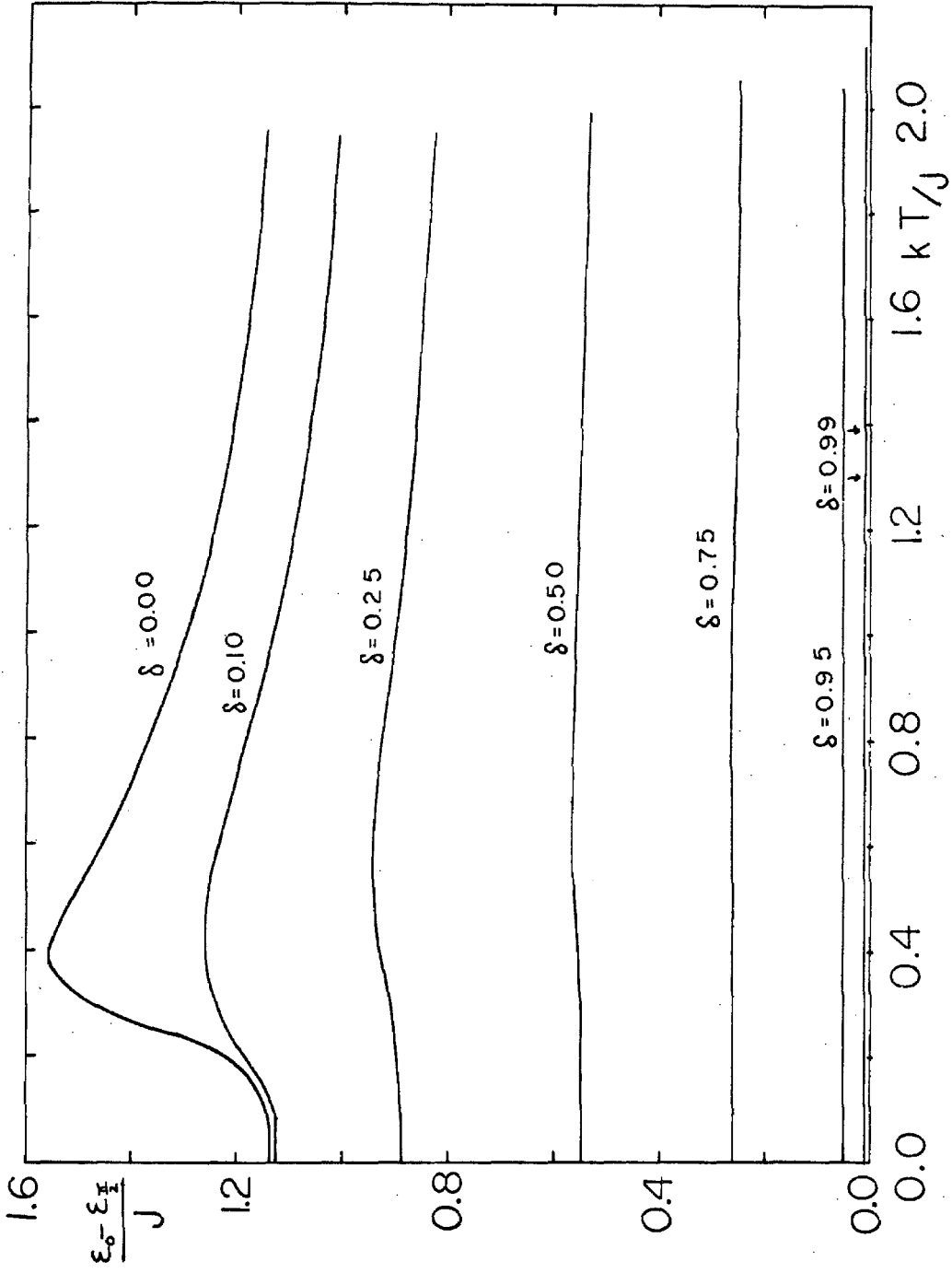
Fig. 9. The temperature dependence of the triplet exciton bandwidth for fixed values of δ.
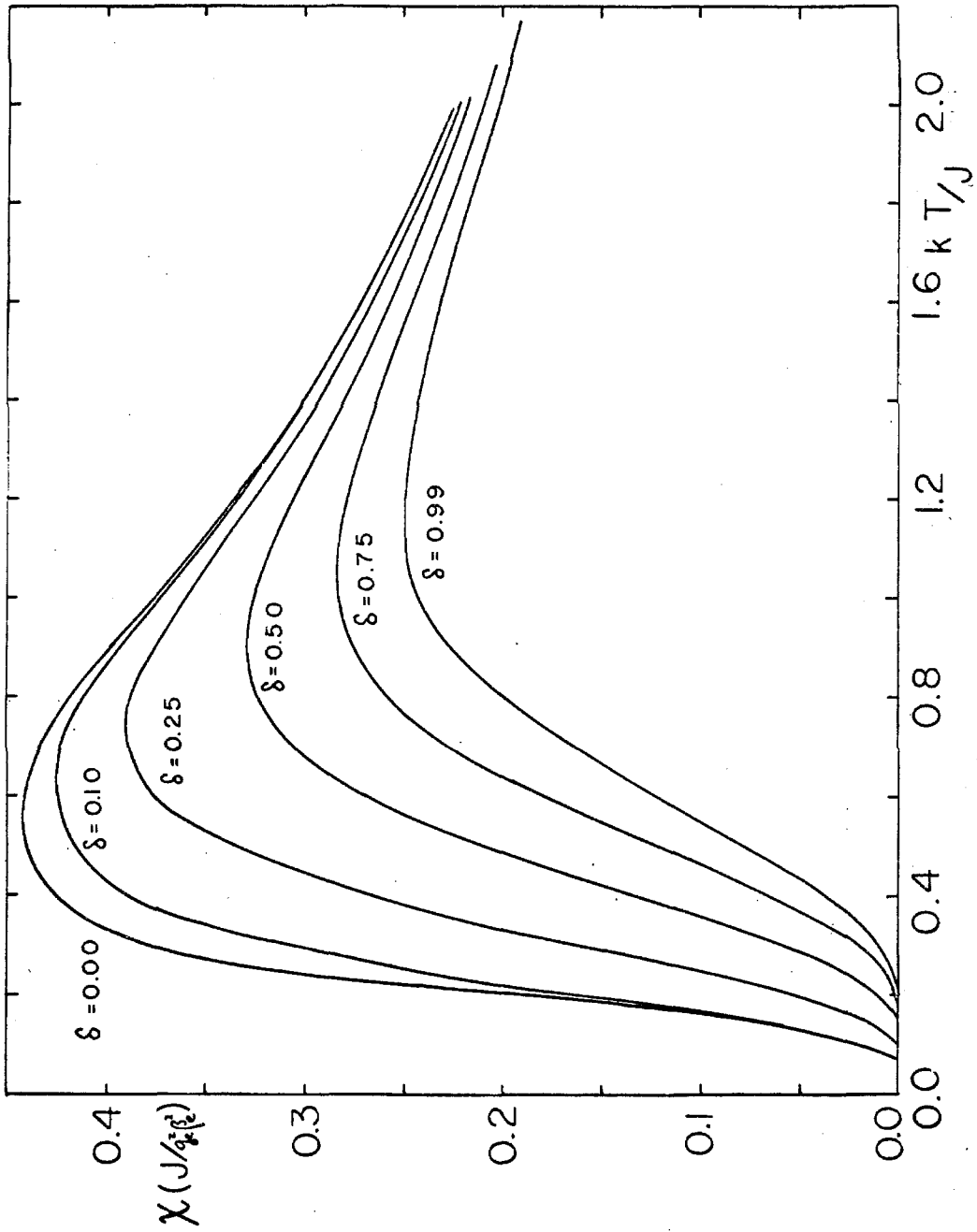
Fig. 10. The paramagnetic susceptibility of the linear antiferromagnet as a function of the reduced temperature for fixed values of δ.

is greater than in the ideal case. The shift in the maximum of $\chi(\delta,T)$ to higher T for large δ is another consequence of the larger energy gap found in the strongly alternating antiferromagnet. The asymptotic behavior, for any δ, is $\chi \rightarrow 1/T$ (to order $1/T^2$), which is the expected result for a paramagnetic gas.

VI. Discussion

In this section, we compare the results of the present method with those obtained in previous theories and with experiment. We consider first the connection with previous theories of the regular antiferromagnet. We then consider the connection with theories of the alternating antiferromagnet, especially in the case of strong alternation and low temperature. Next we consider experimental results and fit the paramagnetic susceptibility of organic crystals, for both the regular and the alternating antiferromagnet. The concluding remarks are concerned with a brief discussion of phonon-coupling.

A. Comparison with the Theory of the Regular Antiferromagnet

The ground-state energy per site of the regular antiferromagnet in the Hartree-Fock approximation ($\Delta = \xi = 0$) is $E/JN = -(1/4 + \frac{1}{\pi} + \frac{1}{\pi^2}) = -0.66923$, as is evident from II.19 since $\beta = \frac{2}{\pi}$ when the $\frac{1}{2}N$ lowest states are occupied. We have reproduced Rodriguez's first result (5). (In his notation, the hamiltonian contains the factor 2J rather than J.) The ground-state energy obtained by Ruijgrok and Rodriguez by a variational calculation (14) is just the solution of $\mathcal{H}_{red}^{(\alpha)}$ at 0°K for $\delta = 0$: $E/JN = -0.68229$. This result is typical of the best zeroth-order estimates available (14,16). It is also essentially the result obtained by a field-theoretic treatment of the quartic term, using the Hartree-Fock states as zeroth-order functions, but without

introducing explicitly the coherence between electrons with unlike S_z (18).

Since the exact ground state energy (28) is, to five significant figures, $E/JN = -0.69312$, it is evident that the effect of coherence is substantial. Using as zeroth-order states the solutions of $\mathcal{H}_{red}^{(\alpha)}$, it is straightforward to find the second-order correction to the ground-state energy. Perturbation theory is expected to give rapidly converging results on account of the energy gap. The second-order correction for the regular antiferromagnet is found in appendix II. We find $E/JN = -0.69257$, which is less than 0.1% higher than the exact result.

Another measure of the accuracy of the ground-state wave function of the regular antiferromagnet is the short-range order. The short-range order, by definition, is

$$\eta = -\frac{2}{N} \left\langle \sum_{j=1}^{N} S_j^3 S_{j+1}^3 \right\rangle,$$

<div align="right">VI.1</div>

where the ground state expectation value is understood. Neglecting $V^{(\alpha)}$ in II.19, we reproduce the result of Ruijgrok and Rodriguez (14): $\eta = 0.295$. The exact value is (28) $\eta = 0.298$, so that the agreement is good even in zeroth order. $\mathcal{H}_{red}^{(\alpha)}$ therefore provides a good description of the ground state of the regular antiferromagnet.

We turn next to the question of an energy gap in the excitation spectrum of the regular antiferromagnet. There is an energy gap in the spectrum of $\mathcal{H}_{red}^{(\alpha)}$, which has been found

explicitly in appendix I. However, for $\delta = 0$, there is no unique

pairing condition; the quadratic part of the hamiltonian is then

diagonal in terms of the a_k's. By pairing, not k, k + π, but,

for instance, k, k + π - ε, we expect to find low energy states

of high multiplicity. (Since there are then fewer than $\frac{1}{2}N$ pair

states, the states we construct will be degenerate in the zeroth

order, and consequently should be assigned high multiplicities.)

Thus we expect to find "collective" excitations for the regular

antiferromagnet. That is, we expect to find excitations in which

a macroscopic number of spins are oriented differently than in

the ground state. That collective modes of some sort should exist

has been shown by Anderson, again in connection with superconduc-

tivity; the regular antiferromagnet corresponds to his "neutral

Fermi gas" (17).

The triplet excitations found by Des Cloizeaux and Pearson

(7) are collective states of the exact hamiltonian. In the Bethe

formalism, the wave number k is allowed to become complex (1).

But, in the case of the ground state and the low-lying triplets,

k is real and is identical with our definition of the wave number.

Since the wave numbers of order N spins are changed from their

ground state values, the triplet excitations found by Des

Cloizeaux and Pearson are collective excitations. They are not

separated from the ground state by an energy gap. They, like the

excitations of $H_{red}^{(\alpha)}$, show the separation of the system into two

sublattices, as shown in figure 3. The separation into sublattices

has been discussed elsewhere (7,14), but it is not completely

understood. Griffiths extended the exact results of Des Cloizeaux and Pearson to states with higher multiplicities. The excitations he considers are also collective; they are essentially excited states of the whole lattice and represent but a few of the possible number of states (8,9).

We identify the states found by Des Cloizeaux and Pearson, and by Griffiths, as the collective excitations we neglected by truncating the hamiltonian. We cannot offer anything like a rigorous justification. The results of Griffiths (9) then show that the thermal properties of the regular antiferromagnet do not depend on the collective excitations at any finite temperature. The reason, as expected, is that there are too few collective states. We summarize these tentative conclusions. The coherence between electrons with unlike S_z introduces, at low temperatures, an energy gap in the single excitation spectrum of the regular antiferromagnet, that is, in the excitations of $\mathcal{H}_{red}^{(\alpha)}$. There also exist collective modes, for which there is no energy gap. The thermal properties of the system are entirely determined by the far more numerous single excitations.

B. Comparison with the Theory of
the Alternating Antiferromagnet

We consider first the limit $\delta = 1$ and $0°K$, the case of a non-interacting system of pairs of electrons on two sites. The ground state energy is, by inspection, $-1.0J$ per site. From III.12, III.13a,b, we have $q = 1$, $\xi = \frac{1}{2}$, and $\gamma = 3/2$. The ground state energy is therefore, from III.16, $-1.0J$ per site,

the exact result. The excitation energy of $\mathcal{H}^{(\alpha)}_{red}$ is, from III.21b, $2J$, and, for both the particles and the holes, the band has collapsed into a $\frac{1}{2}N$-fold degenerate line, as expected. However, the $S_z = 0$ components of the $\frac{1}{2}N$ triplets have excitation energies $4J$. As we have already discussed in connection with the magnetic susceptibility, the appearance of this state with twice the proper excitation energy occurs for all δ and T and is a consequence of the truncation of the hamiltonian. The Hartree-Fock solutions may be obtained by setting $\Delta = \xi = 0$ in the equations describing the alternating antiferromagnet, in which case we reproduce the treatment in reference 19. By taking into account the coherence between antiparallel electrons, we always obtain lower energies.

For $\delta > 0$, the lattice has lower symmetry. An energy gap is expected even from simple band theory. In the Hartree-Fock approximation, the gap is $J\delta_\chi$, while if we include the coherence between antiparallel electrons, the gap is $J\sqrt{\Delta^2 + (\delta_\chi + \xi)^2}$. Furthermore, for $\delta > 0$, the pairing condition is uniquely defined, since, unless k and $k + \pi$ are paired, the quadratic part of the hamiltonian is not diagonalized by the transformation. We do not expect, therefore, to find low-lying collective modes. High-energy collective modes exist: for instance, for small δ and low T, case (a), case (b), and the Hartree-Fock approximation represent three different solutions, with increasing energies per site, in which a macroscopic number of spins have different ground state orientations. In the limit of an infinite system, the solution

with the lowest energy per site is sufficient for an arbitrarily
accurate thermodynamic description.

The hamiltonian for the alternating Heisenberg antiferro-
magnet is the "exciton" hamiltonian in the theory of paramagnetic
excitations in organic crystals (24). Many organic crystals have
structures corresponding to essentially non-interacting chains of
molecules (21); their spin properties may therefore be studied by
one-dimensional models. A successful low-temperature and strong-
alternation theory has been obtained by McConnell, Lynden-Bell,
and Montgomery (16,21,24). We define J_1 and J_2 to be the exchange
integrals J and J' in their notation: $J_1 = J(1 + \delta)$ and $J_2 =$
$J(1 - \delta)$. The excitation spectrum at 0°K is (16)

$$\varepsilon_\varkappa^I = J(1+\delta)^{1/2}\left((1+\delta)-(1-\delta)\cos\varkappa\right)^{1/2}, \qquad \text{VI.2}$$

where $\varkappa = 0, \pm \dfrac{4\pi}{N}, \ \ldots \pm \dfrac{(N-4)\pi}{N}$, π, and the $\frac{1}{2}N$ excitations
are triplets. Since $\varkappa = 2k$ and $\sin^2 k = \frac{1}{2}(1 - \cos 2k)$, we may
rewrite the excitation energies III.21a-b at 0°K to have the same
form as $\varepsilon_\varkappa^I$.

For $\delta < 1$, the derivation of the exciton spectrum VI.2
involves the introduction of unphysical states, but at 0°K and
for $\delta \neq 0$, the number of these states is not large (16). Without
introducing unphysical states, but neglecting exciton-exciton
interactions, Lynden-Bell and McConnell (24) obtained the excita-
tion spectrum

$$\varepsilon_\varkappa^{II} = J\left\{(1+\delta)- \tfrac{1}{2}(1-\delta)\cos\varkappa\right\}, \qquad \text{VI.3}$$

which is just the first two terms of the expansion of VI.2 in $J_2/J_1 < 1$. VI.3 is usually used for comparison with experiment, since it may be used even at finite temperatures, provided only that the exciton concentration is small. In this model, the alternating antiferromagnet is considered to consist of $\frac{1}{2}N$ pairs of two electron sites in position space. The exchange interaction J_1 and the part of J_2 that corresponds to exciton motion are treated exactly. The terms in J_2 that represent exciton-exciton interactions and exciton creation and annihilation processes are to be included by using perturbation theory.

The important parameters, for any treatment of the alternating antiferromagnet at low temperatures, are the energy gap in the excitation spectrum and, to a lesser extent, the excitation bandwidth. The former determines, roughly, how many excitations there are at any temperature, while the latter gives, roughly, the density of states. The minimum energy gap at $0°K$ is $J\sqrt{(1 + \delta)2\delta}$, $\frac{1}{2}J(1 + 3\delta)$, and $J\sqrt{\Delta^2 + (\xi + \delta\gamma)^2}$ for the excitations ϵ_χ^{I}, ϵ_χ^{II}, and those of the present method, respectively. The minimum energy gap is shown as a function of δ in figure 11. The bandwidths for the three cases are, respectively, $J[\sqrt{(1 + \delta)2} \cdot (1 - \sqrt{\delta})]$, $J(1 - \delta)$, and $J(\sqrt{\Delta^2 + (\xi + \delta\gamma)^2} - \sqrt{\Delta^2 + (\gamma + \delta\xi)^2})$, they are shown in figure 12. It is evident that, for $\delta \gtrsim .4$, there is quantitative agreement. The pseudo-spin formalism therefore reduces, for the case of strong alternation and low temperature, to the exciton theories of McConnell, Lynden-Bell, and Montgomery.
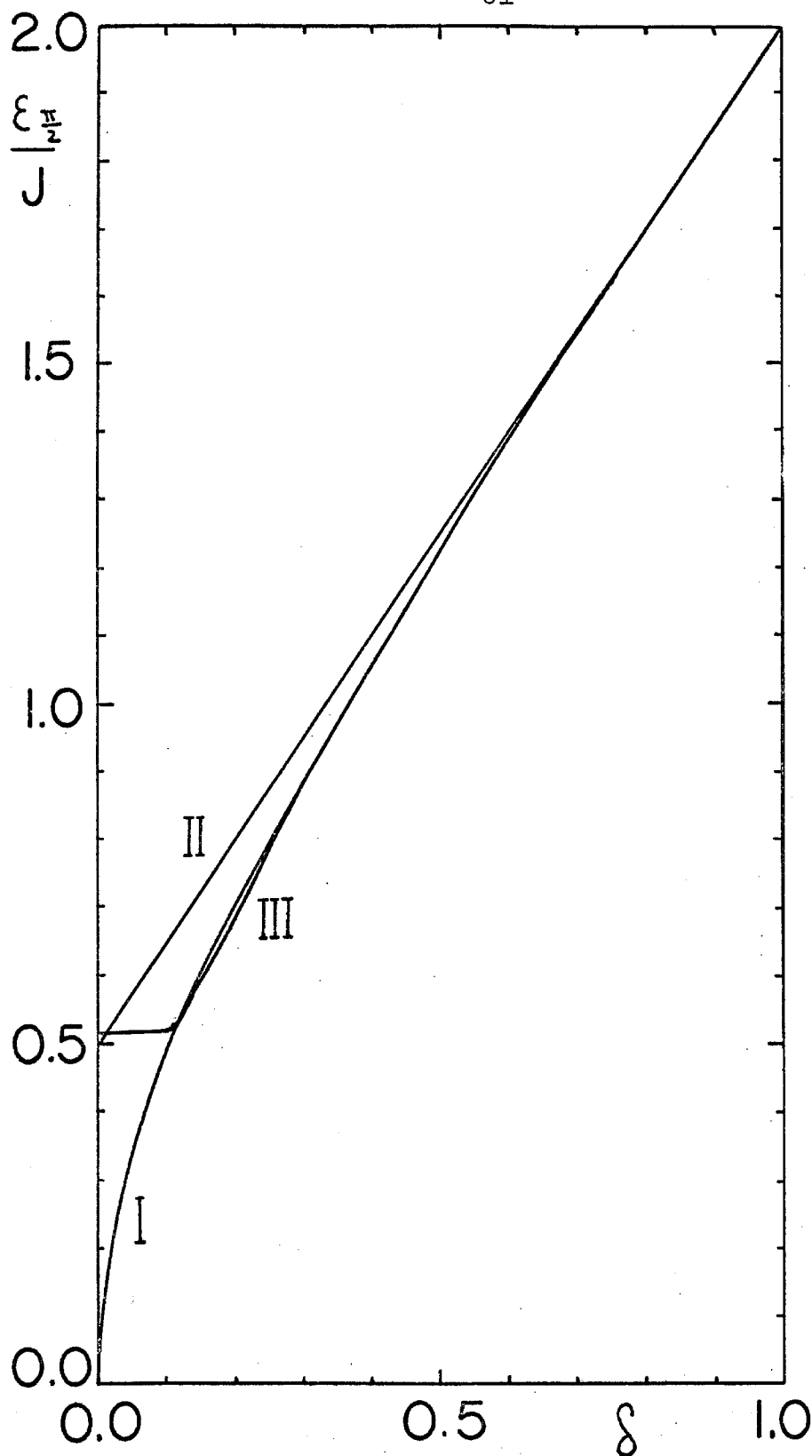
Fig. 11. Comparison of the 0°K minimum energy gap for (I) the exciton theory of Montgomery, (II) the exciton theory of Lynden-Bell and McConnell, and (III) the present work.
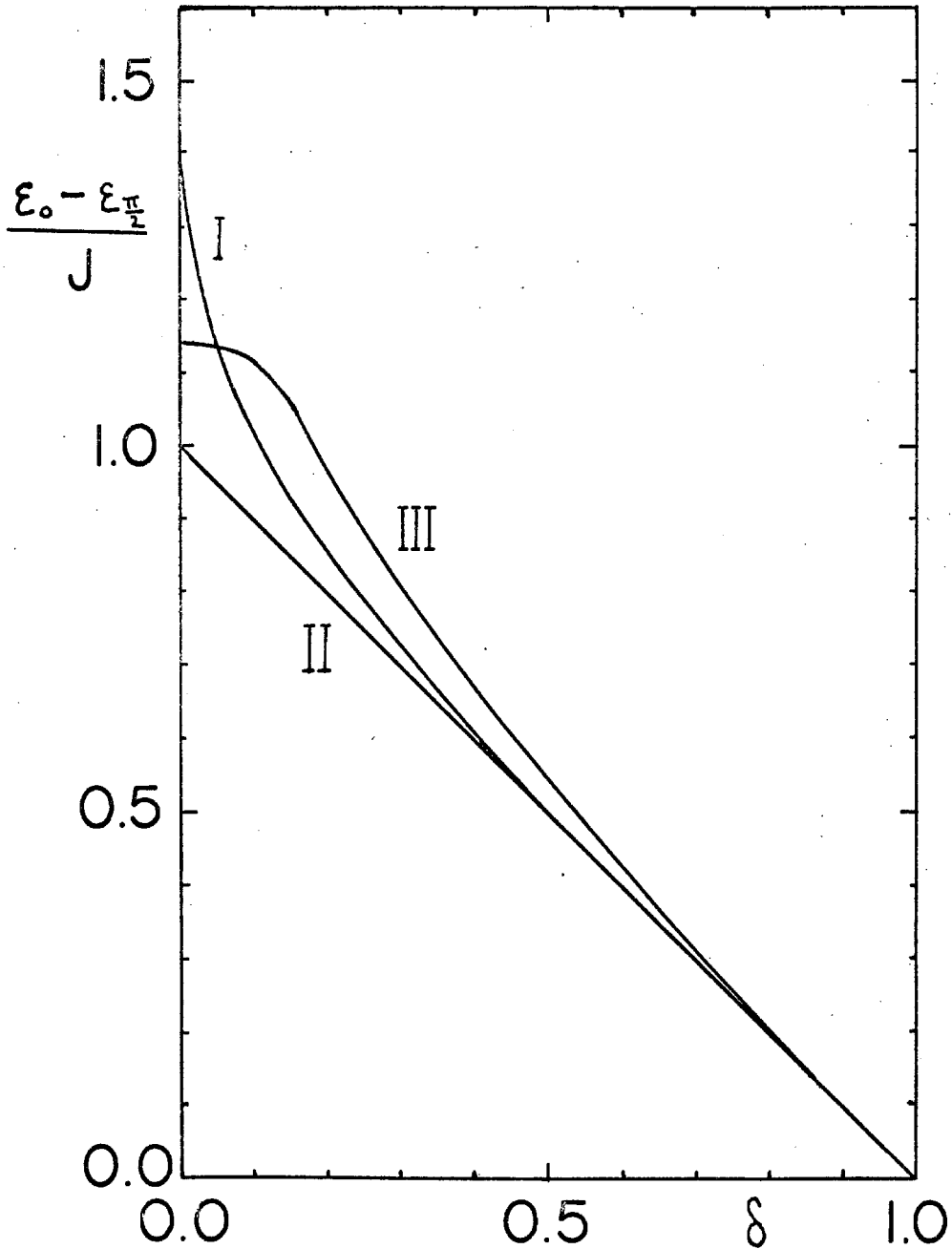
Fig. 12. Comparison of the 0°K triplet exciton bandwidth for (I) the exciton theory of Montgomery, (II) the exciton theory of Lynden-Bell and McConnell, and (III) the present work.

The temperature range over which the results of Lynden-Bell and McConnell are valid may be obtained from figures 9 and 10. As long as the minimum energy gap and the excitation bandwidth are constant, it is a good approximation to neglect exciton-exciton interactions. At higher temperature, the inclusion of exciton-exciton interactions would lead to new quasiparticles. The energy gap and the bandwidth are then temperature-dependent. The temperature-independent parameters are suitable up to moderately high $(kT/J \sim .5)$ temperatures when the alternation is strong.

The decrease in the effective singlet-triplet energy gap with increasing temperature has been observed (33), and a purely phenomenological theory has been proposed by Chesnut (34). Chesnut assumes a hamiltonian that describes triplet excitations with strong attractive interactions, tentatively attributed to lattice distortions. The interactions are neglected in the entropy term. The resulting Gibbs free energy naturally describes a system in which the excitation population increases more rapidly with temperature than if there were no attractive interactions. In effect, he introduces a molecular field whose strength is an arbitrary parameter.

The model we present gives changes in the singlet-triplet energy gap that are of the right order; as shown in figure 9, the energy gap decreases by at least a factor of two. The decrease in the effective singlet-triplet energy gap is a many-body effect arising from the temperature dependence of the parameters

describing the spin system. The excitations, found at any tem-
perature by minimizing the Gibbs free energy, always have spins
$S_z = \pm 1$, but their energies are functions of temperature. Other
properties, which also depend on the coherence, such as the band-
width, are also temperature-dependent, since the amount of
coherence must be determined for every temperature. The excita-
tions are independent in the approximation of neglecting $V^{(\alpha)}$.
Thus the change in the excitation energy is not associated with
either an attraction or a repulsion among the quasiparticles.
Another, probably smaller, change in the singlet-triplet energy
gap, which also has nothing to do with interactions between
excitons, is due to the change in the exchange integrals as the
crystal expands thermally.

C. Comparison with Experiment

We consider the organic crystals BDPA (22,35) and $(C_2H_5)_3$-
$NH^+(TCNQ)_2^-$ (23,33). Their properties are discussed in the
references cited. It is sufficient, for the present discussion,
to note that BDPA may be considered to be a regular antiferromag-
net, while $(C_2H_5)_3NH^+(TCNQ)_2^-$ appears to be a strongly alternating
antiferromagnet. Thus they represent the two extreme cases. We
consider the paramagnetic susceptibility of these crystals. The
diamagnetic contribution to the susceptibility is assumed to
remain constant in the temperature ranges discussed.

An Ising model has been used to describe BDPA in reference
22. The electronic specific heat was used to evaluate the exchange
integrals. The value found, in units of k and in our notation, is

J' = 5.2-6.0°K (35). Since the low-temperature specific heat is dominated by the energy gap, which in the Ising model is J', we set $\Delta J = J'$; thus J = 10-12°K. We use the value J = 11°K in figure 14 to compare with data on the Knight shifts, which are proportional to the magnetic susceptibility. The vertical scale was adjusted arbitrarily. The lowest temperatures correspond to less than 2°K; at such low temperatures, impurities may cause too high a signal and, as shown by the three values at 4°K, the experimental uncertainties are considerable.

The results we present are for a system of non-interacting chains, each of which is a regular Heisenberg antiferromagnet. The dashed curve in figure 14 represents the results of Griffiths (36), who solved numerically the regular antiferromagnet with 10 spins. The Ising model, as shown in reference 22, gives rather poorer fit. This is not surprising, since the hamiltonian is badly truncated in the Ising calculation. Our results, except for the difficult region of very low temperatures, give a somewhat better fit than the numerical results of Griffiths. However, the experimental points show considerable variations (cf. reference 22).

In $(C_2H_5)_3\overset{+}{N}H(TCNQ)_2^-$, there are two unpaired electrons on four TCNQ molecules; the lattice is formed by the TCNQ's. The system is apparently strongly alternating; it is described rather well as a collection of triplets (23,33). The low-temperature singlet-triplet energy gap observed experimentally is 0.034 ev. We set $\delta = 0.99$ and $J(\delta\chi + \xi)$ equal to the energy gap. J is
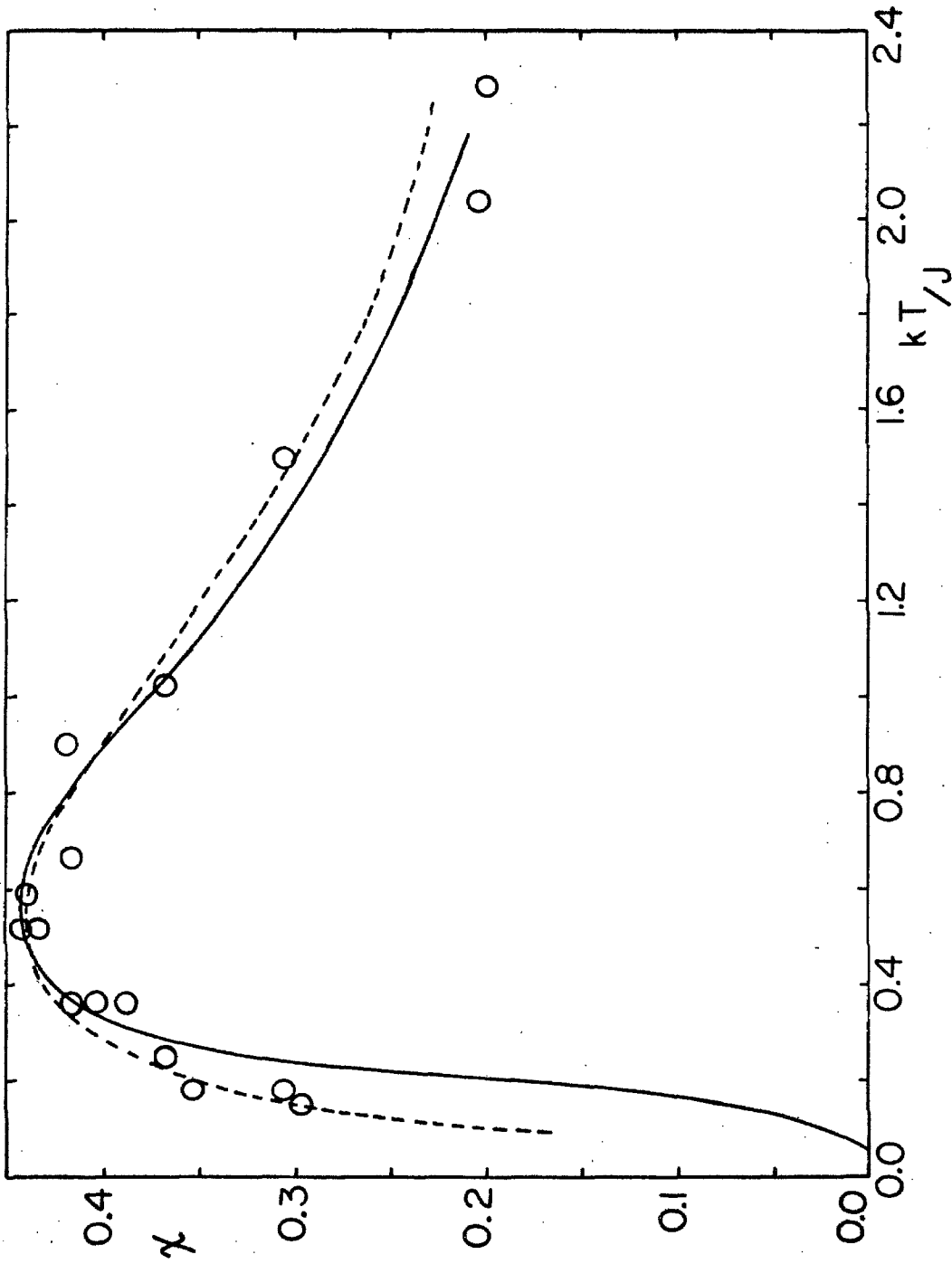
Fig. 13. The paramagnetic susceptibility of BDPA. The experimental points are from Hamilton's Knight shift data; the dashed line is Griffiths's spin numerical calculation; the solid curve is from the present work, for $\delta = 0$.

therefore 0.017 ev. The fit with the experimentally observed susceptibility is shown in figure 14 for J = 0.0175 and an arbitrarily chosen vertical scale. The dashed line represents the susceptibility of non-interacting triplets,

$$\chi \, \propto \, \frac{1}{T} \, \frac{1}{1 + \frac{1}{3} e^{\Delta/kT}} \qquad\qquad VI.4$$

where Δ is the singlet-triplet energy gap. The dashed line is, if the diamagnetic contribution is included, perhaps within experimental uncertainty for kT/J up to the temperature at which the maximum susceptibility is observed (33).

It is evident that, unless the change in the singlet-triplet gap is included, the susceptibility may be fitted either at high or at low temperature, but not at both. At low temperatures, the exciton density is low and the temperature-independent parameters of the Lynden-Bell and McConnell theory give a good description. If, as is usually done, the exchange integrals are estimated from low temperature experiments, then the singlet-triplet gap will be overestimated unless the temperature dependence of the parameters is included.

D. Conclusion: Effects of Lattice Vibrations

The present model gives good agreement both with previous theories and with experiment. The properties of the regular or the alternating antiferromagnet are obtained at any temperature. Since the excitations of $\mathcal{H}_{red}^{(\alpha)}$ are independent, we may easily
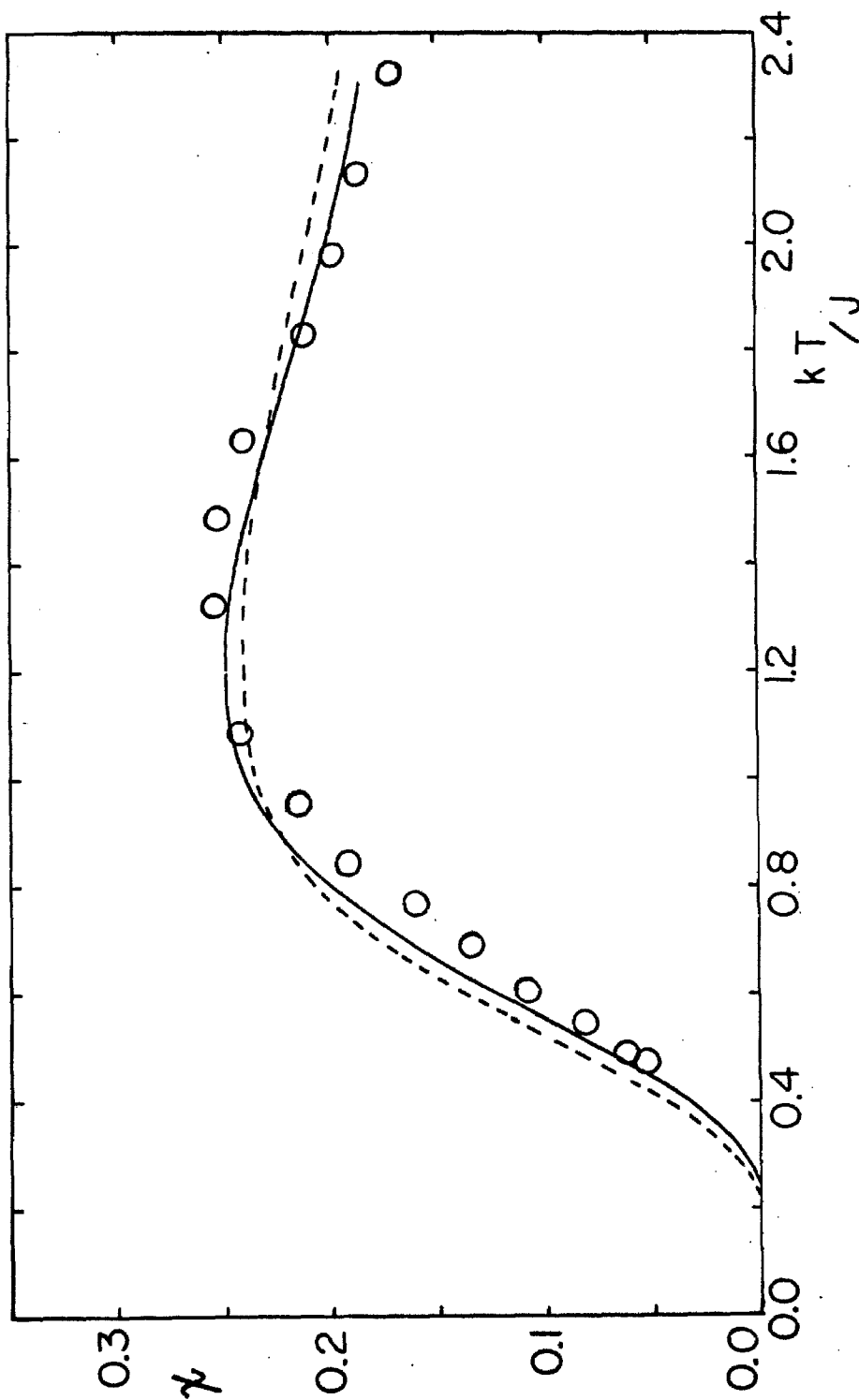
Fig. 14. The paramagnetic susceptibility of $(C_2H_5)_3NH(TCNQ)_2$. The experimental points are from the data of Chesnut and Phillips; the dashed curve is the result for the ideal case of non-interacting triplets; the solid curve is from the present work, for $\delta = 0.99$.

calculate any property of the spins by using statistical mechanics. As we have shown, the truncated hamiltonian $\mathcal{H}_{red}^{(\alpha)}$ is a rather good approximation of the entire hamiltonian. In any case, as shown by the second-order correction to the ground-state energy of the regular antiferromagnet, we may use the solutions of the truncated hamiltonian as zeroth-order functions in perturbation calculations.

We are especially interested in the electronic properties of organic crystals that show paramagnetic excitations. Of course, the molecules on which the electrons are strongly bound are not stationary, but vibrate. Before attempting to calculate more accurately the electronic properties of these crystals via perturbation theory, we must take into account the effects of lattice vibrations. When the two electrons forming a triplet excitation are on adjacent sites, they may interact very strongly with the lattice; for instance, the electronic wave function may well change, as in H_2, from a bonding singlet to an antibonding triplet state, thus increasing the intersite distance (37). The effective mass of the excitons may then be as large as 10^4 or 10^5 electrons (37,38). Such behavior is possible for strongly alternating lattices at low temperatures; the excitons then become diffusional (37).

A measure of the closeness of the electrons forming a triplet excitation is the value of $\eta_{11} - \eta_{10}$. Here η is the order parameter VI.1 and the subscripts indicate that the expectation values are to be taken in the states $S = 1$, $S_z = 1$ and $S = 1$,

$S_z = 0$. z refers to the molecular axes x, y, z that diagonalize the effective spin hamiltonian. The spin hamiltonian VI.5 is usually used to present experimental data (39)

$$\mathcal{H}_{eff} = D S_{\mathfrak{z}}^{2} + E(S_x^2 - S_{\mathfrak{y}}^2).$$ VI.5

The parameters D and E express the dipolar interaction between two electrons, on adjacent sites, that form a triplet (39).

The hamiltonian I.1 for the alternating antiferromagnet is isotropic. Thus we may choose the z-axis along which we quantize the spins to be the z-axis of the frame which diagonalizes VI.5. Furthermore, the expectation value of $\frac{2}{N} \sum_{j} S_j^x S_{j+1}^x$ in the state $S = 1$, $S_x = 0$ is therefore the same as the expectation value of $\frac{2}{N} \sum_{j} S_j^z S_{j+1}^z$ in the state $S = 1$, $S_z = 0$. If $/1,1 >$ and $/1,-1 >$ represent the states $S = 1$, $S_z = 1$ and $S = 1$, $S_z = -1$, then the state $S = 1$, $S_x = 0$ is $\frac{1}{\sqrt{2}} (/1,1 > - /1,-1 >)$. The expectation value $\eta_{11} - \eta_{10}$, in the limit $N \to \infty$, is then easily evaluated,

$$\eta_{11} - \eta_{10} = \frac{1}{2} \left\{ (\delta-1)(\delta-2) + \Delta^2 + \xi^2 + 2\delta\xi\gamma \right\}.$$ VI.6

The behavior of $\frac{3}{4} \frac{1}{(\eta_{11} - \eta_{10})}$ is shown in figure 15. For $\delta = 1$, at $0°K$, the unpaired spins must be adjacent, so that the full value of the dipolar interaction is obtained; we have normalized so that $\frac{3}{4} \frac{1}{(\eta_{11}-\eta_{10})}$ is then unity. The average number of sites on which the triplet is distributed is, very roughly, $\frac{3}{4} \frac{1}{(\eta_{11}-\eta_{10})}$, from the probability that the unpaired spins are adjacent and
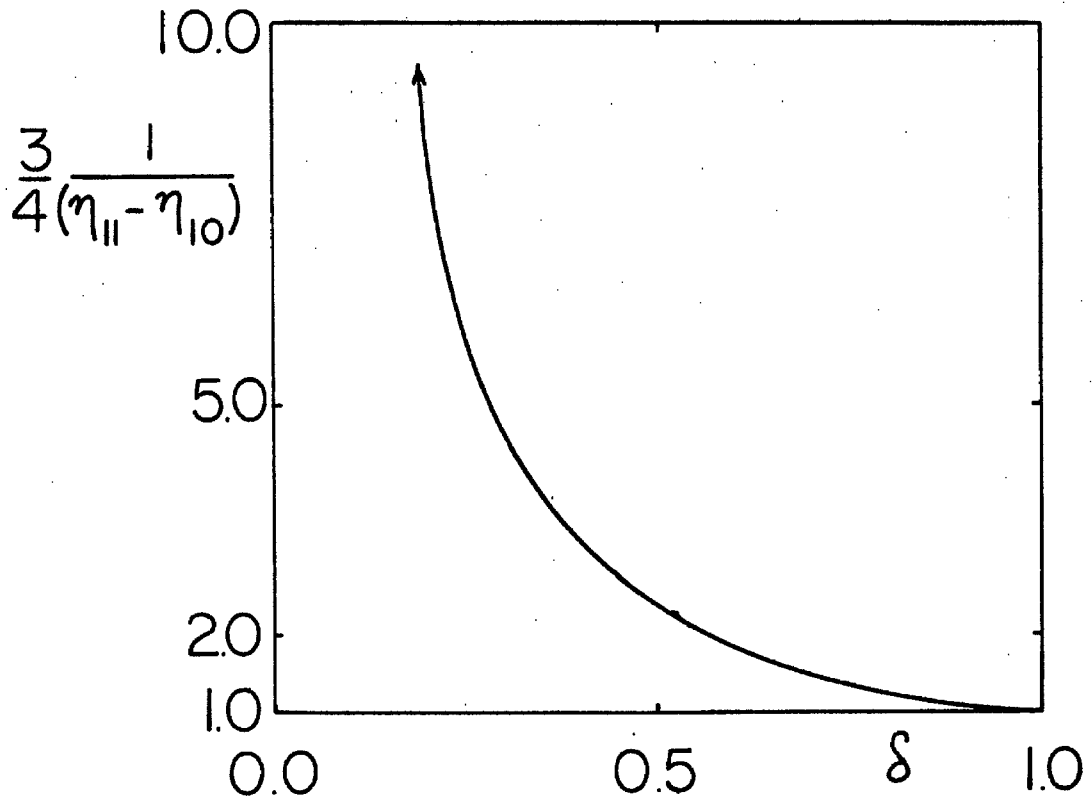
Fig. 15. Rough estimate of the number of sites separating two electrons that form a triplet excitation at 0°K.

since the dipolar interaction is negligible unless the electrons are adjacent. At low temperatures, the two electrons forming a triplet are close together for $\delta \gtrsim .5$. For the regular antiferromagnet at $0°K$, $\eta_{11} - \eta_{10}$ vanishes within the accuracy of a calculation in which $V^{(\alpha)}$ is neglected. The unpaired electrons are then very far from each other. Finally, in the high-temperature limit, since $\gamma \to 1$ and ξ, $\Delta \to 0$, $\eta_{11} - \eta_{10} \to 0$ for any alternation. The triplet excitations then correspond to two noninteracting doublets. At high temperatures, we therefore have, for any alternation, a paramagnetic gas of spin $\frac{1}{2}$ particles, which is the expected result.

When the spins corresponding to a triplet excitation are, on the average, separated by more than one site, they are essentially independent and have no convenient way in which to distort the lattice. Phonon-coupling is then expected to be weak. In the case of a rather strongly alternating lattice and low temperature, although the phonon-coupling is strong, the phonons produce only a few changes in those features of the spin system which are of interest in EPR experiments (37,40).

Appendix I

We calculate the energies of the states of the regular antiferromagnet with $\frac{1}{2}N + 1$ or $\frac{1}{2}N - 1$ fermions. These states form a band and are the lowest-lying excitations of $\mathcal{H}_{red}^{(\alpha)}$. To find the excitation energies, we must calculate the energies per site to order $1/N$ rather than to order 1 as done in section III. The $\frac{1}{2}N$-particle excitations, as discussed in section III, have $S_z = 1$ and are degenerate with the $\frac{1}{2}N$-hole excitations with $S_z = -1$. Since the excited states have opposite parity to that of the ground state, the k-values allowed by II.13 are different. Thus the sums appearing in the solutions must be evaluated again. However, for the $\frac{1}{2}N$ k-values between $-\frac{1}{2}\pi$ and $\frac{1}{2}\pi$, for either $\alpha = 1$ or $\alpha = 2$,

$$\frac{1}{N} \sum_k^{\alpha} f\left(\sin^2(k+\tfrac{\pi}{N})\right) = \frac{1}{N} \sum_k^{\alpha} f(\sin^2 k) + O\left(\tfrac{1}{N^2}\right),$$

1.1

where $f(\sin^2 k)$ is any function of $\sin^2 k$. Since we always have to sum over k, except for a few terms, symmetrically from $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$, there is cancellation, and the sums over the k's may, to order $1/N^2$, be interchanged.

The excited states are states in which the pair state k, $k + \pi$, instead of lying in the subspace of unlike S_z, is in the subspace of like S_z; that is, k and $k + \pi$ are either both filled, which corresponds to a particle excitation, or both empty, which corresponds to a hole excitation. In either case, the subspace of the pseudo-spins, in which we take advantage of the coherence

between states with unlike S_z, is decreased by one pair state, with $-\frac{1}{2}\pi < k < \frac{1}{2}\pi$. We define $\epsilon(k)$ to be the difference between q for the excited state with wave vector $\pm k$ and q for the ground state. For $\delta = 0$, using 1.1, we evaluate $\epsilon(k)$ by finding the difference between the two master equations III.8 which may be written for the excited and the ground states:

$$\epsilon(k) = \frac{1-q^2}{q\,K(q)-\frac{\pi}{2}}\,\frac{\pi}{N}\,\frac{q^2\sin^2 k}{\sqrt{1-q^2\sin^2 k}} \;+\; 0\left(\frac{1}{N^2}\right).\qquad 1.2$$

In 1.2, since the right-hand side is at least of order $1/N$, we may use q and k corresponding to either the excited or the ground state.

The change in energies for the two states is

$$E^T(k) - E^S = \frac{NJ}{\pi^2}\left\{ \sum_{k=-\frac{\pi}{2}}^{\frac{\pi}{2}\alpha} \frac{1}{\sqrt{1-q^2\sin^2 k}} \;-\; \sum_{k'=-\frac{\pi}{2}}^{\frac{\pi}{2}\beta,k} \frac{1}{\sqrt{1-(q+\epsilon(k))^2\sin^2 k'}} \right\},\qquad 1.3$$

where $E^T(k)$ is the energy of the triplet state, E^S is the energy of the ground state, α is the parity of the ground state, and β is the parity of the triplet state. The superscripts β, k denote that the sum is from $k' = -\frac{1}{2}\pi$ to $\frac{1}{2}\pi$, using the values specified in II.13, and that the states k, $k + \pi$ are either both empty or both full. Using 1.1 and 1.2, we find for $-\frac{1}{2}\pi < k < \frac{1}{2}\pi$

$$\frac{E^T(k) - E^S}{NJ} = \frac{1}{N}\sqrt{\gamma^2 + \Delta^2}\sqrt{1-q^2\sin^2 k} + 0\left(\frac{1}{N^2}\right),\qquad 1.3$$

where, to order 1/N, q and k may correspond to their values in
either the ground or the excited state. 1.3 is just the excita-
tion energy III.21a for the case of the regular antiferromagnet.
Therefore, at least for the regular antiferromagnet, the excita-
tion energies are just the magnitude of the molecular field seen
by the pseudo-spins. As discussed in section III, this result
would be true in general if we neglected end effects and is con-
sequently expected to be valid in the limit $N \to \infty$ for the
alternating antiferromagnet.

Appendix II

We consider the regular antiferromagnet and calculate, in
the limit $N \to \infty$, the second-order correction to the ground-state
energy. For $\delta = 0$, the second sum in the perturbation II.21
vanishes. The perturbation is

$$V^{(\alpha)} = \frac{J}{N} \sum_{\substack{q,k,k' \\ q \neq 0,\pi; \ k' \neq k+q, \ k+q+\pi}}^{\alpha} V(q,k,k') = \frac{J}{N} \sum_{q,k,k'}^{\alpha} \cos q \ a_{k+q}^{\dagger} a_{k'-q}^{\dagger} a_{k'} a_{k} , \quad 2.1$$

where $-\pi < q, \ k, \ k' < \pi$. The second-order correction to the
ground-state energy is

$$E^{(2)} = -\frac{J^2}{N^2} \sum_{q,k_1,k_2}^{\alpha} \frac{\langle \Phi_0 | \sum_{q',k_1',k_2'} V(q',k_1',k_2') | q,k_1,k_2 \rangle \langle q,k_1,k_2 | \sum_{q'',k_1'',k_2''} V(q'',k_1'',k_2'') | \Phi_0 \rangle}{E(q,k_1,k_2)} , \quad 2.2$$

where $/ \Phi_0 >$ is the ground state, $/q,k_1,k_2 >$ is the excited state
obtained by operating with $V(q,k_1,k_2)$ on the ground state, and

$E(q, k_1, k_2)$ is the excitation energy of the state $/q, k_1, k_2 >$. We immediately have $\delta_{qq''}$, $\delta_{k_1 k_1''}$, and $\delta_{k_2 k_2''}$, since each term in $V^{(\alpha)}$ produces just one state $/q, k_1, k_2 >$. The operator $V(q, k_1, k_2)$ always annihilates two particles and then creates two particles. There are always two ways of returning to the ground state from the state $/q, k_1, k_2 >$. They correspond to replacing the particles to their original states ($q' = q$, $k_1' = k_1$, $k_2' = k_2$) or to inter-changing them first ($q' = q$, $k_1' = k_2$, $k_2' = k_1$). Thus we have $\delta_{qq'}$, $2\delta_{k_1 k_1'}$, and $\delta_{k_2 k_2'}$. Performing the sums over the δ functions, we obtain

$$E^{(2)} = -\frac{2J^2}{N^2} \sum_{q,k,k'}^{\alpha} \frac{|\langle \Phi_0 | V(q,k,k') | q,k,k' \rangle|^2}{E(q,k,k')} . \qquad 2.3$$

The ground state of the regular antiferromagnet has al-ready been obtained in III.22. Since, for $k \neq k'$, $a_k^+ a_{k+\pi}$ commutes with $a_{k'+\pi}^+$, the ground state may be written

$$|\Phi_0\rangle = \prod_{-\frac{\pi}{2} < k < \frac{\pi}{2}}^{\alpha} \{\cos\tfrac{1}{2}\theta_k \, a_{k+\pi}^+ + \sin\tfrac{1}{2}\theta_k \, a_k^+ \} |0\rangle . \qquad 2.4$$

We take the kth component of the product and operate with a_k, $a_{k+\pi}$, a_k^+, $a_{k+\pi}^+$, respectively, where $-\frac{1}{2}\pi < k < \frac{1}{2}\pi$. a_k and $a_{k+\pi}$ give the vacuum state, with coefficients $v_k = \sin\tfrac{1}{2}\theta_k$ and $u_k = \cos\tfrac{1}{2}\theta_k$, respectively, while a_k^+ and $a_{k+\pi}^+$ give the doubly occupied state $/k, k + \pi >$, with coefficients u_k and v_k, respectively. If we take the k and k' components, with $-\frac{1}{2}\pi < k, k' < \frac{1}{2}\pi$ and $k \neq k'$, we may obtain similar results for the eight possible pairs of

creation and annihilation operators involving k and k'. We now write

$$V^{(\alpha)} = \sum_{q,k,k'}^{\alpha} \sum_{i=1}^{4} V_i(q,k,k'),$$ 2.5

where $-\tfrac{1}{2}\pi < k, k' < \tfrac{1}{2}\pi$ and $-\pi < q < \pi$. It is straightforward to obtain the coefficients in terms of v_k and u_k which result when we operate with $V_i(q,k,k')$ on the ground state.

Finally, each of the four terms of the matrix elements $< q,k,k'/V^{(\alpha)}/\Phi_o >$ is written as a sum of four terms: $-\tfrac{1}{2}\pi + k' < q < \tfrac{1}{2}\pi - k$; $-\tfrac{1}{2}\pi - k < q < -\tfrac{1}{2}\pi + k'$; $\tfrac{1}{2}\pi - k < q < \tfrac{1}{2}\pi + k'$; and $-\pi < q < -\tfrac{1}{2}\pi - k$, $\tfrac{1}{2}\pi + k' < q < \pi$, where we still have $-\tfrac{1}{2}\pi < k, k' < \tfrac{1}{2}\pi$. After some manipulation, it is evident that the various ranges of q may be recombined. Thus

$$E^{(2)} = -\frac{2J^2}{N^2} \sum_{qkk'}^{\alpha} \frac{\cos^2 q}{E(q,k,k')} \left\{ u^2(k+q)v^2(k') + v^2(k+q)u^2(k') \right\} \times$$ 2.6
$$\left\{ u^2(k'-q)v^2(k) + v^2(k'-q)u^2(k) \right\},$$

where $-\pi < q < \pi$, $-\tfrac{1}{2}\pi < k, k' < \tfrac{1}{2}\pi$ and

$$u^2(k) = \tfrac{1}{2}\left(1 + \varkappa \frac{\cos k}{\varepsilon(k)}\right)$$ 2.7a

$$v^2(k) = \tfrac{1}{2}\left(1 - \varkappa \frac{\cos k}{\varepsilon(k)}\right)$$ 2.7b

$$\varepsilon(k) = \sqrt{1 - \varkappa^2 \sin^2 k}$$ 2.7c

$$E(q,k,k') = \frac{\delta}{\chi}(\mathcal{E}(k) + \mathcal{E}(k') + \mathcal{E}(k+q) + \mathcal{E}(k'-q)) \qquad \text{2.7d}$$

In the limit $N \to \infty$, the sums may be replaced by integrals. We simplify by using the symmetry properties of the functions and obtain

$$\frac{E^{(2)}}{JN} = -\frac{\chi}{\delta}\frac{2}{(2\pi)^3}\int_0^{\frac{\pi}{2}}d\mathfrak{z}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}dx\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}dy\frac{\cos^2\mathfrak{z}}{\mathcal{E}(x)+\mathcal{E}(y)+\mathcal{E}(x+\mathfrak{z})+\mathcal{E}(y-\mathfrak{z})}\left\{1+\right.$$
$$\left.\chi^4\frac{\cos x\cos y\cos(x+\mathfrak{z})\cos(y-\mathfrak{z})}{\mathcal{E}(x)\mathcal{E}(y)\mathcal{E}(x+\mathfrak{z})\mathcal{E}(y-\mathfrak{z})}\right\}. \qquad \text{2.8}$$

For $\delta = 0$ and $0°K$, the values of δ and χ are, respectively, 1.57030 and 0.9505389. The integrations were performed numerically with the aid of a computer. The second-order correction to the ground-state energy of the regular antiferromagnet is

$$\frac{E^{(2)}}{JN} = -0.010277. \qquad \text{2.9}$$

Appendix III

The tables presented in this appendix are numerical solutions for the linear antiferromagnets, with $\delta = 0.00, 0.05, 0.10 \ldots 0.95, 0.99$, in the temperature range $0 \leq kT \lesssim 2.2J$.

		TABLE I.	ALTERNATION PARAMETER	$\delta = 0.00$.			
kT/J	γ	ξ	Δ	E/JN	ε_{I}/J	$(\varepsilon_{0}-\varepsilon_{I})/J$	$\chi(J/g_{e}^{2}\beta_{e}^{2})$
0.016520	1.570300	0.	0.513128	-0.682286	0.513128	1.138884	0.18602559E-12
0.023600	1.570300	0.	0.513128	-0.682286	0.513128	1.138884	0.17436288E-08
0.041300	1.570300	0.	0.513126	-0.682285	0.513126	1.138885	0.14896580E-04
0.082593	1.570490	0.	0.512054	-0.682160	0.512054	1.139805	0.54717865E-02
0.117907	1.571710	0.	0.504526	-0.681205	0.504526	1.146177	0.31205536E-01
0.164560	1.575950	0.	0.473673	-0.676996	0.473673	1.171922	0.10039970E-00
0.204539	1.581930	0.	0.418358	-0.669381	0.418358	1.217957	0.18229061E-00
0.268145	1.594620	0.	0.213673	-0.647117	0.213673	1.395199	0.34077430E-00
0.389743	1.558970	0.	0.	-0.507597	0.	1.558970	0.42332958E-00
0.501812	1.505440	0.	0.	-0.566587	0.	1.505440	0.44227429E-00
0.702919	1.405840	0.	0.	-0.494097	0.	1.405840	0.43446428E-00
0.937926	1.313100	0.	0.	-0.431058	0.	1.313100	0.38998852E-00
1.235570	1.235570	0.	0.	-0.381658	0.	1.235570	0.32954869E-00
1.490510	1.192400	0.	0.	-0.355454	0.	1.192400	0.28676677E-00
1.911210	1.146720	0.	0.	-0.328742	0.	1.146720	0.23390002E-00

TABLE 2. ALTERNATION PARAMETER $\delta = 0.05$.

kT/J	γ	ξ	Δ	E/JN	$\varepsilon_{\rm II}/J$	$(\varepsilon_o - \varepsilon_{\rm II})/J$	$\chi(J/g_z^2\beta_e^2)$
0.016495	1.575280	0.137858	0.466641	-0.684996	0.514470	1.135083	0.16434339E-12
0.023565	1.575280	0.137858	0.466641	-0.684996	0.514470	1.135083	0.16008838E-08
0.041239	1.575280	0.137858	0.466640	-0.684995	0.514469	1.135084	0.14209981E-04
0.082470	1.575470	0.137830	0.465493	-0.684875	0.513421	1.135989	0.53533825E-02
0.117734	1.576670	0.137647	0.457364	-0.683930	0.506010	1.142268	0.30756509E-01
0.164326	1.580870	0.137010	0.423595	-0.679753	0.475512	1.167743	0.99434090E-01
0.204262	1.586820	0.136126	0.361423	-0.672189	0.420776	1.213320	0.18097030E-00
0.267813	1.599450	0.134306	0.047952	-0.650015	0.219578	1.387303	0.33890045E-00
0.390441	1.557710	0.081109	0.	-0.611418	0.158994	1.402771	0.40715177E-00
0.502572	1.504880	0.056691	0.	-0.569102	0.131935	1.375780	0.43452802E-00
0.703702	1.405670	0.034613	0.	-0.495493	0.104896	1.302504	0.43144872E-00
1.020730	1.313040	0.022622	0.	-0.431889	0.088274	1.225897	0.36888389E-00
1.236320	1.235550	0.015266	0.	-0.382176	0.077043	1.159270	0.32884715E-00
1.491230	1.192390	0.011820	0.	-0.355836	0.071439	1.121541	0.28632221E-00
1.911910	1.146720	0.008551	0.	-0.329005	0.065887	1.081261	0.23365059E-00

TABLE 3. ALTERNATION PARAMETER $\delta = 0.10$.

kT/J	γ	ξ	Δ	E/JN	$\varepsilon_{\Pi\frac{1}{2}}/J$	$(\varepsilon_o-\varepsilon_{\Pi\frac{1}{2}})/J$	$\chi(J/g_e^2\beta_e^2)$
0.016422	1.590360	0.276850	0.280760	-0.693194	0.518481	1.123742	0.11333289E-12
0.023460	1.590360	0.276850	0.280760	-0.693194	0.518481	1.123742	0.12383594E-08
0.041056	1.590350	0.275849	0.280760	-0.693194	0.518480	1.123742	0.12331232E-04
0.082105	1.590540	0.276795	0.279014	-0.693083	0.517507	1.124590	0.50129589E-02
0.117217	1.591690	0.275446	0.266050	-0.692171	0.510434	1.130610	0.29444367E-01
0.163629	1.595790	0.275216	0.205650	-0.688105	0.480977	1.155309	0.96585203E-01
0.203495	1.600810	0.271451	0.	-0.680797	0.431532	1.196423	0.17520496E-00
0.269127	1.592150	0.226143	0.	-0.664523	0.385358	1.229406	0.26872782E-00
0.392411	1.554370	0.152746	0.	-0.621721	0.308183	1.261462	0.37422781E-00
0.504780	1.503320	0.110238	0.	-0.576317	0.260570	1.253774	0.41720840E-00
0.706019	1.405190	0.068466	0.	-0.499622	0.208985	1.203052	0.42427894E-00
0.940987	1.312880	0.044993	0.	-0.434373	0.176281	1.141098	0.38515715E-00
1.238540	1.235500	0.030436	0.	-0.383727	0.153986	1.084558	0.32710239E-00
1.493410	1.192370	0.023587	0.	-0.356982	0.142824	1.051905	0.28520042E-00
1.914030	1.146710	0.017077	0.	-0.329788	0.131748	1.016670	0.23301563E-00

TABLE 4. ALTERNATION PARAMETER $\delta = 0.15$; $\Delta = 0.0$.

kT/J	δ	ξ	E/JN	$\varepsilon_{\mathrm{I\!I}}/J$	$(\varepsilon_\circ - \varepsilon_{\mathrm{I\!I}})/J$	$\chi\,(J/g_e^2\,\beta_e^2)$
0.0164500	1.592710	0.348585	-0.706199	0.587491	1.057506	0.19404384E-14
0.0234999	1.592710	0.348585	-0.706199	0.587491	1.057506	0.73423821E-10
0.0411249	1.592710	0.348585	-0.706199	0.587491	1.057506	0.25307868E-05
0.0822485	1.592720	0.348349	-0.706138	0.587257	1.057715	0.23378929E-02
0.1174770	1.592750	0.346187	-0.705529	0.585099	1.059579	0.17184748E-01
0.1642940	1.592440	0.336672	-0.702513	0.575538	1.067403	0.62859893E-01
0.2048960	1.590970	0.321315	-0.696947	0.559960	1.079207	0.11726198E-00
0.2711140	1.583830	0.285685	-0.681469	0.523259	1.103423	0.20924029E-00
0.3953820	1.549810	0.211443	-0.636232	0.443914	1.137612	0.33647559E-00
0.5082480	1.500960	0.158549	-0.587353	0.383693	1.141049	0.39482152E-00
0.7097800	1.404430	0.100904	-0.506280	0.311568	1.107997	0.41425223E-00
0.9447540	1.312620	0.066880	-0.438445	0.263773	1.058879	0.38019980E-00
1.2422200	1.235410	0.045416	-0.386283	0.230727	1.011495	0.32453126E-00
1.4970100	1.192320	0.035247	-0.358869	0.214095	0.983512	0.28353629E-00
1.9175400	1.146690	0.025594	-0.331089	0.197598	0.952932	0.23206518E-00

TABLE 5. ALTERNATION PARAMETER $\delta = 0.20$; $\Delta = 0.0$

kT/J	δ	ξ	E/JN	ε_{II}/J	$(\varepsilon_0 - \varepsilon_{II})/J$	$\chi(J/g_e^2\beta_e^2)$
0.0165800	1.583520	0.372414	-0.720529	0.689118	0.968885	0.61407988E-17
0.0236857	1.583520	0.372414	-0.720529	0.689118	0.968885	0.13431744E-11
0.0414500	1.583520	0.372414	-0.720529	0.689118	0.968885	0.26745362E-06
0.0828994	1.583520	0.372338	-0.720503	0.689042	0.968946	0.79420861E-03
0.1184130	1.583520	0.371317	-0.720152	0.688021	0.969762	0.82772250E-02
0.1656360	1.583240	0.365604	-0.717963	0.682252	0.974109	0.38324721E-01
0.2066250	1.581200	0.354992	-0.712685	0.671232	0.980966	0.80970151E-01
0.2735410	1.575820	0.327150	-0.699112	0.642314	0.998936	0.16406611E-00
0.3990950	1.544720	0.258313	-0.653123	0.567257	1.029126	0.29976676E-00
0.5127500	1.498080	0.200856	-0.601237	0.500472	1.037779	0.37030730E-00
0.7148540	1.403420	0.131452	-0.515165	0.412136	1.017574	0.40226503E-00
0.9499220	1.312270	0.088086	-0.444012	0.350540	0.979347	0.37404448E-00
1.2473100	1.235290	0.060121	-0.389816	0.307179	0.940135	0.32127292E-00
1.5020200	1.192260	0.046752	-0.361492	0.285204	0.916406	0.28140527E-00
1.9224300	1.146670	0.033946	-0.332894	0.263280	0.890179	0.23083840E-00

TABLE 6. ALTERNATION PARAMETER δ = 0.25 ; Δ = 0.0.

kT/J	δ	ξ	E/JN	$\varepsilon_{I\!I}/J$	$(\varepsilon_o - \varepsilon_{I\!I})/J$	$\chi(J/q_z^2\beta_z^2)$
0.0167297	1.575110	0.391441	-0.735620	0.785218	0.887752	0.30914892E-19
0.0238996	1.575110	0.391441	-0.735620	0.785218	0.887752	0.33882529E-13
0.0418242	1.575110	0.391441	-0.735620	0.785218	0.887752	0.33794252E-07
0.0836482	1.575110	0.391413	-0.735609	0.785190	0.887773	0.29370853E-03
0.1194880	1.575100	0.390901	-0.735399	0.784676	0.888149	0.42242033E-02
0.1671680	1.574850	0.387317	-0.733787	0.781029	0.890650	0.24285571E-01
0.2085900	1.573780	0.379760	-0.729958	0.773205	0.895515	0.57218163E-01
0.2762860	1.568280	0.357759	-0.717007	0.749829	0.907891	0.13019304E-00
0.4033570	1.539480	0.295776	-0.671288	0.680646	0.932778	0.26645073E-00
0.5180730	1.494890	0.237333	-0.617104	0.611055	0.943168	0.34557668E-00
0.7210870	1.402220	0.159829	-0.525956	0.510384	0.931793	0.38903660E-00
0.9563960	1.311840	0.108453	-0.450956	0.436413	0.902540	0.36696725E-00
1.2537500	1.235130	0.074476	-0.394272	0.383259	0.870490	0.31744198E-00
1.5083800	1.192190	0.058058	-0.364824	0.356106	0.850599	0.27887432E-00
1.9286600	1.146640	0.042243	-0.335197	0.328903	0.828298	0.22936771E-00

TABLE 6. ALTERNATION PARAMETER $\delta = 0.25$; $\Delta = 0.0$.

kT/J	δ	ξ	E/JN	$\varepsilon_{\pi/2}/J$	$(\varepsilon_0 - \varepsilon_{\pi/2})/J$	$\chi \ (J/g_k^2 \beta_e^2)$
0.0167297	1.575110	0.391441	-0.735620	0.785218	0.887752	0.30914892E-19
0.0238996	1.575110	0.391441	-0.735620	0.785218	0.887752	0.33882529E-13
0.0418242	1.575110	0.391441	-0.735620	0.785218	0.887752	0.33794252E-07
0.0836482	1.575110	0.391413	-0.735609	0.785190	0.887773	0.29370853E-03
0.1194880	1.575100	0.390901	-0.735399	0.784676	0.888149	0.42242033E-02
0.1671680	1.574850	0.387317	-0.733787	0.781029	0.890650	0.24285571E-01
0.2085900	1.573780	0.379760	-0.729958	0.773205	0.895515	0.57218163E-01
0.2762860	1.568280	0.357759	-0.717007	0.749829	0.907891	0.13019304E-00
0.4033570	1.539480	0.295776	-0.671288	0.680646	0.932778	0.26645073E-00
0.5180730	1.494890	0.237333	-0.617104	0.611055	0.943168	0.34557668E-00
0.7210870	1.402220	0.159829	-0.525956	0.510384	0.931793	0.38903660E-00
0.9563960	1.311840	0.108453	-0.450956	0.436413	0.902540	0.36696725E-00
1.2537500	1.235130	0.074476	-0.394272	0.383259	0.870490	0.31744198E-00
1.5083800	1.192190	0.058058	-0.364824	0.356106	0.850599	0.27887432E-00
1.9286600	1.146640	0.042243	-0.335197	0.328903	0.828298	0.22936771E-00

TABLE 7. ALTERNATION PARAMETER $\delta = 0.30$; $\Delta = 0.0$

kT/J	δ	ξ	E/JN	ε_π/J	$(\varepsilon_o - \varepsilon_\pi)/J$	$\chi(J/q_c^2\beta_c^2)$
0.0168951	1.567370	0.407106	-0.751309	0.877317	0.812185	0.22600099E-21
0.0241358	1.567370	0.407106	-0.751309	0.877317	0.812185	0.11071242E-14
0.0422376	1.567370	0.407106	-0.751309	0.877317	0.812185	0.49365353E-08
0.0844751	1.567370	0.407096	-0.751304	0.877307	0.812192	0.11647107E-03
0.1206720	1.567370	0.406825	-0.751186	0.877036	0.812381	0.22619227E-02
0.1688500	1.567150	0.404499	-0.749981	0.874644	0.813856	0.15908039E-01
0.2107380	1.566210	0.398987	-0.746786	0.868850	0.817056	0.41498172E-01
0.2792740	1.561230	0.381367	-0.735030	0.849736	0.825904	0.10467774E-00
0.4080320	1.534310	0.326062	-0.690148	0.786355	0.845774	0.23713320E-00
0.5240440	1.491550	0.268608	-0.634314	0.716073	0.856059	0.32173864E-00
0.7283260	1.400880	0.185924	-0.538327	0.606188	0.850469	0.37513705E-00
0.9640730	1.311340	0.127866	-0.459142	0.521268	0.828432	0.35920668E-00
1.2614800	1.234950	0.088420	-0.399609	0.458905	0.802571	0.31313638E-00
1.5160400	1.192090	0.069124	-0.368825	0.426751	0.786076	0.27600129E-00
1.9362100	1.146600	0.050419	-0.337980	0.394399	0.767327	0.22767933E-00

TABLE 8. ALTERNATION PARAMETER $\delta = 0.35$; $\Delta = 0.0$

kT/J	δ	ξ	E/JN	ε_{II}/J	$(\varepsilon_o - \varepsilon_{II})/J$	$\chi(J/q_e^2 \beta_e^2)$
0.0170733	1.560220	0.420290	-0.767488	0.966367	0.740955	0.22600862E-23
0.0243904	1.560220	0.420290	-0.767488	0.966367	0.740955	0.44997475E-16
0.0426831	1.560220	0.420290	-0.767488	0.966367	0.740955	0.81549562E-09
0.0853662	1.560220	0.420285	-0.767485	0.966362	0.740958	0.49056800E-04
0.1219470	1.560220	0.420137	-0.767414	0.966214	0.741054	0.12632769E-02
0.1706530	1.560030	0.418583	-0.766502	0.964593	0.741941	0.10732421E-01
0.2130330	1.559200	0.414481	-0.763820	0.960201	0.744067	0.30770350E-01
0.2824530	1.554650	0.400186	-0.753147	0.944313	0.750402	0.85269821E-01
0.4130290	1.529300	0.350897	-0.709381	0.886152	0.765962	0.21169619E-00
0.5305250	1.488170	0.295437	-0.652424	0.816296	0.775276	0.29936368E-00
0.7364250	1.399430	0.209760	-0.551971	0.699560	0.773286	0.36100533E-00
0.9728400	1.310790	0.146259	-0.468441	0.605035	0.756945	0.35096777E-00
1.2704100	1.234740	0.101902	-0.405761	0.534061	0.736345	0.30845048E-00
1.5249500	1.191990	0.079918	-0.373478	0.497115	0.722847	0.27283528E-00
1.9450200	1.146560	0.058455	-0.341233	0.459751	0.707269	0.22580001E-00

kT/J	δ	ξ	E/JN	ε_{II}/J	$(\varepsilon_o - \varepsilon_{II})/J$	$\chi(J/q^2\beta_e^2)$
0.0172622	1.553590	0.431571	-0.784071	1.053007	0.673211	0.29961535E-25
0.0246603	1.553590	0.431571	-0.784071	1.053007	0.673211	0.22108693E-17
0.0431556	1.553590	0.431571	-0.784071	1.053007	0.673211	0.15005022E-09
0.0863111	1.553590	0.431569	-0.784070	1.053005	0.673213	0.21801373E-04
0.1232990	1.553590	0.431484	-0.784025	1.052920	0.673264	0.73290771E-03
0.1725600	1.553430	0.430421	-0.783327	1.051793	0.673805	0.74386020E-02
0.2154510	1.552680	0.427313	-0.781049	1.048385	0.675220	0.23286863E-01
0.2857890	1.548500	0.415577	-0.771343	1.034977	0.679754	0.70343239E-01
0.4182790	1.524490	0.371553	-0.728816	0.981349	0.691762	0.18974851E-00
0.5374130	1.484820	0.318539	-0.671134	0.912467	0.699769	0.27868874E-00
0.7452540	1.397930	0.231442	-0.566651	0.790614	0.699893	0.34695496E-00
0.9825880	1.310180	0.163599	-0.478703	0.687671	0.687949	0.34242783E-00
1.2804700	1.234510	0.114887	-0.412669	0.608691	0.671774	0.30346411E-00
1.5350500	1.191870	0.090412	-0.378734	0.567160	0.660875	0.26942501E-00
1.9550700	1.146510	0.066333	-0.344932	0.524937	0.648106	0.22375084E-00

TABLE 9. ALTERNATION PARAMETER $\delta = 0.40$; $\Delta = 0.0$.

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TABLE 10. ALTERNATION PARAMETER $\delta = 0.45$; $\Delta = 0.0$.

kT/J	λ	ξ	E/JN	$\varepsilon_{\overline{\tau}}/J$	$(\xi_o - \varepsilon_\pi)/J$	$\chi(J/q_c^2 \beta_c^2)$
0.0174604	1.547430	0.441352	-0.800999	1.137695	0.608343	0.49535229E-27
0.0249434	1.547430	0.441352	-0.800999	1.137695	0.608343	0.1285544E-18
0.0436509	1.547430	0.441352	-0.800999	1.137695	0.608343	0.30395C10E-10
0.0873018	1.547430	0.441351	-0.800999	1.137694	0.608343	0.10175327E-04
0.1247150	1.547420	0.441301	-0.800961	1.137640	0.608365	0.44038380E-03
0.1745530	1.547280	0.440557	-0.800416	1.136833	0.608698	0.52858751E-02
0.2179740	1.546620	0.438165	-0.798482	1.134144	0.609650	0.17960346E-01
0.2892560	1.542750	0.428424	-0.789620	1.122661	0.612879	0.58728800E-01
0.4237350	1.519910	0.388959	-0.748370	1.072918	0.622023	0.17083085E-00
0.5446290	1.481540	0.338540	-0.690244	1.005233	0.628650	0.25976051E-00
0.7547000	1.396390	0.251128	-0.582144	0.879503	0.629894	0.33321030E-00
0.9932120	1.309550	0.179886	-0.489823	0.769183	0.621315	0.33372732E-00
1.2915700	1.234270	0.127350	-0.420277	0.682771	0.608806	0.29825145E-00
1.5462600	1.191750	0.100584	-0.384567	0.636871	0.600141	0.26581535E-00
1.9662900	1.146450	0.074041	-0.349056	0.589943	0.589825	0.22155590E-00

TABLE II. ALTERNATION PARAMETER $\delta = 0.50$; $\Delta = 0.0$

kT/J	δ	ξ	E/JN	ε_{II}/J	$(\varepsilon_o - \varepsilon_{II})/J$	$\chi(J/q_e^2 \beta_e^2)$
0.0176664	1.541670	0.449925	-0.818204	1.220760	0.545873	0.10276516E-28
0.0252377	1.541670	0.449925	-0.818204	1.220760	0.545873	0.87052304E-20
0.0441659	1.541670	0.449925	-0.818204	1.220760	0.545873	0.67226186E-11
0.0883318	1.541670	0.449925	-0.818204	1.220760	0.545873	0.49718003E-05
0.1261870	1.541670	0.449894	-0.818185	1.220729	0.545888	0.27352022E-03
0.1766230	1.541550	0.449362	-0.817754	1.220137	0.546094	0.38451912E-02
0.2205870	1.540950	0.447496	-0.816087	1.217971	0.546727	0.14100219E-01
0.2928350	1.537350	0.439329	-0.807964	1.208004	0.549011	0.49591050E-01
0.4293600	1.515540	0.403799	-0.767972	1.161569	0.555871	0.15450723E-00
0.5521140	1.478360	0.355961	-0.709624	1.095141	0.561200	0.24252008E-00
0.7646680	1.394840	0.268990	-0.598283	0.966410	0.562925	0.31991676E-00
1.0046140	1.308890	0.195143	-0.501674	0.849588	0.556874	0.32498520E-00
1.3036400	1.234000	0.139278	-0.428506	0.756278	0.547361	0.29287753E-00
1.5585200	1.191610	0.110420	-0.390926	0.706225	0.540595	0.26204684E-00
1.9786300	1.146390	0.081565	-0.353592	0.654760	0.532412	0.21923546E-00

TABLE 12. ALTERNATION PARAMETER $\delta = 0.55$; $\Delta = 0.0$.

kT/J	δ	ξ	E/JN	ε_{π}/J	$(\varepsilon_0 - \varepsilon_{\pi})/J$	$\chi(J/q_e^2\,\beta_e^2)$
0.0178792	1.536290	0.457507	-0.835662	1.302466	0.485452	0.25960815E-30
0.0255418	1.536290	0.457507	-0.835662	1.302466	0.485452	0.67734057E-21
0.0446981	1.536290	0.457507	-0.835662	1.302466	0.485452	0.16123191E-11
0.0893960	1.536290	0.457507	-0.835662	1.302466	0.485452	0.25372144E-05
0.1277080	1.536290	0.457488	-0.835650	1.302447	0.485461	0.17535561E-03
0.1787590	1.536190	0.457101	-0.835309	1.302005	0.485590	0.28597801E-02
0.2232790	1.535640	0.455624	-0.833856	1.300226	0.486007	0.11255201E-01
0.2965110	1.532270	0.448713	-0.826375	1.291461	0.487601	0.42323430E-01
0.4351280	1.511390	0.416585	-0.787607	1.247849	0.492662	0.14038166E-00
0.5598200	1.475290	0.371229	-0.729182	1.182638	0.496827	0.22685821E-00
0.7750800	1.393300	0.285208	-0.614937	1.051523	0.498641	0.30716287E-00
1.0167050	1.308210	0.209409	-0.514153	0.928924	0.494460	0.31629340E-00
1.3166000	1.233730	0.150669	-0.437316	0.829220	0.487377	0.28739702E-00
1.5717700	1.191460	0.119910	-0.397778	0.775213	0.482198	0.25815456E-00
1.9920400	1.146330	0.088897	-0.358518	0.719378	0.475845	0.21680851E-00

TABLE 13. ALTERNATION PARAMETER δ = 0.60 ; Δ = 0.0 .

kT/J	δ	ξ	E/JN	$\varepsilon_{\frac{1}{2}}^{II}/J$	$(\varepsilon_o - \varepsilon_{\frac{1}{2}}^{II})/J$	$\chi(J/g_e^2\beta_e^2)$
0.0180981	1.531250	0.464266	-0.853340	1.383016	0.426794	0.78691866E-32
0.0258545	1.531250	0.464266	-0.853340	1.383016	0.426794	0.59945845E-22
0.0452453	1.531250	0.464266	-0.853340	1.383016	0.426794	0.41727091E-12
0.0904906	1.531250	0.464265	-0.853339	1.383015	0.426794	0.13507535E-05
0.1292720	1.531250	0.464253	-0.853331	1.383003	0.426799	0.11592287E-03
0.1809540	1.531160	0.463966	-0.853051	1.382662	0.426878	0.21721651E-02
0.2260410	1.530660	0.462783	-0.851781	1.381179	0.427151	0.91253265E-02
0.3002710	1.527500	0.456885	-0.844868	1.373385	0.428245	0.36480558E-01
0.4410170	1.507450	0.427705	-0.807257	1.332175	0.431898	0.12811507E-0C
0.5677140	1.472330	0.384692	-0.748854	1.268090	0.435055	0.21264680E-00
0.7858700	1.391770	0.299952	-0.631988	1.135014	0.436727	0.29500087E-00
1.0294040	1.307530	0.222733	-0.527180	1.007251	0.433919	0.30772062E-00
1.3303600	1.233450	0.161525	-0.446642	0.901595	0.428770	0.28186151E-00
1.5859200	1.191310	0.129048	-0.405089	0.843834	0.424905	0.25417376E-00
2.0064700	1.146270	0.096029	-0.363812	0.783791	0.420096	0.21429285E-00

TABLE 14. ALTERNATION PARAMETER $\delta = 0.65$; $\Delta = 0.0$

kT/J	λ	ξ	E/JN	ε_{II}/J	$(\varepsilon_0 - \varepsilon_{II})/J$	$\chi(J/g_e^2 \beta_e^2)$
0.0183223	1.526520	0.470329	-0.871207	1.462567	0.369667	0.28285033E-33
0.0261747	1.526520	0.470329	-0.871207	1.462567	0.369667	0.59851224E-23
0.0458058	1.526520	0.470329	-0.871207	1.462567	0.369667	0.11616132E-12
0.0916115	1.526520	0.470329	-0.871207	1.462567	0.369667	0.74978509E-06
0.1308730	1.526510	0.470321	-0.871192	1.462552	0.369666	0.78958711E-04
0.1832000	1.526430	0.470104	-0.870960	1.462283	0.369714	0.16831762E-02
0.2288650	1.525970	0.469146	-0.869839	1.461026	0.369888	0.75077116E-02
0.3041070	1.522990	0.464071	-0.863417	1.454014	0.370622	0.31739636E-01
0.4470110	1.503700	0.437455	-0.826905	1.414860	0.373186	0.11742382E-00
0.5757640	1.469480	0.396633	-0.768597	1.351795	0.375496	0.19974922E-00
0.7969820	1.390270	0.313381	-0.649362	1.217056	0.376911	0.28344836E-00
1.0426400	1.306840	0.235171	-0.540667	1.084617	0.375084	0.29932173E-00
1.3448600	1.233150	0.171858	-0.456425	0.973405	0.371452	0.27631128E-00
1.6009300	1.191150	0.137834	-0.412818	0.912081	0.368661	0.25013115E-00
2.0218600	1.146200	0.102956	-0.369446	0.847986	0.365135	0.21170595E-00

TABLE 15. ALTERNATION PARAMETER $\delta = 0.10$; $\Delta = 0.0$.

kT/J	δ	ξ	E/JN	$\varepsilon_{\mathrm{II}}/J$	$(\varepsilon_{\circ}-\varepsilon_{\mathrm{II}})/J$	$\chi(J/q_e^2\beta_e^2)$
0.0185512	1.522060	0.475802	-0.889233	1.541244	0.313877	0.12274528E-34
0.0265017	1.522060	0.475802	-0.889233	1.541244	0.313877	0.67070455E-24
0.0463780	1.522060	0.475802	-0.889233	1.541244	0.313877	0.34745032E-13
0.0927560	1.522060	0.475802	-0.889233	1.541244	0.313877	0.43413924E-06
0.1325080	1.522060	0.475796	-0.889229	1.541238	0.313879	0.55377333E-04
0.1854930	1.521980	0.475630	-0.889027	1.541016	0.313905	0.13292865E-02
0.2317440	1.521560	0.474845	-0.888032	1.539937	0.314015	0.62618843E-02
0.3080090	1.518740	0.470446	-0.882042	1.533564	0.314488	0.27854401E-01
0.4530950	1.500130	0.446069	-0.846548	1.496160	0.316218	0.10806607E-00
0.5839490	1.466750	0.407280	-0.788390	1.434005	0.317841	0.18803181E-00
0.8083720	1.388800	0.325638	-0.666987	1.297798	0.318949	0.27250755E-00
1.0563500	1.306150	0.246782	-0.554549	1.161087	0.317810	0.29113413E-00
1.3600300	1.232860	0.181681	-0.466633	1.044683	0.315354	0.27077906E-00
1.6167200	1.190990	0.146270	-0.420935	0.979963	0.313416	0.24605376E-00
2.0381600	1.146130	0.109676	-0.375407	0.911967	0.310936	0.20906246E-00

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TABLE 16. ALTERNATION PARAMETER $\delta = 0.15$; $\Delta = 0.0$

kT/J	λ	ξ	E/JN	ε_{II}/J	$(\varepsilon_o - \varepsilon_{II})/J$	$\chi(J/g^2\beta^2)$
0.0187843	1.517860	0.480767	-0.907410	1.619162	0.259273	0.10082065E-35
0.0268348	1.517860	0.480767	-0.907410	1.619162	0.259273	0.84089278E-25
0.0469608	1.517860	0.480767	-0.907410	1.619162	0.259273	0.11182322E-13
0.0939217	1.517860	0.480767	-0.907410	1.619162	0.259273	0.262401193E-06
0.1341730	1.517860	0.480764	-0.907408	1.619159	0.259274	0.39968713E-04
0.1878270	1.517790	0.480635	-0.907238	1.618977	0.259289	0.10688177E-02
0.2346730	1.517400	0.479984	-0.906345	1.618034	0.259354	0.52902408E-02
0.3119720	1.514720	0.476144	-0.900732	1.612184	0.259644	0.246433700E-01
0.4592590	1.496740	0.453730	-0.866194	1.576285	0.260753	0.99839554E-01
0.5922500	1.464130	0.416823	-0.808211	1.514920	0.261827	0.17737336E-00
0.8200010	1.387360	0.336852	-0.684810	1.377372	0.262627	0.262166340E-00
1.0704800	1.305460	0.257623	-0.568768	1.236718	0.261959	0.28318457E-00
1.3758200	1.232560	0.191013	-0.477211	1.115433	0.260387	0.265293100E-00
1.6332500	1.190830	0.154361	-0.429407	1.047483	0.259117	0.241961810E-0C
2.0553200	1.146050	0.116187	-0.381666	0.975724	0.257466	0.20637663E-00

TABLE 17. ALTERNATION PARAMETER $\delta = 0.80$; $\Delta = 0.0$

kT/J	δ	ξ	E/JN	ε_{π}/J	$(\varepsilon_o - \varepsilon_{\pi})/J$	$\chi(J/g_e^2\beta_e^2)$
0.0190212	1.513890	0.485293	-0.925715	1.696405	0.205719	0.58084243E-36
0.0271732	1.513890	0.485293	-0.925715	1.696405	0.205719	0.11814596E-25
0.0475531	1.513890	0.485293	-0.925715	1.696405	0.205719	0.38950118E-14
0.0951062	1.513890	0.485294	-0.925716	1.696406	0.205719	0.16574241E-06
0.1358660	1.513890	0.485291	-0.925713	1.696406	0.205720	0.29668284E-04
0.1901980	1.513830	0.485189	-0.925570	1.696253	0.205728	0.87410687E-03
0.2376470	1.513460	0.484645	-0.924757	1.695413	0.205763	0.45233896E-02
0.3159890	1.510920	0.481270	-0.919489	1.690006	0.205930	0.21966431E-01
0.4654940	1.493510	0.460585	-0.885833	1.655393	0.206585	0.92579065E-01
0.6006520	1.461620	0.425417	-0.828047	1.594713	0.207241	0.16766109E-00
0.8318390	1.385970	0.347135	-0.702801	1.455911	0.207767	0.25240064E-00
1.0849900	1.304780	0.267752	-0.583278	1.311576	0.207406	0.27548846E-00
1.3921600	1.232260	0.199875	-0.488123	1.185683	0.206477	0.25987709E-00
1.6504400	1.190660	0.162116	-0.438198	1.114644	0.205709	0.23787744E-00
2.0732800	1.145970	0.122489	-0.388210	1.039265	0.204696	0.20366140E-00

TABLE 18. ALTERNATION PARAMETER $\gamma = 0.85$; $\Delta = 0.0$

kT/J	δ	ξ	E/JN	$\varepsilon_{\mathbb{I}}/J$	$(\varepsilon_0 - \varepsilon_{\mathbb{I}})/J$	$\chi(J/g_e^2\beta_e^2)$
0.0192616	1.510130	0.489437	-0.944133	1.773047	0.153104	0.61027866E-36
0.0275165	1.510130	0.489437	-0.944133	1.773047	0.153104	0.18814880E-26
0.0481539	1.510130	0.489437	-0.944133	1.773047	0.153104	0.14850456E-14
0.0963078	1.510140	0.489436	-0.944142	1.773055	0.153106	0.10949516E-06
0.1375820	1.510130	0.489434	-0.944131	1.773044	0.153104	0.22623099E-04
0.1926030	1.510080	0.489353	-0.944011	1.772921	0.153109	0.72639368E-03
0.2406620	1.509730	0.488895	-0.943268	1.772165	0.153125	0.39110923E-02
0.3200550	1.507310	0.485909	-0.938299	1.767122	0.153210	0.19717778E-01
0.4717930	1.490430	0.466753	-0.905467	1.733618	0.153552	0.86144947E-01
0.6091430	1.459220	0.433190	-0.847895	1.673527	0.153905	0.15879373E-00
0.8438580	1.384610	0.356589	-0.720913	1.533507	0.154203	0.24318832E-00
1.0998300	1.304120	0.277224	-0.598047	1.385726	0.154034	0.26805522E-00
1.4090000	1.231950	0.208288	-0.499326	1.255445	0.153549	0.25454985E-00
1.6682500	1.190490	0.169544	-0.447285	1.181460	0.153142	0.23381495E-00
2.0919900	1.145900	0.128584	-0.395027	1.102599	0.152597	0.20092784E-00

TABLE 19. ALTERNATION PARAMETER $\delta = 0.90$; $\Delta = 0.0$

kT/J	δ	ξ	E/JN	ε_{II}/J	$(\varepsilon_o - \varepsilon_{II})/J$	$\chi \ (J/q_c^2 \beta_c^2)$
0.0195050	1.506580	0.493243	-0.962667	1.849165	0.101334	0.60266307E-36
0.0278643	1.506580	0.493243	-0.962667	1.849165	0.101334	0.35095926E-27
0.0487624	1.506580	0.493243	-0.962667	1.849165	0.101334	0.63075603E-15
0.0975249	1.506580	0.493243	-0.962667	1.849165	0.101334	0.75685516E-07
0.1393210	1.506580	0.493242	-0.962667	1.849164	0.101334	0.17701937E-04
0.1950380	1.506530	0.493176	-0.962557	1.849053	0.101335	0.61268612E-03
0.2437140	1.506200	0.492786	-0.961874	1.848366	0.101341	0.34168152E-02
0.3241670	1.503880	0.490130	-0.957164	1.843622	0.101375	0.17814773E-01
0.4781480	1.487490	0.472329	-0.925093	1.811070	0.101516	0.80419865E-01
0.6177120	1.456910	0.440250	-0.867734	1.751469	0.101666	0.15068410E-00
0.8560360	1.383300	0.365300	-0.739134	1.610270	0.101800	0.23449699E-00
1.1149600	1.303460	0.286088	-0.613020	1.459202	0.101737	0.26089238E-00
1.4263000	1.231650	0.216274	-0.510802	1.324759	0.101538	0.24932273E-00
1.6866300	1.190320	0.176655	-0.456641	1.247943	0.101367	0.22978809E-00
2.1114100	1.145820	0.134474	-0.402084	1.165712	0.101135	0.19818608E-00

TABLE 20. ALTERNATION PARAMETER $\delta = 0.95$; $\Delta = 0.0$						
kT/J	δ	ξ	E/JN	$\varepsilon_{\perp}/J$	$(\varepsilon_o - \varepsilon_{\perp})/J$	$\chi(J/g_e^2 \beta_e^2)$
0.0197512	1.503210	0.496753	-0.981295	1.924802	0.050323	0.59515085E-36
0.0282160	1.503210	0.496753	-0.981295	1.924802	0.050323	0.82863721E-28
0.0493780	1.503210	0.496753	-0.981295	1.924802	0.050323	0.30480739E-15
0.0987560	1.503210	0.496753	-0.981295	1.924802	0.050323	0.54685C18E-07
0.1410800	1.503200	0.496752	-0.981284	1.924792	0.050322	0.14194150E-04
0.1975020	1.503160	0.496698	-0.981193	1.924700	0.050323	0.52402058E-03
0.2467990	1.502850	0.496364	-0.980565	1.924071	0.050324	0.30136900E-02
0.3283190	1.500630	0.493987	-0.976092	1.919585	0.050332	0.16191722E-01
0.4845540	1.484690	0.477394	-0.944724	1.887849	0.050365	0.75304603E-01
0.6263500	1.454700	0.446686	-0.887572	1.828651	0.050401	0.14324942E-00
0.8683540	1.382030	0.373347	-0.757438	1.686275	0.050434	0.22629835E-00
1.1303500	1.302810	0.294394	-0.628177	1.532063	0.050421	0.25399821E-00
1.4440200	1.231350	0.223857	-0.522516	1.393639	0.050375	0.24420730E-00
1.7055400	1.190150	0.183461	-0.466243	1.314103	0.050334	0.22580761E-00
2.1314900	1.145740	0.140163	-0.409372	1.228616	0.050279	0.19544515E-00

TABLE 21. ALTERNATION PARAMETER $\delta = 0.99$; $\Delta = 0.0$

kT/J	λ	ξ	E/JN	$\varepsilon_{\frac{\pi}{2}}/J$	$(\varepsilon_o - \varepsilon_{\frac{\pi}{2}})/J$	$\chi\ (J/g_e^2\beta_e^2)$
0.0199501	1.500630	0.499373	-0.996256	1.984997	0.010013	0.58921727E-36
0.0285001	1.500630	0.499373	-0.996256	1.984997	0.010013	0.33505648E-28
0.0498751	1.500630	0.499373	-0.996256	1.984997	0.010013	0.18878996E-15
0.0997503	1.500630	0.499373	-0.996256	1.984997	0.010013	0.43477741E-07
0.1425000	1.500620	0.499373	-0.996246	1.984987	0.010012	0.12091333E-04
0.1994910	1.500580	0.499324	-0.996158	1.984898	0.010013	0.46672253E-03
0.2492910	1.500290	0.499030	-0.995577	1.984317	0.010013	0.27433258E-02
0.3316680	1.498130	0.496845	-0.991260	1.979994	0.010013	0.15061545E-01
0.4897130	1.482540	0.481125	-0.960429	1.948840	0.010014	0.71596561E-01
0.6333050	1.452990	0.451441	-0.903435	1.889901	0.010015	0.13774112E-00
0.8782990	1.381040	0.379352	-0.772125	1.746582	0.010017	0.22007461E-00
1.1428300	1.302310	0.300666	-0.640425	1.589953	0.010016	0.24867284E-00
1.4584700	1.231120	0.229649	-0.532048	1.448458	0.010015	0.24019995E-00
1.7210200	1.190010	0.188695	-0.474084	1.366805	0.010013	0.22266324E-00
2.1480000	1.145670	0.144574	-0.415354	1.278787	0.010011	0.19325846E-00

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II. PHONON EFFECTS IN TRIPLET EXCITON THEORY

A LOCALIZED, DIFFUSIONAL MODEL FOR EXCITONS

Abstract

Ionic organic crystals such as Wurster's blue perchlorate
and various TCNQ salts consist of linear chains of free radicals.
The EPR (electron paramagnetic resonance) properties of these
crystals have been successfully discussed in terms of triplet
excitons, especially for low exciton densities. We consider a
deformable lattice and investigate the influence of phonons on
the triplet excitons. For low exciton density (i.e., at low tem-
perature) the excitons, on account of the phonons, are localized
and diffusional; they resemble chargeless polarons in the strong-
coupling limit. A general expression for the rate of an exciton
process in a phonon bath at thermal equilibrium is obtained. The
temperature dependence of the rate is found. In particular, we
obtain the diffusion constant for exciton motion, the activation
energy for diffusion, and the rates of exciton creation and anni-
hilation processes via lattice phonons. We estimate these
parameters for Wurster's blue perchlorate. Even at absolute zero,
diffusional excitons are mobile enough to account for the absence
of hyperfine structure in the EPR spectra. We also obtain the
modifications of the parameters of the effective exciton hamil-
tonian due to the phonons, and we rederive a phonon-coupled
repulsion between excitons.

Introduction

We consider a one-dimensional lattice of free radicals, on each of which there is a tightly-bound unpaired electron. We assume that the lattice alternates, as shown in figure 1. A pair of nearest-neighbor free radicals form a site; the alternating lattice is therefore a regular array of sites. The two unpaired electrons on a site may be in either a spin-paired singlet state or a spin-parallel triplet state. We assume that the coupling is antiferromagnetic, so that the exchange integral is positive. The singlet state is then the ground state. The triplet excited states, on account of the interactions between electrons on adjacent sites, are mobile. These mobile triplet states are the paramagnetic (triplet) excitons that are the lowest-lying excited states of certain organic crystals. The crystals are ionic free radicals, such as various TCNQ salts (1,2) and Wurster's blue perchlorate (3). In these systems, the triplet states are accessible thermally.

The electronic properties of the tightly-bound electrons may be understood from a one-dimensional model (4,5). Lynden-Bell and McConnell have discussed, in a paper we call A (5), the properties of triplet excitons on a rigid, alternating lattice, with exchange integrals $J > J' > 0$. In the approximation of not including ionic states or higher excited states, the hamiltonian is just the exchange hamiltonian (equation 1.1). The conclusions in A may be summarized as follows: to good approximation, the triplet excitons on a rigid lattice are waves; they are

essentially fermions; their energies form a band whose width is J'.

The temperature dependence of the exciton lines observed by EPR (1-3,6) may be understood roughly on the basis of A, provided that J' is some two orders of magnitude smaller than J. However, the alternation of the WBP (Wurster's blue perchlorate) lattice is probably quite small (7); above the transition temperature of 186°K, the lattice does not alternate at all (8). Such a large variation in the relative magnitudes of the exchange integrals is therefore unexpected. Furthermore, the exciton line-broadening and line-merging rates as functions of temperature show different activation energies (2,3); this property cannot be predicted from the model in A. By considering a deformable lattice, McConnell and Soos, in a paper we call B (9), found a spin-independent, phonon-coupled repulsion between triplet excitons. The repulsion explains the temperature dependence of the line broadening (10) and also gives the appropriate exchange narrowing for J' of the order of J. However, the model used is essentially that of localized excitons.

We show that, due to the rapid scattering of excitons by phonons, the delocalized description used in A is inappropriate and that a localized, diffusional model is indicated. In order to do this, we derive the properties of excitons coupled to a phonon bath, which for simplicity we take to be the same as in B. The one-dimensional model we consider is inherently more tractable than the three-dimensional model used in the analogous,

extensively studied problem of the interactions of localized electrons in polar crystals. Diffusional excitons may be considered to be chargeless polarons, with very strong coupling to the lattice. Delocalized excitons, on the other hand, resemble metallic electrons. As in polaron theory, the localized, diffusional picture is appropriate for low exciton concentrations.

The effective masses of the localized, diffusional excitons may be so large that an inverse Born-Oppenheimer approximation is required; the excitons move slowly compared with lattice vibrations. This approximation is valid only at low temperatures. As the temperature is raised, the excitons become increasingly more mobile and, provided that $J' \gtrsim$ typical phonon energies, eventually move rapidly compared with lattice vibrations. Their effective masses decrease by several orders of magnitude. The relative rates of lattice vibrations and quasiparticle (exciton) motion thus determine the appropriate approximation scheme.

In section I, we discuss the model, the exciton-phonon hamiltonian, and the approximations. In section II, we find the distortions of the lattice, both in real and in wave vector space, due to an arbitrary exciton distribution. In section III, we derive a general expression for the rate, and its temperature dependence, of an exciton transition. The site-to-site jumping frequency ω_j and the diffusion constant for localized excitons are found in section IV. We show that the jumping rate is high enough to account for the absence of hyperfine structure, even at very low temperature. This removes what had been the most

serious objection to a localized, diffusional model. The high-temperature activation energy for diffusion is found. In section V, we estimate the rate of exciton creation and annihilation via lattice phonons. Lattice-phonon processes are compared with radiationless transitions via intramolecular phonons. In section VI, we present the justification for a localized, diffusional model and discuss the modifications, due to phonons, of the parameters of the effective exciton hamiltonian.

I. Model for Excitons, Phonons.
The Exciton-Phonon Hamiltonian

The exchange hamiltonian 1.1 is also the hamiltonian for an alternating linear antiferromagnetic chain. Both the regular $(J' = J)$ and the alternating $(J' < J)$ antiferromagnet have been considered several times (for further references, see reference 11). It may be shown (11) that the description used in A is adequate for the case of strong alternation $(J' \lesssim 1/3\ J)$ and low temperature $(kT \lesssim \frac{1}{2}J)$. It is inherent to the model in A that the two electrons forming a triplet excitation are always adjacent in position space. This assumption is satisfied for strong alternation and low temperature (11). Unless the two electrons are adjacent, the electrostatic phonon-coupling we describe does not exist. The two electrons forming a triplet excitation then do not distort the lattice, so that phonon-coupling is expected to be weak. We restrict the discussion to the case of strong alternation and low temperature. The exciton model used in A will always be used in the following.

The triplet excitons of A are now considered on a deformable lattice, shown in figure 1. The exciton hamiltonian for the rigid lattice is (5)

$$H_e^0 = \sum_{\ell=1}^{N/2} \{ J\, \vec{A}_{2\ell} \cdot \vec{A}_{2\ell+1} + J'\, \vec{A}_{2\ell} \cdot \vec{A}_{2\ell-1} \} \qquad 1.1$$

$$= H_0 + H_1 + H_2 + H_3$$
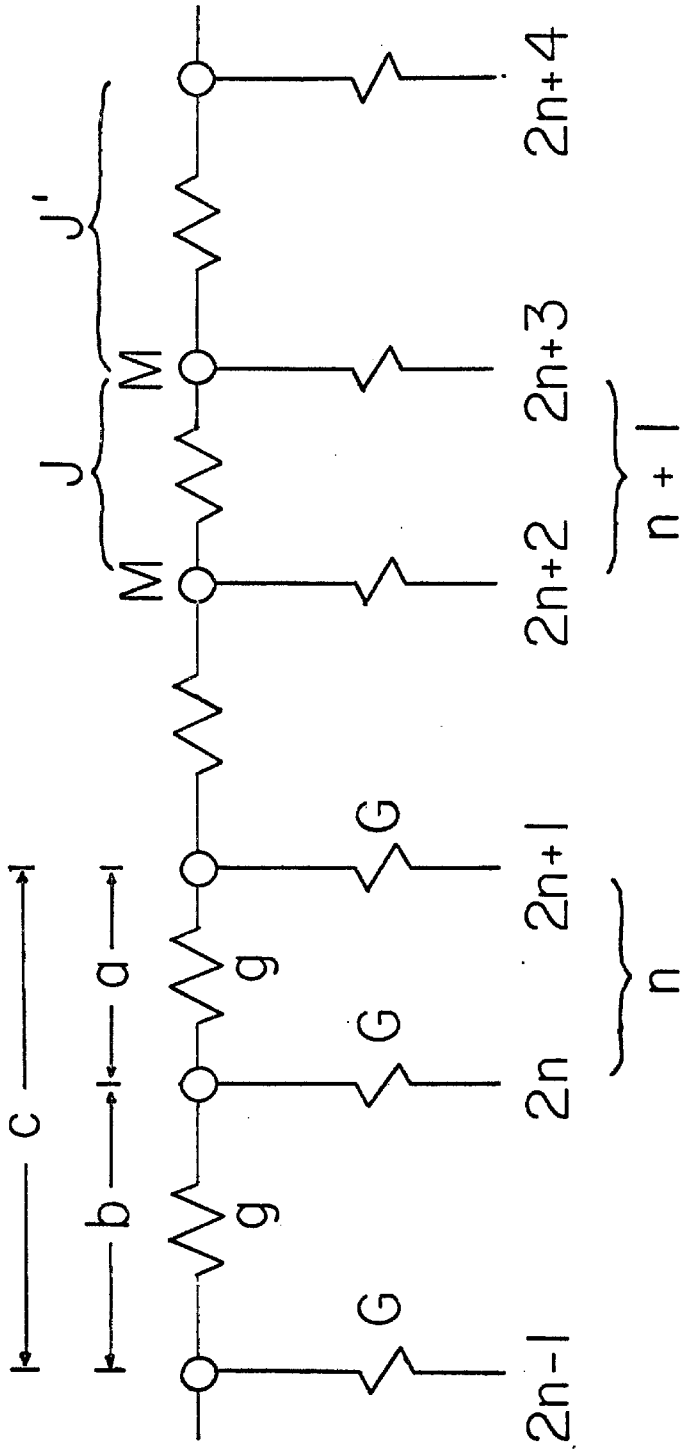
Fig 1. Schematic of alternating linear array of exchange-coupled molecules.

$$\mathcal{H}_o + \mathcal{H}_1 = \sum_{n=1}^{N/2} \{ J t_n^+ t_n - \frac{J'}{4}(t_n^+ t_{n+1} + t_{n+1}^+ t_n) \} \qquad 1.2$$

$$\mathcal{H}_2 = \sum_{n=1}^{N/2} \frac{J'}{4} \vec{S}_n \cdot \vec{S}_{n+1}$$

$$1.3$$

$$\mathcal{H}_3 = \frac{J'}{4} \times \text{terms creating or destroying excitations.}$$

$\vec{J}_n = \frac{1}{2}$ is the electron spin on the nth molecule; the molecules 2n, 2n + 1 are nearest neighbors and form the site n; t_n^+, t_n are the exciton creation and annihilation operators, respectively, for the nth site; $\vec{S}_n = 1, 0$ is the spin at the nth site if there is, or is not, an exciton on the site.

To discuss a deformable lattice, we must consider the phonon-coupling arising, as shown in B, from the distance dependence of the exchange integrals. $\mathcal{H}_{pe}$ is the term in the hamiltonian which describes the coupling due to the linear term in the Taylor expansion of the exchange integrals. We neglect all higher order terms in the expansion. Unless otherwise indicated, all quantities are evaluated at their no-exciton equilibrium positions. Thus we have

$$\mathcal{H}_e = \mathcal{H}_e^o + \mathcal{H}_{pe}, \qquad 1.4$$

where

$$\mathcal{H}_{pe} = \sum_{\ell=1}^{N/2} \left\{ j\,\delta_\ell\, \vec{J}_{2\ell} \cdot \vec{J}_{2\ell+1} + j'\Delta_\ell\, \vec{J}_{2\ell} \cdot \vec{J}_{2\ell-1} \right\},$$

1.5

$$= \mathcal{H}_4 + \mathcal{H}_5 + \mathcal{H}_6 + \mathcal{H}_7,$$

$$\mathcal{H}_4 = \sum_{n=1}^{N/2} j\,\delta_n\, t_n^+ t_n,$$

1.6

$$\mathcal{H}_5 = -\sum_{n=1}^{N/2} \frac{j'}{4}\Delta_n \left(t_n^+ t_{n+1} + t_{n+1}^+ t_n \right).$$

1.7

$j = \frac{\partial J}{\partial x}$ and $j' = \frac{\partial J'}{\partial x}$ are the derivatives of the two exchange integrals with respect to the intermolecular distance; $\delta_n \equiv d_{2n+1} - d_{2n}$, $\Delta_n \equiv d_{2n} - d_{2n-1}$, where d_n is the displacement from equilibrium of the nth molecule; $\mathcal{H}_6$ and $\mathcal{H}_7$ are just $\mathcal{H}_2$ and $\mathcal{H}_3$ multiplied by $j'\Delta_n/J'$ in each term. The alternating lattice consists of N molecules and $\frac{1}{2}N$ sites. M is the mass of a molecule (or free radical, etc.); a, b, and c are the distances specifying the free lengths and the unit cell; G and g are force constants.

We assume that the discussion may be restricted to a harmonic phonon hamiltonian and to an electronic perturbation that is linear in the molecular displacements. A linear perturbation will give new equilibrium positions, but will not change the normal frequencies. This approximation is a frequent starting point for discussions of electron-phonon interactions (12-14).

If an excitation is placed on site m, the electronic wave function
of m is changed from a bonding S=0 to an antibonding S=1 state; by
"bonding" and "antibonding" we of course refer only to the contri-
bution of the two electrons which are unpaired in the free
molecules. The pair 2m, 2m + 1 will move apart. The perturbation
corresponds to a change in the singlet-triplet energy gap and is
just a term of H_4,

$$V_m = -|j| \, \delta_m \, .$$

1.8

Distortions arising from the perturbation 1.8, when there
is an exciton on the mth site, are the only ones we consider.
Thus we explicitly include only j; the effects arising from j'
will be included only in an average way, as discussed in section
VI. In fact, j' has but second-order effects on, for instance,
the line shape (15). It is evident physically that, if we con-
sider a site of the strongly alternating lattice to be a
"molecule," the excitation energies of the "molecules" should
depend on j in the first order and on j' only in higher order.

The lattice is "tied down" to simulate the three-
dimensionality of the actual lattice; G = 0 for the "free"
lattice. It is impossible to separate exactly the longitudinal
and the transverse phonon modes, because in general the polariza-
tion directions on the phonon modes are not simply related to the
lattice directions. The coupling with the roughly transverse
phonons is expected to be weak (14). A general qualitative

feature of the roughly longitudinal mode is that it is shifted to higher energies relative to the free lattice (14). By tying down the lattice, we approximate crudely this feature of the actual, extremely complicated phonon spectrum. The model is, however, entirely inadequate in that it suppresses entirely low-energy phonons (16). We shall return to this point when we discuss the scattering of excitons by phonons in section VI. It is evident, therefore, that we cannot, for instance, discuss the phonon heat capacity in terms of the present model. On the other hand, that the excitations are localized and diffusional does not depend on tying down the lattice.

The force constants between nearest (intra-site) and next nearest (inter-site) molecules are chosen to be the same. This assumption removes the energy gap between the acoustic and the optical phonon modes. The phonon spectrum of the alternating lattice then reduces to the spectrum of a regular lattice with lattice spacing $\frac{1}{2}c = \frac{1}{2}(a + b)$. The more general case of alternating force constants leads to similar results if the lattice is tied down (15).

When there are no excitons on the lattice, the phonon hamiltonian is

$$H_p = \sum_{\ell=1}^{N} \left\{ \frac{p_\ell^2}{2M} + \frac{g}{2}(\lambda d_\ell^2 - 2d_\ell d_{\ell+1}) \right\}, \qquad 1.9$$

where $\lambda = 2 + G/g$ and p_n is the momentum of the nth molecule. We transform to wave vector space. The phonon wave vector q is

restricted to the first Brillouin zone. We obtain

$$\mathcal{H}_P = \sum_q \left\{ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \xi_q \partial \xi_{-q}} + \frac{1}{2} M \omega_q^2 \xi_q \xi_{-q} \right\}$$

$$= \sum_q \frac{1}{2} \hbar \omega_q \left(\zeta_q^2 - \frac{\partial^2}{\partial \zeta_q^2} \right),$$

1.10

where $q = \frac{2\pi m}{cN}$, $m = 0, \pm 1, \ldots \pm(\frac{1}{2}N-1), \frac{1}{2}N$; the dispersion relation is

$$\omega_q = \sqrt{\frac{q}{M} \left(\lambda - 2\cos\frac{qc}{2} \right)} \quad ;$$

1.11

ξ_q are the normal coordinates for the regular lattice

$$\xi_q = \frac{1}{\sqrt{N}} \sum_{\ell=1}^{N} d_\ell \, e^{iq\frac{\ell c}{2}},$$

1.12

and ζ_q are dimensionless, real normal coordinates,

$$\zeta_q = \sqrt{\frac{2M\omega_q}{\hbar N}} \sum_{\ell=1}^{N} \left\{ \begin{array}{ll} d_\ell \cos q\frac{\ell c}{2} & q \geqslant 0 \\ d_\ell \sin q\frac{\ell c}{2} & q < 0 . \end{array} \right.$$

1.13

The ζ_q are convenient for the present problem (17), since we introduce harmonic oscillator functions explicitly.

We summarize below the various approximations. (a) The electrons follow the motion of the nuclei adiabatically; this is the familiar Born-Oppenheimer approximation. (b) The unpaired electron on each molecule is always in the molecular electronic ground state. The triplet excitons are the only electronic

excitations possible at the temperatures considered. (c) The lattice may be approximated by a harmonic model. For the most part, tying down the lattice is not crucial: the consequences of not doing so are that the self-energy (equation 2.9) is increased, while the phonon-coupled interaction between excitons (equation 2.16) vanishes. Thus we not only assume that the lattice is harmonic, but also replace the three-dimensional lattice with an effective one-dimensional model. (d) The interactions of an exciton with the lattice may be approximated by the linear term in the expansion of the exchange integrals. Thus we consider explicitly one-phonon processes only. (e) The lattice is adiabatic with respect to the excitons. This approximation is discussed in the next section and is justified in section VI.

II. Distortion of the Lattice
Due to Localized Excitons

It is known that localized excitons may have very large effective masses (18,19). It may therefore be appropriate to make an inverse Born-Oppenheimer approximation: the molecules follow the motion of the excitons adiabatically. The presence of an exciton on site m will displace the qth normal coordinate by an amount $\varepsilon_m(q)$. The normal frequencies are unchanged, since the perturbation 1.8 is linear. We show in section IV that in fact the exciton remains on a site for a time long compared with lattice vibration periods. We assume therefore that the molecular coordinates have time to rearrange completely for a given exciton distribution.

(a) One Exciton, at Site m

If there is an exciton on site m, the phonon hamiltonian is

$$\mathcal{H}_P^m = \mathcal{H}_P + V_m = \sum_{l=1}^{N} \left\{ \frac{P_l^2}{2M} + \frac{g}{2}(\lambda d_l^2 - 2 d_l d_{l+1}) \right\} - |j|(d_{2m+1} - d_{2m}). \quad 2.1$$

We introduce the coordinates

$$\left. \begin{array}{l} y_{2m+l} = d_{2m+l} - \alpha f_l \\ y_{2m+1-l} = d_{2m+1-l} + \alpha f_l \end{array} \right\} \quad l = 1, 2, 3 \cdots, \qquad 2.2$$

where $\alpha = |j|/g$ and the $f_l(\lambda)$ are undetermined functions. We substitute 2.2 in 2.1 and require that all terms linear in the y_l's vanish. This will be the case, provided that

$$\lambda f_1 + (f_1 - f_2) - 1 = 0$$
$$\lambda f_\ell - (f_{\ell+1} + f_{\ell-1}) = 0 \quad , \quad \ell = 2, 3, \cdots . \qquad 2.3$$

For an infinite ($N \to \infty$) lattice, which we assume, the solutions of 2.3 lead to an infinite continued fraction,

$$\bar{q}(\lambda) = \cfrac{1}{\lambda - \cfrac{1}{\lambda - \cdots}} . \qquad 2.4$$

The solution we seek must have the property that $f_\ell \to 0$ as $\ell \to \infty$, since the effects of the perturbation far from the mth site must be negligible. Using this condition, we find

$$\bar{q}(\lambda) = \frac{\lambda - \sqrt{\lambda^2 - 4}}{2} , \qquad 2.5$$

$$f_1(\lambda) = \frac{1}{2}\left(1 - \sqrt{\frac{\lambda - 2}{\lambda + 2}}\right), \qquad 2.6$$

$$f_\ell(\lambda) = f_1 x^{\ell - 1} , \quad x(\lambda) = \frac{2}{\lambda + \sqrt{\lambda^2 - 4}} , \quad \ell = 2, 3, \cdots . \qquad 2.7$$

Thus we have

$$\mathcal{H}_P^m = \sum_\ell \left\{ \frac{P_\ell^2}{2M} + \frac{q}{2}(\lambda y_\ell^2 - 2 y_\ell y_{\ell+1}) \right\} - \Lambda(\lambda)$$

$$= \sum_q \left\{ \frac{1}{2} \hbar \omega_q \left((\gamma_q^m)^2 - \frac{\partial^2}{\partial(\gamma_q^m)^2} \right) \right\} - \Lambda(\lambda) ; \qquad 2.8$$

$$\Lambda(\lambda) = \frac{\dot{j}^2}{q} \frac{1}{2}\left(1 - \sqrt{\frac{\lambda - 2}{\lambda + 2}}\right) = \frac{\dot{j}^2}{q} f_1(\lambda) . \qquad 2.9$$

$\zeta_q^m = \zeta_q - \epsilon_m(q)$ is the qth dimensionless, real normal coordinate when there is an exciton on site m. The quantity $\Lambda(\lambda)$ is just the self-energy correction evaluated in B by a totally different method.

From 1.13, 2.2, 2.6, and 2.7, we have

$$\epsilon_m(q) = \sqrt{\frac{2M\omega_q}{\hbar N}} \sum_{\ell=-\infty}^{\infty} \alpha(\ell) \begin{cases} \cos\frac{qc}{2}(2m+\ell) & q \geqslant 0 \\ \sin\frac{qc}{2}(2m+\ell) & q < 0 \end{cases}, \qquad 2.10$$

where $\alpha(\ell) = \pm |j| f_\ell(\lambda)/g$ for $\ell > 0$ and $\ell \leq 0$, respectively. We use 2.7 to sum 2.10. After some manipulation, we obtain

$$\epsilon_m(q) = \sqrt{\frac{2M\omega_q}{\hbar N}} \frac{|j|}{g} \frac{-2\sin\frac{qc}{4}}{(\lambda - 2\cos\frac{qc}{2})} \begin{cases} \sin qc(m+\frac{1}{4}), & q \geqslant 0 \\ \cos qc(m+\frac{1}{4}), & q < 0 \end{cases}; \qquad 2.11$$

$$\epsilon_m(q) - \epsilon_{m+1}(q) = \sqrt{\frac{2M\omega_q}{\hbar N}} \frac{|j|}{g} \frac{4\sin\frac{qc}{4}\sin\frac{qc}{2}}{(\lambda - 2\cos\frac{qc}{2})} \begin{cases} \cos qc(m+\frac{3}{4}), & q \geqslant 0 \\ \sin qc(m+\frac{3}{4}), & q < 0 \end{cases}. \qquad 2.12$$

If we sum over the first Brillouin zone the square of 2.11 or 2.12 with an even function of q, we obtain results which are independent of the site m. This property will always guarantee that various results be independent of the site; this must of course be the case, since all the sites are equivalent.

The self-energy is the negative of the energy required to distort the normal coordinates by an amount $\epsilon_m(q)$, as may be verified by evaluating the sum explicitly,

$$\Lambda(\lambda) = \sum_q \frac{1}{2}\hbar\omega_q \left(\epsilon_m(q)\right)^2 = \frac{j^2}{g} \frac{1}{2}\left(1 - \sqrt{\frac{\lambda-2}{\lambda+2}}\right). \qquad 2.13$$

As expected, the new equilibrium positions correspond to a lattice on which each molecule has been moved away from the exciton by an amount $|j| f_{\ell}(\lambda)/g$; this is immediately evident from 2.2 and 2.7. The self-energy, which may also be obtained by summing over the distortions in real space, corrects for the effect of a non-vertical transition. By distorting a site (increasing the equilibrium separation between the two molecules) the creation of an exciton decreases the singlet-triplet energy gap.

(b) Two or More Localized Excitons

We suppose that there is an arbitrary distribution of excitons on the lattice. Since the perturbation 1.8 is linear in the molecular coordinates, the distortion of the qth normal coordinate from its equilibrium position is just the sum of the distortions due to each exciton. As before, the normal coordinates are unchanged. Hence we have

$$H_P' = \sum_q \left\{ \tfrac{1}{2} \hbar \omega_q \left((\zeta_q')^2 - \frac{\partial^2}{\partial (\zeta_q')^2} \right) \right\} - \mathcal{E}(\lambda) , \qquad 2.14$$

where $\zeta_q' = \zeta_q - \sum_{m \,(\text{occupied})} \varepsilon_m(q)$ is the qth normal coordinate for the arbitrary, but fixed, exciton distribution and

$$\mathcal{E}(\lambda) = \sum_{q=-\pi}^{\pi} \tfrac{1}{2} \hbar \omega_q \left\{ \sum_{\substack{m \\ (\text{occupied})}} \varepsilon_m(q) \right\}^2 . \qquad 2.15$$

The square terms in $\mathcal{E}(\lambda)$ will each give rise to a self-energy term. The cross terms may be evaluated directly. They depend on

$|m - m'|$ only; for $m \neq m'$,

$$-\sum_q \frac{1}{2} \hbar \omega_q \, \varepsilon_m(q) \, \varepsilon_{m'}(q) = \frac{j^2}{q} \frac{1}{2} \sum_{p=|m-m'|}^{\infty} \left(1 - \frac{2}{\lambda}\right) \binom{2p}{p-|m-m'|} \frac{1}{\lambda^{2p}} \, , \qquad 2.16$$

where $\binom{2p}{p-|m-m'|}$ is the binomial coefficient and $\lambda > 2$ for $G \neq 0$. We have rederived the phonon-coupled exciton-exciton repulsion described in B. For $\lambda = 3$, the interaction is to good approximation a nearest-neighbor repulsion, which in the notation of B is called $V(2)$. Hence, if we have p excitons, distributed on the lattice so that there are p' pairs of adjacent excitons,

$$\mathcal{E}(\lambda) = p \Lambda(\lambda) - p' V(2) \, . \qquad 2.17$$

For $\lambda = 2$, the "free" lattice, the repulsion vanishes. For λ slightly larger than 2, the repulsion may not be approximated as a nearest-neighbor interaction. We assume, as in B, that λ is about 3.

III. General Expression for Rates of Exciton Processes

The localized exciton states are not even eigenstates of the rigid lattice exciton hamiltonian H_e^0. The time development of approximate eigenstates may be found by using the time-dependent Schrödinger equation. The general expression for the rate of transition from an initial state $/a>$ to a final state $/b>$ is

$$W_{ba} = \frac{2\pi}{\hbar} |\langle b| M | a\rangle|^2 \delta(E_b - E_a) . \qquad 3.1$$

3.1 is one of the forms of the Golden Rule of time-dependent perturbation theory (20). E_b and E_a are the energies of the states $/b>$ and $/a>$, respectively, and M is any operator connecting the two states.

The problem of finding the rates of electronic transitions in the presence of an harmonic phonon field has been extensively studied (21-23,17). The parameters that correspond to $\varepsilon_m(q)$ are usually too difficult to evaluate. The exciton-phonon problem we consider is tractable, however. Firstly, it is a one-dimensional problem; secondly, the nature of the exciton-phonon interaction is straightforward, at least in the first approximation; thirdly, the excitons are described by spin functions, which here, as in general, facilitate the calculation of matrix elements. The discussion of the exciton-phonon problem we present follows closely the electron-phonon discussions given by O'Rourke (22), Vasileff (23), and Trlifaj (17).

(a) Expression for W_{ba}

The initial and the final exciton states are $/a >$ and $/b >$, respectively. The initial state may contain an arbitrary number of localized excitons. The phonon states, for exciton configuration $/a>$, are

$$|\vec{n}^a\rangle \equiv \prod_{q=1}^{N} |n_q^a\rangle,$$ 3.2

where $/n_q^a >$ is a normalized harmonic oscillator function, with energy $n_q^a \hbar\omega_q$. The energy is independent of the configuration, since we consider only the perturbation 1.8. The index $\underline{a}$ denotes that $\zeta_q^a = \zeta_q - \epsilon_a(q)$, where $\epsilon_a(q)$ is the equilibrium displacement of the qth normal coordinate for the exciton configuration $/a >$. Thus the initial state of the (exciton and phonon) system is

$$|a\,\vec{n}^a\rangle = |a\rangle \prod_q |n_q^a\rangle.$$ 3.3

The vector $\vec{n}^a$ has components $(n_{q_1}^a, n_{q_2}^a, \ldots n_{q_N}^a)$. The exciton hamiltonian $\mathcal{H}_e$ (equation 1.4) has matrix elements $M(R)$ connecting $/a >$ and $/b >$. $M(R)$ is expanded about the no-exciton equilibrium position and only the linear term is retained

$$M(R) = M(R_o) + M'(R_o)\Delta, \qquad R = R_o + \Delta.$$ 3.4

Δ is the difference between the coordinates of two adjacent molecules; that is, either $\Delta = \delta_\ell$ or $\Delta = \Delta_\ell$, $\ell = 1, 2, \ldots \frac{1}{2}N$.

The transition rate W_{ba} is found from 3.1 and 3.3,

$$W_{ba} = \frac{2\pi}{\hbar} \sum_{\vec{n}^a, \vec{n}^b} P(\vec{n}^a) |\langle \vec{n}^b b | M + M'\Delta | \vec{n}^a a\rangle|^2 \delta(E_{b\vec{n}^b} - E_{a\vec{n}^a}),$$ 3.5

where M and M' are evaluated at R₀. Equation 3.5 includes all possible phonon paths; $p(\vec{n}^a)$ is a weighting factor expressing the initial phonon populations. $E_{b\vec{n}b}$ and $E_{a\vec{n}a}$ are the final and initial energies of the total system. We always assume that the phonons are in thermal equilibrium. The probability $p(\vec{n}^a)$ of finding the phonon distribution $(n^a_{q_1}, n^a_{q_2}, \ldots n^a_{q_N})$ is

$$P(\vec{n}^a) = \prod_q \left\{ e^{-n^a_q \frac{\hbar\omega_q}{kT}} \Big/ \sum_{n^a_q=0}^{\infty} e^{-n^a_q \frac{\hbar\omega_q}{kT}} \right\}. \qquad 3.6$$

We define $\beta_q = \hbar\omega_q/kT$ and perform the sum in the denominator,

$$P(\vec{n}^a) = \left(\prod_q 2\sinh \frac{\beta_q}{2} \right) \exp\left\{ -\sum_q \beta_q \left(n^a_q + \tfrac{1}{2}\right) \right\}. \qquad 3.7$$

Although n^a_q is independent of $\underline{a}$, we retain the index to specify the state.

The system energy is found from 2.17. The exciton configuration $/a>$ is assumed to have $\underline{a}$ excitons and $\underline{a}'$ pairs of adjacent excitons. The phonon-coupled repulsion is approximated by a nearest-neighbor interaction. J is the singlet-triplet energy gap for the undistorted lattice; $J_0 = J - \lambda$ is the observed (renormalized) singlet-triplet gap. Thus,

$$E_{a\vec{n}^a} = aJ_0 + a'V(2) + \sum_q \hbar\omega_q\left(n^a_q + \tfrac{1}{2}\right). \qquad 3.8$$

We define $\hbar\omega_a = aJ_0 + a'V(2)$ and $\omega_{ba} = \omega_b - \omega_a$,

$$E_{b\vec{n}^b} - E_{a\vec{n}^a} = \hbar\omega_{ba} + \sum_q \hbar\omega_q\left(n^b_q - n^a_q\right). \qquad 3.9$$

Following O'Rourke (22), we introduce the integral representation of the delta function

$$\delta(E_{b\vec{n}^b} - E_{a\vec{n}^a}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, exp\left\{\frac{it}{\hbar}(E_{b\vec{n}^b} - E_{a\vec{n}^a})\right\}$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, exp(i\omega_{ba}t) \, exp(it \sum_q \omega_q (n_q^b - n_q^a)).$$

$$3.10$$

Substituting 3.7 and 3.10 in 3.5, we have

$$W_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \, (exp \, i\omega_{ba}t) \sum_{\vec{n}^a, \vec{n}^b} \left(\prod_q 2\sinh\frac{\beta_q}{2}\right) exp\left\{-\sum_q [(n_q^a + \tfrac{1}{2})\beta_q -\right.$$

$$\left. it(n_q^b - n_q^a)\omega_q]\right\} \prod_q |\langle n_q^b b|M + M'\Delta| n_q^a a\rangle|^2.$$

$$3.11$$

It is shown in appendix II that after expanding $\Delta = \sum_q \Delta(q)$ all the cross terms in 3.11 are negligible. Thus

$$W_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \, (exp \, i\omega_{ba}t) \sum_{\vec{n}^a \vec{n}^b} \left(\prod_q 2\sinh\frac{\beta_q}{2}\right) exp\left\{-\sum_q [(n_q^a + \tfrac{1}{2})\beta_q\right.$$

$$\left. - it(n_q^b - n_q^a)\omega_q]\right\}\left\{\prod_q |M|^2 |\langle n_q^b| n_q^a\rangle|^2 + |M'|^2 \sum_{q'} |\langle n_{q'}^b|\Delta(q')| n_{q'}^a\rangle|^2 \prod_{q \neq q'} |\langle n_q^b| n_q^a\rangle|^2\right\}.$$

$$3.12$$

We now define $G_q(t)$ and $H_q(t)$

$$G_q(t) = \sum_{n_q^a, n_q^b} 2(\sinh\frac{\beta_q}{2}) |\langle n_q^b| n_q^a\rangle|^2 exp\left\{-[(n_q^a + \tfrac{1}{2})\beta_q - it(n_q^b - n_q^a)\omega_q]\right\}, \quad 3.13$$

$$H_q(t) = \sum_{n_q^a, n_q^b} 2(\sinh\frac{\beta_q}{2}) |\langle n_q^b|\Delta(q)| n_q^a\rangle|^2 exp\left\{-[(n_q^a + \tfrac{1}{2})\beta_q - it(n_q^b - n_q^a)\omega_q]\right\}. \quad 3.14$$

Both $G_q(t)$ and $H_q(t)$ play the role of correlation functions. We thus obtain the following expression for W_{ba}:

$$W_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \, (\exp i\omega_{ba}t) \left[|M|^2 \prod_q G_q(t) + |M'|^2 \sum_{q'} H_{q'}(t) \prod_{q \neq q'} G_q(t) \right]. \quad 3.15$$

(b) Evaluation of W_{ba}

Both O'Rourke and Vasileff have evaluated $G_q(t)$; they obtain

$$G_q(t) = \exp\left\{ -\frac{[\mathcal{E}_b(q) - \mathcal{E}_a(q)]^2}{2} [(2\bar{n}_q + 1)(1 - \cos\omega_q t) - i\sin\omega_q t] \right\}, \quad 3.16$$

where $\bar{n}_q = 1/(e^{\beta q} - 1)$ is the mean occupation number; thus we have used the fact that the phonon bath is in thermal equilibrium. Rather than repeat the calculation here, we give in appendix I the evaluation of $H_q(t)$. Once the derivation of $G_q(t)$ is known, any new expression such as $H_q(t)$ is easily evaluated in an analogous manner. We assume (as mentioned above, this is the only case we need consider) that the process considered involves the molecular coordinates d_ℓ and $d_{\ell+1}$. The expansion of $\Delta_\ell = d_{\ell+1} - d_\ell$ is, from 1.13,

$$d_\ell = \sum_q \sqrt{\frac{\hbar}{2MN\omega_q}} \, \zeta_q \begin{cases} \cos q \frac{\ell c}{2} & q > 0 \\ \sin q \frac{\ell c}{2} & q < 0 \end{cases}, \quad 3.17$$

$$\Delta_\ell = \sum_q \Delta_\ell(q) = \sum_q \sqrt{\frac{\hbar}{2MN\omega_q}} \, \zeta_q \begin{cases} -2\sin\frac{qc}{4}\sin\frac{qc}{2}(\ell+\frac{1}{2}) & q > 0 \\ 2\sin\frac{qc}{4}\cos\frac{qc}{2}(\ell+\frac{1}{2}) & q < 0 \end{cases}. \quad 3.18$$

We therefore obtain

$$|\langle n_q^b | \Delta_\ell(q) | n_q^a \rangle|^2 = \frac{\hbar}{MN\omega_q} \, 2\sin^2\frac{qc}{4} \, |\langle n_q^b | J_q | n_q^a \rangle|^2, \quad q \gtrless 0. \qquad 3.19$$

In 3.19 we have grouped $\pm q$ together, since the rest of $H_q(t)$ does not depend on the sign of q. Thus $H_q(t)$, like $G_q(t)$, is independent of the site.

Except for the distortions of at most two excitons at sites ℓ and $\ell + 1$, the distortions are the same for $/a >$ and $/b >$, since except for one or two excitons, they have the same exciton configurations. The mean occupation numbers are also independent of the exciton configuration. Thus $H_q(t)$ and $G_q(t)$ are independent of the exciton distribution on the rest of the lattice. As shown in appendix I, for $-\pi < qc < \pi$,

$$H_q(t) = (\bar{n}_q + \tfrac{1}{2})(\cos^2\frac{\omega_q t}{2})\left\{ -2i\tanh\frac{\beta_q}{2}\tan\frac{\omega_q t}{2} + 1 - \tan^2\frac{\omega_q t}{2} \right\} \times \qquad 3.20$$
$$G_q(t) \, \hbar \sin^2\frac{qc}{4} \, / \, MN\omega_q .$$

Since the sum is symmetric in q, we have divided by two and extended the range of q to include the whole Brillouin zone.

Using 3.16 and 3.20, we evaluate W_{ba}. The integrand in 3.15 is quite small unless t is so small that, for all ω_q, $\omega_q t \ll 1$. But, for such times, we may expand $\sin\omega_q t$ and $\cos\omega_q t$ and thus obtain Gaussian integrals. Following Trlifaj (17), we define

$$A_{ba} = \omega_{ba} + \tfrac{1}{2}\sum_q \omega_q \left(\varepsilon_b(q) - \varepsilon_a(q) \right)^2,$$
$$B_{ba} = \sum_q \left(\varepsilon_b(q) - \varepsilon_a(q) \right)^2 \omega_q^2 (\bar{n}_q + \tfrac{1}{2}). \qquad 3.21$$

The condition for the evaluation of the integrals by the present method are

$$|A_{ba}|, \quad \sqrt{B_{ba}} \gg \omega_q \qquad \text{(all q).} \qquad 3.22$$

W_{ba} is evaluated in appendix III; we find

$$W_{ba} = \frac{1}{\hbar^2}\sqrt{\frac{2\pi}{B_{ba}}}\, e^{-\frac{A_{ba}^2}{2B_{ba}}} \left\{ |M|^2 + |M'|^2 \sum_q \frac{\hbar \sin^2\frac{qc}{4}}{NM\omega_q}\left[(\bar{n}_q+\tfrac{1}{2}) + \frac{\omega_q}{2}\frac{A_{ba}}{B_{ba}}\right]\right\}. \quad 3.23$$

(c) Temperature Dependence of W_{ba}

B_{ba} does not vanish, even at $0°K$, if the distortions $\varepsilon_b(q)$ and $\varepsilon_a(q)$ are different, even though the occupation numbers $\bar{n}_q$ then vanish. Thus the transition rates we consider are finite even at $0°K$. In the high temperature region $kT \gtrsim \hbar\omega_q^{max}$,

$$B_{ba} \approx \frac{2kT(|A_{ba}| - \omega_{ba})}{\hbar}. \qquad 3.24$$

Thus, for high temperature,

$$W_{ba} = \frac{1}{\hbar^2}\sqrt{\frac{\pi\hbar}{kT(|A_{ba}|-\omega_{ba})}}\, e^{-\frac{\hbar A_{ba}^2}{4kT(|A_{ba}|-\omega_{ba})}} \left\{|M|^2 + kT\frac{|M'|^2}{q}\frac{1}{4}\left(1-\sqrt{\tfrac{\lambda-2}{\lambda+2}}\right)\right\}. \quad 3.25$$

The term in $\omega_q A_{ba}/2B_{ba}$ has been omitted; we show in appendix III that it is negligible. We may therefore define the activation energy ΔE_{ba} for the exciton transition $/a> \rightarrow /b>$ to be

$$\Delta E_{ba} = \frac{\hbar A_{ba}^2}{4(|A_{ba}| - \omega_{ba})}. \qquad 3.26$$

It must be stressed that unless the conditions 3.22 are satisfied, we cannot obtain 3.23; the conditions 3.22 are not always fulfilled. If we wish to extend the concept of an activation energy to lower temperatures, we must generalize to include temperature-dependent activation energies such that

$$\lim_{T \to 0} \frac{\Delta E(T)}{kT} < \infty. \tag{3.27}$$

IV. Exciton Jumping Rate.
Activation Energy for Diffusion

The processes described by the hamiltonian 1.1-7 are exciton jumping, exciton creation and annihilation, and exchange interactions between adjacent excitons. The fastest of these is the jumping of an exciton from one site to the next. The relationship between the diffusion constant D and the jumping rate ω_j is simply $D = \omega_j c^2$, where c is the distance between sites (17). ω_j thus gives the basis for a diffusional description of exciton motion. ω_j must satisfy two conditions: it must be large enough, even at very low temperatures, to account for the absence of hyperfine structure in the EPR spectra, and it must be small enough to justify the adiabatic approximation (e).

The matrix element for exciton jumping is obtained from $\mathcal{H}_1$ and $\mathcal{H}_5$ (1.2 and 1.5, respectively)

$$ M(R) = \frac{J'(R_0)}{4} + \frac{j'(R_0)}{4}\Delta, \qquad 4.1 $$

where J' and j' are evaluated at the no-exciton equilibrium position. We consider the process in which an exciton on site m jumps to site m + 1. Site m + 1 must therefore be empty originally; the probability that site m + 1 is unoccupied is $1 - \rho e^{-\frac{V(2)}{kT}}$ ~ 1, where ρ is the exciton density. Since the distortions are additive, $\epsilon_a(q) - \epsilon_b(q)$ reduces to $\epsilon_m(q) - \epsilon_{m+1}(q)$. Since ω_q is an even function of q, A_{ba}, B_{ba}, and ω_j are independent of the site m. We assume for the moment that there are no excitons on the sites m - 1 and m + 2. The initial and the final states are

then degenerate and ω_{ba} in 3.9 vanishes. We have from 3.23

$$\omega_j = \frac{1}{\hbar}\sqrt{\frac{2\pi}{B_j}}\; e^{-\frac{A_j^2}{2B_j}}\left\{\left(\frac{J^j}{4}\right)^2 + \left(\frac{j'}{4}\right)^2 \sum_q \frac{\hbar \sin^2\frac{qc}{4}}{MN\omega_q}\left[(\bar{n}_q+\tfrac{1}{2}) + \frac{\omega_q}{2}\frac{A_j}{B_j}\right]\right\};\qquad 4.2$$

$$A_j = \tfrac{1}{2}\sum_q \omega_q\left(\varepsilon_m(q)-\varepsilon_{m+1}(q)\right)^2 = \frac{1}{\hbar}\left(2\Lambda(\lambda)+V(2)\right),\qquad 4.3$$

$$B_j = \sum_q \omega_q^2\left(\varepsilon_m(q)-\varepsilon_{m+1}(q)\right)^2\left(\bar{n}_q+\tfrac{1}{2}\right).$$

2.16 and 2.17 have been used to evaluate A_j. At $0°K$,

$$B_j^o = \frac{j^2}{g}\;\frac{\frac{g}{M}}{\hbar\sqrt{\frac{g}{M}}}\;\frac{2}{\sqrt{\lambda}}\;.\qquad 4.4$$

and, for $kT \ll \hbar\omega_q$, very approximately,

$$B_j \approx B_j^o\left(1+\frac{4}{\sqrt{2\pi}}\sqrt{\frac{kT}{\hbar}}\left(\frac{M\lambda}{g}\right)^{\frac{1}{2}}\right).\qquad 4.5$$

We estimate the magnitudes of the parameters for WBP. We use the estimates from paper B. $\lambda = 2 + G/g \sim 3$ is reasonable; j^2/g is a typical energy term that occurs in the self-energy and the exciton-exciton repulsion; it is estimated to be between 1000 and 8000 cm^{-1}, with the smaller value perhaps more probable; $h(g/M)^{\frac{1}{2}}$ is a typical phonon energy, or about 30 to 60 cm^{-1}; thus $B_j^o \sim 50\, g/M$. The values of Λ and $V(2)$ may be found in paper B or calculated from 2.9 and 2.16; $2\Lambda + V(2) \sim 0.60\, j^2/g$. Thus

$$\frac{A^2}{2B_j^o} \sim \frac{(.6)^2}{100}\left(\frac{j^2}{g}\frac{1}{\hbar\sqrt{\frac{g}{M}}}\right)^2 \sim 9\;.\qquad 4.6$$

Finally, to obtain a number, we set $J' = 100$ cm^{-1} and $(j')^2/g = 1000$ cm^{-1}; at $0°$K,

$$\omega_j^o \approx \frac{1}{\hbar^2} \sqrt{\frac{2\pi}{B_j^o}} \, e^{-g} \left\{ \left(\frac{J'}{4}\right)^2 + \frac{(j')^2}{g} \frac{1}{64} \hbar \sqrt{\frac{g}{M}} \right\} \sim 4 \times 10^8 \text{ sec}^{-1}, \qquad 4.7$$

while, for moderate temperatures ($\bar{n}_q \sim \frac{1}{2}$ or $T \sim 60\text{-}70°$K), the jumping rate is about 10^{10} sec^{-1}. Although the estimates above are very definitely of the order of magnitude variety, it is evident that ω_j is substantial even at $0°$K. The estimate of ω_j agrees with the order of magnitude estimate (10) of the jumping rate required to account for the absence of hyperfine structure. Furthermore, the jumping rate is some two orders of magnitude smaller (at moderate temperatures) than typical phonon frequencies. Thus the approximation that the molecules are adiabatic with respect to the excitons is a good one.

The exciton model we have been using neglects exciton-exciton interactions that are quadratic in the exciton density; it is therefore restricted to low exciton densities (11). In the following, we shall mean by "high" temperature the temperature range $\hbar\omega_q^{max} \lesssim kT \lesssim \frac{1}{2}J_o$, where J_o is the observed singlet-triplet separation. The high temperature form of the jumping rate is obtained from 3.26

$$\omega_j = \left(1 - \rho e^{-\frac{V(2)}{kT}}\right) \frac{1}{\hbar^2} \sqrt{\frac{\hbar}{kT|A_j|}} \, e^{-\frac{\hbar|A_j|}{4kT}} \left\{ \left(\frac{J'}{4}\right)^2 + kT \frac{(j')^2}{g} \frac{1}{64}\left(1 - \sqrt{\frac{\lambda-2}{\lambda+2}}\right) \right\}, \qquad 4.8$$

$$A_j = \frac{1}{\hbar}(2\Lambda + V(2)).$$

Using 3.27, we obtain the activation energy for diffusion

$$\Delta E_j = \frac{\hbar |A_j|}{4} = \frac{\Lambda(\lambda)}{2} + \frac{V(2)}{4}.$$

4.9

ΔE_j has a straightforward physical interpretation. If we imagine that the "activated complex" is half an exciton on adjacent sites, ΔE_j is just the energy difference between the intermediate and the initial state. The activation energy is the energy needed to delocalize an exciton equally on two adjacent sites. We note that a well-defined, temperature-independent activation energy is found only when the phonon field is reasonably populated.

For completeness, we mention that there are two other exciton jumping frequencies. They correspond to having one exciton on either site m - 1 or m + 2 initially. The former is the rate at which an exciton adjacent to another exciton jumps to the next site; the latter is the rate at which an exciton which is one site removed from another exciton jumps to the site next to the exciton. For these processes, $\hbar\omega_{ba}$ is - and + V(2), respectively, rather than 0. It is easy to find the modifications to 4.7-9. Since, in the model we use, the excitons repel each other, the former rate is slightly higher and the latter slightly lower than the rate when $\omega_{ba} = 0$. The high-temperature activation energies for diffusion are, respectively,

$$\Delta E_1 = \left(\frac{\Lambda}{2} + \frac{V(2)}{4}\right)\frac{1}{1 + \frac{V(2)}{2\Lambda + V(2)}} \approx E_0\left(1 - \frac{V(2)}{2\Lambda}\right),$$

$$\Delta E_2 = \left(\frac{\Lambda}{2} + \frac{V(2)}{4}\right)\frac{1}{1 - \frac{V(2)}{2\Lambda + V(2)}} \approx E_0\left(1 + \frac{V(2)}{2\Lambda}\right).$$

4.10

In 4.10, we have set E_0 equal to the activation energy for diffusion when $\omega_{ba} = 0$ and have used the property that $\gg V(2)$.

V. Creation and Annihilation of Excitons

We consider in this section exciton creation and annihilation processes via lattice phonons. However, phonons corresponding to intramolecular vibrations are also important. The connection between the high energy (>300 cm^{-1}) intramolecular modes and the low energy (<100 cm^{-1}) lattice modes is discussed by Davydov (24). He shows that the intramolecular normal frequencies are split into narrow, quasi-continuous bands in a crystal. For the complicated crystals in which triplet excitons are observed, there are therefore some 3n-6 phonon bands corresponding to internal vibrations, where n is the number of atoms per molecule. These modes should provide phonons throughout the energy range 300-3000 cm^{-1}. The dispersion relations would be difficult to find, even for a harmonic model, and it would also be necessary to have detailed knowledge of the force constants.

A detailed qualitative analysis of the radiationless decay of a triplet via intramolecular phonons is available (25). Since the excitons are on a pair of molecules, whose internal vibrations are almost completely independent of each other, the coupling with intramolecular phonons is expected to be much weaker than in the case discussed in reference 25, where the triplet is on a single molecule. Exciton creation and annihilation via intramolecular phonons is therefore expected to be negligibly slow compared with lattice phonon processes. The intramolecular transition rate is essentially temperature independent.

Examination of the exciton hamiltonian 1.1 shows that there are two radiationless creation and annihilation processes. Two adjacent excitons may be created or annihilated; an exciton may be created next to an exciton and one of a pair of adjacent excitons may be annihilated. The exciton spin S and the z component of spin S_z are conserved in each process. All the processes involve the exchange integral J'.

We consider first exciton annihilation and begin with pair annihilation. The initial state contains a pair of adjacent excitons; the final state has two fewer excitons and no excitons on the sites occupied by the pair. For simplicity, the sites adjacent to the pair are assumed to be empty. Using 3.8, 3.9, and 3.21, we find

$$\omega_{a2} = -2J_0 - V(2)$$
$$\hbar A_2 = -2(J_0 - \Lambda + V(2)).$$

5.1

Since $\Lambda \gtrsim J_0$, $\hbar A$ is not large compared with $\hbar\omega_q$, and the integrals cannot be evaluated by the method of section III. We consider next the annihilation of one exciton from an isolated pair of adjacent excitons,

$$\omega_{a1} = -J_0 - V(2)$$
$$\hbar A_{a1} = -(J_0 - \Lambda + V(2)).$$

5.2

Again, the condition that $\hbar A \gg \hbar\omega_q$ is not satisfied. The calculation of annihilation rates therefore requires a more accurate integration in 3.15.

Fortunately, the inequalities 3.22 are satisfied for creation processes. If the system is in thermal equilibrium, we thus also know the annihilation rates. For the creation of an isolated pair of excitons,

$$\hbar A_{c2} = 2(J_0 + \Lambda),$$

5.3

while for the creation of an exciton next to an exciton,

$$\hbar A_{c1} = J_0 + \Lambda + V(2).$$

5.4

The A's satisfy the inequality 3.22; the B's are always comparable to B_j, which satisfied 3.22,

$$B_{c2} = \sum_q (\varepsilon_m(q) + \varepsilon_{m+1}(q))^2 \omega_q^2 (\bar{n}_q + \tfrac{1}{2}),$$

$$B_{c1} = \sum_q (\varepsilon_m(q))^2 \omega_q^2 (\bar{n}_q + \tfrac{1}{2}).$$

5.5

For low temperatures, we set $B = B^\circ$, its value at $0^\circ K$, and neglect ρ compared with unity,

$$W_{c2}^\circ = \frac{1}{\hbar^2} \sqrt{\frac{2\pi}{B_{c2}^\circ}} \, e^{-A_{c2}^2/2B_{c2}^\circ} \left\{ \left(\frac{J'}{2}\right)^2 + \frac{(j')^2}{q} \hbar \sqrt{\frac{q}{M}} \frac{1}{16} \right\},$$

5.6

$$W_{c1}^\circ = \rho \frac{1}{\hbar^2} \sqrt{\frac{2\pi}{B_{c1}^\circ}} \, e^{-A_{c1}^2/2B_{c1}^\circ} \left\{ \left(\frac{J'}{3}\right)^2 + \frac{(j')^2}{q} \hbar \sqrt{\frac{q}{M}} \frac{1}{36} \right\}.$$

5.7

The high-temperature expressions are easily obtained. Since

$$B_{c2} \approx \frac{2}{\hbar^2} kT(2\Lambda - V(2)),$$

5.8

$$B_{c1} \approx \frac{2}{\hbar^2} kT \Lambda, \tag{5.8}$$

we find

$$W_{c2} = (1-\rho)(1-\rho e^{-\frac{V(2)}{kT}}) \frac{1}{\hbar^2} \sqrt{\frac{2\pi}{B_{c2}}} e^{-A_{c2}^2/2B_{c2}} \left\{ \left(\frac{J'}{2}\right)^2 + kT \frac{(q')^2}{q} \frac{1}{16} \left(1-\sqrt{\frac{\lambda-2}{\lambda+2}}\right) \right\}, \tag{5.9}$$

$$W_{c1} = \rho(1-\rho e^{-\frac{V(2)}{kT}}) \frac{1}{\hbar^2} \sqrt{\frac{2\pi}{B_{c1}}} e^{-A_{c1}^2/2B_{c1}} \left\{ \left(\frac{J'}{3}\right)^2 + kT \frac{(q')^2}{q} \frac{1}{36} \left(1-\sqrt{\frac{\lambda-2}{\lambda+2}}\right) \right\}. \tag{5.10}$$

The activation energies ΔE_{c2} and ΔE_{c1} are found from 3.27, 5.3, 5.4, and 5.8,

$$\Delta E_{c2} = \frac{(J_0 + \Lambda)^2}{2\Lambda - V(2)}, \tag{5.11}$$

$$\Delta E_{c1} = \frac{(J_0 + \Lambda + V(2))^2}{4\Lambda}. \tag{5.12}$$

That $2\Delta E_{c1} > \Delta E_{c2}$ is as expected. The site adjacent to an exciton is compressed and therefore a poor site on which to create another exciton. As is the case of exciton jumping, there are several other, almost equal, transition rates. They correspond to creation processes in which the final state is not an isolated pair but a pair adjacent to an exciton.

The approximate values of the WBP parameters introduced in the previous section are used to make rough estimates. In addition, we assume that $J_0 \gtrsim \frac{1}{2}\Lambda$, which is probably good to

within a factor of two. At moderate temperatures ($n_q \sim \frac{1}{2}$ or $T \sim$ 60-70°K),

$$W_{c2} \sim 10^4 \text{ sec}^{-1}$$

$$W_{c1} \sim \rho 10^7 \text{ sec}^{-1}$$

5.13

The very rough estimates 5.13 show again that the exponential $e^{-A^2/2B}$ which dominates the rates at low temperatures is basically a phonon effect.

The rates discussed above are faster than intramolecular radiationless transitions except at very low temperatures. In contrast to the allowed electronic transitions we have been considering, the intramolecular process involves a forbidden transition and is an example of spin-lattice relaxation. It is typical that there should be several mechanisms, each of which can be estimated only very roughly. Exciton creation and annihilation, by any available process, may also be considered to be random motion of the excitons, since in the steady-state systems we discuss the number of excitons remains constant. The creation and annihilation of excitons therefore also contribute to the averaging out of the hyperfine structure. However, they are negligibly slow compared with the jumping rate.

VI. Discussion

(a) Localized Exciton Approximation

We have presented in the preceding sections some of the properties of a simple model for phonons and localized, diffusional excitons. In this section, the assumption of a localized and diffusional model is justified for dilute exciton systems. The problem of delocalization is considered first.

It is straightforward to show that if the exchange energy varies linearly with lattice distortions, an exciton on an harmonic lattice will have an energy minimum if it is localized on one site. We consider N uncoupled harmonic oscillators and put 1/N exciton on each. The perturbation 1.8 is $-|j| x/N$, where x is the distortion of each site. The energy is

$$E(N) = J - \sum_{n=1}^{N} \frac{|j|}{g} x_n + \sum_{n=1}^{N} \left(\frac{P_n^2}{2M} + \frac{1}{2} g x_n^2 \right) \qquad 6.1$$

$$E(N) = J + \sum_{n=1}^{N} \left(\frac{P_n^2}{2M} + \frac{1}{2} g d_n^2 \right) - \frac{1}{2} \frac{j^2}{g N} . \qquad 6.2$$

where $d_n = x_n - |j|/gN$. The energies of the displaced oscillators are unchanged, since the force constants are unchanged. E(N) has a minimum for N = 1. This conclusion holds quite generally even for tied down or coupled oscillators. The important assumptions are that the exchange energy is linear, that there are few excitons, and that the coupling is a distortion of the sites (that is, that the two electrons forming a triplet state are always

neighbors in real space, an assumption that is valid for J' << J
at low temperatures (11)). Delocalized excitons form a band with
width J'. The center of the band is Λ higher than the localized
exciton energy levels. Since the self-energy is of the order of
the observed singlet-triplet energy gap J_0, at low temperatures
(kT << Λ ~ J_0) the excitons are essentially completely in the
localized states.

The problem of delocalization has been thoroughly investi-
gated in another context, in polaron theory (26). A dilute system
of excess electrons in a polar crystal gives rise to polarization
wells. Localizing an electron in its polarization well substan-
tially improves its energies compared with free electron energies.
Pekar considers a fixed polarization well, that is, a fixed
electron, and solves for the motion of the nuclei (27). This is
entirely in the spirit of section II, where the molecular motions
were found for a fixed exciton. Pekar's treatment has since been
replaced by a calculation which, although physically more involved,
gives substantially better energies (28,29). Basically, this
result reflects the fact that it is not a very good approximation
in polar crystals to assume that the nuclei are adiabatic with
respect to the polarons. We therefore need to consider the exciton
problem in greater detail when the jumping frequency ω_j approaches
the phonon frequencies; that is, for elevated temperatures. At
high temperatures, however, the exciton model we have been con-
sidering fails.

Chesnut has proposed a purely phenomenological theory for dense exciton systems (30). Phonon-coupling plays a significant role in his theory, as it is taken to be the probable cause of the decrease in the singlet-triplet energy gap with increasing temperature (cf. 6.4). Within the framework of the Lynden-Bell and McConnell exciton theory (5), it is straightforward to reproduce Chesnut's results, provided it is assumed that the lattice is distorted, not locally, but uniformly by each exciton. The perturbation 1.8 then becomes, for exciton density ρ,

$$V(\rho) = -|J|\rho\delta .$$ 6.3

The exchange integrals J and J' are now temperature dependent, and J decreases with increasing temperature,

$$J(\rho) = J(0) - \frac{J^2}{9}\frac{2}{\lambda+2}\rho ,$$

$$J'(\rho) = J'(0) + \frac{J^2}{9}\frac{2}{\lambda+2}\rho .$$ 6.4

The coefficient of the term in ρ in 6.4 corresponds to Chesnut's ϵ_1 (30) both in sign and in magnitude. If we introduce further simplifying assumptions, we may reproduce Chesnut's theory in its entirety. It is evident that the crucial assumption is that the distortions are uniform. This would be the case if the excitons moved rapidly compared with molecular vibrations, so that the lattice could not rearrange locally. A molecular field approximation such as Chesnut's is then appropriate.

At low temperatures, for strong alternation (J' < 1/3 J), the distortions are local and the excitons are diffusional.

Therefore Chesnut's model is restricted to high temperatures and, perhaps, to weakly alternating systems. A self-consistent solution of the rigid-lattice exciton hamiltonian 1.1, for any J' between 0 and J, predicts the decrease in the singlet-triplet energy gap with increasing temperature (11); the decrease has been observed experimentally (31). Thus it is not clear that the phonon-coupled interaction of Chesnut has to be postulated. That the phonon-coupling remains unchanged with increasing temperature is also untenable, since the mean separation between the electrons forming a triplet excitation increases with temperature, thus changing, and probably weakening, the phonon-coupling (11).

(b) Diffusional Exciton Approximation

It is an obvious improvement of the theory to use the translational symmetry of the lattice and to classify the excitons by their wave vectors. $\mathcal{H}_0$ and $\mathcal{H}_1$ in 1.2 may be diagonalized by transforming to the Fermi creation and annihilation operators a_k^+ and a_k in wave vector space (32,33)

$$\mathcal{H}_0 + \mathcal{H}_1 = \sum_k \varepsilon_k \, a_k^+ a_k \qquad 6.5$$

where

$$\varepsilon_k = J - \tfrac{1}{2}J' \cos kc$$

$$k = \frac{2\pi m}{c\left(\frac{N}{2}\right)}, \qquad m = 0, \pm 1, \dots \pm \tfrac{N}{4}-1, \tfrac{N}{4}. \qquad 6.6$$

The k-state description and the possibility of local deformations were discussed from the first for triplet excitons (34). We show

now that, except for a very rigid lattice, the k-state description gives negligible improvements in the energy and is misleading.

We construct exciton k-states from the localized exciton states and the distorted harmonic oscillator functions 3.3. For one exciton,

$$|k\rangle = \frac{1}{\sqrt{\frac{N}{2}}} \sum_{j=1}^{N/2} |j\rangle \, e^{ikjc} \prod_q |n_q^j\rangle, \qquad 6.7$$

where k is the wave vector of the exciton and is restricted to the first Brillouin zone, $|j\rangle$ is the spin function indicating that there is only one triplet, at site j, on the lattice, and the normalization shows that there are $\frac{1}{2}N$ sites. The phonon functions are normalized individually and, at the end, we always assume that the phonons are in thermal equilibrium, so that the occupation numbers n_q are replaced by the mean occupation numbers $\bar{n}_q$.

We define J'_{eff} as the effective exchange integral for exciton jumping. As shown in appendix IV,

$$J'_{eff} = J' \prod_q \langle \bar{n}_q^{j+1} | \bar{n}_q^j \rangle. \qquad 6.8$$

J'_{eff} is the parameter that replaces J' in the dispersion relation 6.6; it represents the parameter in the effective exciton hamiltonian that describes exciton motion. The evaluation of $\prod_q \langle \bar{n}_q^{j+1} | \bar{n}_q^j \rangle$ for the lattice in thermal equilibrium is given in appendix IV;

we find

$$\prod_q \langle \bar{n}_q^{j+1} | \bar{n}_q^{j} \rangle = \exp\left\{ -\frac{j^2}{q\hbar\sqrt{\frac{q}{M}}} 4 \int_0^\pi \frac{d\theta}{\pi} \frac{\sin^2\theta \,(1-\cos\theta)}{(\lambda - 2\cos\theta)^{3/2}} (\bar{n}_\theta + \tfrac{1}{2}) \right\},\qquad 6.9$$

where $qc/2 = \theta$ and $\bar{n}_\theta = \bar{n}_q$. If the lattice were rigid, which amounts to setting $j = 0$ (since, as is evident from 1.8, the lattice is then unperturbed) the overlap would be unity, as expected. As the temperature is raised, the overlap decreases. Physically, raising the temperature increases the mean energy and gives increasingly rapidly oscillating phonon wave functions; rapidly oscillating functions have small overlaps when displaced. That the exciton bandwidth is decreased by phonons is known (34,35); it is also known that the bandwidth decreases with increasing temperature in polaron theory (36).

The overlap is estimated in appendix IV at 0°K, where it is largest. We use again the WBP parameters estimated in section IV and find

$$\prod_q \langle \bar{n}_q^{j+1} | \bar{n}_q^{j} \rangle \sim 10^{-3}.\qquad 6.10$$

Thus the improvement in the exciton energy for k states is very small, less than 0.1% per exciton. It therefore seems to be largely a matter of convenience whether to use k states or localized states.

However, the excitons are rapidly scattered by the phonons. The terms $\mathcal{H}_4$ and $\mathcal{H}_5$ (given by 1.6 and 1.7,

respectively) scatter excitons from one k state to another, as is evident from their representation in wave vector space,

$$H_4 + H_5 = \sum_{q,k} \sqrt{\frac{2\hbar}{MN\omega_q}} \left(\sin\frac{qc}{4}\right) e^{-i\frac{qc}{4}} |J| \left\{ 1 - \frac{J'}{2J} e^{-i\frac{qc}{4}} \cos\left(\frac{c}{2}(k+\frac{q}{2})\right) \right\} (b_q^+ - b_{-q}) a_k^+ a_{k+q} \cdot 6.11$$

The Bose operators b_q^+ and b_q are the phonon creation and annihilation operators; q and k are the phonon and the exciton wave vectors, respectively. The transverse phonons have been omitted in 6.11. Two-phonon Orbach processes have also been neglected. Thus it is a consequence of the approximations that there are apparently no phonons with sufficiently low energies to be used in 6.11 for the very narrow, of order J'_{eff}, exciton band.

In any actual lattice, there will be low-energy phonons, both longitudinal and transverse. Using the Golden Rule for time-dependent perturbation theory, we make a rough estimate of the scattering rate. Depending on whether a phonon is created or annihilated (37),

$$W_1 \sim (\bar{n}_q + \tfrac{1}{2}) \frac{J'^2}{q J'_{eff}} \sqrt{\frac{q}{M}} \, , \qquad \text{(creation)} \qquad 6.12$$

$$W_2 \sim \bar{n}_q \frac{J'^2}{q J'_{eff}} \sqrt{\frac{q}{M}} \, . \qquad \text{(annihilation)} \qquad 6.13$$

It is emphasized that 6.12 and 6.13 are only rough estimates. The phonons used are not in the model we have been using; their dispersion relations are not known. The exciton dispersion relation is given in 6.6. The phonon density is assumed to be $N/2\pi c$ and

$\bar{n}_q$ represents the mean occupation numbers of the low energy longi-
tudinal phonons used in 6.12, 13.

Using the estimates for WPB, we have

$$W_1 \sim (\bar{n}_q + 1) \, 10^{15} \, \sec^{-1},$$
$$W_2 \sim \bar{n}_q \, 10^{15} \, \sec^{-1}.$$

<div align="right">6.14</div>

Even if the estimates in 6.14 are high by two or three orders of
magnitude, the scattering is rapid. For an exciton near the
bottom of the band, $\frac{1}{2}J'_{eff}(1-\cos kc) = J'_{eff}(kc/2)^2$ is the kinetic
energy and $v = \hbar k/M$ is the velocity; hence we have the effective
mass M of order 10^{-22} gm, which is of the order of the mass of a
Wurster's blue radical ion, and v of the order of 10^{11} sites per
second. Thus the exciton is scattered many times in going from
one site to the next. The rapidly scattered exciton would in fact
appear to be undergoing a random walk motion. A diffusional model
is therefore appropriate.

(c) <u>Parameters of the Effective Exciton Hamiltonian</u>

An exciton system placed in a phonon bath may be described
by an effective spin hamiltonian, as given in appendix IV. In
spite of the interactions with the phonons, the excitons must
still be described by a singlet-triplet energy gap and by other
parameters that express exciton motion, exciton-exciton inter-
actions, and exciton creation and annihilation. Only a term such
as a phonon-coupled interaction between excitons changes the <u>form</u>
of the exciton hamiltonian. Otherwise, the effect of the phonons

is to alter the meaning of the various parameters appearing in the exciton hamiltonian for the rigid lattice

We have shown in section II that the singlet-triplet energy gap, the parameter appearing in the term $\mathcal{H}_0$ (1.2), is renormalized. We have also shown that J'_{eff} for exciton motion, the parameter in the term $\mathcal{H}_1$ (1.2), involves a phonon overlap integral (see 6.8) and is consequently small. Similarly, it may be shown that the parameters appearing in $\mathcal{H}_3$ (1.3), which describe exciton creation and annihilation processes, are all J' times a phonon overlap integral. They are therefore also substantially smaller than the rigid lattice parameter J'. The exchange interaction between adjacent excitons, given by the term $\mathcal{H}_2$ (1.3), connects states with the same exciton distributions. Hence the lattice distortions are all the same and the phonon overlap is equal to unity. The parameter expressing exciton exchange is therefore $1/4$ J', evaluated at the equilibrium position of the adjacent molecules of a pair of adjacent occupied sites.

We therefore have a narrow exciton band of order J'_{eff}, localized, diffusional excitons with large effective masses, and a phonon-coupled repulsion between excitons. At the same time, J' may be of the order of J. The reconciliation of these properties, as suggested in the introduction, indicates that our diffusional model is consistent with the available low temperature experimental data. The present discussion is not easily extended to high ($kT > \frac{1}{2}J$) temperatures, since then both the exciton model

and the exciton-phonon interaction must be reexamined. It appears that the excitons then move rapidly compared with lattice vibrations. Since the electrons forming an exciton are, on the average, increasingly separated, the phonon-coupling changes, and probably decreases, with increasing temperature (11).

The model we have presented is an oversimplification of both the phonons and the excitons. In particular, the phonon spectrum must in detail be quite different from the one-dimensional spectrum we consider. Even such a minor change as the slight alternation of the force constants, which is physically obvious since the free lengths alternate, introduces an optical branch. Although the nature of the results are unchanged, the mathematics become far less tractable. At present, the uncertainties in the various parameters describing the excitons are such that we could have consistently replaced the dimensionless sums over the phonon frequencies ω_q by unity. As long as we are interested primarily in the excitons, the exact nature of the phonon spectrum is in fact not crucial.

Appendix I. Evaluation of $H_q(t)$

The basic identity used to evaluate G_q, H_q, and similar expressions is the Slater sum (22),

$$\rho(x\,x'|\xi) = \sum_{k=0}^{\infty} \frac{e^{-(k+\frac{1}{2})\xi}}{\sqrt{\pi}\; 2^k\, k!}\; H_k(x) H_k(x') \exp\{-\tfrac{1}{2}(x^2+(x')^2)\}$$

$$= \frac{1}{\sqrt{2\pi \sinh\xi}}\; \exp\{-\tfrac{1}{4}[(x+x')^2\tanh\tfrac{1}{2}\xi + (x-x')^2\coth\tfrac{1}{2}\xi]\}, \qquad \text{I.1}$$

where $H_k(x)$ is the kth Hermite polynomial. Introducing

$$\lambda_q = \beta_q + i\omega_q t, \qquad \mu_q = -i\omega_q t, \qquad \text{I.2}$$

we write, following O'Rourke (22),

$$G_q(t) = \frac{\sinh\frac{1}{2}\beta_q}{\pi\sqrt{\sinh\lambda_q \sinh\mu_q}} \iint_{-\infty}^{\infty} dx\,dy\, \exp\{-\tfrac{1}{4}[(x+y-2\mathcal{E}_b(q))^2\tanh\tfrac{1}{2}\mu_q$$

$$+ (x-y)^2\coth\tfrac{1}{2}\mu_q + (x+y-2\mathcal{E}_a(q))^2\tanh\tfrac{1}{2}\lambda_q + (x-y)^2\coth\tfrac{1}{2}\lambda_q]\}. \qquad \text{I.3}$$

Using 3.14, 3.19, and I.3, we obtain

$$H_q(t) = \frac{\sinh\frac{1}{2}\beta_q}{\pi\sqrt{\sinh\lambda_q \sinh\mu_q}}\; \frac{\hbar \sin^2\frac{qc}{4}}{MN\omega_q} \iint_{-\infty}^{\infty} xy\,dx\,dy\, \exp\{-\tfrac{1}{4}[$$

$$(x+y-2\mathcal{E}_b(q))^2\tan\tfrac{1}{2}\mu_q + (x-y)^2(\coth\tfrac{1}{2}\mu_q+\coth\tfrac{1}{2}\lambda_q) + (x+y-2\mathcal{E}_a(q))^2\times$$

$$\tan\tfrac{1}{2}\lambda_q]\}. \qquad \text{I.4}$$

We define

$$\Omega_q^2 = \tanh\tfrac{1}{2}\lambda_q + \tanh\tfrac{1}{2}\mu_q,$$
$$\Lambda_q^2 = \coth\tfrac{1}{2}\lambda_q + \coth\tfrac{1}{2}\mu_q, \qquad \text{I.5}$$
$$\xi_q = \mathcal{E}_b(q)\tanh\tfrac{1}{2}\mu_q + \mathcal{E}_a(q)\tanh\tfrac{1}{2}\lambda_q.$$

Using the definitions I.5, we have

$$H_q(t) = \frac{\sinh\frac{1}{2}\beta_q}{\pi\sqrt{\sinh\lambda_q \sinh\mu_q}} \frac{\hbar\sin^2\frac{qc}{4}}{MN\omega_q} \exp\left\{-\xi_b^2(q)\tanh\frac{1}{2}\mu_q - \xi_a^2(q)\tanh\frac{1}{2}\lambda_q\right\} \cdot$$

$$\int_{-\infty}^{\infty} y\,dy \exp\left\{-\frac{1}{4}\left[y^2(\Omega_q^2+\Lambda_q^2)-4y\xi_q\right]\right\} \int_{-\infty}^{\infty} x\,dx \exp\left\{-\frac{1}{4}\left[x^2(\Omega_q^2+\Lambda_q^2) + 2x(4(\Omega_q^2-\Lambda_q^2)-2\xi_q)\right]\right\}.$$

$$\text{I.6}$$

The integral is evaluated by completing the square in the exponent. We obtain

$$H_q(t) = \frac{\sinh\frac{1}{2}\beta_q}{\pi\sqrt{\sinh\lambda_q \sinh\mu_q}} \frac{\hbar\sin^2\frac{qc}{4}}{MN\omega_q} \frac{2\pi}{\Omega_q\Lambda_q} \left[\frac{\Lambda_q^2-\Omega_q^2}{2\Lambda_q^2\Omega_q^2} + \frac{\xi_q^2}{\Omega_q^4}\right].$$

$$\exp\left\{-\xi_b^2(q)\tanh\frac{1}{2}\mu_q - \xi_a^2(q)\tanh\frac{1}{2}\lambda_q + \frac{\xi_q^2}{\Omega_q^2}\right\}.$$

$$\text{I.7}$$

It is straightforward to prove the identities:

$$\frac{2\sinh\frac{1}{2}\beta_q}{\sqrt{\sinh\lambda_q \sinh\mu_q}} \frac{1}{\Omega_q\Lambda_q} = 1 \quad ;$$

$$-\xi_b^2(q)\tanh\frac{1}{2}\mu_q - \xi_a^2(q)\tanh\frac{1}{2}\lambda_q + \frac{\xi_q^2}{\Omega_q^2} = -\frac{1}{2}\left(\xi_b(q)-\xi_a(q)\right)^2\left[(2\bar{n}_q+1)\cdot(1-\cos\omega_q t) - i\sin\omega_q t\right].$$

$$\text{I.8}$$

Since ξ_q^2/Ω_q^4 is of order $1/N$ smaller than $\Lambda_q^2 - \Omega_q^2/\Lambda_q^2\Omega_q^2$,

$$\frac{\Lambda_q^2-\Omega_q^2}{2\Lambda_q^2\Omega_q^2} + \frac{\xi_q^2}{\Omega_q^2} \simeq \left(\bar{n}_q+\frac{1}{2}\right)\left(\cos^2\frac{1}{2}\omega_q t\right)\left(1-2i\tanh\frac{\beta_q}{2}\tan\frac{\omega_q t}{2}-\tan^2\frac{\omega_q t}{2}\right). \quad \text{I.9}$$

We therefore obtain

$$G_q(t) = \exp\left\{-\tfrac{1}{2}(\mathcal{E}_b(q)-\mathcal{E}_a(q))^2\left((2\bar{n}_q+\tfrac{1}{2})(1-\cos\omega_q t)-i\sin\omega_q t\right)\right\},$$

$$H_q(t) = \frac{\hbar\sin^2\tfrac{qc}{4}}{NM\omega_q}(\bar{n}_q+\tfrac{1}{2})(\cos^2\tfrac{\omega_q t}{2})(1-2i\tanh\tfrac{\beta_q}{2}\tan\tfrac{\omega_q t}{2}-\tan^2\tfrac{\omega_q t}{2})G_q(t). \qquad \text{I.10}$$

Appendix II. Derivation of Equation 3.12

We show that the cross terms in 3.11 vanish, so that the transition rate W_{ba} may be written as in 3.12. We define $L_q(t)$,

$$L_q(t) = \sum_{n_q^a, n_q^b} 2(\sinh\tfrac{\beta_q}{2})\langle n_q^b | n_q^a\rangle\langle n_q^b |\Delta(q)| n_q^a\rangle\exp\Big\{- \qquad \text{II.1}$$
$$[(\bar{n}_q+\tfrac{1}{2})\beta_q - it(n_q^b - n_q^a)\omega_q]\Big\}.$$

The cross terms in 3.11 may be written in terms of $G_q(t)$ and $L_q(t)$,

$$W'_{ba} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\,(\exp i\omega_{ba}t)\Big\{2MM'\sum_{q'}L_{q'}(t)\prod_{q\neq q'}G_q(t) + $$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{II.2}$$

$$2|M'|^2\sum_{q',q''}'L_{q'}(t)L_{q''}(t)\prod_{q\neq q',q''}G_q(t)\Big\}.$$

where $\sum_{q',q''}'$ means $q'\neq q''$. We wish to show that W'_{ba} vanishes. If the normal coordinates were not distorted, the proof would be trivial. Then $L_q(t)$ vanishes identically, since for two different harmonic oscillator functions the overlap vanishes, while for the same function, the expectation value of the position coordinate vanishes.

Using the Slater sum I.1 and the definition I.2,

$$L_q(t) = \frac{\sinh\frac{\beta q}{2}}{\pi\sqrt{\sinh\lambda_q \sinh\mu_q}} \sqrt{\frac{\hbar}{MN\omega_q}}\, I_q(t) \begin{cases} -2\sin\frac{qc}{4}\sin\frac{qc}{2}(\ell+\frac{1}{2}) & q \geqslant 0 \\ 2\sin\frac{qc}{4}\cos\frac{qc}{2}(\ell+\frac{1}{2}) & q < 0 \end{cases}, \quad \text{II.3}$$

$$I_q(t) = \int\!\!\!\int_{-\infty}^{\infty} x\,dx\,dy\,\exp\Big\{-\tfrac{1}{4}\Big[(x+y-2\varepsilon_b(q))^2\tanh\tfrac{1}{2}\mu_q +$$
$$(x-y)^2(\coth\tfrac{1}{2}\mu_q + \coth\tfrac{1}{2}\lambda_q) + (x+y-2\varepsilon_a(q))^2\tanh\tfrac{1}{2}\lambda_q\Big]\Big\}. \quad \text{II.4}$$

We have assumed that the process considered involves the adjacent molecular coordinates d_ℓ and $d_{\ell+1}$; we have also used that M and M' are real, which is a property of the exciton hamiltonian 1.1. Using I.6, integrating as in appendix I, and using the identities I.8, we have

$$I_q(t) = \frac{2\pi}{\Omega_q \Lambda_q}\frac{\xi_q}{\Omega_q^2}\, G_q(t), \quad \text{II.5}$$

$$L_q(t) = \sqrt{\frac{\hbar}{MN\omega_q}}\frac{\xi_q}{\Omega_q^2}\, G_q(t) \begin{cases} -2\sin\frac{qc}{4}\sin\frac{qc}{2}(\ell+\frac{1}{2}) & q \geqslant 0 \\ 2\sin\frac{qc}{4}\cos\frac{qc}{2}(\ell+\frac{1}{2}) & q < 0 \end{cases}. \quad \text{II.6}$$

The first part of II.6 is just $\Delta_\ell(q)$, as given in 3.18, except that ζ_q has been integrated out. This expression is independent of the number of excitons on the lattice. Thus $\Delta_\ell = \sum_q \Delta_\ell(q)$ is completely determined by the particular form of the lattice distortions arising from the excitons on site ℓ or $\ell + 1$. In all the cases that arise with the exciton hamiltonian 1.1, the perturbation is a distortion involving the coordinates of adjacent molecules.

On the other hand, ξ_q does depend on the exciton configurations $/a>$ and $/b>$. We generalize 2.11,

$$\xi_q = \mathcal{E}_b(q)\tanh\tfrac{1}{2}\mu_q + \mathcal{E}_a(q)\tanh\tfrac{1}{2}\lambda_q \qquad \text{II.7}$$

$$\mathcal{E}_{b,a}(q) = \sum_{\substack{\ell \\ \text{(occupied in } b,a)}} \sqrt{\frac{2M\omega_q}{\hbar N}}\ \frac{|\ell|}{g}\ \frac{(-2\sin\frac{qc}{4})}{(\lambda - 2\cos\frac{qc}{2})}\begin{cases} \sin\frac{qc}{2}(\ell+\tfrac{1}{2}) & q \gtrless 0 \\ \cos\frac{qc}{2}(\ell+\tfrac{1}{2}) & q < 0. \end{cases} \quad \text{II.8}$$

The sum is over the sites that are occupied in $|b\rangle, |a\rangle$. We assume, as in section II, that the lattice is infinite ($N \to \infty$); there are then an infinite number of excitons at any finite temperature. Furthermore, since the excitons interact only through short-range forces, the exciton distribution is random. Then the sum over the occupied sites in II.8 gives

$$\mathcal{E}_b(q) = \mathcal{E}_a(q) = 0 . \qquad \text{II.9}$$

However, a quantity like $\epsilon_a(q) - \epsilon_b(q)$ does not necessarily vanish. For the processes examined in sections IV and V, $/b>$ and $/a>$ differ by either the position or the existence of one or two excitons. Thus, regardless of the overall exciton distribution, there is exact cancellation of all but the distortions due to one or two excitons. Therefore $\epsilon_b(q) - \epsilon_a(q)$ is of order $1/\sqrt{N}$.

The cross terms therefore vanish because the system is large. They may be divided into two classes which contain one and two factors of $L_q(t)$, respectively. While they are of order

$1/N$ and $1/N^2$, respectively, of the analogous square terms, there are N and N^2 times as many of them. It may be verified by direct integration that the size of $L_q(t)$ is not enough to justify the neglect of the square terms.

Appendix III. Evaluation of W_{ba} (3.15)

We consider the first term in the integrand of equation 3.15,

$$\prod_q G_q(t) = \exp\left\{-\sum_q \tfrac{1}{2}(\mathcal{E}_b(q)-\mathcal{E}_a(q))^2\left[(2\bar{n}_q+1)(1-\cos\omega_q t)-i\sin\omega_q t\right]\right\}. \quad \text{III.1}$$

As we show below, there exists a $t = \tau$ such that, for any ω_q, $\omega_q\tau \ll 1$ and that the integrand is negligible for $t > \tau$. We expand $\cos\omega_q t$ and $\sin\omega_q t$ and neglect terms beyond the quadratic. The integral then reduces to a Gaussian integral if we complete the square,

$$W_{ba}^{(1)} = \frac{|M|^2}{\hbar^2} \int_{-\infty}^{\infty} dt \, \exp\left\{it A_{ba} - \frac{t^2}{2} B_{ba}\right\}, \quad \text{III.2}$$

where A_{ba} and B_{ba} are defined in 3.21. Integrating, we have

$$W_{ba}^{(1)} = \frac{|M|^2}{\hbar^2} \sqrt{\frac{2\pi}{B_{ba}}} \, e^{-A_{ba}^2/2B_{ba}}. \quad \text{III.3}$$

It is evident from III.2 that the integrand oscillates rapidly for $t \gtrsim \tau$ if $A_{ba} \gg \omega_q$; and that the integrand is small for $t \gtrsim \tau$ if $\sqrt{B_{ba}} \gg \omega_q$. These conditions are given in 3.22 and justify the approximations made to obtain III.3.

The second part of 3.15 is evaluated in the same way. The conditions 3.22 are again needed. Using 3.20 and III.1, we find after some manipulation

$$W_{ba}^{(2)} = \frac{|M'|^2}{\hbar^2} e^{-A_{ba}^2/2B_{ba}} \sum_q \frac{\hbar \sin^2 \frac{qc}{4}}{MN\omega_q} \sqrt{\frac{2\pi}{B_{ba}}} \Big\{$$

$$(\bar{n}_q + \tfrac{1}{2})\Big(1 + \tfrac{3}{8}\frac{\omega_q^2}{B_{ba}^2}(A_{ba}^2 - B_{ba})\Big) + \frac{\omega_q}{2}\frac{A_{ba}}{B_{ba}}\Big\}. \qquad \text{III.4}$$

Since $B_{ba} \gg \omega_q^2$ and $(A_{ba}^2 - B_{ba})/B_{ba} < 1$, we may neglect the second term. Thus, we find

$$W_{ba}^{(2)} = \frac{|M'|^2}{\hbar^2} e^{-A_{ba}^2/2B_{ba}} \sqrt{\frac{2\pi}{B_{ba}}} \sum_q \frac{\hbar \sin^2 \frac{qc}{4}}{MN\omega_q}\Big\{\bar{n}_q + \tfrac{1}{2} + \frac{\omega_q}{2}\frac{A_{ba}}{B_{ba}}\Big\}. \qquad \text{III.5}$$

At high temperatures, $kT > \hbar\omega_q$, and if $\omega_{ab} = 0$,

$$\frac{\omega_q A_{ba}}{2B_{ba}} \sim \frac{\hbar\omega_q}{4kT}. \qquad \text{III.6}$$

Hence we introduce no serious error by neglecting the second term at high temperatures. Replacing the sum in III.5 by an integral (that is, letting $N \to \infty$), we obtain

$$W_{ba}^{(2)} \approx \frac{|M'|^2}{q\,\hbar^2} \sqrt{\frac{\pi\hbar}{kT(|A_{ba}| - \omega_{ba})}} e^{-\frac{\hbar(|A_{ba}| - \omega_{ba})}{4kT}} \tfrac{1}{4}\Big(1 - \sqrt{\tfrac{\lambda-2}{\lambda+2}}\Big). \qquad \text{III.7}$$

We combine III.3 and III.5 to obtain W_{ba} in 3.23.

Appendix IV. Evaluation of $\prod_q < \bar{n}_q^{j+1} / \bar{n}_q^j >$

As in paper B, the effective exciton hamiltonian may be written

$$\mathcal{H}_{eff} = \sum_n \left\{ J_0 t_n^+ t_n - \tfrac{1}{4} J'_{eff} (t_n^+ t_{n+1} + t_{n+1}^+ t_n) \right\} + \mathcal{H}_2 + \mathcal{H}_3 + \mathcal{H}_i , \qquad \text{IV.1}$$

where the self-energy correction is included in the first term to give the observed singlet-triplet splitting J_0. The parameter describing exciton motion is J'_{eff} and is found below. The parameters J' appearing in 1.3 must be suitably reinterpreted, as discussed in section VIc; otherwise, $\mathcal{H}_2$ and $\mathcal{H}_3$ in 1.3 and in IV.1 are identical. $\mathcal{H}_i$ is the phonon-coupled repulsion between excitons, which we are approximating by a nearest-neighbor interaction,

$$\mathcal{H}_i = \tfrac{1}{2} \sum_n V(2) t_n^+ t_n t_{n+1}^+ t_{n+1} . \qquad \text{IV.2}$$

The effective exciton hamiltonian IV.1 is obtained by integrating out the phonons from the matrix elements of the exciton-phonon hamiltonian 1.4. For instance, we use the wave functions 6.7 and the part of the hamiltonian expressing exciton motion to find J'_{eff};

$$\langle k | \mathcal{H}_{motion} | k \rangle = -\frac{J'}{4} \left\{ e^{ikc} \prod_q \langle n_q^j | n_q^{j+1} \rangle + e^{-ikc} \prod_q \langle n_q^j | n_q^{j+1} \rangle \right\}. \qquad \text{IV.3}$$

Since $< n_q^j/n_q^{j+1} > = < n_q^j/n_q^{j-1} >$,

$$\langle k | H_{motion} | k \rangle = - \frac{J'}{2} (\cos kc) \prod_q \langle n_q^j | n_q^{j+1} \rangle . \qquad \text{IV.4}$$

Thus the parameter expressing exciton motion is

$$J'_{eff} = J' \prod_q \langle \bar{n}_q^j | \bar{n}_q^{j+1} \rangle . \qquad \text{IV.5}$$

We consider the overlap between two displaced harmonic oscillator wave functions. We suppose that the displacement of one with respect to the other is known. The Hermite polynomial centered at a may be expressed in terms of Hermite polynomials centered at the origin (38).

$$H_n (x-a) = \sum_{m=0}^{n} \frac{(-2a)^{n-m} n!}{m! (n-m)!} H_m (x) . \qquad \text{IV.6}$$

We wish to evaluate the overlap between the two **n**-quantum harmonic oscillator functions $\Psi_n(x)$ and $\Psi_n(x-a)$, centered at the origin and at a, respectively. We have

$$\langle \Psi_n (x) | \Psi_n (x-a) \rangle = N_n^2 e^{-\frac{a^2}{4}} \int_{-\infty}^{\infty} e^{-y^2} dy \, H_n(y+\tfrac{a}{2}) H_n(y-\tfrac{a}{2}) . \qquad \text{IV.7}$$

where $N_n = 1/(\sqrt{\pi} \, 2^n n!)^{\frac{1}{2}}$. Using the expansion IV.6 and the orthogonality of the Hermite polynomials, we obtain

$$\langle \Psi_n (x) | \Psi_n (x-a) \rangle = e^{-\frac{a^2}{4}} \sum_{k=0}^{n} \frac{n!}{k! (n-k)!} \left(-\frac{a^2}{2}\right)^{n-k} , \qquad \text{IV.8}$$

$$\prod_q \langle n_q^{j+1} | n_q^j \rangle = \prod_q e^{-\frac{a_q^2}{2}} \sum_{k=0}^{n_q} \frac{n_q!}{k!(n_q-k)!} \left(-\frac{a_q^2}{2}\right)^{n_q-k}. \qquad \text{IV.9}$$

Since we have expanded $/n_q^{j+1} >$ about the equilibrium position of $/n_q^j >$, $a_q = \varepsilon_{j+1}(q) - \varepsilon_j(q)$. Using 2.12 and combining $\pm q$, we obtain

$$a_q^2 = \frac{2M\omega_q}{\hbar N} \frac{j^2}{q} \frac{16 \sin^2 \frac{qc}{4} \sin^2 \frac{qc}{2}}{(\lambda - 2\cos \frac{qc}{2})^2}, \qquad q \geqslant 0. \qquad \text{IV.10}$$

a_q^2 goes as $1/N$. We expand the product to order $1/N^2$, take the limit $N \to \infty$, and rearrange,

$$\prod_q \langle n_q^{j+1} | n_q^j \rangle = \exp\left\{-\sum_q \frac{a_q^2}{2}(n_q + \tfrac{1}{2})\right\}. \qquad \text{IV.11}$$

The phonon overlap has been calculated for an arbitrary phonon distribution. We now specialize to the thermal equilibrium distribution. As expected, the overlap does not depend on the site j,

$$\prod_q \langle \bar{n}_q^{j+1} | \bar{n}_q^j \rangle = \exp\left\{-\frac{4 j^2}{q \hbar \sqrt{\frac{q}{M}}} \int_0^\pi \frac{d\theta}{\pi} \frac{\sin^2\theta(1-\cos\theta)}{(\lambda - 2\cos\theta)^{3/2}}(\bar{n}_\theta + \tfrac{1}{2})\right\}. \text{IV.12}$$

Using the parameters for WBP estimated in section III, we have, at 0°K,

$$\prod_q \langle \bar{n}_q^{j+1} | \bar{n}_q^j \rangle \sim 10^{-3}. \qquad \text{IV.13}$$

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III. PROPOSITIONS

Proposition I:

Derivation of the Chronoamperometric Constant for Unshielded,

Circular, Planar Electrodes[1]

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We have calculated the chronoamperometric constant for a circular electrode of finite size and have shown that it can be expanded as a power series in $\sqrt{Dt}/\rho_0$. The coefficient of the term in $\sqrt{Dt}/\rho_0$ is 2.26 and is in agreement with experiment. This coefficient is calculated by exploiting the equivalence between this problem and the corresponding heat conduction problem.

I. Introduction

The familiar Cottrell equation[2]

$$\frac{it^{1/2}}{AC} = \frac{n\mathfrak{F}D^{1/2}}{\pi^{1/2}} \qquad (1.1)$$

does not adequately describe the current–time behavior observed with electrodes of finite size at times longer than a few seconds.[3] Therefore, we have calculated the current–time behavior for a circular electrode of radius ρ_0 and have shown that the chronoamperometric constant can be expanded as a power series in $\sqrt{Dt}/\rho_0$; the coefficient of the term in $\sqrt{Dt}/\rho_0$ is calculated. To do this, we have exploited the similarity between this problem and analogous heat conduction problems by adding current sources in direct analogy to the heat sources added in heat conduction problems. We discuss only the mixed boundary condition problem in which the concentration is fixed at the surface of the electrode; the solution to the Neumann problem (chronopotentiometry) may be obtained analogously.

If we neglect the effect of turbulence and of convective stirring, then the current passing through the area $\vec{A}$ is simply

$$i = n\mathfrak{F} \frac{\mathrm{d}\vec{N}}{\mathrm{d}t} \cdot \vec{A} = n\mathfrak{F}D\nabla\bar{\mu} \cdot \vec{A} \qquad (1.2)$$

where i is the current in amperes, n is the number of equivalents per mole, D is the diffusion coefficient in cm.^{2}/sec., and $\bar{\mu}$ is the electrochemical potential. If the solution contains a large concentration of supporting electrolyte, the transference number of the electro-

active species is essentially zero. Under these conditions,[4] the diffusion equation reduces to

$$\frac{\partial C_i}{\partial t} = D_i\nabla^2 C_i \qquad (1.3)$$

where C_i is the concentration in moles/cc. of the ith electroactive species.

In the presence of excess supporting electrolyte, the compact double layer[5,6] can be approximated by a parallel plate condenser whose plates are separated by one or two molecular diameters. Therefore, the charge on the double layer for a circular electrode of radius ρ_0 will be uniform until $\rho - \rho_0$ approaches the thickness of the compact double layer (cf. Fig. 1). Since the metallic electrode is an equipotential surface, the uniformity of the double-layer charge requires that the potential at the outer Helmholtz plane also be uniform until $\rho - \rho_0$ approaches the thickness of the compact double layer. Very close to the edge, the potential at the outer Helmholtz plane will decrease with respect to the solution potential.

Therefore, it is very reasonable to assume that the concentration of the electroactive species will be uni-

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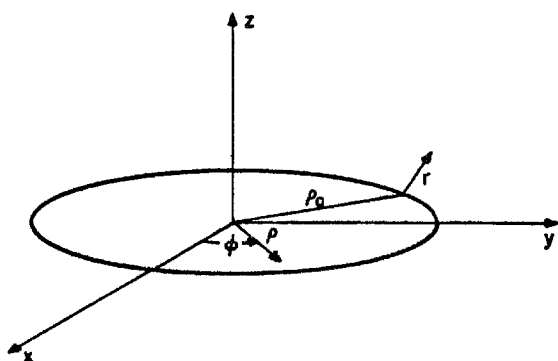
Figure 1. Model for the circular disk electrode.

form at the outer Helmholtz plane of metallic electrodes of finite size and in the presence of excess supporting electrolyte if the concentration is governed by the Nernst equation.

II. Formal Solution

We will first consider the oxidation of a single insoluble species to give a soluble product, e.g., the generation of silver ion into a solution initially free of silver. Our electrode is a circular planar disk of radius ρ_0 situated in the $z = 0$ plane (cf. Fig. 1). This electrode is potentiostated at a fixed potential E, and it is assumed that the Nernst equation is obeyed. This guarantees that diffusion and not the electron-transfer step will control the current. Observe that under these conditions, the concentration at the surface of the electrode will continuously increase with potential and no limiting current will be achieved. This approach is purely one of convenience and is taken to achieve greater generality as will become evident in the Discussion section.

The cylindrical symmetry enables us to write the concentration as $C(\rho,z,t)$. The boundary conditions for $C(\rho,z,t)$ are

$$C(\rho,0,t) = \begin{cases} C^0(E) & \rho \leq \rho_0 & t \geq 0^+ \\ 0 & \rho > \rho_0 & t = 0^+ \end{cases}$$

$$\frac{\partial C}{\partial z}(\rho,0,t) = 0 \qquad \rho > \rho_0 \qquad t \geq 0^+ \qquad (2.1)$$

$$C(\rho,z,0) = 0 \qquad z > 0$$

$$\lim_{\rho \to \infty} C(\rho,z,t) = \lim_{z \to \infty} C(\rho,z,t) = 0$$

$$(2.2)$$

$$\lim_{t \to \infty} C(\rho,z,t) = C^0(E)$$

We use the superposition theorem and write

$$C(\rho,z,t) = C^I(\rho,z,t) + C^{II}(\rho,z,t) \qquad (2.3)$$

In general, the surface of an electrode can be represented by a continuum of current sources whose distribution and strengths are time dependent. The source distribution for an infinite planar electrode is time independent and is uniform over the surface of the electrode. The time-dependent sources of $C^I(\rho,z,t)$ are chosen to be equivalent to such a uniform distribution for $\rho \leq \rho_0$ at $t = 0^+$. Therefore, $C^I(\rho,z,t)$ is equivalent, initially, to the concentration distribution at a circular section of an infinite electrode. At later times, radial diffusion causes the sources of $C^I(\rho,z,t)$ to decrease near the edge of the electrode and apparent sources to appear at $\rho > \rho_0$. The sources of $C^{II}(\rho,z,t)$ could be chosen so that the boundary condition (2.1) is satisfied at all times. Alternatively, the sources of $C^{II}(\rho,z,t)$ might be chosen so that the total flux from the finite electrode into the region $\rho \leq \rho_0$ is the same as from the infinite electrode. We shall adopt the second condition because we wish to approximate the sources for $C^{II}(\rho,z,t)$ by a line source. Such an approximation gives a nonuniform concentration at the surface of the electrode. Obviously, an exact solution must satisfy both conditions simultaneously.

The analogous heat conduction problem is that of a circular hot plate whose sources are chosen so as to keep the heat flux from the plate into the region $\rho \leq \rho_0$ the same as the flux from a circular section of an infinite hot plate whose temperature is uniform and time independent.

The initial conditions for $C^I(\rho,z,t)$ are

$$C^I(\rho,0,0^+) = \begin{cases} C^0(E) & \rho \leq \rho_0 \\ 0 & \rho > \rho_0 \end{cases} \qquad (2.4)$$

Since the diffusion equation contains only a first derivative with respect to time, it is convenient to make the partial separation

$$C^I(\rho,z,t) = C^0 g(\rho,t) f(z,t) \qquad (2.5)$$

where $C^0(E)$ is the concentration at the outer Helmholtz plane and $f(z,t)$ and $g(\rho,t)$ are dimensionless functions to be determined. It is evident that under certain conditions, such as $t \to 0$ or $\rho \to 0$, the solution must reduce to the solution for the infinite planar electrode. Hence, $f(z,t)$ corresponds to the well-known solution for the infinite planar electrode[7]

$$f(z,t) = 1 - \mathrm{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \qquad (2.6)$$

and $g(\rho,t)$ represents the effect of diffusion in the radial direction. Furthermore, the initial condition for $g(\rho,t)$ is

(7) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter 3.

$$g(\rho,0^+) = \begin{cases} 1 & \rho \leq \rho_0 \\ 0 & \rho > \rho_0 \end{cases} \qquad (2.7)$$

$g(\rho,t)$ must satisfy the radial portion of the diffusion equation.

$g(\rho,t)$ may be obtained *via* a Hankel transform.[8] Only zeroth-order Bessel functions appear because of the cylindrical symmetry. The integrand is a solution to the diffusion equation for each value of k, and hence $g(\rho,t)$ is a solution.

$$g(\rho,t) = \int_0^\infty k\,dk\, f(k) e^{-Dk^2 t} J_0(k\rho)$$

$$f(k) = \int_0^\infty \rho\,d\rho\, g(\rho,0^+) J_0(k\rho) \qquad (2.8)$$

As is shown in Fig. 2, $g(\rho,t)$ is a step function at $t = 0^+$; at later times, the time dependence of (2.8) gives different superpositions of the Bessel functions and the step-function decays. This decay expresses the fact that there is radial diffusion.

Since $C^I(\rho,z,t)$ satisfies the boundary conditions only at $t = 0^+$, it is evident that a current source must be added toward the edge of the electrode to maintain a uniform concentration distribution. This current source will produce the concentration $C^{II}(\rho,z,t)$. Once we have calculated $C^I(\rho,z,t)$, we will be able to determine the position and the strength of the current sources that produce $C^{II}(\rho,z,t)$.

The current flowing through the electrode is given rigorously by the gradient with respect to z of the concentration evaluated at $z = 0$, $\rho \leq \rho_0$. Therefore, the current density corresponding to $C^I(\rho,z,t)$ is

$$\frac{i}{\pi\rho_0^2} = n\mathfrak{F}D\, \frac{2}{\rho_0^2} \int_0^{\rho_0} \left(\frac{\partial C^I}{\partial z}\right)_{z=0} \rho\,d\rho =$$

$$-\frac{n\mathfrak{F}DC^0}{\sqrt{\pi Dt}} \int_0^{\rho_0} \rho\,d\rho\, g(\rho,t) \quad t > 0 \qquad (2.9)$$

$$g(\rho,t) = \int_0^\infty k\,dk\, e^{-Dk^2 t} J_0(k\rho) \times$$

$$\int_0^\infty \rho'd\rho'g(\rho',0^+)J_0(k\rho') \qquad (2.10)$$

By reversing the orders of integration freely, it is possible to show that for an arbitrary $g(\rho,0^+)$ the current density is an expansion in powers of $\sqrt{Dt}/\rho_0$.

III. Special Case: One-Component System

A. Expressions for $g(\rho,t)$. We now consider in detail the properties of $C^I(\rho,z,t)$. The initial conditions are fixed by (2.4); $f(z,t)$ is given by (2.6); $g(\rho,0^+)$ is the step function defined by (2.8). We integrate (2.8) to obtain

$$f(k) = \int_0^\infty \rho'd\rho'g(\rho',0^+)J_0(k\rho') = \rho_0\frac{J_1(k\rho_0)}{k} \qquad (3.1)$$

The exponential in (2.10) is now expanded in a Hankel transform. Only zeroth-order Bessel functions appear because of the symmetry in the k-plane. The inverse transformation reduces to a Laplace transform.[9]

$$e^{-Dk^2 t} = \int_0^\infty q\,dq\,J_0(kq)f(q) \qquad (3.2)$$

$$f(q) = \int_0^\infty k\,dk\,e^{-Dk^2 t}J_0(kq) =$$

$$\frac{1}{2Dt}\int_0^\infty dy\,e^{-y}J_0\left(\frac{q}{\sqrt{Dt}}\sqrt{y}\right) = \frac{1}{2Dt}e^{-\frac{q^2}{4Dt}} \qquad (3.3)$$

Combining (2.9), (2.10), (3.2), and (3.3), we obtain

$$g(\rho,t) = \frac{\rho_0}{2Dt}\int_0^\infty q\,dq\,e^{-\frac{q^2}{4Dt}} \times$$

$$\int_0^\infty J_0(kq)J_0(k\rho)J_1(k\rho_0)dk \qquad (3.4)$$

The integral over the Bessel functions is a special case of the formula of Sonine and Dougall.[10]

$$g(\rho,t) = \frac{1}{2\pi Dt}\int_0^\infty q\,dq\,e^{-q^2/4Dt}A(\rho,\rho_0,q) \qquad (3.5)$$

$A(\rho,\rho_0,q) =$

$$\begin{cases} \pi & \rho_0^2 > (\rho + q)^2 \\ \cos^{-1}\left(\dfrac{\rho^2 + q^2 - \rho_0^2}{2q\rho}\right) & (\rho + q)^2 > \rho_0^2 > (\rho - q)^2 \\ 0 & (\rho - q)^2 > \rho_0^2 \end{cases}$$

$$(3.6)$$

Hence

$$\rho \leq \rho_0 \quad g(\rho,t) = 1 + \frac{1}{\pi}\int_{\rho_0-\rho}^{\rho_0+\rho} dq\,e^{-\frac{q^2}{4Dt}} \times$$

$$\frac{\partial}{\partial q}\left(\cos^{-1}\left(\frac{\rho^2 + q^2 - \rho_0^2}{2q\rho}\right)\right) \qquad (3.7)$$

$$\rho > \rho_0 \quad g(\rho,t) = \frac{1}{\pi}\int_{\rho-\rho_0}^{\rho+\rho_0} dq\,e^{-\frac{q^2}{4Dt}} \times$$

$$\frac{\partial}{\partial q}\left(\cos^{-1}\left(\frac{\rho^2 + q^2 - \rho_0^2}{2q\rho}\right)\right) \qquad (3.8)$$

(8) P. M. Morse and H. Feshbach, "Methods of Theoretical Physics," McGraw-Hill Book Co., New York, N. Y., 1953.

(9) W. Magnus and F. Oberhettinger, "Formulas and Theorems for the Functions of Mathematical Physics," Chelsea Publishing Co., New York, N. Y., 1949, p. 132.

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In order to evaluate the integrals in (3.7) and (3.8), we first evaluate $\partial g/\partial\rho(\rho,t)$. We can easily verify (or observe from the boundary conditions) that $\partial g/\partial\rho(\rho,0^+)$ is a δ-function of unit strength.

$$t = 0^+ \quad \frac{\partial g}{\partial\rho}(\rho,0^+) = -\rho_0 \int_0^\infty kdkJ_1(k\rho)J_1(k\rho_0)$$

$$\text{(3.9)}$$

$$= -\delta(\rho - \rho_0)$$

$$t > 0^+ \quad \frac{\partial g}{\partial\rho}(\rho,t) = -\frac{\rho_0}{2}\int_0^\infty dye^{-Dty}J_1(\rho\sqrt{y})J_1(\rho_0\sqrt{y})$$

$$\text{(3.10)}$$

$$= -\frac{\rho_0}{2Dt}I_1\left(\frac{\rho\rho_0}{2Dt}\right)e^{-\frac{\rho^2+\rho_0^2}{4Dt}}$$

The Laplace transform[10] in (3.10) gives the modified Bessel function of the first order.

We define $\Delta g(\rho,t)$ to be the deviation of $g(\rho,t)$ from the step function $g(\rho,0^+)$.

$$\Delta g(\rho,t) = g(\rho,t) - 1 \qquad \rho \leq \rho_0$$
$$= g(\rho,t) \qquad \rho > \rho_0 \quad \text{(3.11)}$$

We now obtain an expression for $\Delta g(\rho,t)$, $\rho \leq \rho_0$. It is evident from (3.7) that $g(0,t) = 1$ for all $t > 0$. Equation 3.10 then gives

$$\Delta g(\rho,t) = g(\rho,t) - g(0,t) = \int_0^\rho \frac{\partial g}{\partial\rho'}(\rho',t)d\rho' \quad \rho \leq \rho_0$$

$$\text{(3.12)}$$

$$= -\frac{\rho_0}{2Dt}\int_0^\rho I_1\left(\frac{\rho'\rho_0}{2Dt}\right)e^{\frac{-(\rho')^2+\rho_0^2}{4Dt}}d\rho'$$

If we set $\chi = \rho\rho_0/2Dt$, $\chi_0 = \rho_0^2/2Dt$, and $\beta = Dt/\rho_0^2 = 1/2\chi_0$, we find

$$\Delta g(\chi,t) = -e^{-\chi_0/2}\int_0^\chi I_1(x)e^{-\beta x^2}dx \quad \text{(3.13)}$$

We use the properties of the modified Bessel functions[11] and integrate (3.13) by parts repeatedly.

$$\Delta g(\chi,t) = -e^{-\chi_0/2}\left\{\sum_{\nu=0}^\infty (2\beta\chi)^\nu I_\nu(\chi)e^{-\beta\chi^2} - 1\right\}$$

$$\text{(3.14)}$$

$$= e^{-\chi_0/2}\left\{1 - e^{-\rho^2/4Dt}\sum_{\nu=0}^\infty \left(\frac{\rho}{\rho_0}\right)^\nu I_\nu\left(\frac{\rho\rho_0}{2Dt}\right)\right\},$$

$$\rho \leq \rho_0$$

where I_ν is the modified Bessel function of order ν.

B. *Correction to the Current Density.* Expressions 3.13 and 3.14 will be used to evaluate $g(\rho,t)$. Before we perform this calculation, which requires a variety of special conditions, we will evaluate the decay in the current density *at the electrode* due to the apparent motion of the current sources for $C^1(\rho,z,t)$ to $\rho > \rho_0$ in the $z =$

0 plane. We replace $g(\rho,t)$ in (2.9) by $\Delta g(\rho,t)$; except for constants, we have

$$\int_0^{\rho_0} \rho d\rho\Delta g(\rho,t) = \frac{\rho_0^2}{2}e^{-\frac{\chi_0}{2}} -$$

$$\int_0^{\rho_0} \rho d\rho e^{-\frac{\rho_0^2+\rho^2}{4Dt}}\sum_{\nu=0}^\infty \left(\frac{\rho}{\rho_0}\right)^\nu I_\nu\left(\frac{\rho\rho_0}{2Dt}\right)$$

$$\text{(3.15)}$$

$$= e^{-\frac{\chi_0}{2}}\left\{\frac{\rho_0^2}{2} - \left(\frac{2Dt}{\rho_0}\right)^2\sum_{\nu=0}^\infty \int_0^{\chi_0} (2\beta x)^\nu e^{-\beta x^2}I_\nu(x)xdx\right\}$$

We integrate by parts repeatedly to obtain

$$\int_0^{\chi_0} x^{\nu+1}e^{-\beta x^2}I_\nu(x)dx =$$

$$\sum_{\mu=\nu+1}^\infty \frac{(2\beta\chi_0)^\mu}{2\beta^{\nu+1}}I_\mu(\chi_0)e^{-\beta\chi_0^2} \quad \text{(3.16)}$$

Substituting (3.16) in (3.15), we have

$$\int_0^{\chi_0} \rho d\rho\Delta g(\rho,t) = e^{-\frac{\rho_0^2}{4Dt}}\times$$

$$\left\{\frac{\rho_0^2}{2} - 2Dte^{-\frac{4Dt}{\rho_0^2}}\sum_{\nu=0}^\infty \nu I_\nu\left(\frac{\rho_0^2}{2Dt}\right)\right\} \quad \text{(3.17)}$$

Using the recursion relations for the modified Bessel functions, we find

$$\frac{1}{2x}\sum_{\nu=1}^\infty \nu I_\nu(x) = \frac{1}{2}\sum_{\nu=1}^\infty \{I_{\nu-1}(x) - I_{\nu+1}(x)\}$$

$$\text{(3.18)}$$

$$= \frac{1}{2}\{I_0(x) + I_1(x)\}$$

Substituting (3.18) in (3.17), we obtain

$$\int_0^{\chi_0} \Delta g(\rho,t)\rho d\rho = -\frac{\rho_0^2}{2}e^{-\frac{\rho_0^2}{2Dt}}\times$$

$$\left\{I_0\left(\frac{\rho_0^2}{2Dt}\right) + I_1\left(\frac{\rho_0^2}{2Dt}\right) - e^{+\rho_0^2/4Dt}\right\} \quad \text{(3.19)}$$

Hence

$$\frac{\Delta i}{\pi\rho_0^2} = \frac{n\mathfrak{F}DC^0}{\sqrt{\pi Dt}}e^{-\frac{\rho_0^2}{2Dt}}\left\{I_0\left(\frac{\rho_0^2}{2Dt}\right) + I_1\left(\frac{\rho_0^2}{2Dt}\right) -\right.$$

$$\left. e^{+\rho_0^2/4Dt}\right\} \quad \text{(3.20)}$$

Equation 3.20 is an exact expression. The current sources for $C^1(\rho,z,t)$ have an initial uniform distribution over the surface of the electrode that is identical with the time-independent distribution of the current sources

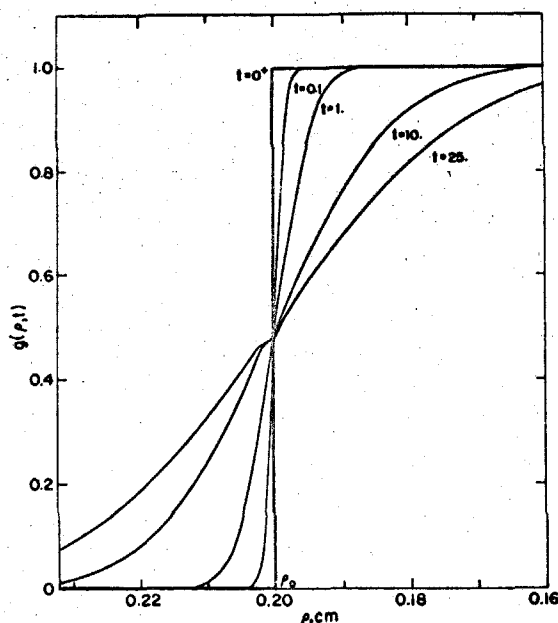(11) H. B. Dwight, "Tables of Integrals and Other Mathematical Data," The Macmillan Co., New York, N. Y., 1961.

Figure 2. Plot of $g(\rho,t)$ as a function of ρ illustrating the redistribution of the sources of $C^I(\rho,z,t)$. $\rho_0 = 0.2$ cm., $D = 1 \times 10^{-4}$ cm.^{2}/sec.

for the infinite planar electrode. However, the current sources for $C^I(\rho,z,t)$ are redistributed in time because of radial diffusion; the sources near the edge of the electrode decay, and apparent sources are found outside the electrode ($\rho > \rho_0$). $g(\rho,t)$ is identically unity for the infinite planar electrode since there is no radial diffusion in that case.

C. Evaluation of $g(\rho,t)$ for Experimental Conditions. In order to find $g(\rho,t)$, $\rho < \rho_0$, and thus determine the position of the sources that we shall use for $C^{II}(\rho,z,t)$, it is convenient to specialize the experimental conditions, i.e., $\rho_0 \gtrsim 0.2$ cm., $D \sim 10^{-5}$ cm.^{2}/sec., $t \lesssim 100$ sec. Under these conditions, $\rho_0^2/4Dt = \chi_0/2 > 10$. From the definition of $I_\nu(x)$, it is evident that $I_{\nu+1}(x) < I_\nu(x)$ for all ν when $x > 0$. Hence, we have from (3.14)

$$|\Delta g(\rho,t)| < e^{-\frac{\rho_0^2+\rho^2}{4Dt}} I_0\left(\frac{\rho\rho_0}{2Dt}\right) \sum_{\nu=0}^{\infty}\left(\frac{\rho}{\rho_0}\right)^\nu =$$

$$e^{-\frac{\rho_0^2+\rho^2}{4Dt}} I_0\left(\frac{\rho\rho_0}{2Dt}\right)\frac{1}{1-\rho/\rho_0}, \quad \rho \le \rho_0 \quad (3.21)$$

For $\rho = \rho_0/4$, $\chi_0/4 \gtrsim 5$, and we may use the large argument expansion of I_0.[11] We then have, for $0 < \rho \le \rho_0/4$

$$|\Delta g(\rho,t)| < |\Delta g(\rho_0/4,t)| \approx$$

$$^4/_2\frac{e^{-\frac{9\chi_0}{32}}}{\sqrt{\frac{\pi\chi_0}{2}}}\left[1+\frac{1}{2\chi_0}\cdots\right] \sim e^{-7} \quad (3.22)$$

Hence we observe that $\Delta g(\rho,t)$ is negligible for $\rho \le \rho_0/4$. Equation 3.21 is an upper bound for $|\Delta g(\rho,t)|$, since, in it, we have replaced all of the modified Bessel functions by I_0. For example, eq. 3.21 gives $|\Delta g(0,t)| \lesssim e^{-10}$ while $\Delta g(0,t) \equiv 0$ (for all t) from eq. 3.14. For $\rho_0/4 < \rho \le \rho_0$, we may use the large argument expansion of the modified Bessel functions in eq. 3.12 throughout the entire range of the integration.

$$\Delta g(\chi,t) = -e^{-\beta\chi_0^2}\int_{\chi_0/4}^{x} e^{-\beta\nu^2}e^\nu \frac{\mathrm{d}y}{\sqrt{2\pi y}}\left(1-\frac{3}{8y}\cdots\right)$$

$$(3.23)$$

$$= -\int_{\chi_0/4}^{x} e^{-\beta(\chi_0-y)^2}\frac{\mathrm{d}y}{\sqrt{2\pi y}}\left(1-\frac{3}{8y}\cdots\right)$$

Since $\chi_0/4 > 5$, it is straightforward to integrate (3.23). Hence

$$\Delta g(\rho,t) =$$

$$\begin{cases} -^1/_2\left(1-\mathrm{erf}\left(\frac{\rho_0-\rho}{2\sqrt{Dt}}\right)\right)-\frac{1}{2\sqrt{\pi}}\frac{\sqrt{Dt}}{\rho_0}\times \\ \quad e^{-\frac{(\rho_0-\rho)^2}{4Dt}}+0\left(\left(\frac{\sqrt{Dt}}{\rho_0}\right)^3\right) \quad \frac{\rho_0}{4}<\rho\le\rho_0 \\ \\ \hfill (3.24) \\ \\ 0 \hfill \rho\le\frac{\rho_0}{4} \end{cases}$$

Expression 3.24, which has the expected form, may be obtained directly from (3.7) by taking $\rho = \rho_0 - \Delta$ and letting $\Delta \to 0$ *after* the integration. If we set $\rho = \rho_0$ in (3.7), the integrand is indeterminate at $q = 0$; when the integration is now performed, only the second term of (3.24), evaluated at $\rho = \rho_0$, is obtained.

Since the derivative of $g(\rho,t)$ is continuous for $t > 0$, we may use an expression similar to (3.12) to evaluate $g(\rho,t)$ for $\rho > \rho_0$.

$$\Delta g(\rho,t) = 1 + \Delta g(\rho_0,t) - \frac{\rho_0}{2Dt}\int_{\rho_0}^{\rho} I_1\left(\frac{\rho'\rho_0}{2Dt}\right)\times$$

$$e^{-\frac{(\rho')^2+\rho_0^2}{4Dt}}\mathrm{d}\rho' \quad \rho > \rho_0$$

$$(3.25)$$

$$= ^1/_2\left(1-\mathrm{erf}\left(\frac{\rho-\rho_0}{2\sqrt{Dt}}\right)\right)-\frac{1}{2\sqrt{\pi}}\frac{\sqrt{Dt}}{\rho_0}\times$$

$$e^{-\frac{(\rho-\rho_0)^2}{4Dt}}+0\left(\left(\frac{\sqrt{Dt}}{\rho_0}\right)^3\right)$$

The next term in eq. 3.24 or 3.25 is negligible for the times of interest. Since $f(0,t) = 1$, the deviation of $C^I(\rho,0,t)$ from C^0 for $\rho \leq \rho_0$ is C^0 times expression 3.24.

D. Sources for and Calculation of $C^{II}(\rho,z,t)$. $g(\rho,t)$ is plotted as a function of ρ for various values of t in Fig. 2. It is evident that, for $t \lesssim 25$ sec., deviations from the step-function initial condition are important only within 0.02 to 0.03 cm. of the edge of the electrode. Of course, this is precisely what is expected, especially if the analogous heat problem is considered. Therefore, we need a current source of radius of about 0.01 cm. at the perimeter of the electrode, placed so that the outer edge of the source is at $\rho = \rho_0$ if the boundary condition (2.4) is to be satisfied for all times. Such a time-dependent source, which arises from the decomposition of the concentration in (2.3), defines the diffusion problem for $C^{II}(\rho,z,t)$.

As a first approximation, we consider a time-independent source at $\rho = \rho_0$. This should be a good approximation for short times since, for short times, (3.24) shows that the source is essentially at the edge and, as is evident from the large argument expansion of the modified Bessel functions, (3.20) shows that $\Delta i/\pi\rho_0^2$ is essentially time independent.

$$\frac{\Delta i}{A} = \frac{n\mathfrak{F}D2C^0}{\pi\rho_0^2}\left\{1 + 0\left(\frac{Dt}{\rho_0^2}\right)\right\} \quad (3.26)$$

In the same spirit, we may, for short times, approximate the source by an infinitely long, straight wire and express the concentration at a distance r from the wire as

$$C^{II}(r,t) = \frac{C^0\alpha}{2\pi}\int_{r/2\sqrt{Dt}}^{\infty}\frac{dx}{x}e^{-x^2} =$$
$$-\frac{C^0\alpha}{4\pi}Ei\left(-\frac{r^2}{4Dt}\right) \quad (3.27)$$

where $Ei(x)$ is the exponential integral. α is the strength of the source and will be evaluated below. This solution is borrowed from the analogous heat conduction problem.[12]

It is not convenient to satisfy the boundary condition (2.1) by requiring that the sum of $C^I(\rho,z,t)$ and $C^{II}(\rho,z,t)$ be uniform and time independent at the face of the electrode, since, by lumping the corrections into a line source, we have introduced a singularity. We may, however, as an alternative condition, match fluxes. Since the exact sources of $C^{II}(\rho,z,t)$ have "radii" of about 0.01 cm. for $t \lesssim 25$ sec., the approximation of a line source should be excellent for $r \gtrsim 0.01$ cm. (*cf.* Fig. 2). Once outside the source distribution, its detailed composition becomes unimportant; as in a multipole expansion, the major effect is found by put-

ting a point source at the center of the distribution. We will approximate even further and place the source at the edge of the electrode instead of near the edge.

The current flowing from a straight wire is radial by symmetry. At a line source of strength α, the current per unit length is

$$i_s = n\mathfrak{F}D2\pi r\frac{\partial}{\partial r}C^{II}(r,t)\big|_{r=0} = -n\mathfrak{F}DC^0\alpha \quad (3.28)$$

It is evident from Fig. 1 that the symmetry in the $z = 0$ plane requires that the flux flowing into the region where $z > 0$ is just half the total flux from a source whose intensity is twice the intensity of the actual source. Thus (3.28) will be correct if α is taken to be the actual intensity per unit length of the line source. Furthermore, at least for short times, the flux into the region $\rho < \rho_0$ is the same, by symmetry, as the flux into the region $\rho > \rho_0$. The total flux from a line source of length $2\pi\rho_0$ is

$$\frac{i_s}{\pi\rho_0^2} = -\frac{2}{\rho_0}n\mathfrak{F}DC^0\alpha \quad (3.29)$$

Half of this current will flow into the region $z > 0$, $\rho < \rho_0$. Hence

$$\frac{1}{2}i_s = -\Delta i \quad (3.30)$$

where Δi is given by (3.20). These two currents have opposite signs since the source for $C^{II}(\rho,z,t)$ is to correct for the effects of radial diffusion. Thus we obtain

$$\alpha = \frac{2}{\pi} \quad (3.31)$$

The correction current density is therefore

$$\frac{i_s}{\pi\rho_0^2} = -\frac{n\mathfrak{F}DC^0}{\sqrt{\pi Dt}}\frac{4}{\sqrt{\pi}}\frac{\sqrt{Dt}}{\rho_0} \quad (3.32)$$

E. Total Current Density and Concentration Profiles.
The total current density is the sum of the current sources for $C^I(\rho,z,t)$ and eq. 3.32. The *total* current density due to the sources of $C^I(\rho,z,t)$ is (*cf.* eq. 2.9)

$$\frac{i_1}{\pi\rho_0^2} = -n\mathfrak{F}C^0\sqrt{\frac{D}{\pi t}}\int_0^{\infty}g(\rho,t)\rho d\rho$$
$$= -n\mathfrak{F}C^0\sqrt{\frac{D}{\pi t}}\left\{1 + 0\left(\frac{Dt}{\rho_0^2}\right)\right\} \quad (3.33)$$

Therefore, the total current is

(12) L. R. Ingersoll, O. J. Zobel, and A. C. Ingersol, "Heat Conduction," McGraw-Hill Book Co., New York, N. Y., 1948, p. 146.

$$\frac{i}{\pi\rho_0{}^2} = -\frac{n\mathfrak{F}DC^0}{\sqrt{\pi Dt}}\left\{1 + \frac{4}{\sqrt{\pi}}\frac{\sqrt{Dt}}{\rho_0} + 0\left(\frac{Dt}{\rho_0{}^2}\right)\right\}$$

$$(3.34)$$

Although the boundary condition (2.1) is not satisfied in detail on the electrode, it is evident that, if the line charge is redistributed near the edge, the concentration could be calculated even at the face of the electrode. The current correction would, however, be very nearly the same since the flux from a source distribution may be found by calculating the flux from the equivalent point source.

We have overestimated the correction in (3.30) since the center of the correction source is actually at $\rho < \rho_0$ rather than at $\rho = \rho_0$. Thus slightly more than half of the flux goes into the region $\rho < \rho_0$. This effect is only of the order of a few per cent for $t \lesssim 25$ sec. At longer times, when this effect becomes larger, the assumption that the added current is a line source approximated by a straight wire also becomes untenable.

$C^{\mathrm{I}}(\rho,z,t)$ and $C^{\mathrm{II}}(\rho,z,t)$ are given by (2.4), (2.6), (3.24), (3.25), and (3.27). As discussed above, $C^{\mathrm{II}}(\rho, z,t)$ is a poor approximation for distances smaller than the dimensions of the sources of $C^{\mathrm{II}}(\rho,z,t)$. The dimensions of the sources of $C^{\mathrm{II}}(\rho,z,t)$ may be estimated from Fig. 2 which shows the region for $\rho < \rho_0$ where $\Delta g(\rho,t)$ is appreciably different from zero. For $t \lesssim 25$ sec., a distance of about 0.01 cm. from the edge of the electrode is sufficient to ensure being outside the source. We therefore have, for $t \lesssim 25$ sec. and $r \gtrsim 0.01$ cm.

$$C(\rho,z,t) = C^{\mathrm{I}}(\rho,z,t) + C^{\mathrm{II}}(\rho,z,t)$$

Figure 3. Typical concentration profiles for $C(\rho,z,t)$ and $C^{\mathrm{II}}(\rho,z,t)$: $z = 0.01$ cm., $\rho_0 = 0.2$ cm., $D = 1 \times 10^{-5}$ cm.^{2}/sec.

of line sources and then replacing each line source by a finite source. The strength of such sources is still determined by $\Delta g(\rho,t)$. As is evident, such a procedure approximates the exact solution more and more accurately. However, in order to obtain the exact solution, both the location and the strength of the sources

$$C^{\mathrm{I}}(\rho,z,t) = C^0\begin{cases} 1 - \mathrm{erf}\left(\dfrac{z}{2\sqrt{Dt}}\right) & 0 \leq \rho < \dfrac{\rho_0}{4} \\[2ex] \left[\frac{1}{2}\left(1 + \mathrm{erf}\left(\dfrac{\rho_0 - \rho}{2\sqrt{Dt}}\right)\right) - \dfrac{1}{2\sqrt{\pi}}\dfrac{\sqrt{Dt}}{\rho_0}e^{-\left(\frac{\rho_0-\rho}{4Dt}\right)^2}\right]\left(1 - \mathrm{erf}\left(\dfrac{z}{2\sqrt{Dt}}\right)\right) & \dfrac{\rho_0}{4} \leq \rho \leq \rho_0 \\[2ex] \left[\frac{1}{2}\left(1 - \mathrm{erf}\left(\dfrac{\rho - \rho_0}{2\sqrt{Dt}}\right)\right) - \dfrac{1}{2\sqrt{\pi}}\dfrac{\sqrt{Dt}}{\rho_0}e^{-\left(\frac{\rho-\rho_0}{4Dt}\right)^2}\right]\left(1 - \mathrm{erf}\left(\dfrac{z}{2\sqrt{Dt}}\right)\right) & \rho_0 < \rho \leq \infty \end{cases}$$

$$(3.35)$$

$$C^{\mathrm{II}}(\rho,z,t) = C^0\begin{cases} -\dfrac{1}{2\pi^2}Ei\left(-\dfrac{r^2}{4Dt}\right) & 0 < r < \dfrac{\rho_0}{2} \\[2ex] 0 & \dfrac{\rho_0}{2} \leq r < \infty \end{cases}$$

$$(3.36)$$

where $r = [z^2 + (\rho - \rho_0)^2]^{1/2}$.

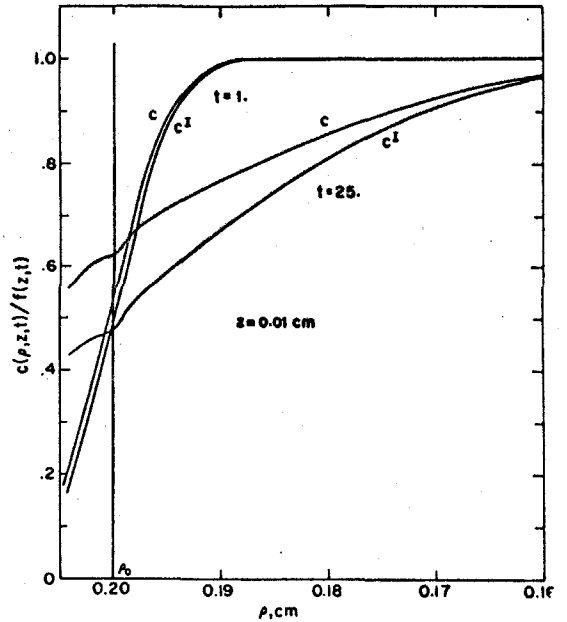Near the electrode, the concentration may be found more accurately by replacing our line source by a series

for $C^{\mathrm{II}}(\rho,z,t)$ must be time dependent. Thus, the mathematics becomes considerably less tractable. The simple model discussed in this paper is therefore useful in that it provides an accurate value of the total current density and, except very near the electrode, accurate concentration profiles.

IV. Discussion

A. Generalization. Our solution can be readily converted into the more usual situation where the solu-

tion originally contains the electroactive species at concentration C^0 and the product is insoluble. This is done by the simple transformation

$$C'(\rho,z,t) = C^0 - C(\rho,z,t) \qquad (4.1)$$

where $C'(\rho,z,t)$ is the transformed concentration and $C(\rho,z,t)$ is given by (2.3). Under these conditions, eq. 3.34 will be valid at all points on the i–E curve if C^0 is replaced by $C^0 - C(\rho,0,t,E)$.

This treatment can be extended to include the more general system where both the oxidized and reduced species are soluble and the solution is initially free of the reduced species. We decompose the concentration of both the oxidized and reduced species into the two components $C_t^{\mathrm{I}}(\rho,z,t)$ and $C_t^{\mathrm{II}}(\rho,z,t)$. We require the additional boundary conditions that the ratio of the concentrations of the two components at the outer Helmholtz plane is fixed by the Nernst equation and that the sum of their fluxes is zero at the electrode.[7] The current on the diffusion plateau will be independent of the reduced species and will again be given by eq. 3.34.

It is evident that an analogous approach can be used to obtain a solution under different boundary conditions, such as a constant concentration gradient at $z = 0$.

B. *Comparison with Experiment.* The theoretical value of the chronoamperometric constant is obtained by rearranging eq. 3.34.

$$\frac{it^{1/2}}{AC^0} = n\mathfrak{F}\sqrt{\frac{D}{\pi}}\left\{1 + \frac{4}{\sqrt{\pi}}\frac{\sqrt{Dt}}{\rho_0} + 0\left(\frac{Dt}{\rho_0^2}\right)\right\} \qquad (4.2)$$

The coefficient of the first term has been evaluated experimentally for $\rho_0 = 0.258$ cm. and $0.01 < \sqrt{Dt}/\rho_0 < 0.08$ for a variety of systems.[3] The experimental value of this coefficient is 2.12 ± 0.11 (95% confidence level) and is in agreement with the theoretical value of 2.26; the agreement is especially good since the latter is a slight overestimate.

Proposition II:

Phonon-Coupled Interactions between Paramagnetic Excitons*

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It is shown that exciton–phonon coupling in solid free radicals leads to a spin-independent repulsion between paramagnetic excitons. This repulsion may make a significant contribution to the activation energy for spin-exchange line broadening that is observed in the paramagnetic resonance of a number of solid free radicals.

INTRODUCTION

PREVIOUS theoretical treatments[1,2] of paramagnetic excitons in solid free radicals have neglected exciton–phonon coupling, even though it is quite likely that the exciton–phonon coupling is large. This neglect is justifiable from a phenomenological point of view to the extent that the form of the spin Hamiltonian for the problem is independent of exciton–phonon coupling. In the present paper we shall describe briefly a *spin-independent* repulsion between triplet excitons that is not represented by the previously described triplet exciton spin Hamiltonian. This phonon-coupled interaction between triplet excitons may make a significant contribution to the activation energy for spin-exchange line broadening that is observed in the paramagnetic resonance of a number of solid free radicals.[3-6]

MODEL

In the solid free radicals that show triplet exciton paramagnetic resonance,[3-6] the exciton motion is principally along linear free radical chains. The simplest example to consider is Wurster's Blue perchlorate where each radical in the chain is a positive ion, and where the distances between the ions are presumed to alternate in the low temperature crystal structure.[6] A schematic of this alternating linear array is given in Fig. 1. The spin exchange interactions between the spin $\mathfrak{S}_n$ on the nth molecule and its nearest neighbors are given by

the spin Hamiltonian[2]

$$\mathfrak{K}_e = \sum_{n=1,3,5,\ldots} J \mathfrak{S}_n \cdot \mathfrak{S}_{n+1} + J' \mathfrak{S}_n \cdot \mathfrak{S}_{n-1}. \quad (1)$$

Here $\mathfrak{S}_n = \frac{1}{2}$. As has been pointed out previously,[2] this Hamiltonian can be written in the form

$$\mathfrak{K}_e = \mathfrak{K}_0 + \mathfrak{K}_1 + \mathfrak{K}_2 + \mathfrak{K}_3, \quad (2)$$

where

$$\mathfrak{K}_0 = J \sum_{n=1,3,5,\ldots} l_n^+ l_n, \quad (3)$$

$$\mathfrak{K}_1 = -\tfrac{1}{4} J' \sum_{n=1,3,5,\ldots} l_n^+ (l_{n+2} + l_{n-2}), \quad (4)$$

$$\mathfrak{K}_2 = \tfrac{1}{4} J' \sum_{n=1,3,5,\ldots} \mathbf{S}_n \cdot \mathbf{S}_{n+1}, \quad (5)$$

$$\mathfrak{K}_3 = \tfrac{1}{4} J' X (\text{terms creating or destroying excitations}). \quad (6)$$

In these equations l_n^+ and l_n are operators creating and destroying triplet excitations on the pairs of molecules n and $n+1$, and $\mathbf{S}_n$ is the total spin angular momentum operator for the pair of molecules n and $n+1$, $\mathbf{S}_n = \mathfrak{S}_n + \mathfrak{S}_{n+1}$. In Eqs. (3)–(5), n takes on only odd values, $n = 1, 3, 5, \cdots$. The Hamiltonian term $\mathfrak{K}_2$ gives the spin dependent exchange interaction between adjacent triplet excitations. As in the previous work,[2] we assume that $J \gg J' > 0$. The eigenstates of the free exciton gas Hamiltonian $\mathfrak{K}_0 + \mathfrak{K}_1$ are given elsewhere; the elementary excitations have fermionlike properties.[2,7,8] The term in $\mathfrak{K}_3$ can be neglected (or simply treated by perturbation theory) when $J \gg J'$. The term in $\mathfrak{K}_2$ which gives a spin-dependent exciton–exciton interaction is probably small compared to the repulsion between the excitons due to the phonon-coupled interaction described below.

We consider only the phonon spectrum of the linear lattice sketched in Fig. 1. The displacement of each molecule from its equilibrium position in the chain direction is d_n and the molecule–molecule interaction is assumed to be harmonic, $\tfrac{1}{2} g(d_n - d_{n+1})^2$. For simplicity, the same force constant g is used for the cou-

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[6] D. D. Thomas, H. Keller, and H. M. McConnell, "Exciton Magnetic Resonance in Wurster's Blue Perchlorate" J. Chem. Phys. (to be published). See also H. M. McConnell, D. Pooley, and A. Bradbury, Proc. Natl. Acad. Sci. (U.S.) 48, 1480 (1962).
[7] D. B. Chesnut and A. Suna, J. Chem. Phys. 39, 146 (1963).
[8] H. M. McConnell and C. G. Montgomery, J. Chem. Phys. 39, 252 (1963).

pling of molecules n and $n+1$ as for n and $n-1$. The three-dimensional character of the real lattice is introduced by including in the potential energy of the phonon Hamiltonian terms of the form $Gd_n{}^2+Gd_{n+1}{}^2+\cdots$ which hinder the otherwise free translational motion of the linear lattice in the chain direction. With these potential terms the phonon Hamiltonian is (except for zero-point energy)

$$\mathcal{3C}_p=\sum_k \hbar\omega_k b_k{}^+ b_k, \qquad (7)$$

$$\omega_k=\{2g[(\tfrac{1}{2}\lambda)-\cos k]/m\}^{\frac{1}{2}}, \qquad (8)$$

where $b_k{}^+$ and b_k are phonon creation and annihilation operators, and where m is the mass of each molecule, and $\lambda=2+G/g$.

The exciton–phonon coupling arises through the distance dependence of the exchange integrals

$$J=J_0+j(d_{n+1}-d_n)+\cdots. \qquad (8)$$

We include only this linear term in the displacement, and neglect the distance dependence of the much smaller exchange integral J'. The exciton–phonon coupling Hamiltonian $\mathcal{3C}_c$ can then be written

$$\mathcal{3C}_c=\sum_{n=1,3,5,\ldots}\mathcal{3C}_c(n), \qquad (9)$$

$$\mathcal{3C}_c(n)=jt_n{}^+ t_n(d_{n+1}-d_n),$$

or

$$\mathcal{3C}_c(n)=jN^{-\frac{1}{2}}t_n{}^+ t_n\sum_k (2\hbar/m\omega_k)^{\frac{1}{2}}\sin\tfrac{1}{2}k$$

$$\times \exp[-ik(n+\tfrac{1}{2})](b_k{}^++b_{-k}). \qquad (10)$$

Here N is the number of atoms in the chain. For $J'\ll\hbar\omega_0$, $\mathcal{3C}_c$ can be treated as a second-order perturbation on the momentum eigenstates of $\mathcal{3C}_0+\mathcal{3C}_1$, or on the localized eigenstates of $\mathcal{3C}_0$. In the latter case, the second-order energy $V(n-n')$ that depends on the distance between the localized excitations n and n' is

$$V(n-n')=-2\sum_k (\hbar\omega_k)^{-1}\langle n,\,n';\,0\mid \mathcal{3C}_c(n)\mid n,\,n';\,k\rangle$$

$$\times\langle n,\,n';\,k\mid \mathcal{3C}_c(n')\mid n,\,n';\,0\rangle, \qquad (11)$$

where $\mid n,\,n';\,0\rangle$ and $\mid n,\,n';\,k\rangle$ represent quantum states of the linear chain where spin pairs n, $n+1$, and n', $n'+1$ are excited to their triplet states and where there are no phonons ($\mid n,\,n';\,0\rangle$) and a single phonon of wavevector k ($\mid n,\,n';\,k\rangle$). When $\lambda\gg2$, the above summation is readily evaluated by a power series expansion, with the result

$$V(n-n')=j^2/g\lambda^{|n-n'|}. \qquad (12)$$

Equation (12) gives the lowest-order contribution to $V(n-n')$ for a given $|n-n'|$. An exact expansion good for all values of λ (but only valid to second-order
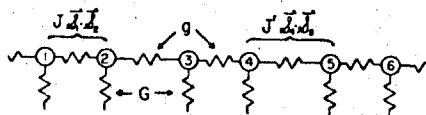

Fig. 1. Schematic of alternating linear array of exchange-coupled molecules.

perturbation theory) is

$$V(n-n')=\frac{j^2}{g}\left(1-\frac{2}{\lambda}\right)\sum_{p=\frac{1}{2}|n-n'|}^{\infty}\left(\frac{2p}{p-\frac{1}{2}|n-n'|}\right)\frac{1}{\lambda^{2p}}, \qquad (13)$$

where

$$\left(\frac{2p}{p-\frac{1}{2}|n-n'|}\right)$$

is the binomial coefficient.

From the foregoing results we see that the effect of the phonon coupling of the triplet excitons is to give rise to an effective Hamiltonian of the form

$$\mathcal{3C}_4=\tfrac{1}{2}\sum_{n,n'}{}' V(n-n')t_n{}^+ t_n t_{n'}{}^+ t_{n'}. \qquad (14)$$

For $n=n'$ in Eq. (11) one obtains the "self-energy" for a single exciton, which is

$$V(0)=-j^2/2g\{1-[(\lambda-2)/(\lambda+2)]^{\frac{1}{2}}\}.$$

DISCUSSION

The model used above for the calculation of phonon-coupled interactions between triplet excitons is certainly sufficiently realistic to show the existence of this effect. Although it is difficult to make a reliable order-of-magnitude estimate of the repulsion potential $V(n-n')$ for a particular crystal at the present time, the discussion given below does strongly suggest that this potential may be very large indeed in the crystals of interest.

It is known that the Wurster's Blue ion, and also TCNQ ions, dimerize in solution.[9,10] The shortest intermolecular distances between the ions are almost certainly of the order of $R\sim3-3.5$ Å. At this distance the exchange or bonding force[11] pulling the molecules together is of the order of $j=\partial J/\partial R$, and the dominant force pushing the molecules apart is the coulomb repulsion, of order e^2/R^2. Thus, at the equilibrium intermolecular distances, $j\sim e^2/R^2$. In the crystal lattice of Wurster's Blue, the dominant contributions to the force constant g must be of the order of the contribu-

[9] K. H. Hausser and J. N. Murrell, J. Chem. Phys. 27, 500 (1957).

[10] D. B. Chesnut (private communication).

[11] It should be noted that our arguments are essentially independent of the extent to which charge-transfer effects contribute to J and j providing that the intermolecular charge transfer does not approach 100% in the singlet ground state of a free-radical pair.

tions of the coulomb repulsions between the molecules, which is $g \sim e^2/R^3$. Thus, the factor j^2/g that appears in Eqs. 12 or 13 for $V(n-n')$ is of the order of e^2/R, which is of the order of 1 eV. Further, if we assume that the two force constants g and G are of the same order of magnitude, then the repulsion potential is quite large for adjacent localized excitations. For example, when $g=G$, the factors involving λ in Eq. (13) give $V(2) = 0.064 j^2/g$, which is of the order of 500 cm^{-1}.

The above repulsion potential must contribute to the activation energy for exchange broadening of the fine structure lines of exciton paramagnetic resonance spectra. That is, in all the solid free radical exciton spin-resonance spectra that have been observed thus far, the exciton concentration varies as $\sim \exp(-J/kT)$ (at low temperatures) whereas the spin exchange line broadening varies as $\exp(-\Delta E/kT)$, and in general, $\Delta E > J$. For example, the excess activation energy for spin-exchange broadening, $\Delta E - J$, is equal to 146 cm^{-1} in Wurster's Blue perchlorate, and is even larger in some of the TCNQ salts.[3] In Wurster's Blue perchlorate it has been shown that this excess activation energy cannot be attributed to an activation energy for diffusion.[6] In the light of the present calculations this excess activation energy may very well arise from the phonon-coupled repulsion between the triplet excitons.

Proposition III

Motional Narrowing in One-Dimensional Exciton Systems

Abstract

The hyperfine interaction between a triplet exciton and nuclear spins is averaged out if the excitons are not stationary. We consider motional narrowing for localized, diffusional excitons. We show that, in a one-dimensional system, both the exciton jumping frequency ω_j and the lifetime of the excited state $1/\omega_L$ must be included, even when $\omega_j \gg \omega_L$. When $\omega_j \gg \omega_L$, a Lorentzian line is found, in agreement with experiment. Also, the dependence of the line-width on the jumping frequency agrees with McConnell's result. The calculation we present is a specialization of Anderson's theory of motional narrowing to a one-dimensional system.

I. Introduction

The theory of line-shapes in magnetic resonance is intimately connected with the theory of relaxation and is consequently of central importance. A general theory of magnetic resonance absorption has been presented by Kubo and Tomita (1). The theory of line-shapes and relaxation has been further considered by Kubo (2). The narrowing of spectral lines has been of interest from the first. Exchange narrowing was demonstrated by Gorter and Van Vleck (3) and by Anderson and Weiss (4). Motional narrowing was discussed by Bloembergen, Purcell, and Pound (5), and a mathematical model based on their ideas was proposed by Anderson (6).

It is the purpose of such theories to relate the absorption spectrum to a correlation function. The correlation function then characterizes a system; it must be guessed or calculated for each case considered. Our purpose in the following is to study the motional narrowing of the hyperfine interaction in one-dimensional exciton systems. We modify Anderson's theory (6) to fit a one-dimensional model.

II. The Model

The low-temperature electronic properties of certain organic crystals may be described in terms of paramagnetic (triplet) excitons (7,8,9). The crystal structure is such that a one-dimensional model is indicated (8). There is a tightly-bound unpaired electron on each of the molecules forming a linear array. If we neglect the molecular vibrations and all but the low-lying triplet electronic excitations, the hamiltonian describing the tightly-bound electrons is

$$\mathcal{H} = \sum_{j=1}^{N/2} \left\{ J \vec{S}_{2j} \cdot \vec{S}_{2j+1} + J' \vec{S}_{2j} \cdot \vec{S}_{2j-1} \right\}, \tag{1}$$

where there are N molecules in the chain, $\vec{S}_{2j}$ is the electron spin on the 2jth molecule, and $J \geq J' > 0$ are the exchange integrals for antiferromagnetic coupling. This phenomenological hamiltonian is due to Heisenberg (10) and has long been the basis for theoretical investigations of ferromagnetism and antiferromagnetism. We will consider only the case of strong alternation $(J' < 1/3J)$ and low temperature $(kT < 1/2J)$. Under these

conditions (11), the excitations are triplets and the two unpaired electrons forming a triplet exciton are adjacent in real space. By considering the effect of longitudinal phonons, it may be shown that the triplet excitons are localized and diffusional (12). The triplet excitons are confined to a random-walk along the chain. The jumping rate is ω_j.

We consider the transitions between the levels of the triplet exciton. In high magnetic field, the transitions are between the Zeeman levels of the exciton; in zero field, they are the zero-field transitions that arise from the dipolar interaction between two electrons forming an exciton. For intermediate magnetic fields, linear combinations of the Zeeman and the zero-field levels are required. We concentrate on a particular transition, with frequency ω_t. The pair of adjacent molecules to which a localized exciton is restricted contains a number of nuclei with spins. The hyperfine interaction between the exciton spin and the nuclear spins modifies slightly the transiton frequency ω_t. We define $\Delta\omega = \omega - \omega_t$ to be the deviation of the transition frequency if the nuclear spins are included. In general, $\omega_t \gg /\Delta\omega/$ and $\Delta\omega$ is symmetric about ω_t. We also define ω_p^2 to be the mean square breadth of the line in the absence of motion.

The nuclear spin orientations are random. To simplify, we assume that the nuclear spin orientations may be considered to be fixed. Since each of the pair of molecules contains a number of nuclei, the frequency distribution $\Delta\omega$ is Gaussian; the Gaussian approximation is rather good even if there are but 6-10

nuclear spins (4). Even if we include nuclear spin relaxation, the nuclear spin distribution is independent of time for a system in thermal equilibrium. The preceding may be summarized by saying that $\Delta\omega(t)$ is a stationary Gaussian random function. In the absence of motion, a Gaussian line, or if the hyperfine lines can be resolved, peaks whose envelope is a Gaussian line, would be observed. The line would be centered at ω_t and its width would be ω_p.

Finally, we need to know the lifetime $1/\omega_L$ of an excited state. In a one-dimensional system, ω_L is important even if the jumping frequency ω_j is much larger than ω_L. The reason is that, in one dimension, a random walk is highly correlated: there is a 50% probability that the exciton jumps to the site it has just vacated. Thus the usual three-dimensional approximation that there is no back-jumping breaks down. We note that ω_L may contain contributions that affect the line shape in different manners. For instance, there is the relaxation, due to the hyperfine interaction, of the exciton levels (S_z changes but S remains fixed). There is also relaxation, due to vibronic coupling, in which the triplet state is annihilated (S is not conserved). Finally, there are exciton creation and annihilation processes via lattice phonons (S and S_z are conserved). These processes, unlike the relaxation processes, do not broaden the line directly. In general, we must have $\omega_L \geq \omega_p$. If ω_L is entirely determined by relaxation processes, then $\omega_L = \omega_p$; if there are exciton creation

and annihilation processes which do not broaden the line directly, then $\omega_L > \omega_p$.

III. The Correlation Function

We construct first the function $g_{\Delta\omega}(\tau) = \phi_{\Delta\omega}(\tau)\omega_p^2$. $g_{\Delta\omega}(\tau)$ expresses the probability that if, at time $t = 0$, the transition occurs at $\omega_t + \Delta\omega$, than at $t = \tau$ the transition still occurs at $\omega_t + \Delta\omega$. We construct an ensemble in each of whose replicas there is, at $t = 0$, an exciton on a site such that the transition frequency is $\omega_t + \Delta\omega$. Since the frequency distribution $\Delta\omega$ is symmetric about $\Delta\omega = 0$, it is straightforward to show that

$$g_{\Delta\omega}(\tau) = P(0,\tau) , \qquad (2)$$

where $P(0,\tau)$ is the probability that the exciton is at its original position at $t = \tau$.

We assume for a moment that $\omega_L = 0$; that is, that the only interruption of the resonance is by exciton diffusion. Since the exciton is executing a random walk in one dimension, the probability distribution expressing the exciton distribution at $t = \tau$ is a Gaussian centered at the site on which the exciton was at $t = 0$. Using the identity

$$\sum_{n=-\infty}^{\infty} e^{-tn^2} = \sqrt{\frac{\pi}{t}} \sum_{n=-\infty}^{\infty} e^{-\pi^2 n^2/t} , \qquad (3)$$

it is easy to show that, to better than 10%

$$P(0,\tau) = \begin{cases} 1 & 0 \leq \tau \leq \frac{1}{2\pi\omega_j} \\ \frac{1}{\sqrt{2\pi\omega_j\tau}} & \frac{1}{2\pi\omega_j} < \tau < \infty \end{cases} . \tag{4}$$

We now remove the restriction that $\omega_L = 0$. The finite lifetime of the excited state on a given site gives an exponential decay. Thus we obtain

$$q_{\Delta\omega}(\tau) = \omega_p^2 \varphi_{\Delta\omega}(\tau) = \begin{cases} e^{-\omega_L\tau} & 0 \leq \tau \leq \frac{1}{2\pi\omega_j} \\ \frac{e^{-\omega_L\tau}}{\sqrt{2\pi\omega_j\tau}} & \frac{1}{2\pi\omega_j} < \tau < \infty \end{cases} \tag{5}$$

The case of interest is $\omega_j \gg \omega_L \geq \omega_p$. The approximation for $\phi_{\Delta\omega}(\tau)$ is always better than 10% and, for $\tau > 1/\pi\omega_j$, better than 1%.

We restrict the discussion to a single electronic transition, with mean frequency ω_t. As shown by Anderson (6), the absorption spectrum is

$$I(\Delta\omega) = \int_{-\infty}^{\infty} d\tau \, e^{i\Delta\omega\tau} \varphi(\tau) . \tag{6}$$

$\phi(\tau)$ is the correlation function. If $\Delta\omega(\tau)$ is a stationary Gaussian random function (6),

$$\varphi(\tau) = \exp\left\{-\omega_p^2 \int_0^\tau dx (\tau-x) \varphi_{\Delta\omega}(x)\right\} . \tag{7}$$

We now calculate $\phi(\tau)$. Substituting in equation (7), we find

$$\varphi(\tau) = exp\left\{-\frac{\omega_p^2}{\sqrt{2\pi}\omega_j\omega_L}\left[\tau\sqrt{\pi}\,erf\sqrt{\omega_L\tau} + \frac{\sqrt{\omega_L\tau}\,e^{-\omega_L\tau}}{\omega_L} + \frac{\sqrt{\pi}}{2\omega_L}erf\sqrt{\omega_L\tau}\right]\right\}, (8)$$

where we have neglected the contribution from the region $0 \leq x \leq \frac{1}{2\pi\omega_j}$. For $\tau < 2/\omega_L$, if $\omega_j \gg \omega_L$, $\varphi(\tau) \sim 1$. For $\tau > 2/\omega_L$,

$$\varphi(\tau) = exp\left\{-\frac{\omega_p^2\tau}{\sqrt{2}\omega_j\omega_L}\right\}. \tag{9}$$

Although, for $\tau < 2/\omega_L$, $\varphi(\tau)$ is more complicated, it may be shown that $\varphi(\tau)$ is a monotonically decreasing function. $\varphi(\tau)$ may be approximated to better than 1% by $\varphi(\tau)$ as in equation (9), even for $0 \leq \tau \leq 2/\omega_L$, provided that $10^{-4} \omega_j \sim \omega_L \sim \omega_p$.

We use equation (9) to perform the integration in equation (6),

$$I(\Delta\omega) = \frac{2\frac{\omega_p^2}{\sqrt{2}\omega_j\omega_L}}{(\Delta\omega)^2 + (\frac{\omega_p^2}{\sqrt{2}\omega_j\omega_L})^2} \tag{10}$$

The absorption line is Lorentzian, with width

$$\lambda = \frac{\omega_p^2}{\sqrt{2}\omega_j\omega_L}. \tag{11}$$

In the three-dimensional problem, the width is ω_p^2/ω_j (6). The restriction to a one-dimensional random walk necessitates the inclusion of ω_L as well as ω_j. As perhaps should have been expected from the greater correlation, due to back jumping, in

one dimension, there is less motional narrowing. Motional narrowing still occurs when $\omega_j \gg \omega_p$, since $\omega_L \gtrsim \omega_p$. For $\omega_j < \omega_L$, the approximations made to evaluate $\emptyset(\tau)$ must be modified. In the case of slow jumping, the expected line is the unnarrowed Gaussian.

IV. Discussion

The preceding calculation is restricted to localized, diffusional excitons. The justification for such a model is given elsewhere (12). Since we have entirely neglected all exciton-exciton interactions, the calculation is restricted to low temperatures. For instance, to temperatures such that the mean time between an exciton-exciton collision is greater than the lifetime of the excited state. The parameters we have introduced may be estimated. The exciton jumping frequency ω_j may be evaluated explicitly (12). The frequency ω_L is more difficult to evaluate, since it includes several effects. The creation and annihilation of excitons via lattice phonons may be calculated (12). At very low temperatures, relaxation processes are the dominant mechanisms. Thus, at least as a first approximation, ω_L may be set equal to the observed line-width.

By setting ω_L equal to the line-width W_{hf} of the observed Lorentzian line, McConnell has obtained a qualitative estimate of motional narrowing for localized, diffusional excitons (13). We set $A = \omega_p$ to be the hyperfine interaction in the absence of motion. Substituting in equation (11), we obtain

$$W_{h.f.} = A \left(\frac{W_{h.f.}}{2\omega_j} \right)^{1/4} .$$

(12)

Except for the factor of 2 in front of ω_j, this result is identical with McConnell's. ~~estimate,~~ We may now turn the argument around and use equation (12) to estimate the jumping frequency ω_j. The estimates are consistent with the calculated values (12). It appears, therefore, that the motional narrowing of the hyperfine interaction in paramagnetic exciton crystals may be understood on the basis of previously derived theories of line-shapes. We note that, because of back jumping, the correlation function for the one-dimensional system we have considered is qualitatively different from the correlation function for the equivalent three-dimensional system.

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Proposition IV

A Suggestion for Many-Body Calculations

Abstract

It is proposed that field-theoretic techniques be applied to many-body problems after the best possible zeroth-order basis set has been obtained by canonical transformations. A criterion is suggested to help decide what are the best zeroth-order states. Although highly non-rigorous, it is hoped that the discussion will suggest how to attack many-body problems.

I. Introduction

It is now accepted that perturbation theory, even to infinite order, will not necessarily solve a quantum-mechanical problem. A somewhat less shocking statement is that, in other cases, perturbation theory must be carried to infinite order to obtain meaningful results. The failure of what may be called "second-order perturbation theory" has resulted in a number of attempts at reformulating the problem of a closed system of inter-acting particles. The field-theoretic techniques developed by Feynman, Dyson, and others for quantum electrodynamics became the foundation of a variety of many-body treatments.

Recently, there has been great interest in many-body tech-niques in several areas of physics. After their introduction in quantum electrodynamics and in nuclear physics, many-body techniques were extended to older problems in solid state physics.

Examples are the problems of metallic electrons, of polarons, of superconductivity, and of superfluidity. An excellent set of reprints of solid state problems may be found in The Many-Body Problem, edited by Pines (1). Another established area in which many-body techniques are increasingly used is that of quantum statistical mechanics. The possibility of working with strongly-interacting systems and of considering easily finite temperatures are the main advantages of the field-theoretic formulation. A detailed discussion may be found in the Methods of Quantum Field Theory in Statistical Physics by Abrikosov (2).

The reprints in Pines's book suggest that the primary goal of the early investigators was to reformulate specific problems, rather than to create general field theories. Also, that considerable intuition was used to pick out the important processes and to make the problems more tractable. Hence the variety of names associated with rather similar operations in different problems. It is largely because to the physical insight used in connection with each problem that such mathematically formidable problems could be handled. On the other hand, field theory, like perturbation theory, is a formal framework. In principle, all that is required is a knowledge of the statistics, either Bose or Fermi, that the particles or the quasiparticles obey. No physical insight is needed.

Canonical transformations have long been a standard tool in physics. Perhaps the most ubiquitous is the transformation connecting real and momentum space. In principle, a canonical

transformation is capable of giving the best possible one-particle functions and energies; that is, the best possible zeroth-order basis set. This is the natural basis set to use in further calculations, whether by perturbation theory or by field theory. The success of the Bloch electron model in metals, of the Hartree-Fock treatment of electronic structure, or the Bardeen, Cooper, Schrieffer (B.C.S.) theory of superconductivity suggests that most of the physics may be understood if the best possible basis set has been found. There is always an element of uncertainty and intuition in the choice of a basis set, even though of course the evaluation of energies for a given basis set is completely rigorous. For instance, the Bloch states must be replaced by the B.C.S. states for electrons close to the Fermi surface in superconductors below the transition temperature.

II. Discussion

It is evident that a criterion is needed to indicate what is the best basis set. In particular, we need to know in what instances the usual zeroth-order states, which are largely obtained from symmetry considerations, are inadequate. Then we could use physical insight to construct, via a canonical transformation, the best basis set. Either perturbation theory or field theory may then be used to study the effects of correlations; the latter is more general. Rather than providing two general methods of handling many-body problems, canonical transformations and field theories complement each other.

We consider briefly metallic electrons. If the inter-
action between electrons is entirely positive, like the repulsive
Coulomb interaction, the Bloch states, which reflect the symmetry
of the crystal, form the appropriate basis set. On the other
hand, if the net interaction is negative, that is, attractive,
then the B.C.S. states are the correct basis set. It appears,
therefore, that improvements upon states dictated primarily by
symmetry considerations are possible only when there exists at
least a region in which the interaction between particles is
negative. This is a necessary, rather than a sufficient, con-
dition. Physically, it is obvious to attempt to improve the
total energy by using, wherever possible, quasiparticles which
include the attractive interaction between the real particles.
Thus, in the B.C.S.-Bogoliubov formulation, only electrons very
near the Fermi surface, where the interaction is the most negative,
are in states different from the Bloch states. Similarly, for the
linear Heisenberg antiferromagnet, whether regular or alternating,
the Bloch states are modified the most near the Fermi surface (3).

Although we have no definite criterion for obtaining the
best zeroth order functions, we have at least a clue: to look
for regions in which the interaction between particles or quasi-
particles is negative.

In conclusion, we note that neither perturbation theory
nor field theory is likely to yield results except after con-
siderably more manipulation than is usually required. For an
isotropic system in a macroscopic box, a pair-wise interaction

in real space gives, in momentum space, the interaction term

$$V(k_2-k_3)a^+_{k_1}a^+_{k_2}a_{k_3}a_{k_4} \qquad (k_1 + k_2 + k_3 + k_4 + 2\pi\nu$$
$$\nu = 0, \pm 1, \ldots) \tag{1}$$

For fermions, the creation and annihilation operators a^+_k, a_k are Fermi operators; for bosons, they are Bose operators; the restriction on the k's expresses the conservation of pseudo-momentum. In the case of fermions, the Bogoliubov canonical transformation is

$$\eta_k = u_k a_k + v_k a^+_{-k}$$
$$\eta^+_k = u^*_k a^+_k + v^*_k a_{-k}, \tag{2}$$

with the restrictions

$$/u_k/^2 + /v_k/^2 = 1$$
$$u_k v_{-k} + u_{-k} v_k = 0 . \tag{3}$$

The operators η^+_k, η_k are also Fermi operators. They define the appropriate quasiparticles when there is an attractive interaction between the real particles. (Otherwise, u_k and v_k are never both different from zero.)

In general, the integral equations that yield u_k, v_k may only be solved for the separable potential $V(k,k') = V(k)V(k')$. Let us assume that we have obtained this solution. Now, to do either perturbation theory or field theory using the η_k's as a basis set, we must transform the interaction term, using the

inverse of the transformation (2). The potential then contains 16 terms, ranging from terms containing 4 creation operators to terms containing 4 annihilation operators. Even if the terms are combined, there remain 5 types of terms, with operator structures $\eta^+_{k_1}\eta^+_{k_2}\eta^+_{k_3}\eta^+_{k_4}$, $\eta^+_{k_1}\eta^+_{k_2}\eta^+_{k_3}\eta_{k_4}$, $\eta^+_{k_1}\eta^+_{k_2}\eta_{k_3}\eta_{k_4}$, $\eta^+_{k_1}\eta_{k_2}\eta_{k_3}\eta_{k_4}$, and $\eta_{k_1}\eta_{k_2}\eta_{k_3}\eta_{k_4}$. Only the third term conserves the number of quasi-particles. A similar result is found in Bose systems. An interesting calculation by Hugenholtz and Pines (4) for an interacting Bose system at absolute zero, in which the Bose condensation is explicitly included, demonstrates the possibility (and the difficulty) of applying field-theoretic techniques to problems in which the operator structure of the interaction term is more complicated than in (1).

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Proposition V

Formal Model for Second-Order Transitions

Abstract

A model is presented for transitions of the second order. The model is based on a "phase" parameter η which is discrete for first-order transitions and continuous for second-order transitions. A minor difficulty in the formal representation of second-order transitions is thus resolved.

I. Introduction

Discussions of second-order transitions and phase changes may be found in standard texts (1,2). The usual definition of a first-order phase change is that, at the transition temperature and pressure, the Gibbs free energies of the two phases, $G_I(T,P)$ and $G_{II}(T,P)$, obey the relations (2)

$$G_I = G_{II}$$

$$\frac{\partial G_I}{\partial T} \neq \frac{\partial G_{II}}{\partial T}.$$

(1)

We omit the possibility of such metastable states as those involving superheating or supercooling. The observed free-energy curve for a system in thermal equilibrium is shown in figure 1; it is the curve corresponding to the phase with the lower free energy. The discontinuity in the slope at the transition temperature gives the entropy change,
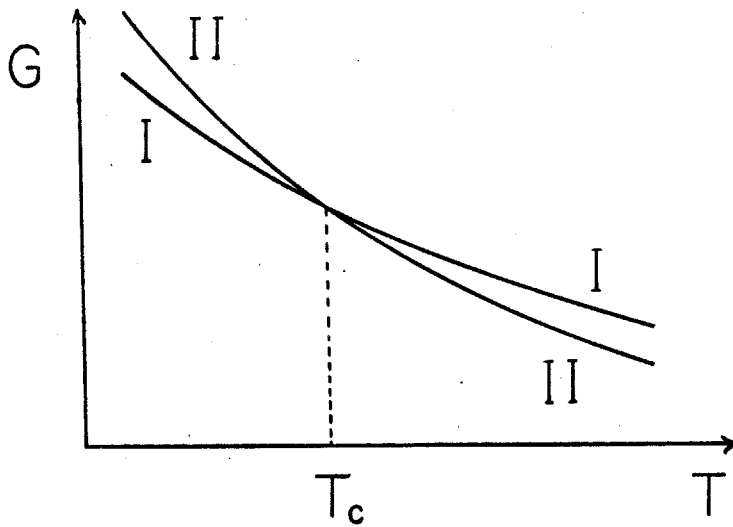
Fig. 1. Schematic representation of a first-order phase change. The Gibbs free energy for the system in thermal equilibrium is the curve corresponding to phase I for $T < T_c$ and to phase II for $T > T_c$.

$$\Delta S = S_{II} - S_{I} = \frac{\partial G_I}{\partial T} - \frac{\partial G_{II}}{\partial T} . \tag{2}$$

In the same way, a second-order transition obeys the relations

$$G_I = G_{II}$$
$$\frac{\partial G_I}{\partial T} = \frac{\partial G_{II}}{\partial T} \tag{3}$$
$$\frac{\partial^2 G_I}{\partial T^2} \neq \frac{\partial^2 G_{II}}{\partial T^2}$$

at the transition temperature T_c. The second derivative of the free energy with respect to temperature is discontinuous at T_c. The change in the constant pressure heat capacity is given by

$$\Delta C = C_{II} - C_I = T_c \left\{ \frac{\partial^2 G_I}{\partial T^2} - \frac{\partial^2 G_{II}}{\partial T^2} \right\}. \tag{4}$$

It is straightforward to generalize to transitions of arbitrarily high order (2). A similar set of relations may be found if the pressure, rather than the temperature, is varied.

We wish to draw a diagram such as figure 1 to describe a second-order transition. We suppose that the free energies and their first derivatives with respect to temperature are equal at T_c, but that the second derivatives are not equal. Then, as shown in figure 2, the curves cannot cross and no transition occurs; one of the phases has a lower Gibbs free energy both above and below T_c. If the curves cross and the first derivatives are equal, then the second derivatives must also be equal at T_c;
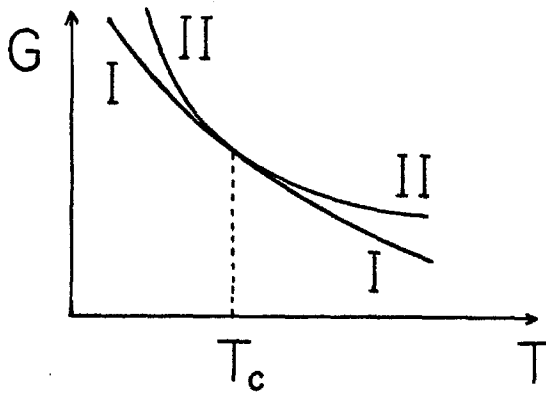
Fig. 2. Attempted representation of a second-order transition. $G_I = G_{II}$ and $G'_I = G'_{II}$ at T_c, but $G''_I \neq G''_{II}$.

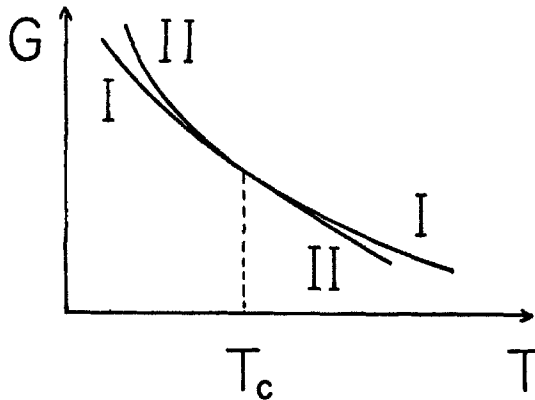There is no phase transition, as phase I always has lower free energy than phase II.

Fig. 3. Attempted representation of a second-order transition. $G_I = G_{II}$ and $G'_I = G'_{II}$ at T_c, and the curves cross. But the second temperature derivatives of the free energies must be equal at T_c, so that the transition is of the __third__ order.

this situation is shown in figure 3. A <u>third</u>-order transition would occur. Guggenheim shows his awareness of the difficulty by refusing, for physical reasons, to extend the free energy curve for one of the phases below the critical temperature (2).

II. The Model

It is not our purpose here to discuss the physical differences between first and second-order transitions. We merely note that second-order transitions usually involve continuous rearrangements in crystals or in liquids and are consequently intimately related with order-disorder phenomena. Let us define a "phase" parameter η such that $\eta = 0$ for a system well below its transition temperature and $\eta = 1$ for the system well above its transition temperature. For instance, in the first order transition ice $\to$ water, $\eta = 0$ refers to ice and $\eta = 1$ to water. For second-order transitions, η may be defined in terms of the order. We leave the specification of η deliberately open; it may be defined rigorously for any given system. Examples of second-order transitions are the Curie point in ferromagnetic substances, where η would be related to the spontaneous magnetization, and the 2.2°K transition in liquid helium.

It is proposed that the difference between first and second-order transitions may be formally understood from the temperature dependence of η. In first-order transitions, η changes discontinuously at the transition temperature. Alternatively, we may think of η as a many-valued function at the transition

temperature. Thus a system with a first-order transition is not
uniquely characterized if the transition temperature and pressure
are given; η must also be specified. Two phases may coexist at
the critical temperature; the situation is described schematically
in figure 1, except at the critical temperature, where the diagram
does not contain enough information. A second-order transition,
on the other hand, is characterized by a continuous, single-valued
η. Thus we have a continuum of phases, corresponding to $0 \leq \eta \leq 1$,
each of which successively represents the lowest free energy
phase. This scheme is shown in figure 4. The observed free
energy is the envelope of the curves in figure 4. It is evident
that two different phases never coexist, even at T_c.

Several consequences follow immediately from the model.
First, the difficulty mentioned about the formal representation
of second-order transitions has been resolved. By plotting
$S = -\frac{\partial G}{\partial T}$, it is evident that, although the first derivative of
the free energy, the envelope of the curves in figure 4, is con-
tinuous, the second may be discontinuous. Second, the transition
occurs over some interval ΔT, which in most cases is rather small.
Formally, a second-order transition resembles a succession of
first-order transitions which are "infinitesimal" in the sense
that the entropy changes are very small. Hence the difficulty,
in cases with very small ΔS, in distinguishing between first and
second-order transitions. Finally, we note that although second-
order transitions are frequently called "phase changes," they
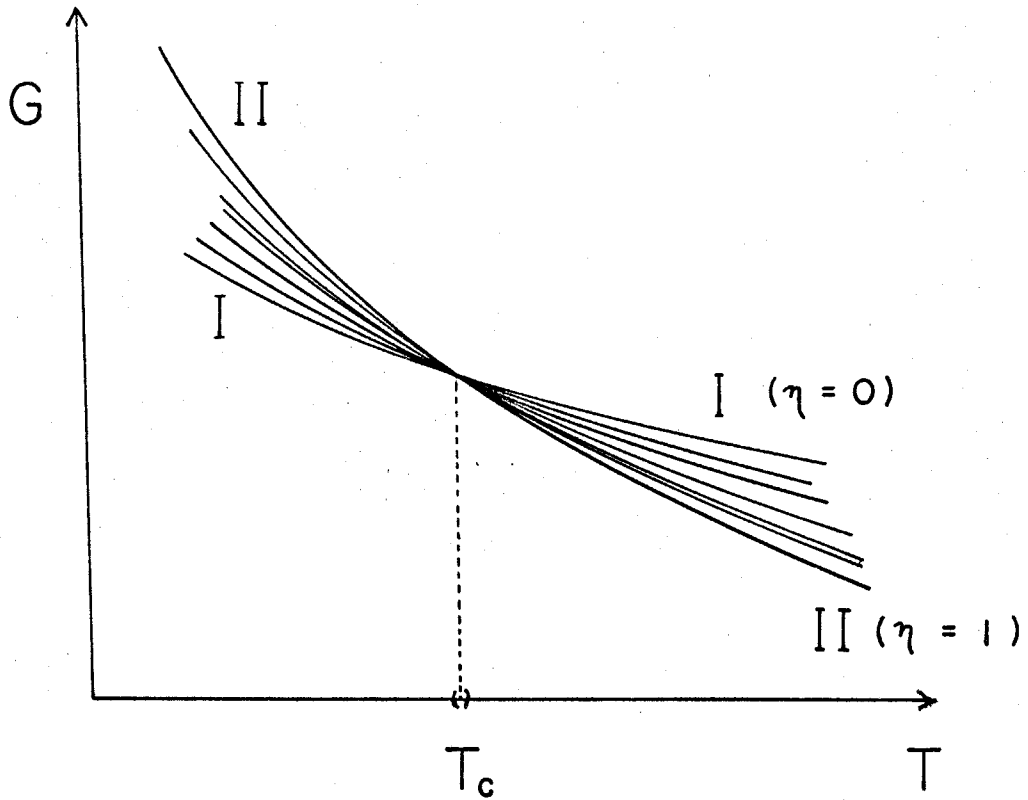
Fig. 4. Schematic representation of a second-order
transition. The Gibbs free energy is the envelope
of the curves.

never correspond to phases in equilibrium. Even at T_c, there is only one phase present for a system in thermal equilibrium.

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