ONE - DIMENSIONAL EXCITONS IN ORGANIC MOLECULAR CRYSTALS

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Abstract

A number of organic molecular crystals contain topologically linear chains of interacting molecules, coupled relatively weakly to the rest of the crystal lattice. The hamiltonian operators for several systems of this sort are represented as quadratic forms in Bose or Fermi creation and annihilation operators. A theorem is presented which permits the diagonalization of these forms by linear canonical transformations of the operators. This method is applied to the study (using a quasi-boson approximation) of the low-lying energy states of a chain of spin-$\frac{1}{2}$ ions with the hamiltonian

$$H = \sum_{i \text{ odd}} J S_i \cdot S_{i+1} + \sum_{i \text{ even}} J' S_i \cdot S_{i+1} ,$$

where $J \geq J \geq 0$. The effects of anisotropic coupling and of an external magnetic field are included. Qualitative agreement with existing experimental data on crystals containing such chains is good. When

$J' = J$, the system is the Heisenberg antiferromagnet; the results obtained in this limit are in good quantitative agreement with theoretical treatments of that system.

A fermion representation of the electronic states of certain linear-chain molecular crystals is developed. The method of canonical transformations can then be applied to crystals with strong intermolecular interactions due to dispersion forces or to intermolecular charge transfer. The treatment of dispersion interactions extends the Davydov singlet exciton theory into the range of strong coupling, where the elementary excitations of the system may have unusually small energies and are associated with distributed ferroelectric-type electronic polarization. Change transfer effects in linear chains of alternating donor and acceptor molecules are treated, with cooperative Coulomb effects included in a self-consistent field approximation. The energy spectrum of the current-carrying elementary excitations is calculated. The calculation is also applicable to the problem of the electronic states of N/2 mobile electrons on a regular linear array of N molecules.

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Chapter I - Introduction

Much of the attention devoted to an understanding of the solid state of matter has been concentrated on inorganic crystals. Organic crystals, however, have received comparatively little study; phenomena peculiar to them are generally less completely understood. Powerful tools for the analysis of the electrical and magnetic properties of inorganic crystals are provided by the high symmetry of common periodic arrangements of simple molecules or ions, and the concepts of free or nearly-free electron theory have permitted at least a general understanding of the phenomena most frequently encountered in these systems. These techniques are less satisfactory for a complete understanding of the behavior of crystals made up of complex organic molecules. The properties of organic crystals are strongly influenced by the cooperative behavior of large numbers of their constituent elements. A study of even the simplest collective properties of some organic molecular or free-radical crystals shows striking effects of such cooperative behavior, and can reveal, in fact, the existence of qualitatively new phenomena.

It is a significant difference between organic and inorganic crystals that the former are composed of generally less symmetrical units. As a consequence the structures in which these units arrange themselves tend to possess lower symmetry than the arrays most typical of inorganic crystals. Many known aromatic crystals exist, for example, each molecule or ion of which interacts most strongly with only one or two of its neighbors. Crystals with these properties have been labelled class I and class II, respectively, by McConnell and Lynden-Bell.(1) A class II crystal contains topologically linear chains of ions, with couplings along each chain stronger than couplings of the chain to its surroundings in the crystal. Such systems present a number of appealing problems. The mathematical representation and analysis of these problems are simplified by their one-dimensional character. The calculations presented here may provide insight into the effects of more general three-dimensional processes; at the same time they should be directly applicable to actual physical systems.

In organic molecular or free-radical crystals, the interactions between the molecules or ions are generally small compared with their internal energies. The simplest electronic excitations of these systems correspond to excitations of single molecules or ions.

The presence of intermolecular interactions results in the existence of non-zero matrix elements of the hamiltonian describing the system among states differing in the locations of excited molecules. Consequently, the degeneracies associated with the distribution of excitations are lifted, and the elementary excitations of the system are distributed throughout the crystal. A localized excitation introduced at a point in the lattice will tend to move. Such mobile excitations are known as excitons.

Another result of interactions between molecules is that in general the number of excitations is not conserved. The ground-state energy of the system is lowered by a virtual excitation and de-excitation of the molecules. The lowering of the ground-state energy may be thought of as the zero-point energy associated with the elementary excitations of the system. The elementary excitations are "collective" in the sense that the virtual processes introduce a more-than-pairwise correlated excitation distribution in the energy eigenstates.

These general characteristics of the solutions of the many-body problems presented by molecular crystals may be seen in the results of several calculations concerned with particularly simple physical systems. The method used here for their investigation relies on the fact that it is possible to represent the hamiltonian operators governing the behavior of a number of systems as quadratic forms in creation and annihilation operators obeying either Bose or Fermi commutation relations. Quadratic forms in boson or fermion operators may be diagonalized by linear canonical transformations of the operators. Such transformations have been used in treating many phenomena, notably those associated with superconductivity, superfluidity, etc.(2-4) The following general theorem may be stated. Let B_i be a a set of boson or fermion operators satisfying the commutation relations

$$[B_i, B_j]_{\pm} = 0 ,$$

$$[B_i, B_j^{\dagger}]_{\pm} = \delta_{ij} .$$

Consider the hermitian form

$$F = F_o + \sum_{i,j} A_{ij} B_i^{\dagger} B_j + \sum_{i,j} C_{ij} B_i B_j + \sum_{i,j} C^*_{ij} B_j^{\dagger} B_i^{\dagger}$$

with

$$F_o = F_o^* , \quad A_{ij} = A_{ji}^* , \quad C_{ij} = \mp C_{ji} .$$

The canonical transformation

$$B_i = \sum_\rho (u_{\rho i} B_\rho + v_{\rho i}^* B_\rho^\dagger) , \qquad (1)$$

with the conditions

$$E_\rho u_{\rho i} = \sum_j A_{ij} u_{\rho j} \mp 2 \sum_j C_{ij}^* v_{\rho j} ,$$

$$-E_\rho v_{\rho i} = \sum_j A_{ij}^* v_{\rho j} \mp 2 \sum_j C_{ij} u_{\rho j} ,$$

puts F in the diagonal form

$$F = F_o - \sum_{\rho, i} E_\rho |v_{\rho i}|^2 + \sum_\rho E_\rho B_\rho^\dagger B_\rho .$$

The upper sign of the ±'s refers to fermions, the lower to bosons. The conditions ensuring that the transformation is canonical and a proof of the theorem are given in Appendices A and B.

(A diagonalization process for Bose operators similar to the above is referred to by Agranovich(4) as due to Tyablikov. A book in Russian by Bogoliubov(5) is cited. The present author has been unable to locate a copy; the material in the appendices was independently derived.)

Canonical transformation of fermion operators having the form given in equation (1) are generally known as Bogoliubov-Valatin transformations.(6,7) A widely used special case of the general transformation is one which mixes only special pairs of creation and annihilation operators.(3,8) From a given set of fermion or boson operators B_k, $B_k^\dagger$ one may form new operators

$$\mathfrak{B}_k = u_k^* B_k \pm v_k^* B_{-k}^\dagger \,, \quad \mathfrak{B}_k^\dagger = u_k B_k^\dagger \pm v_k B_{-k} \,, \qquad (2)$$

which have the same commutation relations as B_k, $B_k^\dagger$ if

$$u_k v_{-k} \pm u_{-k} v_k = 0 \,,$$

$$| u_k |^2 \pm | v_k |^2 = 1 \,.$$

The inverse transformation is

$$B_k = u_k \mathfrak{B}_k + v^*_{-k} \mathfrak{B}^\dagger_{-k} \quad .$$

The single index k is written so that for each k there is one other with the same magnitude and opposite sign. This transformation may be used to diagonalize the form

$$F = \sum_k A_k B^\dagger_k B_k + \sum_k C_k B_k B_{-k} + \sum_k C^*_k B^\dagger_{-k} B^\dagger_k$$

with

$$A_k = A_{-k} \quad \text{and} \quad C_k = \mp C_{-k} \quad .$$

The eigenvalue equations are

$$(E_k - A_k)\, u_k \pm 2\, C^*_k v_k = 0$$

$$(-E_k - A_k)\, v_k \pm 2\, C_{-k} u_k = 0$$

with solutions

$$E_k = (A^2_k \pm 4\ |C_k|^2)^{\frac{1}{2}} \quad ,$$

$$|u_k|^2 = \frac{E_k + A_k}{2E_k} ,$$

$$|v_k|^2 = \left| \frac{E_k - A_k}{2E_k} \right| .$$

The diagonalized form may be written

$$F = -\frac{1}{2} \sum_k |E_k - A_k| + \sum_k E_k \mathfrak{B}_k^\dagger \mathfrak{B}_k .$$

It was first shown by Valatin(8) that in the fermion case the vacuum state of the new operators, defined by

$$\mathfrak{B}_k \, |\varphi\rangle = 0 ,$$

is given by

$$|\varphi\rangle = \prod_{k>0} (u_k^* + v_k^* B_{-k}^\dagger B_k^\dagger) \, |0\rangle ,$$

where $|0\rangle$ is the vacuum of the original operators:

$$B_k \, |0\rangle = 0 .$$

A similar representation for the new vacuum state in the boson case is not difficult to find. We try a similar product of commuting factors:

$$|\varphi\rangle = \prod_{k>0} \Gamma_k |0\rangle ,$$

where

$$\Gamma_k = \sum_{n=0}^{\infty} a_{nk} \, (B_{-k}^{\dagger} B_k^{\dagger})^n \quad .$$

For k greater than zero we have

$$\mathfrak{B}_k \Gamma_k |0\rangle = \sum_{m=0}^{\infty} [(m+1) u_k^* a_{m+1,k} - v_k^* a_{m,k}] \, (B_k^{\dagger})^m (B_{-k}^{\dagger})^{m+1} |0\rangle ,$$

which vanishes identically when

$$a_{m,k} = \frac{1}{m!} \left(\frac{v_k^*}{u_k^*} \right)^m a_{ok} \quad .$$

The same condition ensures that

$$\mathfrak{B}_{-k} \Gamma_k |0\rangle = 0 \quad .$$

The state $| \varphi >$ is normalized by requiring that

$$< 0 | \Gamma^{\dagger}_{k} \Gamma_{k} | 0 > = 1 \quad ,$$

which gives

$$| a_{ok} |^2 = \frac{1}{| u_k |^2} \quad .$$

The normalized vacuum state may then be written, to within a phase factor, as

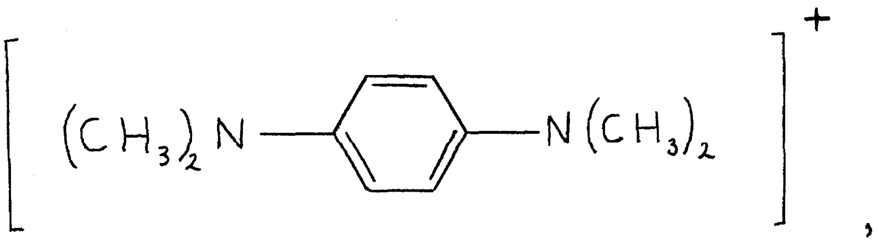
$$| \varphi > = \prod_{k > 0} \left(\frac{1}{| u_k |} \exp \left[\frac{v_k^*}{u_k^*} B^{\dagger}_{-k} B^{\dagger}_{k} \right] \right) | 0 > .$$

Both the simplified transformation of equation (2) and the more general form in equation (1) are used in what follows to diagonalize quadratic forms which represent the hamiltonian operators for a variety of one-dimensional arrays of molecules undergoing interactions typical of organic crystals. Chapters II and III treat linear chains of free radicals coupled by the interaction of neighboring electronic spins, the strength of the coupling alternating along the chains. Crystals containing such chains are exemplified by Wurster's blue perchlorate. The ground-state energy and the energies of the simplest elementary excitations, which are triplet (spin-one) excitons, are calculated in a quasi-boson approximation. The isotropic part of the spin hamiltonian is treated in Chapter II; the effects of anisotropic interactions are included in Chapter III. The results of these calculations are relevant to the problem of the one-dimensional Heisenberg antiferromagnet. Chapter IV applies some conclusions of the previous chapters to the examination of a possible explanation for the observed dimerization of elements in the chains at low temperatures. In Chapter V is a treatment of linear systems in which intramolecular charge resonance is found. The fermion representation developed there permits the extension of the Davydov singlet exciton theory into the region of strong dispersion forces, where several interesting features appear. The final problem, considered in Chapter VI, is concerned with the effects of intermolecular charge transfer in chains of alternating donor and acceptor molecules. The cooperative Coulomb effects are treated in a self-consistent Hartree-like approximation. The calculation is also applicable to the problem of the electronic states of N/2 mobile electrons on a regular linear array of N molecules.

Chapter II - Triplet Excitons

A number of molecular crystals containing linear chains of free radicals are found to have electron-spin-resonance spectra characteristic of triplet excitons. It is the purpose of this section to examine a model which should represent a class of these physical systems. In particular, the treatment should be applicable to crystals of Wurster's blue perchlorate, a compound which has been studied experimentally in some detail.

Wurster's blue perchlorate is a solid ionic free radical salt. Its room-temperature crystal structure has been determined by J. D. Turner and A. C. Albrecht.(9) For the purposes of this discussion, the most significant feature of its structure is the presence of linear chains of the Wurster's blue ion. This positive ion (known to chemists as the N,N,N',N' tetramethyl-p-phenylene diamine cation),



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carries a single unpaired electron, which resides essentially in p-orbitals centered on the two nitrogen atoms. Figure 1 shows a projection of the crystal structure at room temperature. The Wurster's blue ions, seen edge-on as straight lines, form regular chains parallel to the axis labelled a_o. Each WB ion is surrounded by six perchlorate ions. The perchlorate ions do not lie in the plane of the chains.

At a temperature of 186°K, WBP exhibits a phase change. This is apparently due to a dimerization of the positive ions. The spacings of the ions along the chains alternate at low temperatures.(10,11) The transition is marked by a sharp decrease in the magnetic susceptibility.(12,13) At low temperatures, the spin-resonance spectra show absorption peaks corresponding to the existence of S = 1 excitations;(11,13,14) the absence of hyperfine structure in the spectra indicates that the excitations possess a high degree of mobility.

The interaction of adjacent ions in the chains is dominated by the coupling of their electron spins. This may be represented by the spin hamiltonian

$$H = \sum_{i=1}^{2N} J_i \vec{S}_i \cdot \vec{S}_{i+1} + \sum_{i=1}^{2N} D_i S^z_i S^z_{i+1} + \sum_{i=1}^{2N} E_i (S^x_i S^x_{i+1} - S^y_i S^y_{i+1}).$$

Here $\vec{S}_i$ represents the spin on the i^{th} ion, and $J_i > 0$ is the usual exchange integral. At high temperatures, the quantities J_i, D_i and E_i are independent of i. The system is a class II crystal, and the spin hamiltonian is that of a linear Heisenberg antiferromagnet. At low temperatures, where the interionic distances alternate along each chain, the quantities J_i, D_i and E_i should also alternate; the system is then in class I. It is expected that under these conditions, the close pairs tend to be in singlet configurations, which leads to the observed decrease of the magnetic susceptibility. Each chain may then be thought of as a (class II) collection of interacting "molecules" with singlet ground states and triplet excited states. The transition between these two structures is a cooperative one, since the formation of one singlet pair encourages the pairing of its neighbors: the phase change should be quite abrupt. We now wish to examine more closely the properties of the crystal in its low-temperature configuration. In a later section we shall consider a possible explanation for the occurrence of the phase change.

The system described above may be studied in terms of a formal representation which is similar to that developed by Agranovich(4) for the study of general crystal excitations. Each chain is considered as an array of N pairs of strongly coupled spins which interact with neighboring pairs through a weaker spin coupling. For the moment we shall consider only the isotropic part of the hamiltonian; the effects of anisotropy are easily included later. The hamiltonian may be written

$$H = \sum_{p=1}^{N} H_p + \sum_{p,p'=1}^{N} V_{p,p'} \quad ; \qquad (3)$$

$$H_p = J \vec{S}_{p,\ell} \cdot \vec{S}_{p,r} \quad ;$$

$$V_{p,p'} = \delta_{p',p+1} J' \vec{S}_{p,r} \cdot \vec{S}_{p+1,\ell} \quad ;$$

$$J \geq J' > 0 \quad ,$$

where r and ℓ represent the right-hand (toward $p = N$) and left-hand spins of the pairs. We take $V_{N,1} \equiv V_{1,2}$ and assume cyclic boundary conditions. The eigenstates of H_p are $|\alpha>$, the antisymmetric singlet with energy $-3/4\ J$; and $|\beta>$, $|f_1>$, $|f_2>$, the symmetric triplet states with spin projections 0, +1, -1 respectively and energies $+\frac{1}{4} J$.

A basis set of states describing the system is

$$| \ldots N_p(f) \ldots > \; ; \; p = 1, \ldots, N \; ; \; f = \alpha, \beta, f_1, f_2 \; .$$

There are four occupation numbers $N_p(f)$ for each value of p. Each is unity if the p^{th} pair is in the state f, or zero if it is not. Since each pair can be in one and only one state at a time, the occupation numbers must satisfy the conditions

$$\sum_f N_p(f) = 1 \; ; \; \sum_{p,f} N_p(f) = N \quad . \tag{4}$$

Following Agranovich, we define operators acting on these states:

$$b_{p'f'} |\ldots N_p(f) \ldots > = N_{p'}(f') |\ldots N_p(f) - \delta_{p,p'}\delta_{f,f'} \ldots > \; ;$$

$$b^{\dagger}_{p'f'} |\ldots N_p(f) \ldots > = [1 - N_{p'}(f')] |\ldots N_p(f) + \delta_{p,p'}\delta_{f,f'} \ldots > \; .$$

A single b_{pf} acting on a state which satisfies the conditions (4) will, of course, yield a state which does not satisfy these conditions. Any pair $b^{\dagger}_{pf} b_{pf'}$, however, preserves the properties (4), and all physically meaningful operators are made up of such pairs. It may be seen that

$$b^{\dagger}_{pf} b_{pf} = N_p(f) \quad ,$$

and that the operators obey Pauli statistics; that is,

$$[b_{pf}, b_{p'f'}] = 0 \; ;$$

$$[b_{pf}, b^{\dagger}_{p'f'}] = 0 \quad \text{for} \quad (p,f) \neq (p', f') \; ;$$

$$(b_{pf})^2 = 0 \; ;$$

$$b^{\dagger}_{pf} b_{pf} + b_{pf} b^{\dagger}_{pf} = 1 \quad .$$

The hamiltonian (3) may be written in terms of these operators as

$$H = \sum_{p,f} E^f_p \, N_p(f)$$

$$+ \sum_{p,p'} \sum_{f,f',f'',f'''} < ff' \mid V_{pp'} \mid f''f''' > b^{\dagger}_{pf} b^{\dagger}_{p'f'} b_{pf''} b_{p'f'''} \, .$$

The Pauli statistics of the operators b_{pf} are the natural ones for single-molecule excitations in a crystal. The commutativity of operators with different indices reflects the independence of the sites in the original basis, while the unit anticommutator of an operator with its hermitian conjugate follows from the fact that each molecule is in one and only one state. This mixture of boson- and fermion-like properties, however, can make the application of many common field theoretic techniques quite difficult. Two different attacks on such difficulties have been made by H. L. Davis (15) and by Mills, Kenan, and Korringa(16) in their treatments of the Heisenberg antiferromagnet. Each method succeeds in making possible a more or less direct use of formalisms developed originally for the problems of quantum electrodynamics; both, however, pay the price of increased computational complexity. An interesting inversion of this point of view is provided by Whitlock and Zilsel(17), who approximate the effect of hard-core potentials in dense boson systems by a change from Bose to Pauli statistics. The techniques used here, while less general than those adapted from field theory, are perhaps more clearly related to the physically important processes occurring in our model systems.

Let us define the approximately Bose operators:

$$B_{p\beta} = b^{\dagger}_{p\alpha} b_{p\beta} \quad ;$$

$$B_{pf_1} = b^{\dagger}_{p\alpha} b_{pf_1} \quad ;$$

$$B_{pf_2} = b^{\dagger}_{p\alpha} b_{pf_2} \quad .$$

These have the properties

$$B^{\dagger}_{pf} B_{pf} = N_p(f) \; , \tag{5a}$$

$$[B_{pf}, B_{pf}] = 0 \; , \tag{5b}$$

$$[B_{pf}, B^{\dagger}_{pf}] = 1 - 2\,N_p(f) - \sum_{f' \neq f} N_p(f') \; . \tag{5c}$$

(Here, and in what follows, we shall take the index f not equal to α.)

All combinations which differ in the indices p and f commute. The operator $B^{\dagger}_{pf}$ raises the pth pair of spins from their singlet ground state to the component of the triplet specified by the index f. We may also introduce the obvious notation

$$S_p^z = N_p(f_1) - N_p(f_2) \quad ,$$

$$S_p^+ = B^\dagger_{pf_1} B_{p\beta} + B^\dagger_{p\beta} B_{pf_2} \quad ,$$

$$S_p^- = B^\dagger_{p\beta} B_{pf} + B^\dagger_{pf_2} B_{p\beta} \quad .$$

$S_p{}^z$, $S_p{}^x = (S_p^+ + S_p{}^-)/2$, and $S_p{}^y = i(S_p^- - S_p^+)/2$ are the spin components of the spin-one triplet excitation of the p^th pair of radicals.

The explicit representation of the isotropic hamiltonian in terms of these operators is:

$$H = H_1 + H_2 + H_3 \quad ; \tag{6a}$$

$$H_1 = \sum_p E_p{}^\alpha + H_\beta + H_f \, ; \tag{6b}$$

$$H_\beta = J \sum_p B^\dagger_{p\beta} B_{p\beta} - \frac{J'}{4} \sum_p (B^\dagger_{p\beta} + B_{p\beta})(B^\dagger_{p+1,\beta} + B_{p+1,\beta}) \quad , \tag{6c}$$

$$H_f = J \sum_p (B^{\dagger}_{pf_1} B_{pf_1} + B^{\dagger}_{pf_2} B_{pf_2})$$

$$+ \frac{J'}{4} \sum_p \Big\{ (B_{pf_1} - B^{\dagger}_{pf_2})(B_{p+1,f_2} - B^{\dagger}_{p+1,f_1}) \qquad (6d)$$

$$+ (B_{pf_2} - B^{\dagger}_{pf_1})(B_{p+1,f_1} - B^{\dagger}_{p+1,f_2}) \Big\} \quad ;$$

$$H_2 = \frac{J'}{4} \sum_p (S_p{}^z B^{\dagger}_{p+1,\beta} - B^{\dagger}_{p\beta} S_{p+1}{}^z$$

$$+ \frac{S_p{}^+}{\sqrt{2}} B^{\dagger}_{p+1,f_2} - B^{\dagger}_{pf_2} \frac{S_{p+1}{}^+}{\sqrt{2}} + B^{\dagger}_{pf_1} \frac{S_{p+1}{}^-}{\sqrt{2}} - \frac{S_p{}^-}{\sqrt{2}} B^{\dagger}_{p+1,f_1})$$

$$+ \text{ hermitian conjugate ;}$$

$$H_3 = \frac{J'}{4} \sum_p \vec{S}_p \cdot \vec{S}_{p+1} \quad .$$

H_1, H_2, and H_3 are of successively higher orders in the operators B_{pf} and their hermitian conjugates. In physical terms it can be said that H_1 is of the order of the occupation numbers $N_p(f)$, while H_2 and H_3 are of higher orders. Thus at very low temperatures, where the expectation value of any $N_p(f)$ is small, H_1 is the most important part of the hamiltonian. There are three types of terms in H_1. The products $B^{\dagger}_{pf} B_{pf}$ give the contribution to the crystal energy of the triplet excited states of pairs of spins. Products such as $B^\dagger_{pf}B_{p+1,f}$ represent transfer processes, in which an excited triplet gives up its energy to a neighboring pair. These terms describe the mobility of the excitations and lead in the usual way to a band structure in the energy spectrum of the system. Products such as $B^\dagger_{pf}B^\dagger_{p+1,f}$ represent directly the simultaneous excitation of two adjacent pairs to their triplet states. This process also affects the mobility of the excitations, even at very low excitation densities.

H_2 represents processes in which a pair of spins in its singlet state is excited to a triplet state next to an already present excited pair. The spin state of the latter pair may or may not change, depending on the spin state of the newly excited triplet. H_3, finally, represents the interaction of neighboring excited pairs. The interaction has the standard $\vec{S}\cdot\vec{S}$ form.

At very low temperatures, the operators B_{pf} closely resemble boson operators, since the expectation value of the right-hand side of equation (5c) is very nearly equal to unity in all the states of interest. This fact suggests the use of the so-called "quasi-boson" approximation. We may define operators $\mathcal{B}_{pf}$ which obey exact Bose commutation relations:

$$\mathfrak{B}_{p'f'} \; | \dots N_p(f) \dots >$$

$$= \sqrt{N_{p'}(f')} \; | \dots N_p(f) - \delta_{pp'}\delta_{ff'} \dots > \quad .$$

These operators are defined in a space which is much larger than that of the operators B_{pf}; states are included which do not satisfy equations (4). An operator $\mathfrak{B}_{pf}\,(1 - \mathfrak{B}^{\dagger}_{pf}\mathfrak{B}_{pf})$, however, has the same matrix elements as B_{pf} among the physically realizable states. If the hamiltonian is rewritten with each B_{pf} replaced by $\mathfrak{B}_{pf}\,(1 - \mathfrak{B}^{\dagger}_{pf}\mathfrak{B}_{pf})$, its matrix elements within the physical space are unchanged, and it connects physical states only with other physical states. Furthermore, the non-physical states in the basis of the $\mathfrak{B}_{pf}$'s are in general states with larger numbers of excitations. Thus one would expect the lowest eigenstates of the new hamiltonian to lie mostly in the physical subspace of the entire basis. In considering states with low excitation densities, those that are important at low temperatures, we may drop all terms in the hamiltonian of higher than second order in the operators $\mathfrak{B}_{pf}$ and $\mathfrak{B}^{\dagger}_{pf}$. This procedure is formally equivalent to retaining H_1, equation (6), and assuming the operators B_{pf} are actually Bose operators.

We have now an approximate hamiltonian which is a Hermitian quadratic form in operators obeying Bose statistics. This may be diagonalized by a linear canonical transformation; the general method is given in the Appendices. We shall treat the two parts H_β and H_f separately. For the former, an appropriate transformation is given by

$$B_{p\beta} = N^{-\frac{1}{2}} \sum_k [u_\beta(k)\; e^{ikp} B_{\beta k} + \overset{*}{v}_\beta(k)\; e^{-ikp} B^\dagger_{\beta k}] \quad .$$

The imposition of cyclic boundary conditions restricts the values of k to

$$k = 0,\ \pm\frac{2\pi}{N},\ \ \pm\frac{4\pi}{N},\ \ldots\ \pm\frac{N-1}{N}\pi \quad \text{for N odd} ,$$

$$k = 0,\ \pm\frac{2\pi}{N},\ \ldots\ \ \pm\frac{N-2}{N}\pi,\ \pi \quad \text{for N even} \quad .$$

The inverse transformation is

$$B_{\beta k} = N^{-\frac{1}{2}} \sum_p e^{-ikp}\ [\overset{*}{u}_\beta(k)\ B_{p\beta} - \overset{*}{v}_\beta(k)\ B^\dagger_{p\beta}] \quad .$$

The transformation is canonical—that is, the new operators $B^{\dagger}_{\beta k}$, $B_{\beta k}$ obey boson commutation relations—when

$$u_{\beta}(k)\ v_{\beta}(-k) = u_{\beta}(-k)\ v_{\beta}(k) \ ,$$

which we shall satisfy in this case by choosing $u_{\beta}(k)$ and $v_{\beta}(k)$ each real and even in k; and when

$$|u_{\beta}(k)|^{2} - |v_{\beta}(k)|^{2} = 1 \ .$$

The secular equations ensuring that H_{β} is diagonalized by the transformation are

$$E_{\beta}(k)\ u_{\beta}(k) = (J - \frac{J'}{2}\cos k)\ u_{\beta}(k) - \frac{J'}{2}\cos k\ \ v_{\beta}(k) \ ;$$

$$-E_{\beta}(k)\ v_{\beta}(k) = (J - \frac{J'}{2}\cos k)\ v_{\beta}(k) - \frac{J'}{2}\cos k\ u_{\beta}(k) \ .$$

Solutions are

$$E_{\beta}(k) = +\sqrt{J^{2} - J\,J'\cos k} \ ; \qquad (7a)$$

$$u_{\beta}(k) = +\sqrt{\frac{E_{\beta}(k) + J - \frac{J'}{2}\cos k}{2\,E_{\beta}(k)}} \ ; \ v_{\beta}(k) = +\sqrt{u_{\beta}(k)^{2} - 1} \ . \qquad (7b)$$

Under this transformation H_β becomes

$$H_\beta = \tfrac{1}{2}\sum_k [E_\beta(k) - J] + \sum_k E_\beta(k)\, B^\dagger_{\beta k} B_{\beta k} \quad .$$

It is instructive to perform the diagonalization of H_f in two steps. We first introduce the operators

$$B_{p\gamma} = \frac{1}{\sqrt{2}} \left(B_{pf_1} + B_{pf_2}\right) \quad ,$$

$$B_{p\delta} = \frac{1}{\sqrt{2}} \left(B_{pf_1} - B_{pf_2}\right) \quad .$$

This transformation separates H_f into two forms, each similar to H_β:

$$H_f = H_\gamma + H_\delta \quad ;$$

$$H_\gamma = J \sum_p B^\dagger_{p\gamma} B_{p\gamma} + \frac{J'}{4} \sum_p (B_{p\gamma} - B^\dagger_{p\gamma})(B_{p+1,\gamma} - B^\dagger_{p+1,\gamma}) ,$$

$$H_\delta = J \sum_p B^\dagger_{p\delta} B_{p\delta} - \frac{J'}{4} \sum (B_{p\delta} + B^\dagger_{p\delta})(B_{p+1,\delta} + B^\dagger_{p+1,\delta}) \quad .$$

These are put in diagonal form by the transformations

$$B_{p\gamma} = N^{-\frac{1}{2}} \sum_k [u_\gamma(k)\; e^{ikp}\; B_{\gamma k} + \overset{*}{v}_\gamma(k)\; e^{-ikp}\; B^\dagger_{\gamma k}]$$

$$B_{p\delta} = N^{-\frac{1}{2}} \sum_k [u_\delta(k)\; e^{ikp}\; B_{\delta k} + \overset{*}{v}_\delta(k)\; e^{-ikp}\; B^\dagger_{\delta k}]$$

where $u_\gamma(k) = u_\delta(k) = u_\beta(k)$

and $v_\delta(k) = -v_\gamma(k) = v_\beta(k)$

The energy spectra of both forms are identical with that of H_β:

$$E_\gamma(k) = E_\delta(k) = E_\beta(k) \quad .$$

The three branches of H_1 may then be written

$$H_1 = \sum_p E_p^\alpha + \varepsilon_o + \sum_k [E_\beta(k)\; B^\dagger_{\beta k} B_{\beta k} + E_\gamma(k)\; B^\dagger_{\gamma k} B_{\gamma k} + E_\delta(k)\; B^\dagger_{\delta k} B_{\delta k}] \quad . \tag{8}$$

The quantity $\mathcal{E}_o$ represents the decrease of the ground-state energy below that of the vacuum state due to the virtual creation and annihilation processes. The new operators $B^\dagger_{\beta k}$, $B^\dagger_{\gamma k}$, and $B^\dagger_{\delta k}$ may be considered as creation operators for the three types of spin-one elementary excitations of the system, which are non-interacting in this approximation. The energy degeneracy of the three branches has not been removed, of course, since the hamiltonian considered is isotropic. Equation (8) has been left in its more explicit form, however, since the inclusion of non-isotropic interaction will affect the separate terms differently.

The constant terms in the preceding expression for H_1 represent the ground-state energy of the system. They may be written explicitly as

$$\mathcal{E} = \sum_p E_p{}^\alpha + \mathcal{E}_o = - 9/4\ NJ + \frac{3}{2} \sum_k E_\beta(k) \ .$$

In the limit of large N (the approximation made can be valid only for large N), the summation over k may be replaced by integration,

$$\sum_{k} \longrightarrow \frac{N}{2\pi} \int_{-\pi}^{\pi} dk \quad ,$$

and, since all terms are even in k, we have

$$\varepsilon = -\frac{9}{4} NJ + \frac{3NJ}{2\pi} \int_{0}^{\pi} [1 - \frac{J'}{J} \cos k]^{\frac{1}{2}} dk \quad ,$$

or

$$\varepsilon/NJ = -\frac{9}{4} + \frac{3}{\pi} \sqrt{1 + \frac{J'}{J}}\; E\left(\sqrt{\frac{2J'}{J + J'}}\right) \quad . \tag{9}$$

Here E (λ) is the complete elliptic integral of the second kind:

$$E(\lambda) = \int_{0}^{\pi/2} [1 - \lambda^2 \sin^2 x]^{\frac{1}{2}} dx \quad .$$

The ground-state energy given by equation (9) is plotted in Figure 2 as a function of J'/J. Also shown in this figure in the approximate ground-state energy obtained by Bulaevskii$^{(18)}$, using a representation of the hamiltonian quartic in fermion operators and a zero-temperature Hartree-Fock approximation. The curves are qualitatively alike, with the greatest differences appearing for large J'.

Some care must be taken in estimating the accuracy of this treatment. The approximate eigenstates obtained do not lie wholly in the subspace which represents possible physical states of the system; the admixture of unphysical states increases as J' approaches J. The method used here relies fundamentally on the fact that there is a difference between J' and J. The greater this difference, the tighter the binding of the singlet states of pairs of spins relative to the triplet excited states and to the interactions between pairs. One expects the results of the calculation to be most accurate when J'/J is quite small compared to unity. The following characteristics of the solutions obtained give some indication of the applicability of the approximation techniques.

For small J', the predicted ground-state and single-excitation energies agree with perturbation theory results through quadratic terms in J'/J. The solution is, in this sense, exact in the limit of small J'. When

J'/J becomes larger, the unphysical states in the space spanned by the boson operators contribute more significantly to the ground state. This unfortunately makes impractical attempts to estimate higher-order corrections to the energies, since the matrix elements of higher-order terms among the non-physical states are overestimated to a much greater extent than those of the quadratic terms.

A measure of the consistency of the technique is provided by the fraction of the N pairs which are in triplet configurations in the calculated ground state. This is given by

$$\frac{1}{N}\sum_{p}\sum_{f\neq\alpha} N_{p}(f) = \frac{3}{N}\sum_{k} \left| v_{\beta}(k) \right|^{2}$$

$$= -\frac{3}{2} + \frac{3}{2\pi}\left\{\sqrt{\frac{J + J'}{J}}\; E\left(\sqrt{\frac{2J'}{J + J'}}\right) + \sqrt{\frac{J}{J + J'}}\; F\left(\sqrt{\frac{2J'}{J + J'}}\right)\right\} ,$$

sample values of which are tabulated in Table (1). $F(\lambda)$ is the complete elliptic integral of the first kind:

Table (1)

Fraction of spin pairs excited in the calculated ground state *versus* J'/J.

J'/J	Fraction excited
0	0
0.111	0.0021
0.250	0.0061
0.429	0.0198
0.667	0.0612
0.818	0.1242
0.980	0.4356
1.000	$+\infty$

$$F(\lambda) = \int_0^{\pi/2} \frac{dx}{\sqrt{1 - \lambda^2 \sin^2 x}} \quad .$$

It was assumed that this quantity was small; in fact it remains reasonably small for a large range of J'/J, even though it does diverge in the limit of equal J and J'. Another indication of consistency is the fact that the energy of the lowest-lying excitation is greater than zero for all J' less than J, so that at very low temperatures the number of excitations should be small. The ratio of J' to J in Wurster's blue perchlorate at low temperatures is difficult to measure experimentally. Comparison of the observed electron-spin-resonance spectra with the results of a theoretical line-shape calculation(19) indicates that J'/J may be a few percent at most, so that the present calculation should indeed be applicable to this system.

The results of this calculation are most open to question when J' approaches J. In this limit, the system is simply the one-dimensional Heisenberg antiferromagnet, which has been the subject of a great many investigations.(20-27) Comparison of the results obtained above with various treatments in the literature is quite interesting. An approximate value for the ground-state energy of a linear antiferromagnet is given by equation (9) with $J' = J$, and is listed together with the exact and approximate results of several different calculations in Table (2). The agreement between the exact value and the present approximation is surprisingly good. The nature of the energy spectrum of the low-lying states also agrees well with that found by other authors. There is no gap in the spectrum for equal J and J'. The dispersion relation for the lowest energy band is found from equation (7a):

$$E(k) = \sqrt{2}\, J \; \left| \cos \frac{k}{2} \right| \; .$$

This may be compared with the approximate results of Anderson,(21)

$$E(k) = J \; \left| \cos \frac{k}{2} \right| \quad ,$$

and Bulaevskii,(18)

$$E(k) = \left(1 + \frac{2}{\pi}\right) J \; \left| \cos \frac{k}{2} \right| \quad ,$$

Table (2)

Ground-state energy of the linear Heisenberg antiferromagnet, as given by several different calculations.

Calculation	$-\mathcal{E}/NJ$
Rodriguez(23)	0.8393
Oguchi(27)	.862
Ruijgrok and Rodriguez(24)	.8646
Bulaevskii(18)	.870
Exact solution(20)	.8863
Present work	.8998

and with the exact value proposed by des Cloizeau and Pearson,(26)

$$E(k) = \frac{\pi}{2} J \ \left| \cos \frac{k}{2} \right| \quad .$$

An advantage possessed by this calculation is the fact that the correct degeneracy and spin of the lowest excited states follow directly from the original representation used. A final comparison with the exact antiferromagnetic ground state, the calculation of the short-range order, will be possible when the effects of anisotropic interactions are included in the following chapter. The agreement of the value found there for the short-range order parameter with the exact value calculated by Orbach(22) is very good.

All in all, it appears that many of the approximate conclusions provided by this calculation are quite accurate. The approximation technique, however, was a fairly crude one, and several properties of the solutions are patently wrong. The implication is that somehow the total neglect of higher-order interactions was largely compensated for by the introduction of erroneous statistics in the quasi-boson approximation. Why this should be so is far from clear; a satisfactory explanation will probably not be found until the exact solutions to this problem are better understood.

Chapter III - Anisotropic Interactions

The spin-spin coupling considered in the preceding chapter was the isotropic Heisenberg interaction. The effect of an anisotropy in the interaction may be found by including in the spin hamiltonian terms of the form

$$H_D = \sum_{i=1}^{2N} D_i S_i^z S_{i+1}^z \tag{10a}$$

and

$$H_E = \sum_{i=1}^{2N} E_i \left(S_i^x S_{i+1}^x - S_i^y S_{i+1}^y \right) \quad . \tag{10b}$$

As before, we assume that D_i and E_i alternate in magnitude:

$$D_i = \begin{cases} D & i \text{ odd} \\ D' \leq D & i \text{ even} \end{cases} ,$$

$$E_i = \begin{cases} E & i \text{ odd} \\ E' \leq E & i \text{ even} \end{cases} .$$

The new terms lift the degeneracy of the spin-pair triplet states. The eigenstates of each single-site hamiltonian H_p are $|\alpha>$, $|\beta>$, $|\gamma>$, $|\delta>$, as defined in the previous chapter; their eigenvalues are $(-3J/4 - D/4)$, $(J/4 - D/4)$, $(J/4 + D/4 + E)$, and $(J/4 + D/4 - E)$, respectively. The complete hamiltonian, in the quasi-boson approximation, may be written

$$H = -\frac{(3J + D)}{4} N + \sum_{\mu = \beta, \gamma, \delta} H_\mu \quad ; \qquad (11a)$$

$$H_\mu = \sum_{p=1}^{N} a_\mu B^\dagger_{p\mu} B_{p\mu} + \sum_{p=1}^{N} b_\mu (B^\dagger_{p\mu} B_{p+1,\mu} + B_{p\mu} B^\dagger_{p+1,\mu}) + \sum_{p=1}^{N} c_\mu (B_{\beta\mu} B_{p+1,\mu} + B^\dagger_{p\mu} B^\dagger_{p+1,\mu}) \qquad (11b)$$

The coefficients are tabulated below:

μ =	β	γ	δ
a_μ =	J	$J + \frac{D}{2} + E$	$J + \frac{D}{2} - E$
b_μ =	$-\frac{(J' + D')}{4}$	$-\frac{(J' - 2E')}{4}$	$-\frac{(J' + 2E')}{4}$
c_μ =	$-\frac{(J' + D')}{4}$	$+\frac{(J' + 2E')}{4}$	$-\frac{(J' - 2E')}{4}$

Each of the independent branches may be diagonalized by a canonical transformation,

$$B_{p\mu} = N^{-\frac{1}{2}} \sum_{k} [u_\mu(k)\ e^{ikp}\ B_{\mu k} + v_\mu(k)\ e^{-ikp}\ B^\dagger_{\mu k}\ ] , \quad (12a)$$

$$B_{\mu k} = N^{-\frac{1}{2}} \sum_{p} e^{-ikp}\ [u_\mu(k)\ B_{p\mu} - v_\mu(k)\ B^\dagger_{p\mu}\ ] . \quad (12b)$$

with the coefficients

$$u_\mu(k) = \left[\frac{E_\mu(k) + a_\mu + 2b_\mu \cos k}{2E_\mu(k)}\right]^{\frac{1}{2}} , \quad (13a)$$

$$v_\mu(k) = -\ u_\mu(k) \left[\frac{a_\mu + 2b_\mu \cos k - E_\mu(k)}{2c_\mu}\right], \quad (13b)$$

$$E_\mu(k) = [a_\mu{}^2 + 4a_\mu b_\mu \cos k + 4\ (b_\mu{}^2 - c_\mu{}^2)\ \cos^2 k]^{\frac{1}{2}}. \quad (13c)$$

The transformation is convergent when all the $E_\mu(k)$ are real (otherwise the eigenvalues of the approximate hamiltonian are not bounded below). The transformed hamiltonian is

$$H = -\frac{3}{4}(3J + D)N + \frac{1}{2}\sum_{k,\mu} E_{\mu}(k) + \sum_{k,\mu} E_{\mu}(k)\, B^{\dagger}_{k,\mu} B_{k,\mu} \, .$$

In the limit of large N, the summation of the eigenergies $E_{\mu}(k)$ may be replaced by integration and the ground-state energy written in terms of complete elliptic integrals of the first, second, and third kinds. The reduction to standard form depends, however, on the relative sizes of the coefficients J, D, E, etc.—the rather cumbersome expressions that result are omitted here.

The spin system is also affected in a non-isotropic fashion by its interaction with an externally applied magnetic field. In a strong field (of magnitude $|\Delta/g\beta_e|$), the spin hamiltonian may be approximated by

$$\begin{aligned} H = \sum_{i=1}^{2N} J_i \vec{S}_i \cdot \vec{S}_{i+1} + \sum_{i=1}^{2N} D_i S_i^{z} S_{i+1}^{z} \\ + \Delta \sum_{i=1}^{2N} S_i^{z} \, . \end{aligned} \tag{14}$$

Here the z-direction is taken to be that of the magnetic field. The quantities D_i are not the same as those used before—they represent an appropriate average of the previous D and E terms along the new z-axis, about which the spins precess in the presence of the magnetic field.

The simplest way to diagonalize equation (14) is to start with the transformations defined above in equations (12) and (13), but setting $E = E' = 0$. Then

$$E_\gamma(k) = E_\delta(k) \quad ;$$

$$u_\gamma(k) = u_\delta(k) \quad ; \quad v_\gamma(k) = - v_\delta(k) \quad .$$

The interaction with the magnetic field may be written

$$\Delta S^z = \Delta \sum_p (B^\dagger_{p\gamma} B_{p\delta} + B^\dagger_{p\delta} B_{p\gamma})$$

$$= \Delta \sum_k (B^\dagger_{\gamma k} B_{\delta k} + B^\dagger_{\delta k} B_{\gamma k}),$$

so that the hamiltonian (14) becomes

$$H = -\frac{3}{4}(3J + D)N + \frac{1}{2}\sum_{\mu,k} E_{\mu}(k) + \sum_{k} E_{\beta}(k)\, B^{\dagger}_{\beta k} B_{\beta k}$$

$$+ \sum_{k} E_{\gamma}(k)(B^{\dagger}_{\gamma k} B_{\gamma k} + B^{\dagger}_{\delta k} B_{\delta k}) + \sum_{k} \Delta(B^{\dagger}_{\gamma k} B_{\delta k} + B^{\dagger}_{\delta k} B_{\gamma k}) \, .$$

The last two terms may be rewritten in terms of

$$B_{1k} = \frac{1}{\sqrt{2}}(B_{\gamma k} + B_{\delta k}) \; ; \quad B_{2k} = \frac{1}{\sqrt{2}}(B_{\gamma k} - B_{\delta k}) \; :$$

$$H = -\frac{3}{4}(3J + D)N + \frac{1}{2}\sum_{\mu,k} E_{\mu}(k) + \sum_{k} E_{\beta}(k)\, B^{\dagger}_{\beta k} B_{\beta k}$$

$$+ \sum_{k} (E_{\gamma}(k) + \Delta)\, B^{\dagger}_{1k} B_{1k} + \sum_{k} (E_{\gamma}(k) - \Delta)\, B^{\dagger}_{2k} B_{2k} \, . \qquad (15)$$

We see that the β-type excitations are unaffected by the magnetic field, and that the other two branches are displaced in energy by an amount proportional to the field. It is easy to see that the elementary excitations created by $B^{\dagger}_{1k}$ and $B^{\dagger}_{2k}$ have z-projections of their spins equal to 1 and -1 respectively, since

$$[S^z, B_{1k}^\dagger] = B_{1k}^\dagger \quad ,$$

$$[S^z, B_{2k}^\dagger] = - B_{2k}^\dagger \quad .$$

It is instructive to write these operators more explicitly as

$$B_{1k}^\dagger = \frac{1}{\sqrt{2}} (B_{\gamma k}^\dagger + B_{\delta k}^\dagger) = \frac{1}{\sqrt{N}} \sum_p e^{ikp} [u_\gamma(k)\ B_{pf_1}^\dagger - v_\gamma(k)\ B_{pf_2}],$$

$$B_{2k}^\dagger = \frac{1}{\sqrt{2}} (B_{\gamma k}^\dagger - B_{\delta k}^\dagger) = \frac{1}{\sqrt{N}} \sum_p e^{ikp} [u_\gamma(k)\ B_{pf_2}^\dagger - v_\gamma(k)\ B_{pf_1}].$$

Thus $B_{1k}^\dagger$ creates excitons with spin "up" and annihilates excitons with spin "down", and conversely for $B_{2k}^\dagger$. The isotropic hamiltonian treated earlier could just as well have been diagonalized by a direct transformation to these operators.

The ground-state energy in equation (15) becomes, in the limit of large N,

$$\varepsilon = \frac{3}{4}(3J + D)N + \frac{N}{\pi}\sqrt{J(J + J' + D')}\,E\left(\sqrt{\frac{2(J' + D')}{J + J' + D'}}\right)$$

$$+ \frac{2N}{\pi}\sqrt{(J + \frac{D}{2})(J + J' + \frac{D}{2})}\;E\left(\sqrt{\frac{2J'}{J + J' + \frac{D}{2}}}\right),$$

where $E(\lambda)$ is the elliptic integral defined earlier. Using this expression, we may evaluate the short-range order parameter,

$$\eta = < \frac{2}{N} \sum_{i=1}^{2N} S_i^z S_{i+1}^z > \quad .$$

This quantity is a measure of the extent to which the spins of the system are arranged alternately "up" and "down", as they would be if the interaction were that of the Ising model. For perfect alternation, $\eta = -1$. Since

$$\frac{\partial H}{\partial D} = \sum_{i\ \mathrm{odd}} S_i^z S_{i+1}^z$$

and

$$\frac{\partial H}{\partial D'} = \sum_{i \text{ even}} S_i^z S_{i+1}^z ,$$

Feynman's theorem implies that in any eigenstate of the hamiltonian

$$< \sum_i S_i^z S_{i+1}^z > = \frac{\partial < H >}{\partial D} + \frac{\partial < H >}{\partial D'} .$$

Specifically, in the ground state,

$$\eta = \frac{2}{N} \left(\frac{\partial \varepsilon}{\partial D} + \frac{\partial \varepsilon}{\partial D'}\right) = - \frac{3}{2} + \frac{1}{\pi} \left\{ \sqrt{\frac{J + J' + D/2}{J + D/2}}\, E\left(\sqrt{\frac{2J'}{J + J' + D/2}}\right) \right.$$

$$+ \sqrt{\frac{J + D/2}{J + J' + D/2}}\, F\left(\sqrt{\frac{2J'}{J + J' + D/2}}\right)$$

$$+ \frac{\sqrt{J(J + J' + D')}}{(J' + D')}\, E\left(\sqrt{\frac{2(J' + D')}{J + J' + D'}}\right) \qquad (16)$$

$$\left. - \frac{J\sqrt{J}}{(J' + D')\sqrt{J + J' + D'}}\, F\left(\sqrt{\frac{2(J' + D')}{J + J' + D'}}\right) \right\} .$$

Orbach has computed this quantity for the exact ground state of the linear antiferromagnet.(22) We may obtain a value comparable with his in the limit of vanishing anisotropy by letting D and D' vanish and taking J = J' in equation (16). Our result is -0.5996; Orbach's is -0.596. Again, this approximate calculation yields a result in good accord with exact values. It is worthy of note that this agreement suggests that not only the energy, but also the nature of the ground state, are predicted with some accuracy.

It is possible to diagonalize the approximate hamiltonian describing this system under the influence of both the general anisotropic interaction including H_D and H_E, equation (10), and an external magnetic field of arbitrary strength in an arbitrary direction. For convenience, we return to the coordinate system in which x, y, and z are the principal axes of the spin-spin interaction. The hamiltonian is

$$H = \sum_p E_p^{\alpha} + \sum_{\mu = \beta, \gamma, \delta} H_{\mu} + \Delta_x S^x + \Delta_y S^y + \Delta_z S^z .$$

The first terms on the right-hand side are those of equation (11); the magnetic field terms may be written

$$\Delta_z \sum_p (B^\dagger_{p\gamma} B_{p\delta} + B^\dagger_{p\delta} B_{p\gamma}) + \Delta_x \sum_p (B^\dagger_{p\gamma} B_{p\beta} + B^\dagger_{p\beta} B_{p\delta})$$

$$+ i\Delta_y \sum_p (B^\dagger_{p\beta} B_{p\gamma} - B^\dagger_{p\delta} B_{p\beta}) \quad .$$

The three branches are mixed by the field.

We seek a diagonalizing transformation of the form

$$B_{p\mu} = N^{-\frac{1}{2}} \sum_{k,\rho} [e^{ikp} u_{\rho,\mu}(k)\ B_{\rho k} + e^{-ikp} v^*_{\rho,\mu}(k)\ B^\dagger_{\rho k}] \quad .$$

The new branch index ρ takes on three values. The ortho-normality conditions on the coefficients are

$$\sum_\mu [u_{\rho\mu}(k)\ v_{\sigma\mu}(-k) - u_{\sigma\mu}(-k)\ v_{\rho\mu}(k)\ ] = 0 \quad ,$$

$$\sum_\mu [u_{\rho\mu}(k)\ \overset{*}{u}_{\sigma\mu}(k) - v_{\rho\mu}(k)\ \overset{*}{v}_{\sigma\mu}(k)\ ] = \delta_{\rho\sigma} \quad .$$

Six equations in E_ρ, $u_{\rho,\mu}$, and $v_{\rho,\mu}$ provide for the diagonalization of the hamiltonian. To save space, we do not write them out explicitly; they are obtained by the direct application of the general theorem of Appendix B. The vanishing of the secular determinant of the set yields a cubic equation for the squares of the eigenenergies E_ρ:

$$
\begin{aligned}
&E_\rho^{\,6} - E_\rho^{\,4}\left\{\xi_\beta + \xi_\gamma + \xi_\delta + 2\,(\Delta_x^{\,2} + \Delta_y^{\,2} + \Delta_z^{\,2})\right\} \\
&+ E_\rho^{\,2}\Big\{\xi_\beta\xi_\gamma + \xi_\gamma\xi_\delta + \xi_\delta\xi_\beta + 2\Delta_x^{\,2}(\xi_\delta - \chi_\delta) \\
&+ 2\Delta_y^{\,2}(\xi_\gamma - \chi_\gamma) + 2\Delta_z^{\,2}(\xi_\beta - \chi_\beta) + (\Delta_x^{\,2} + \Delta_y^{\,2} + \Delta_z^{\,2})^2\Big\} \\
&- \xi_\beta\xi_\gamma\xi_\delta + 2\Delta_x^{\,2}\xi_\delta\chi_\delta + 2\Delta_y^{\,2}\xi_\gamma\chi_\gamma + 2\Delta_z^{\,2}\xi_\beta\chi_\beta \\
&- 2\Delta_x^{\,2}\Delta_y^{\,2}\,\chi_\beta - 2\Delta_x^{\,2}\Delta_z^{\,2}\,\chi_\gamma - 2\Delta_y^{\,2}\Delta_z^{\,2}\,\chi_\delta \\
&+ \Delta_x^{\,4}\xi_\delta + \Delta_y^{\,4}\xi_\gamma + \Delta_z^{\,4}\xi_\beta = 0 \quad .
\end{aligned}
$$

In this equation

$$\xi_\beta = J^2 - J(J' + D')\cos k \;,$$

$$\chi_{\beta} = (J + \frac{D}{2})^2 - E^2 - (JJ' + \frac{DJ'}{2} + 2EE') \cos k \ ,$$

$$\xi_{\gamma} = (J + \frac{D}{2} + E)^2 - (J + \frac{D}{2} + E)(J' - 2E') \cos k$$

$$- 2J'E' \cos^2 k \ ,$$

$$\chi_{\gamma} = J(J + \frac{D}{2} - E) - (JJ' + \frac{JD'}{2} + \frac{DJ'}{2} + JE' - J'E + \frac{DD'}{2}$$

$$- ED') \cos k + (J' + D') E' \cos^2 k \ ,$$

and ξ_{δ} and χ_{δ} are the same as ξ_{γ} and χ_{γ}, respectively, but with E replaced by (−E) and E' by (−E').

Explicit solution for the eigenenergies and transformation coefficients would probably best be achieved by numerical methods. As before, the transformation is acceptable when the quantities $E_{\rho}(k)$ are all real. The diagonalized hamiltonian is

$$H = - \frac{3}{4} N(3J + D) - \sum_{\rho,k} E_{\rho}(k) \ |v_{\rho k}|^2 + \sum_{\rho,k} E_{\rho}(k) \ B^{\dagger}_{\rho k} B_{\rho k} \ .$$

These calculations show that quite complicated problems may be handled using the quasi-boson approximation. The uncertainties discussed in the previous chapter make precise estimates of the accuracy obtained difficult. When the basic assumption of relatively weak coupling among excitations and the restriction to low-energy states are justified, however, the technique of canonical transformation provides a simple and useful tool for understanding the effects of even highly complex physical processes in molecular crystals.

Chapter IV - Periodic Distortion of Linear Chains

The dimerization of positive ions in crystals of Wurster's blue perchlorate at low temperatures is one example of a transition from a class II to a class I crystal. It has been suggested by McConnell and Lynden-Bell(1) that such shifts may be quite common in molecular aggregates containing topologically linear arrays of interacting elements. Several sorts of one-dimensional systems are known to be unstable with respect to distortions yielding an alternation of inter-particle spacings along the arrays.(28-30) In this chapter we present a calculation which suggests that the cooperative effects induced by excitation transfer and virtual creation processes in the linear chains of interacting spins treated in the two previous chapters actually make dimerization along the chains energetically favorable.

The starting point for this calculation is the approximate ground-state energy of the alternating spin system, expressed as a function of the stronger and weaker coupling coefficients J and J':

$$\mathcal{E} = -\frac{9NJ}{4} + \frac{3NJ}{\pi}\sqrt{1+\frac{J'}{J}}\,E\left(\sqrt{\frac{2J'}{J+J'}}\right) . \qquad (17)$$

The rather surprising accuracy of this expression even in the limit of equal J and J' suggests that it is close to the true value everywhere. This makes it possible to examine in some detail the tendency of this system to undergo a periodic distortion, so that the separations between successive radicals alternate in size. We may suppose, for example, that the individual spins of one chain are bound harmonically at equally spaced points along the chain, and that the magnitude of the coupling between two adjacent spins varies linearly with the distance between them. A hamiltonian describing this situation is

$$H = \sum_{i=1}^{2N} \frac{a}{2} X_i^2 + \sum_{i=1}^{2N} J_o(1 + bX_i)\,\vec{S}_i \cdot \vec{S}_{i+1} .$$

Here X_i is the displacement of the spacing between the i^{th} and $(i + 1)^{st}$ spins from its value when all couplings are equal. We wish to compare the energies of states in which the interparticle distances alternate with that for a regular antiferromagnet ($X_i = 0$). Let $|x> =$

$| bX >$ represent the state in which the displacements alternate so that

$$X_i = (-1)^{i + 1} X .$$

In this state, we take the energy contribution from the spin-spin interaction to be given by equation (17), where we put

$$J = J_o(1 + x) \quad ; \quad J' = J_o(1 - x) .$$

The ground-state energy of this configuration is then

$$< x \; | H | \; x > = NaX^2 + NJ_o(1 + x) \cdot$$

$$\cdot \left\{ - \frac{9}{4} + \frac{3\sqrt{2}}{\pi\sqrt{1 + x}} \; E\left(\sqrt{1 - x}\right) \right\} \qquad ,$$

which we may put in dimensionless form as

$$\frac{< H >}{NJ_o} \equiv \varepsilon(x,S) = Sx^2 - \frac{9}{4}(1 + x) + \frac{3\sqrt{2}}{\pi}\sqrt{1 + x}\, E\left(\sqrt{1 - x}\right); \qquad (18)$$

$$S = \frac{a}{b^2 J_o} \quad .$$

The optimum value of x for each value of the parameter S is given by the requirement that $\mathcal{E}(x, S)$ be a minimum. We consider the set of pairs of corresponding values x and S which satisfy equation (18) and

$$\frac{\partial \mathcal{E}}{\partial x} = 0 = 2xS - \frac{9}{4} + \frac{3\sqrt{2}}{\pi} \frac{1}{(1 - x)\sqrt{1 + x}} \left[(1 + x) F\left(\sqrt{1 - x}\right) - 2xE\left(\sqrt{1 - x}\right) \right] . \qquad (19)$$

Here $F(\lambda)$ is the complete elliptic integral of the first kind, defined in Chapter II.

Two critical points divide the range of x into three parts, each corresponding to a different type of solution to the physical problem. For x greater than x_B, there exist local minima of $\mathcal{E}$ for some value of S between zero and S_B for which $\mathcal{E}(x, S)$ is less than $\mathcal{E}(0, S)$. These represent stable distortions of the chain. At $x = x_B$ the minimum value of $\mathcal{E}$ equals the value for no distortion. For x between x_A and x_B (S between S_A and S_B) there exist local minima of $\mathcal{E}$, but they lie higher than the undistorted energy. For these values of S, the ground state has no distortion, but there is a "metastable" state with a finite distortion. Finally, at $x = x_A$ the energy determined by equations (18) and (19) reaches a maximum. For x less than x_A, the only local extrema of $\mathcal{E}$ are maxima; only the undistorted state is stable, even with respect to infinitesimal fluctuations. Values of S greater than S_A provide no extrema. The criteria for stability of distorted states may therefore be summarized in terms of S as follows:

For $0 < S < S_B$ the distorted state with $1 > x > x_B$ is stable.

For $S_B \leq S \leq S_A$ the distorted state with $x_B \geq x \geq x_A$ is "metastable"; $|x = 0>$ is stable.

For $S > S_A$ no distorted state is stable; $| x = 0 >$ is stable.

Table 3 presents values of x, S, $\mathcal{E}(x, S)$, and the corresponding values of J'/J satisfying equations (18) and (19). The critical values of S are

$$S_A = 2.1 \qquad x_A = 0.06$$

$$S_B = 1.5 \qquad x_B = 0.17 \quad .$$

Table 3: Stable distortions of the one-dimensional antiferromagnet, linear variation of J.

Values of S in parentheses do not correspond to minima of $\mathcal{E}(x,S)$.

x	S	$\mathcal{E}(x,S)$	J'/J	
0.000	(- ∞)		1.000	
0.01	(-7.265)		0.980	
0.02	(-1.395)		.961	
0.03	(+1.053)		.942	
0.04	(1.806)		.923	
0.05	(1.955)		.905	
0.06	2.113	- .8896	.887	A
0.07	2.092	- .8898	.869	
0.08	2.038	- .8906	.852	
0.10	1.897	- .8912	.818	
0.12	1.754	- .8931	.786	
0.14	1.623	- .8952	.754	
0.16	1.507	- .8977	.724	
0.17	1.455	- .8991	.709	B
0.18	1.405	- .9007	.695	
0.20	1.316	- .9040	.667	
0.30	0.9963	- .9233	.538	
0.40	.8024	- .9469	.429	
0.50	.6725	- .9730	.333	
0.60	.5597	-1.0080	.250	
0.70	.5097	-1.0301	.176	
0.80	.4549	-1.0611	.111	
0.90	.4112	-1.0923	0.053	

critical points

The greatest inaccuracies in the above calculation lie in the assumption that the molecular binding is exactly parabolic and that the variation of J is linear. More precisely, the former assumption requires that

$$x << \frac{3a^{3/2}}{V'''(0)\ S^{\frac{1}{2}}\ J_o^{\frac{1}{2}}} \quad ,$$

where $V'''(0)X^3/3!$ is the neglected cubic term in the binding energy; the latter requires that

$$x << \frac{2a^{\frac{1}{2}}b}{J''(0)\ J_o^{3/2}\ S^{\frac{1}{2}}} \quad ,$$

where $J''(0)\ X^2/2$ is the first neglected term in the expansion of

$$J = J_o + J_o b\ X + \frac{1}{2!}\ J''(0)\ X^2 + \ldots$$

It should be emphasized, however, that the expression (17) for $\varepsilon_o(J, J')$ is accurate to a few percent even for $J = J'$ and should be better as J and J' differ more greatly. Any dependences of the molecular binding and the exchange integrals may be treated in an entirely comparable way to provide accurate criteria for distortional stability.

Since it seems likely that the linearity of J is the least sure to be exact, a similar calculation was carried out for an exponential dependence:

$$J(X) = J_o e^{\beta X}$$

The energy for a given distortion and binding is given by

$$\mathcal{E} = \frac{\langle H \rangle}{NJ_o} = S\,x^2 - \frac{9}{4}\,e^x + \frac{3}{\pi}\sqrt{e^{2x}+1}\;E\left(\sqrt{\frac{2}{e^{2x}+1}}\right). \quad (20)$$

The condition that $\mathcal{E}$ be an extremum is

$$\frac{\partial \mathcal{E}}{\partial x} = 0 = 2\,S\,x - \frac{9}{4}\,e^x + \frac{3}{\pi}\,\frac{e^{2x}}{\sqrt{e^{2x}+1}}\;F\left(\sqrt{\frac{2}{e^{2x}+1}}\right). \quad (21)$$

Here

$$S = \frac{a}{\beta^2 J_o} \;; \quad x = \beta X \quad .$$

The qualitative features of the locus described by equations (20) and (21) are the same as before, except for large x, where the dependence of $\mathcal{E}$ becomes exponential rather than quadratic. In this region $\mathcal{E}(x, S)$ can have only relative maxima, which occur for larger and larger values of S as x increases. The minimum value of S occurs at a point we denote by C. As before, for S greater than S_A no stable distortions exist; for S between S_A and S_B there is a "metastable" distortion possible, but the ground state is undistorted; for S between S_B and S_C the ground state has a finite stable distortion. For S greater than S_C, however, the exponential variation of J becomes dominant and the predicted distortion is complete collapse of the pairs. Such a collapse could not be expected physically, of course, since for large x the molecular binding must become strongly repulsive; the actual distortion would be finite. The critical points of significance are thus A and B. The values of S and x at these points are

$$S_A = 2.6 \qquad x_A = 0.07$$
$$S_B = 1.9 \qquad x_B = 0.17 \quad .$$

Table 4 presents values of x, S, $\varepsilon(x, S)$ and J'/J given by equations (20) and (21). It is seen that the results for an exponential variation of J do not differ greatly from those for a linear variation. One would seem justified in concluding that for values of S greater than about three, no distortions will be found, and that for S less than about unity distortions will occur.

Rough estimates of the binding forces and exchange integrals in Wurster's blue perchlorate(31) suggest that in this crystal S is likely to be quite small (a few percent) but might be as large as one. As a matter of fact, the small value of S obtained from these crude estimates would correspond to a quite small value of J'/J, the order of magnitude of that suggested by comparison of calculated and observed spin-resonance line shapes.(19) This should not be taken too seriously, since the corresponding distortion predicted is so large that the harmonic binding approximation is certainly not reasonable.

This calculation ignores, of course, all dynamical phonon effects. It is difficult, therefore, to draw any conclusions as to whether the "metastable"

Table 4: Stable distortions of the one-dimensional antiferromagnet, exponential variation of J.

x	S	$\mathcal{E}(x,S)$	J'/J	
0.000	(− ∞)		1.000	
0.010	(−12.96)		.980	
0.020	(− 0.9496)		.960	
0.030	(+ 1.496)		.942	
0.040	(2.250)		.923	
0.050	(2.472)		.905	
0.060	(2.554)		.987	
0.070	2.562	− .8896	.869	A
0.080	2.480	− .8903	.852	
0.090	2.411	− .8905	.835	
0.100	2.337	− .8912	.818	
0.121	2.193	− .8929	.786	
0.141	2.061	− .8951	.754	
0.161	1.945	− .8981	.724	
0.172	1.893	− .8994	.709	B
0.182	1.843	− .9010	.695	
0.203	1.753	− .9052	.667	
0.310	1.436	− .9245	.538	
0.424	1.248	− .9493	.429	
0.549	1.130	− .9767	.333	
0.693	1.056	−1.1459	.250	
0.867	1.017	−1.3513	.176	C
1.099	1.019	−1.6938	.111	
1.472	1.109	−2.4539	.053	

distortions predicted might actually be observed in real crystal systems. The appearance of stable distortions, for appropriate values of S, does seem definitely indicated. More detailed calculations concerned with phonon-exciton interactions(19,31) (which do not treat the spin-system energies so explicitly) also show a tendency for dimerization to occur, or if already present, to be increased. It is interesting that the present calculation predicts that infinitely small distortions of the lattice are never stable. In particular, this implies that J and J' should differ by at least about ten percent for any stable distortion, so that experimental searches for distortions in other systems should give unambiguous results. Of course, other mechanisms favoring dimerization may be important in many actual crystals; this calculation suggests that, even without them, dimerization of linear chains should sometimes occur.

Chapter V - Singlet Excitons: Intramolecular Charge Resonance

The preceding calculations, while concerned with a rather special physical situation, yield results in accord with very general ideas about the nature of systems containing regular arrays of interacting elements. The existence of long-range correlations in the low-lying energy eigenstates of the system and the nature of the spectrum of the (approximate) elementary excitations are understandable in terms of the concepts discussed earlier of the zero-point oscillations associated with mobile excitations. Furthermore, the specific results obtained followed directly from simple and fundamental properties of the hamiltonian of the system. It is reasonable, then, to look about for other systems with these same basic properties, which should be amenable to similar analysis.

There are, in fact, several physical processes frequently of importance in molecular crystals, processes in which interactions between neighboring elements of a crystal induce collective behavior in low-lying energy states. In some cases, the interactions of significance involve only the two lowest energy configurations of each molecule or radical. In treating problems with such a property in one-dimensional systems, it is possible to dispense with the quasi-boson approximation used in earlier chapters. The states of a linear chain of elements, each of which is in either its ground state or a singlet excited state, may be described completely by a set of second-quantization creation and annihilation operators with Fermi commutation relations.(32,33)

To define such a representation, we may start with a set of second-quantized operators $P_n^\dagger$, P_n. $P_n^\dagger$ raises the nth element in a linear system to its lowest excited state from its ground state. These operators are equivalent to the operators $B_{pf}^\dagger$, B_{pf} defined in Chapter II, except that because there is only one excited state, f, they have Pauli commutation relations:

$$[P_n, P_m]_- = 0 \quad ,$$

$$[P_n, P_m^\dagger]_- = 0 \quad \text{for } m \neq n \; ,$$

$$P_n^\dagger P_n + P_n P_n^\dagger = 1 \quad ,$$

$$(P_n)^2 = 0 \quad .$$

We may now define fermion creation and annihilation operators:

$$f_n^\dagger = (-1)^{\sigma_n} P_n^\dagger \quad ,$$

$$f_n = (-1)^{\sigma_n} P_n \quad ,$$

where

$$\sigma_n = \sum_{m=1}^{n-1} P_m^\dagger P_m = \sum_{m=1}^{n-1} f_n^\dagger f_n \quad .$$

It is easily verified that

$$[f_n, f_m]_+ = 0 \quad ,$$

$$[f_n, f_m^\dagger]_+ = \delta_{mn} \quad .$$

The relationship between the P_n's and the f_n's is a rather complicated one, because of the appearance of the operators σ_n; it has, however, a very useful property. Any product of two Pauli operators corresponding to the same or adjacent sites is equivalent to a similar product of (only) two Fermi operators. For example,

$$P_n^\dagger P_n = f_n^\dagger f_n \ ,$$

$$P_n^\dagger P_{n+1} = f_n^\dagger f_{n+1} \ ,$$

$$P_n P_{n+1} = -f_n f_{n+1} \ .$$

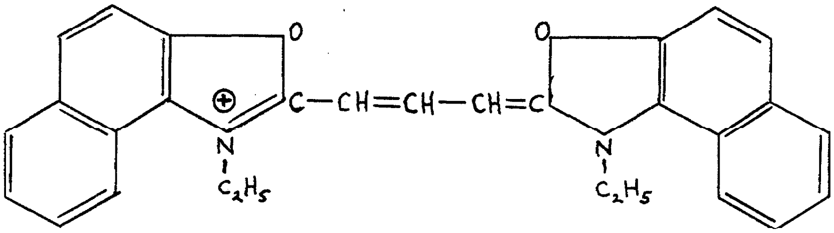
This means that a hamiltonian which is quadratic in the operators $P_n^\dagger$, P_n and involves only nearest-neighbor interactions is also quadratic in the fermion operators $f_n^\dagger$, f_n. Our method for diagonalizing fermion quadratic forms thus enables us to diagonalize quadratic hamiltonian functions describing linear systems of singlet excitons with nearest-neighbor interactions. Furthermore, it is not necessary to impose restrictions on the excitation density, as it was in the quasi-boson method: a complete set of energy eigenstates is obtained. There is, of course, a physical limitation on the applicability of this method to highly excited states. When the excitation density of the system is sufficiently large, the neglect of all excited states of each element above the first is presumably no longer justifiable.

Two problems which lend themselves well to analysis in terms of a fermion representation such as that described above are considered in this and the following chapter. We first treat the electronic states of a linear molecular chain in which dispersion interactions between molecules may be comparable in magnitude to the single-molecule excitation energies.

(After the work described in the remainder of this chapter was completed, it was discovered that a significant part of the mathematical formalism is equivalent to that used elsewhere for a physically quite different problem.(25) Since the present application of the mathematical formalism calls for the investigation of different properties of the solutions, as well as a totally new interpretation of their physical significance, it is felt best to present the complete analysis in a self-contained form. The calculations of Chapter VI use those of this chapter as a starting point.)

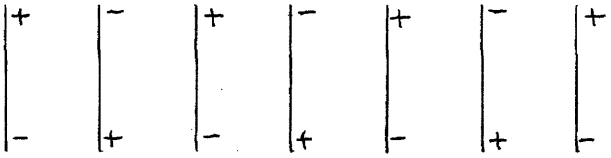
There exists an extensive literature on intermolecular forces due to dispersion or van der Waals interactions.(34) Although these interactions are often regarded as weak, it may be anticipated that in some molecular crystals these forces are so strong that the electronic structures of the molecules in the crystal lattice are grossly different from the structures of the isolated molecules, even though no conventional chemical bonds between the molecules are formed. Here, and below, we shall use the terminology "charge resonance" instead of "dispersion" or "van der Waals", since these latter terms conventionally suggest weak interactions.

Unusually strong charge resonance interactions might be expected, for example, in crystals containing linear arrays of such elements as the cation (3, 3'-diethyl-4, 5, 4', 5'-dibenzo-oxacarbocyanine) shown below:



The positive charge on this radical is concentrated in the vicinity of the two nitrogen nuclei. Symmetric and antisymmetric combinations of the "right-hand" and "left-hand" locations of the charge characterize the ground state and the lowest excited state. Coulomb interactions of the charge on neighboring ions in a linear chain would then tend to produce a collective polarization of the radicals. The way in which the radicals were arranged in the crystal would determine whether the polarization would be ferroelectric or antiferroelectric; the two extreme cases are sketched below, with the charge distributions encouraged by the interaction.

ferroelectric (b < 0)



antiferroelectric (b > 0)

We shall consider, then, a closed linear chain of N identical equally-spaced molecules, denoted by 1, 2, ... N. Only the ground electronic state and first singlet excited state of each molecule are considered, and are represented by wave functions φ_n and φ'_n respectively. Each molecule is assumed to have a center or symmetry that coincides with a center of symmetry of the linear chain. φ_n is assumed to be symmetric, and φ'_n antisymmetric with respect to inversion, and $\varphi_n \rightarrow \varphi'_n$ is a strong allowed electric dipole transition. The hamiltonian for the problem is chosen to be of the simple form

$$H = \sum_{n=1}^{N} (H_n + V_{n,\, n+1}) \quad , \qquad (22)$$

where $V_{N,\, N+1} \equiv V_{N,\, 1}$. Electron exchange between neighboring molecules is neglected, and only nearest-neighbor interactions are considered. H_n is the hamiltonian for the isolated n^{th} molecule; $V_{n,\, n+1}$ is the Coulomb interaction between molecules n and n + 1. The zero of energy is chosen such that

$$(\varphi'_n, H_n \varphi'_n) = \varepsilon \quad ,$$

$$(\varphi_n, H_n \varphi_n) = 0 \quad .$$

The charge distributions corresponding to φ_n and φ'_n are assumed, for simplicity, to be identical. This is, of course, never exactly true for two distinct electronic states. However, it is expected that the charge densities on atoms are relatively unaffected by a transition to the first excited singlet states in such systems as neutral, even alternant aromatic molecules, symmetrical cyanine dye molecules, and probably other symmetrical molecules as well.

As a result of this assumed equivalence of the charge distributions of φ_n and φ'_n, the following matrix elements are equal:

$$(\varphi_n\varphi_{n+1}, V_{n,n+1}\, \varphi_n\varphi_{n+1})$$

$$= (\varphi'_n\varphi'_{n+1}, V_{n,n+1}\, \varphi'_n\varphi'_{n+1}) .$$

Matrix elements of the form

$$(\varphi_n\varphi_{n+1}, V_{n,n+1}\, \varphi'_n\varphi_{n+1})$$

occur in pairs which always cancel out. The hamiltonian can be written, to within an additive constant, in terms of matrix elements of the following two types:

$$(\varphi'_n \varphi_{n+1}, V_{n,n+1}\, \varphi_n \varphi'_{n+1}) ,$$

$$(\varphi_n \varphi_{n+1}, V_{n,n+1}\, \varphi'_n \varphi'_{n+1}) .$$

The first matrix element corresponds to *excitation transfer*, and the second to *excitation-pair creation* and *annihilation*. These matrix elements are equal to one another; their common value will be denoted by b.

With these simplifying assumptions, the eigenstates and excitation spectrum for the hamiltonian of equation (22) are determined below for all values of ε and b.

The hamiltonian, equation (22), can be written in the second-quantization representation as

$$H = \varepsilon \sum_{n=1}^{N} P_n^\dagger P_n + b \sum_{n=1}^{N-1} (P_n^\dagger + P_n)(P_{n+1}^\dagger + P_{n+1})$$

$$+ b\, (P_N^\dagger + P_N)(P_1^\dagger + P_1) .$$

In terms of the fermion operators defined above, this is

$$H = \epsilon \sum_{n=1}^{N} f_n^\dagger f_n + b \sum_{n=1}^{N-1} (f_n^\dagger f_{n+1}^\dagger + f_{n+1} f_n + f_{n+1}^\dagger f_n + f_n^\dagger f_{n+1}) - (-1)^\sigma \, b(f_N^\dagger f_1 + f_N^\dagger f_1^\dagger + f_1^\dagger f_N + f_1 f_N) \tag{23}$$

Here σ is the operator for the total excitation number of the system:

$$\sigma = \sum_{n=1}^{N} P_n^\dagger P_n$$

The parity operator, $(-1)^\sigma$, commutes with any quadratic form in fermion operators f_n and $f_n^\dagger$, and consequently commutes with H. It then follows that all non-degenerate eigenstates of the hamiltonian are necessarily eigenstates of the parity operator, and that we can choose a complete set of states to be simultaneous eigenstates of $(-1)^\sigma$ and H. We shall call eigenstates of $(-1)^\sigma$ with eigenvalue +1 even states, and those with eigenvalue -1 odd states. We introduce the two quadratic forms

$$H^{(\alpha)} = \epsilon \sum_{n=1}^{N} f_n^\dagger f_n + b \sum_{n=1}^{N-1} (f_n^\dagger f_{n+1} + f_n^\dagger f_{n+1}^\dagger$$

$$+ f_{n+1}^\dagger f_n + f_{n+1} f_n) - (-1)^\alpha b (f_N^\dagger f_1 + f_N^\dagger f_1^\dagger + f_1^\dagger f_N + f_1 f_N),$$

where $\alpha = 1, 2.$

This differs from equation (23) in that α is a c-number, whereas σ appearing in equation (23) is an operator. $H^{(1)}$ and $H^{(2)}$ have the property that odd eigenstates of $H^{(1)}$ and even eigenstates of $H^{(2)}$ are eigenstates of the hamiltonian H.

It is convenient to represent $H^{(\alpha)}$ in terms of new fermion operators $F_k^\dagger$ and F_k:

$$F_k = N^{-\frac{1}{2}} \sum_{n=1}^{N} e^{ikn} f_n \tag{24}$$

$$F_k^\dagger = N^{-\frac{1}{2}} \sum_{n=1}^{N} e^{-ikn} f_n^\dagger \quad .$$

The values assumed by k in this set of transformations are chosen so that $e^{ikN} = -(-1)^\alpha$, and are given below for the four distinct cases that occur:

$\alpha = 1$, N even $k = 0, \pm 2\pi/N, \pm 4\pi/N, \ldots + \pi$

$\alpha = 1$, N odd $k = 0, \pm 2\pi/N, \pm 4\pi/N, \ldots \pm (N-1)\, \pi/N$

$\alpha = 2$, N even $k = \pm \pi/N, \pm 3\pi/N, \ldots \pm (N-1)\, \pi/N$

$\alpha = 2$, N odd $k = \pm \pi/N, \pm 3\pi/N, \ldots + \pi$.

$H^{(\alpha)}$ expressed in terms of $F_k^\dagger$, F_k is

$$H^{(\alpha)} = \sum_k E_k^o F_k^\dagger F_k + ib \sin k \,[F_{-k}^\dagger F_k^\dagger - F_k F_{-k}] \quad , \qquad (25)$$

where $E_k^o = \epsilon + 2b \cos k$.

It is to be understood that equation (25) represents four different quadratic forms, each with appropriate k values which depend upon N and α.

$H^{(\alpha)}$ can now be diagonalized by a Bogoliubov-Valatin transformation to new fermion operators $G_k^\dagger$ and G_k :

$$G_k = u_k^* F_k + v_k^* F_{-k}^\dagger ,$$

$$G_k^\dagger = u_k F_k^\dagger + v_k F_{-k} .$$

This transformation is canonical when

$$u_k v_{-k} + u_{-k} v_k = 0$$

and
$$|u_k|^2 + |v_k|^2 = 1 .$$

The inverse transformation is

$$F_k = u_k G_k + v_{-k}^* G_{-k}^\dagger$$

$$F_k^\dagger = u_k^* G_k^\dagger + v_{-k} G_{-k} .$$

$H^{(\alpha)}$ is reduced to diagonal form when

$$u_k(E_k^o - E_k) - 2ib \sin k\, v_k = 0$$

$$2ib \sin k\, u_k + (E_k^o + E_k) v_k = 0 .$$

Solutions are

$$E_k = [(E_k^o)^2 + 4b^2\sin^2 k]^{\frac{1}{2}}$$

$$= [\epsilon^2 + 4b^2 + 4\epsilon b \cos k]^{\frac{1}{2}} \qquad (26a)$$

and

$$u_k = \frac{2ib \sin k}{\sqrt{2E_k(E_k - E_k^o)}} \qquad (26b)$$

$$v_k = \sqrt{\frac{E_k - E_k^o}{2E_k}} \ . \qquad (26c)$$

Positive square roots are taken throughout. Under this transformation equation (25) becomes

$$H^{(\alpha)} = E_{vac} + \sum_k E_k G_k^\dagger G_k \ ,$$

where

$$E_{vac} = -\tfrac{1}{2}\sum_k (E_k - E_k^o) \ .$$

The eigenstates of the hamiltonian, equation (23), are (only) the odd eigenstates of $H^{(1)}$ and (only) the even eigenstates of $H^{(2)}$. The parity operator, $(-1)^{\sigma}$, anticommutes with a single f_n or $f_n^{\dagger}$, and therefore anticommutes with any $G_k^{\dagger}$. Thus, the parity of any eigenstate of $H^{(\alpha)}$ with an odd number of $G_k^{\dagger}$ excitations will be opposite to that of the corresponding G_k vacuum, while states with an even number of excitations will have the same parity as the vacuum. The parities of the G_k vacuum states are determined below for the several special cases that can occur.

Let $|0>$ be the vacuum state of the F_k; i.e., $F_k|0> = 0$ for all k. This is an even state. Consider the normalized state

$$|\Phi> = \prod_{0<k<\pi} (\overset{*}{u}_k + \overset{*}{v}_k F_{-k}^{\dagger} F_k^{\dagger})|0> \quad . \quad (27)$$

Then

$$G_k|\Phi> = 0, \text{ for } k \neq 0, \pi \quad .$$

For N even and $\alpha = 2$, k is never 0 or π; thus $|\Phi>$ is the G_k vacuum in this case. Since $|\Phi>$ is an even state, it is an eigenstate of the hamiltonian for even N.

Next, consider N odd and $\alpha = 2$ so that $0 < |k| \leq \pi$. Here,

$$E_{\pi} = |E^{o}_{\pi}| = |\epsilon - 2b| \quad .$$

If $\epsilon - 2b > 0$, we see from equations(26b) and (26c) that $v_{\pi} = 0$, $u_{\pi} = i$. Thus, for $\epsilon - 2b > 0$, $G_{\pi} = -iF_{\pi}$, and $G_k |\Phi> = 0$ for all k, whence $|\Phi>$ is again the vacuum. If, however, $\epsilon - 2b < 0$, $u_{\pi} = 0$, $v_{\pi} = 1$, so that $F^{\dagger}_{\pi} |\Phi>$ is the vacuum of $H^{(2)}$ for even N. The state $F^{\dagger}_{\pi} |\Phi>$ is an odd eigenstate of $H^{(2)}$, and therefore not an acceptable eigenstate of the hamiltonian H.

Similar arguments can be used to determine the vacuum states in the other cases. The results are summarized in Table 5. Also given in Table 5 are the eigenstates of the physical hamiltonian, H, associated with each vacuum. These are obtained by selecting the odd eigenstates of $H^{(1)}$ and the even eigenstates of $H^{(2)}$.

In the limit of large N, the differences between the vacuum eigenvalues of $H^{(\alpha)}$ go to zero like 1/N, and the spectra of $H^{(1)}$ and $H^{(2)}$ become identical. It is for this limit that we now discuss the spectrum of the hamiltonian equation (23), for the various ranges of

Table 3: Eigenstates of the intramolecular charge resonance hamiltonian

α	N	Range of k	Vacuum State	Parity of Vacuum	States of $\mathcal{H}$
1	even	$0 \leq \lvert k \rvert \leq \pi$	$\lvert\Phi\rangle$ if $\epsilon + 2b > 0$ and $\epsilon - 2b > 0$	even	$G_k^\dagger \lvert\Phi\rangle$, $G_{k''}^\dagger G_{k'}^\dagger G_k^\dagger \lvert\Phi\rangle$, etc.
			$F_\pi^\dagger \lvert\Phi\rangle$ if $\epsilon + 2b > 0$ and $\epsilon - 2b < 0$	odd	$F_\pi^\dagger \lvert\Phi\rangle$, $G_k^\dagger G_{k'}^\dagger F_\pi^\dagger \lvert\Phi\rangle$, etc.
			$F_0^\dagger \lvert\Phi\rangle$ if $\epsilon + 2b < 0$ and $\epsilon - 2b > 0$	odd	$F_0^\dagger \lvert\Phi\rangle$, $G_k^\dagger G_{k'}^\dagger F_0^\dagger \lvert\Phi\rangle$, etc.
			$F_0^\dagger F_\pi^\dagger \lvert\Phi\rangle$ if $\epsilon + 2b < 0$ and $\epsilon - 2b < 0$	even	$G_k^\dagger F_0^\dagger F_\pi^\dagger \lvert\Phi\rangle$, $G_{k''}^\dagger G_{k'}^\dagger G_k^\dagger F_0^\dagger F_\pi^\dagger \lvert\Phi\rangle$, etc.
1	odd	$0 \leq \lvert k \rvert < \pi$	$\lvert\Phi\rangle$ if $\epsilon + 2b > 0$	even	$G_k^\dagger \lvert\Phi\rangle$, $G_{k''}^\dagger G_{k'}^\dagger G_k^\dagger \lvert\Phi\rangle$, etc.
			$F_0^\dagger \lvert\Phi\rangle$ if $\epsilon + 2b < 0$	odd	$F_0^\dagger \lvert\Phi\rangle$, $G_{k'}^\dagger G_k^\dagger F_0^\dagger \lvert\Phi\rangle$, etc.
2	even	$0 < \lvert k \rvert < \pi$	$\lvert\Phi\rangle$	even	$\lvert\Phi\rangle$, $G_{k'}^\dagger G_k^\dagger \lvert\Phi\rangle$, etc.
2	odd	$0 < \lvert k \rvert \leq \pi$	$\lvert\Phi\rangle$ if $\epsilon - 2b > 0$	even	$\lvert\Phi\rangle$, $G_{k'}^\dagger G_k^\dagger \lvert\Phi\rangle$, etc.
			$F_\pi^\dagger \lvert\Phi\rangle$ if $\epsilon - 2b < 0$	odd	$G_k^\dagger F_\pi^\dagger \lvert\Phi\rangle$, $G_{k''}^\dagger G_{k'}^\dagger G_k^\dagger F_\pi^\dagger \lvert\Phi\rangle$, etc.

the physical parameters ε and b. Without loss of generality we may take $\varepsilon \gtrsim 0$.

When the molecular excitation energy is greater than twice the charge resonance coupling, $\varepsilon > 2|b|$, the ground state of the hamiltonian is $|\Phi>$ for both even and odd N, and is non-degenerate. The excitation energy to the bottom of the first exciton band is $\varepsilon - 2|b|$, and the width of the first band is $4|b|$. When $\varepsilon >> 2|b|$ we get the usual dispersion (van der Waals) stabilization of the crystal ground state, and the results reduce to the familiar singlet exciton theory of Davydov. As $|b|$ increases and approaches $\varepsilon/2$, the gap to the bottom of the first band approaches zero; the ground state becomes doubly degenerate at $\varepsilon = 2|b|$. A sketch of the exciton band, for large N, when $\varepsilon = 2|b|$, is given in Figure 3. A crystal having molecular chains with an excitation spectrum of this form would obviously show unusual thermodynamic, transport, and optical properties.

Even more unusual physical properties are predicted for $\varepsilon < 2|b|$. Here, for all cases, all eigenstates of the hamiltonian are (at least) two-fold degenerate. Associated with this degeneracy is an electronic ferroelectric - or antiferroelectric - type polarization. The characteristics of the spectra obtained in this range can be predicted for $\varepsilon = 0$ by observing that the hamiltonian is then equivalent to the one-dimensional Ising hamiltonian. In this representation, the electronic state $(\varphi_n + \varphi_n')/\sqrt{2}$ corresponds to "spin up", and $(\varphi_n - \varphi_n')/\sqrt{2}$ to "spin down". When $b < 0$, the ground state is evidently ferroelectric; the two-fold degeneracy can be understood as corresponding to the two possible directions of the ferroelectric electronic polarization. The gap separating the ground state from the first band is $4|b| - 2\varepsilon$ (in the limit of $\varepsilon = 0$, we observe that the energy of an elementary excitation, $4|b|$, is the energy required to reverse the direction of a single molecular electronic moment in the ferroelectric ground state). The exciton band width is 2ε.

For $2b > \varepsilon \geq 0$, the degeneracy and excitation spectrum can be easily understood in terms of the antiferroelectric linear chain. When N is odd, and $\varepsilon = 0$, the ground state is 2N-fold degenerate (as are all excited states). When $\varepsilon \neq 0$ these degenerate states split into bands, each member of which remains doubly degenerate. The gap is zero in this case. The width of each band is 2ϵ, and the separation between bands is $4b-2\epsilon$.

When $2b > \epsilon \geq 0$ and N is even, the (doubly degenerate, antiferroelectric) ground state is separated from the first band by a gap of $4b-2\epsilon$; the band width is again 2ϵ. In the range $\epsilon < 2|b|$ the crystal excitations may be thought of as running waves of electrical polarization.

At present it is not certain what particular molecular crystals may exhibit strong charge resonance coupling, especially in the interesting region $|2b| > \epsilon$. Rough calculations indicate that such strong interactions may well be found in crystals of large dye-like molecules, such as the example given above, and perhaps even in molecular aggregates that play a role in photosynthesis or other biological phenomena.

Chapter VI - Intermolecular Charge Transfer

Intermolecular charge transfer between aromatic donor molecules, D, and acceptor molecules, A, in one-to-one DA complexes in solution has been widely studied.(35) Molecular crystals of D and A molecules are also known, and X-ray studies show that many of these crystals contain regular linear chains of alternating D and A molecules in a tilted face-to-face arrangement. These linear chains may be represented schematically,

--- DADADA----- .

In a DA chain one may anticipate a cooperative intermolecular charge transfer. That is, if there is, say, "10%" charge transfer from D to A in a particular isolated 1:1 DA complex, then the extent of this charge transfer may be significantly greater than "10%" in the chain, since the <u>neighbors</u> of any given DA pair have average charges that decrease the effective excitation energy of the given DA pair to the ionized state, D^+A^-. Indeed, in some molecular crystals this charge transfer may be so extensive as to yield almost fully ionic chains, ---$D^+A^-D^+A^-$------ , even through the corresponding isolated 1:1 DA complexes are not fully ionic.

In many cases the problem of intermolecular charge transfer in a DA chain can be considered to be an "N-electron problem". That is, in an N-molecule chain (N/2 molecules of A, and N/2 molecules of D) one may for convenience consider only two kinds of molecular orbitals: (1) the doubly-occupied, highest-energy non-degenerate orbital of an isolated D molecule in its electronic ground state, and (2) the lowest-energy unoccupied non-degenerate orbital of an isolated A molecule in its electronic ground state. The state D^+A^- of a given DA pair has one electron in the molecular orbital on D and one electron in the molecular orbital on A.

In the present work intermolecular electron spin exchange is neglected. Also, the method of fermion operators used below cannot handle the spin degeneracy for the N-electron problem where both D^+ and A^- have spin $S = \frac{1}{2}$. Because of this difficulty we only consider spin states where the spin on D^+ is always "up" ($S = \frac{1}{2}$, $S_z = \frac{1}{2}$) and the spin on A^- is always "down" ($S = \frac{1}{2}$,

$S_z = -\frac{1}{2}$). Thus, there are two approximations used here in this N-electron problem: a <u>dynamical</u> approximation in which intermolecular electron spin exchange is neglected, and a <u>statistical</u> approximation in which only a subset of all possible spin states are considered. Although these approximations obviously falsify the magnetic properties of the system, it does appear that the essential features of the interactions that lead to molecular ionization and intermolecular charge resonance are retained in the calculation.

We also consider an "N/2-electron problem", corresponding to a lattice of N orbitals, and N/2 electrons. It is known, for example, that certain ionic free radicals based on the acceptor A = TCNQ with the stochiometry $X^+A_2^-$ are built up from linear chains of A molecules with some (unknown) negative charge distributions such that there are N/2 electrons on N molecules in the chain.(36) In our theoretical discussion we assume that the chain is regular; i.e., all nearest neighbor AA^- distances in the chain direction are the same. (This may very well <u>not</u> be the case in the known TCNQ ion radical salts.) In the N/2-electron problem transitions to doubly charged molecules such as

$A^{=}$ are neglected, so no statistical approximation of the type required above for the N-electron problem is necessary. The dynamical approximation does remain, however, in this case. For clarity, we first develop the mathematical notation for the N-electron problem, and then show how it can be immediately applied to the N/2-electron problem.

We imagine a cyclic linear chain containing an even number of molecules. Let the molecules be labelled n = 1, 2, ... , N: odd values of n correspond to A molecules, and even values to D molecules. Let the state of the ---DADA--- chain in which all molecules are neutral be designated $|0>$. We define fermion creation and annihilation operators, analogous to those of the preceeding section, which here describe the charge states of the molecules: $f_n^\dagger$ creates a negative ion (A^-) on site n if n is odd, and creates a positive hole (D^+) on site n if n is even. For the present problem the excitation number

$$\sigma = \sum_{n=1}^{N} f_n^\dagger f_n$$

is always even, a result of the conservation of charge, and only even eigenstates of $(-1)^{\sigma}$ need be considered. The hamiltonian may be written

$$H = \varepsilon_D \sum_{n \text{ even}} f_n^{\dagger} f_n - \varepsilon_A \sum_{n \text{ odd}} f_n^{\dagger} f_n$$

$$+ \gamma \sum_{n=1,2,3\ldots}^{N-1} (f_n^{\dagger} f_{n+1}^{\dagger} + f_{n+1} f_n) - \gamma (f_N^{\dagger} f_1^{\dagger} + f_1 f_N) + H_{int}. \qquad (28)$$

Here ε_D is the ionization potential of a D molecule in a neutral DA chain; ε_A is the electron affinity $(\varepsilon_A > 0)$ of an A molecule in the chain; and γ is the matrix element:

$$< 0 \,|\, H_e \, f_n^{\dagger} f_{n+1}^{\dagger} \,|\, 0 > \quad ,$$

where H_e is the complete Schrödinger hamiltonian. γ is the fundamental intermolecular charge-resonance matrix element.

H_{int} represents the Coulomb interaction among the charges on ionized molecules, and is quartic in fermion operators. We shall use a "molecular field" or

Hartree-type approximation to H_{int}:

$$H_{int} = \sum_n \epsilon_1 \rho \, f_n^\dagger f_n$$

$$\rho = < \sigma >/N \quad . \tag{29}$$

In this approximation the charge on site n undergoes a Coulomb interaction with the average charge distribution in the whole three-dimensional crystal. This term thus includes long-range Coulomb forces both along an individual chain and between different chains.

Since

$$\sum_{n = 1,3,5\ldots} f_n^\dagger f_n = \sum_{n = 2,4,6\ldots} f_n^\dagger f_n = \tfrac{1}{2} \sum_{n = 1,2,3\ldots} f_n^\dagger f_n$$

in all the states under consideration, the hamiltonian in equation (28) may be written

$$H = \sum_{n=1}^{N} (\epsilon_0 + \epsilon_1 \rho) f_n^\dagger f_n + \gamma \sum_{n=1}^{N-1} (f_n^\dagger f_{n+1}^\dagger + f_{n+1} f_n)$$

$$- \gamma \, (f_N^\dagger f_1^\dagger + f_1 f_N) \quad , \tag{30}$$

where $\varepsilon_0 = \frac{1}{2}(\varepsilon_D - \varepsilon_A)$.

It is expected that the coefficient ε_1 is negative in nearly all cases of physical interest. If ε_1 is negative, we may take the quantity $\varepsilon_0 + \varepsilon_1 \rho$ to be positive without loss of generality, by interchanging the significance of f_n and $f_n^\dagger$ if necessary. That is, if the electron affinity of the acceptors is greater than the ionization potential of the donors in the DA chain, we take as the zeroth-order state $|0>$ the completely ionized state; the operator $f_n^\dagger$ then de-ionizes the nth molecule.

The hamiltonian given by equation (30) is also appropriate for the "N/2-electron problem". In this case, the state $|0>$ is taken to be that in which the odd-numbered molecules are uncharged and the even-numbered ones charged. The fermion operator $f_n^\dagger$ then produces a charge on the nth site if n is odd, and destroys one if n is even. Since the units of the chain are equivalent, $\varepsilon_A = \varepsilon_D$. As before, we represent H_{int} by the Coulomb interaction of each ion with the average charge distribution in the crystal. The charge transfer terms are unchanged. The hamiltonian takes the form

$$H = \epsilon_0(1-\rho)\sum_{n=1}^{N} f_n^\dagger f_n + \gamma \sum_{n=1}^{N-1} (f_n^\dagger f_{n+1}^\dagger + f_{n+1} f_n) \tag{31}$$

$$- \gamma\, (f_N^\dagger f_1^\dagger + f_1 f_N) \quad .$$

As before, we require that $\rho = 1/N < \sum_n f_n^\dagger f_n >$.

This expression for the hamiltonian is equivalent to equation (30) with $\epsilon_1 = - \epsilon_0$.

The diagonalization of the charge-transfer hamiltonian equation (30) follows closely the treatment of the charge-resonance problem in Chapter V. The quantity ρ is treated as a number during the diagonalization, and then the requirement is imposed that it be equal to the expectation value of $N^{-1}\sum f_n^\dagger f_n$ in the states obtained to ensure self-consistency. Fermion operators F_k and $F_k^\dagger$ of the form given by equation (24) are defined for

$$k = \pm \pi/N,\ \pm 3\pi/N,\ \ldots,\ \pm (N-1)\,\pi/N.$$

In terms of these operators, the hamiltonian is

$$H = \sum_k E^o F_k^\dagger F_k + i\gamma \sin k \, (F_{-k}^\dagger F_k^\dagger - F_k F_{-k}) \quad ,$$

where

$$E^o = \epsilon_0 + \epsilon_1 \rho \tag{32}$$

As before the hamiltonian is diagonal when expressed in terms of the fermion operators

$$G_k = \overset{*}{u}_k F_k + \overset{*}{v}_k F_{-k}^\dagger \quad .$$

The coefficients u_k and v_k are given by equation (26) where E_k^o is replaced by E^o and b is replaced by γ. The eigenenergies are

$$E_k = [(E^o)^2 + 4\gamma^2 \sin^2 k]^{\frac{1}{2}} \; .$$

The vacuum state of the hamiltonian is the state $|\Phi>$ given in equation (27). The desired eigenstates of the hamiltonian are obtained by the application of an even number of $G_k^\dagger$ operators to this ground state.

We now wish to impose the condition that the quantity ρ in equation (32) is consistent with equation (29). We observe that an arbitrary eigenstate $G^\dagger_{k_1} G^\dagger_{k_2} \ldots G^\dagger_{k_n} | \Phi >$ has an energy

$$E = E_{vac} + \sum_{k_1, k_2 \ldots} E_k ; \qquad (33a)$$

$$E_{vac} = \tfrac{1}{2} NE^o - \tfrac{1}{2} \sum_{all\ k} E_k . \qquad (33b)$$

The excitation density of such a state may be obtained most simply by application of the Hellman-Feynman theorem:

$$\rho = 1/N < \sum_n f^\dagger_n f_n > = 1/N < \partial H/\partial E^o > = 1/N \ \partial E/\partial E^o ,$$

from which

$$\rho = \rho_{vac} + 1/N \sum_{k_1, k_2, \ldots} E^o/E_k ; \qquad (34a)$$

$$\rho_{vac} = \tfrac{1}{2} - 1/2N \sum_{all\ k} E^o/E_k . \qquad (34b)$$

The problem of solving equations (33) and (34) simultaneously for an arbitrary eigenstate of the hamiltonian is difficult. We are primarily interested, however, in the state of lowest energy, which may or may not by the vacuum state $|\Phi>$. We show now that for $E^o > 0$ and $\epsilon_1 < 0$, the vacuum is indeed the ground state. Consider first a state with a fixed number of excitations. We differentiate its energy, given by equation (33), with respect to $\sin^2 k_i$, where k_i is the wave number of one of the excitations present, keeping ϵ_0, ϵ_1 and γ fixed. The result may be written

$$dE/d(\sin^2 k_i) = 2\gamma^2/E_{k_i}\left\{1 - \rho(E^o)^2/(E_{k_i})^2[2E^o/\epsilon_1 + 1 + 1/N \sum_{k_1,k_2,\ldots} (E^o)^3/(E_k)^3 - 2/N \sum_{\text{all } k} (E^o)^3/(E_k)^3]^{-1}\right\}.$$

For $E^o > 0$ and $\epsilon_1 < 0$, this is always positive. Therefore, of all states with a given number of excitations, the state with the excitations having the smallest possible values of $\sin^2 k$ will have the lowest energy.

We now consider the lowest energy state with μN excitations. The energy and excitation density of this state may be expressed, in the limit of large N, by the equation,

$$E = 2N\,|\gamma|\,[\lambda'/\lambda + 1/\pi\, E(\lambda)/\lambda - 2/\pi\, E(\lambda,\alpha)/\lambda] \quad ; \qquad (35)$$

$$\rho = \tfrac{1}{2} + 1/\pi\,\lambda'\,F(\lambda) - 2/\pi\,\lambda' F\,(\lambda,\alpha) \quad . \qquad (36)$$

Here $E(\lambda,\alpha)$ and $F(\lambda,\alpha)$ are incomplete elliptic integrals:

$$E(\lambda,\alpha) = \int_0^\alpha \sqrt{1 - \lambda^2 \sin^2\theta}\;\, d\theta \; ;$$

$$F(\lambda,\alpha) = \int_0^\alpha \frac{d\theta}{\sqrt{1 - \lambda^2 \sin^2\theta}} \quad ;$$

$$E(\lambda) \equiv E\,(\lambda, \pi/2) \quad ; \quad F(\lambda) \equiv F\,(\lambda, \pi/2) \; .$$

Their arguments are given by

$$\lambda^2 = 1 - \lambda'^2 = 4\gamma^2\,[(E^o)^2 + 4\gamma^2]^{-1} \; ; \qquad (37)$$

$$\alpha = (1 - \mu)\,\pi/2 \; .$$

To find the optimum number of excitations, μN, we seek the value of α for which E in equation (35) is a minimum.

The condition that E have an extremum may be put in the form

$$- \epsilon_0/\epsilon_1 = \lambda\lambda' E/2N |\gamma| + \rho\lambda'^2/(1 - \lambda^2 \sin^{-2}\alpha) + \tfrac{1}{2} \lambda^2 + 2\lambda^2\lambda'/\pi \frac{\sin\alpha \cos\alpha}{\sqrt{1 - \lambda^2 \sin^2 \alpha}} \quad . \tag{38}$$

Numerical investigations of equations (35), (36), and (37) show that the lowest value of E actually occurs for $\mu = 0$ for the values of ϵ_0 and ϵ_1 being considered. The ground state of the hamiltonian is the state with no excitations.

The energy E_{vac} and excitation density ρ_{vac} of the vacuum state are given by equations (33b) and (34b). Figures (4) and (5) show self-consistent values of the energy and excitation-density as a function of the parameter $|\gamma|/\epsilon_0$ for the particular case that $\epsilon_1/\epsilon_0 = - 1$. Such graphs are most simply constructed as follows:

E_{vac} and ρ_{vac} are written in terms of elliptic integrals with argument λ, as given by equation (37). Each value of λ determines a value of ρ. When this value of ρ is inserted in the expression for λ, the corresponding values of ϵ_1/ϵ_0 and $|\gamma|/\epsilon_0$ are easily obtained.

For the ranges of ϵ_0 and ϵ_1 under consideration, the ground-state excitation density ρ is always between zero and one-half, and increases monotonically with $|\gamma/\epsilon_0|$. The ground-state energy likewise becomes more and more negative as $|\gamma|$ increases. In general, these properties result from the occurrence of resonant excitation-deexcitation processes, intermolecular correlations, and the consequent binding of the ground state.

To find self-consistent solutions to equations for an arbitrary excited state would be a complicated task. It is not difficult, however, to understand the nature of the simplest elementary excitations above the ground electronic state. For this purpose we may assume that the density of (real, not virtual) excitations is so small that the average charge density on each molecule is essentially the same as in the ground state.

The excited states are then obtained by the application of pairs of operators $G_k^\dagger$, $G_k^\dagger$, on the ground state $| \Phi >$. These operators, being linear combinations of the $f_n^\dagger$ operators, produce a correlated change in the charge distribution of the system; that is, they introduce a transfer of charge. It is not difficult to isolate the particular combinations of the $G_k^\dagger$'s which correspond to the simplest current-carrying excitations. Consider the operators

$$A_k^\dagger \equiv \frac{1}{\sqrt{2}} \left(G_k^\dagger + G_{k-\pi}^\dagger \right) \qquad \pi \geq k \geq 0$$

$$= \frac{1}{\sqrt{2}} \left[\overset{*}{u}_k \sum_{n \text{ odd}} e^{-ikn} f_n^\dagger + \overset{*}{v}_k \sum_{n \text{ even}} e^{-ikn} f_n \right]$$

and

$$D_k^\dagger \equiv \frac{1}{\sqrt{2}} \left(G_k^\dagger - G_{k-\pi}^\dagger \right) \qquad \pi \geq k \geq 0$$

$$= \frac{1}{\sqrt{2}} \left[\overset{*}{u}_k \sum_{n \text{ even}} e^{-ikn} f_n^\dagger + \overset{*}{v}_k \sum_{n \text{ odd}} e^{-ikn} f_n \right] .$$

$A_k^\dagger$ ionizes the A molecules and de-ionizes the D molecules; $D_k^\dagger$ has the opposite effect. The operator representing the total charge on the chain can be written as

$$\hat{q} = - \sum_n (-1)^n f_n^\dagger f_n \quad .$$

whence

$$[\hat{q}, A_k^\dagger]_- = - A_k^\dagger$$

and

$$[\hat{q}, D_k^\dagger]_- = \quad D_k^\dagger \quad .$$

Thus, $A_k^\dagger$ decreases the net charge on the chain by one unit, and $D_k^\dagger$ increases it by the same amount.

Since the excitation energy $E_k = E_{k - \pi}$, we can write the hamiltonian as

$$H = E_{vac} + \sum_{k \geq 0} E_k \, (A_k^\dagger A_k + D_k^\dagger D_k)$$

The simplest current-carrying states of the chain can be written

$$A_{k'}^\dagger \, D_k^\dagger \, | \Phi >, \; A_{k'''}^\dagger \, A_{k''}^\dagger \, D_{k'}^\dagger \, D_k^\dagger \, | \Phi >, \text{ etc.}$$

The states chosen are those with the same charge as $|\Phi>$. The state $A_{k'}^{\dagger}, D_k^{\dagger}|\Phi>$, for example, contains running waves of negative and positive charge, with momenta 2k' and 2k respectively. Each running wave carries unit charge. The dispersion relation for <u>each</u> charge carrying excitation is simply E_k, and the charge carrier band width is

$$\sqrt{(E^0)^2 + 4\gamma^2} - |E^0| .$$

According to the present calculation, there is always a finite energy gap for excitation to the charge-carrying states, even in the special case where $\rho = \frac{1}{2}$. This is especially noteworthy for the N/2-electron problem, where, in the conventional band approximation, one expects metallic behaviour for a regular linear chain.

Appendix A: Canonical Transformations of Fermi or Bose Operators

Given a set of operators satisfying the commutation relations

A1) $$[B_i, B_j]_\pm = 0 \, , \qquad [B_i, B_j^\dagger]_\pm = \delta_{ij} \, .$$

A2) The transformation $B_\rho = \sum_i (\overset{*}{u}_{\rho i} B_i \pm \overset{*}{v}_{\rho i} B_i^\dagger)$

has an inverse if

A3) $$\sum_\rho (u_{\rho i} \overset{*}{v}_{\rho j} \pm \overset{*}{v}_{\rho i} u_{\rho j}) = 0 \quad ,$$

A4) $$\sum_\rho (u_{\rho i} \overset{*}{u}_{\rho j} \pm \overset{*}{v}_{\rho i} v_{\rho j}) = \delta_{ij} \quad .$$

Proof: From equation (A2),

$$u_{\rho i} B_\rho + \overset{*}{v}_{\rho i} B_\rho^\dagger = \sum_j (u_{\rho i} \overset{*}{u}_{\rho j} \pm \overset{*}{v}_{\rho i} v_{\rho j}) \, B_j$$

$$+ \sum_j (\overset{*}{v}_{\rho i} u_{\rho j} \pm u_{\rho i} \overset{*}{v}_{\rho j}) \, B_j^\dagger \quad .$$

Equations (A3) and (A4) then imply

A5) $$B_i = \sum_\rho (u_{\rho i} B_\rho + \overset{*}{v}_{\rho i} B^\dagger_\rho) \quad .$$

A6) If furthermore $\sum_i (u_{\rho i} v_{\sigma i} \pm u_{\sigma i} v_{\rho i}) = 0$,

A7) $$\sum_i (u_{\rho i} \overset{*}{u}_{\sigma i} \pm v_{\rho i} \overset{*}{v}_{\sigma i}) = \delta_{\rho\sigma} \quad ,$$

the transformation is canonical, i.e.

A8) $$[B_\rho, B_\sigma]_\pm = 0; \quad [B_\rho, B_\sigma] = \delta_{\rho\sigma} \quad .$$

Proof: Equation (A2) with (A1) implies

$[B_\rho, B_\sigma]_\pm = \sum_{ij} (\overset{*}{v}_{\rho i} \overset{*}{u}_{\sigma j} \pm \overset{*}{u}_{\rho i} \overset{*}{v}_{\sigma j}) \delta_{ij} = 0$ by (A6);

$[B_\rho, B^\dagger_\sigma]_\pm = \sum_{ij} (\overset{*}{u}_{\rho i} u_{\sigma j} \pm \overset{*}{v}_{\rho i} v_{\sigma j}) \delta_{ij} = \delta_{\rho\sigma}$ by (A7).

The following converse may be stated: If the transformation (A2) has an inverse and is canonical, then equations (A3), (A4), (A6), (A7) are satisfied.

Proof: We write the inverse as

$$B_i = \sum_\rho (\alpha_{\rho i} B_\rho + \beta_{\rho i} B^\dagger_\rho) .$$

Using equations (A1) and (A8),

A9) $$[B_i, B_\rho]_\pm = \sum_\sigma \beta_{\sigma i} [B^\dagger_\sigma, B_\rho]_\pm + \alpha_{\sigma i} [B_\sigma, B_\rho]_\pm$$

$$= \sum_j \overset{*}{u}_{\rho j} [B_i, B_j]_\pm \pm \overset{*}{v}_{\rho j} [B_i, B^\dagger_j]_\pm$$

or

$$\beta_{\rho i} = \overset{*}{v}_{\rho i} .$$

A10) Similarly $[B_i, B^\dagger_\rho]_\pm = \alpha_{\rho i} = u_{\rho i}$.

Equation (A5) follows.

Equations (A3, 4, 6, 7) are obtained by direct substitution of (A5) in (A1) and (A2) in (A8).

Appendix B: Diagonalization of Hermitian Quadratic Forms

Any Hermitian quadratic form in Fermi or Bose operators may be written

B1) $$F = F_o + \sum_{ij} A_{ij}\, B_i^\dagger B_j + \sum_{ij} C_{ij}\, B_i B_j + \sum_{ij} C_{ij}^*\, B_j^\dagger B_i^\dagger ,$$

where $F_o = F_o^*$; $A_{ij} = A_{ji}^*$; $C_{ij} \pm C_{ji} = 0$.

The canonical transformation $B_i = \sum_\rho (u_{\rho i} B_\rho + v^*_{\rho i} B^\dagger_\rho)$,

B2) with the conditions $$E_\rho u_{\rho i} = \sum_j A_{ij} u_{\rho j} + 2\sum_j C^*_{ji} v_{\rho j} ,$$

B3) $$-E_\rho v_{\rho i} = \sum_j A^*_{ij} v_{\rho j} + 2\sum_j C_{ji} u_{\rho j} ,$$

diagonalizes F:

B4) $$F = F_o - \sum_{\rho,i} E_\rho\, |v_{\rho i}|^2 + \sum_\rho E_\rho B^\dagger_\rho B_\rho .$$

Proof: Using the identity

$$[XY,Z]_- = X[Y,Z]_\pm \mp [X,Z]_\pm Y ,$$

and equations (A9) and (A10), we may evaluate

$$[F, B_\rho^\dagger]_- = \sum_i B_i^\dagger [\sum_j (A_{ij} u_{\rho j} \mp 2\, C_{ij}^* \, v_{\rho j})]$$

$$+ \sum_i B_i \, [\sum_j (\pm A_{ij}^* v_{\rho j} + 2\, C_{ij} u_{\rho j})] \quad .$$

Then, by virtue of equations (B2) and (B3),

$$[F, B_\rho^\dagger]_- = E_\rho \sum_i (u_{\rho i} B_i^\dagger \pm v_{\rho i} B_i) = E_\rho B_\rho^\dagger \quad .$$

It follows that F may be written

$$F = \sum_\rho E_\rho B_\rho^\dagger B_\rho + \text{constant.}$$

The constant is simply the expectation value of F in the vacuum state of the operators $B_\rho^\dagger$:

$$< F > = F_o + \sum_{\rho, i, j} A_{ij} v_{\rho i} \overset{*}{v}_{\rho j} + \sum_{\rho, i, j} C_{ij} u_{\rho i} \overset{*}{v}_{\rho j}$$

$$+ \sum_{\rho, i, j} C_{ij}^* v_{\rho j} \overset{*}{u}_{\rho i} \quad .$$

We multiply equation (B3) by $\overset{*}{v}_{\rho i}$, sum over i, and add the result to its complex conjugate. A simple rearrangement of indices yields

$$- 2E_\rho \sum_i |v_{\rho i}|^2 = 2 \sum_{i,j} (A_{ij} v_{\rho i} \overset{*}{v}_{\rho j} + C_{ij} u_{\rho i} \overset{*}{v}_{\rho j}$$

$$+ C^*_{ij} v_{\rho j} \overset{*}{u}_{\rho i}) \quad ,$$

so that

$$F = F_o - \sum_{\rho, i} E_\rho |v_{\rho i}|^2 + \sum_\rho E_\rho B^\dagger_\rho B_\rho \quad , \qquad \text{q.e.d.}$$

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Legends to Figures

Figure 1. Projection of the room-temperature structure of Wurster's blue perchlorate, taken from the unpublished manuscript of J. D. Turner and A. C. Albrecht with their kind permission.

Figure 2. Ground-state energy of the linear antiferromagnet vs the ratio of coupling strengths J'/J, as calculated by Bulaevskii (dashed line) and the present work (solid line). The exact value at $J'/J = 1$ is due to Orbach.

Figure 3. Dispersion curve for elementary excitation energies of the intramolecular charge-resonance system, when $\varepsilon = 2|b|$. The energy gap vanishes for $k = 0$.

Figure 4. Ground-state energy of the intramolecular charge-transfer hamiltonian vs $|\gamma|/\varepsilon_0$ for $\varepsilon_0 = -\varepsilon_1 > 0$.

Figure 5. Excitation density in ground state vs $|\gamma|/\varepsilon_0$ for $\varepsilon_0 = -\varepsilon_1 > 0$.

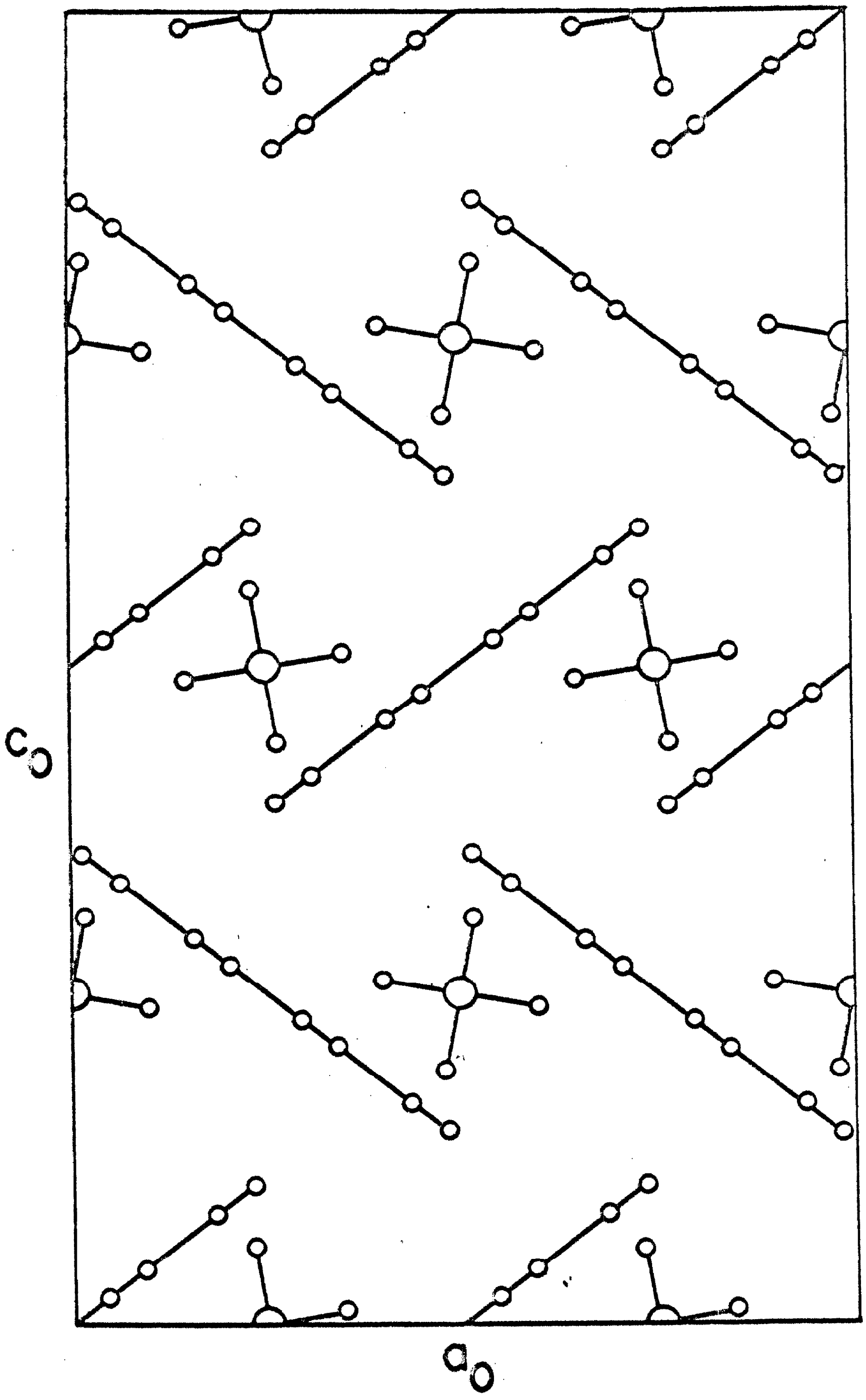

Figure 1

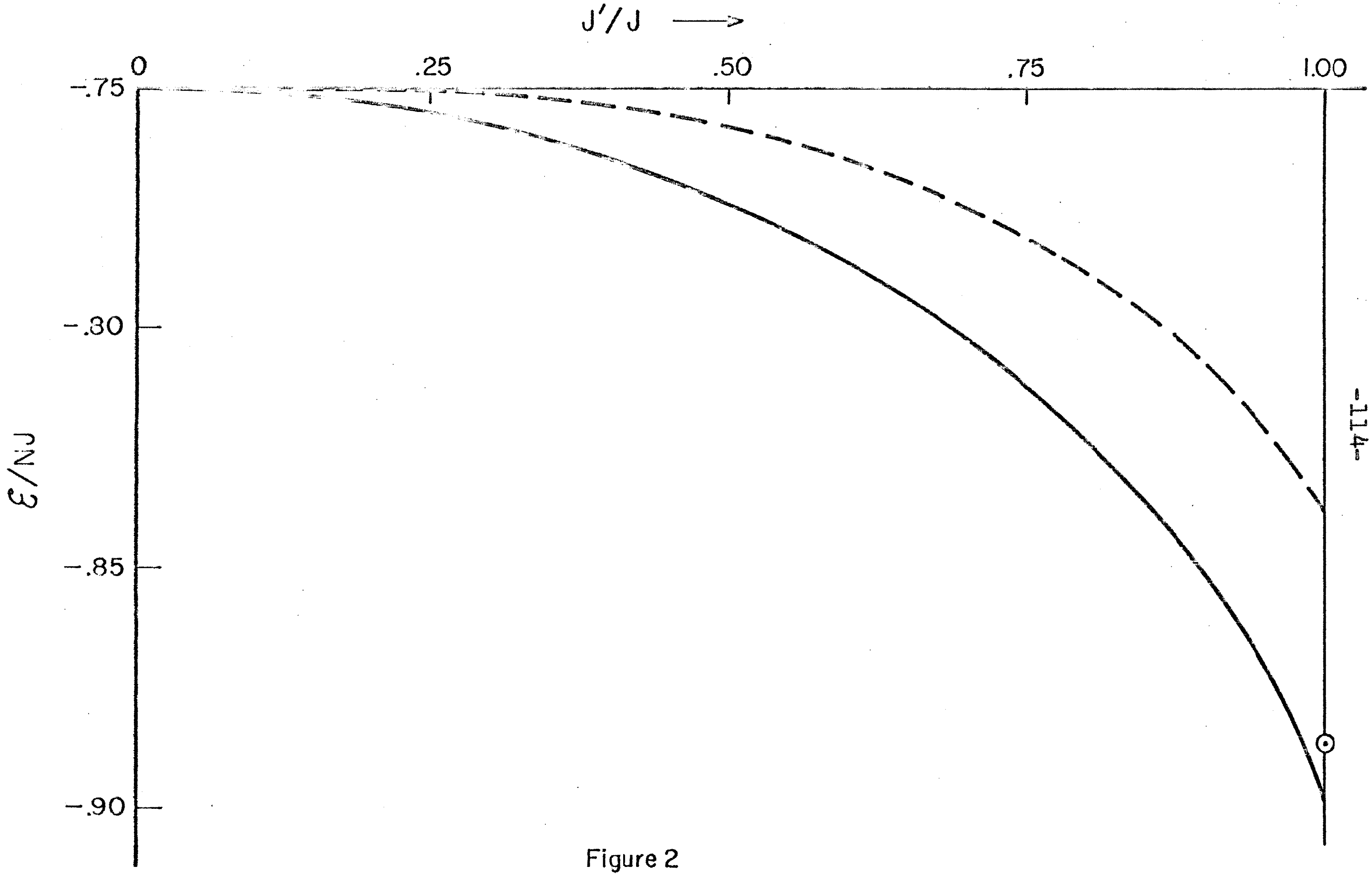

Figure 2

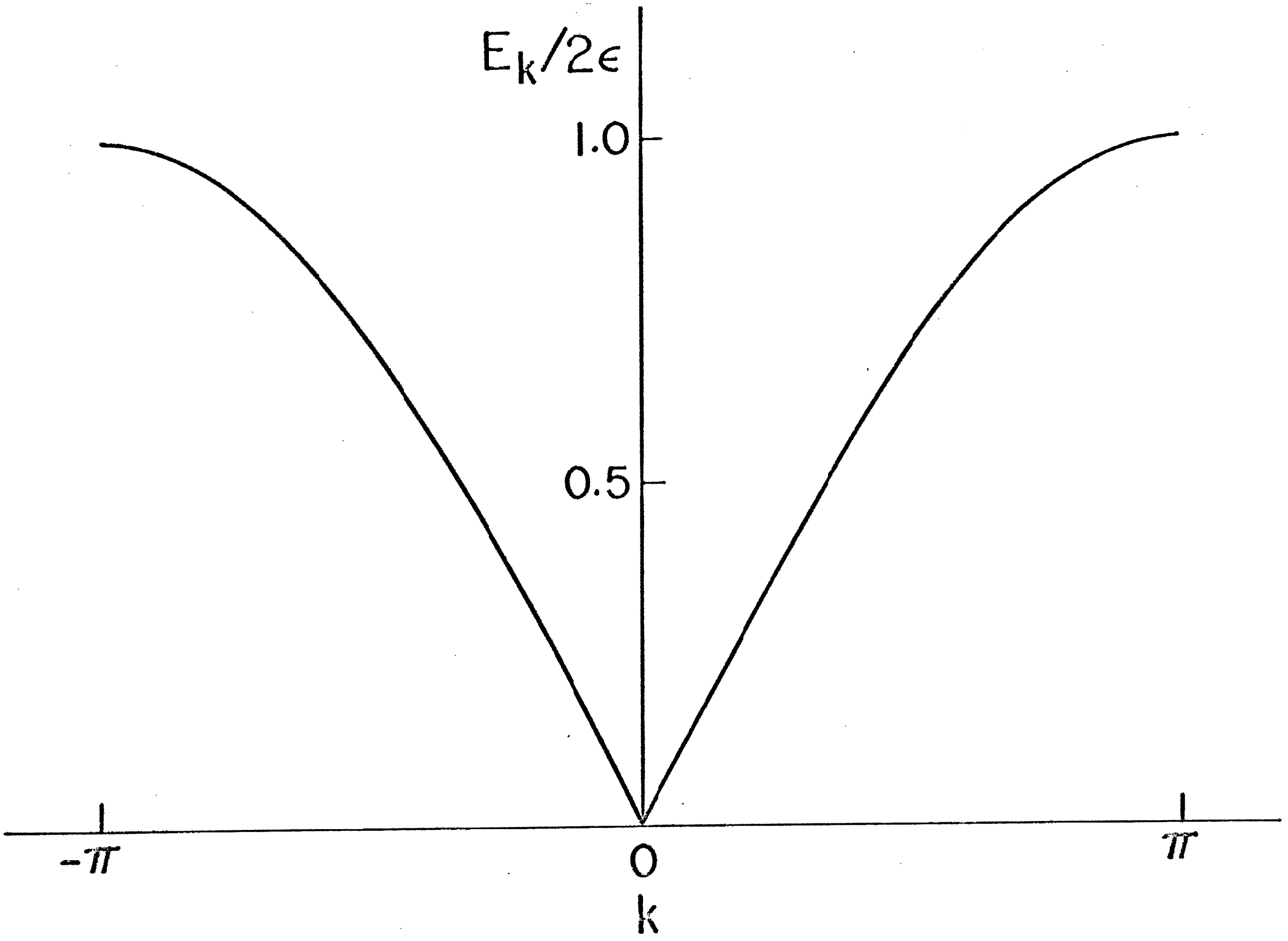

Figure 3

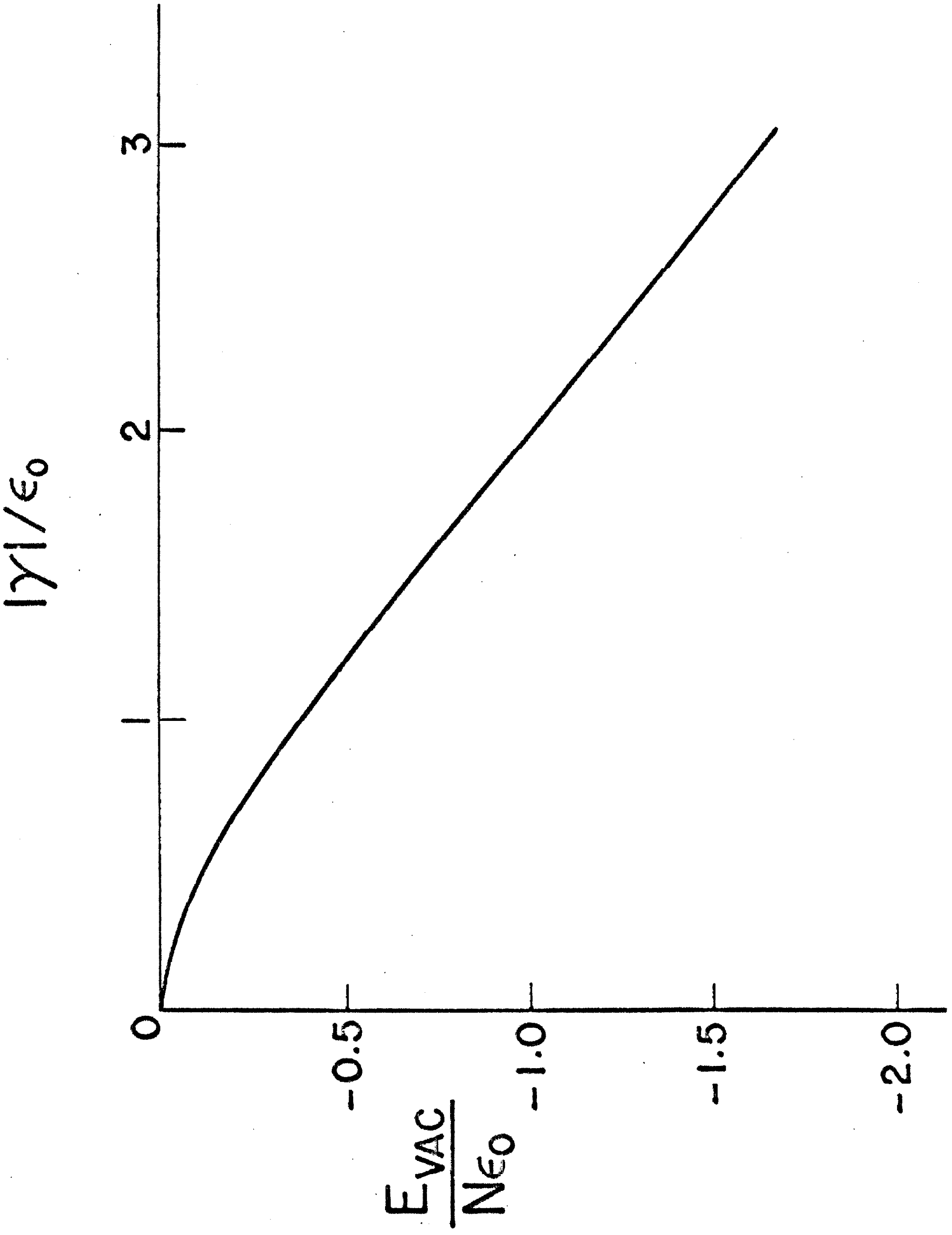

Figure 4

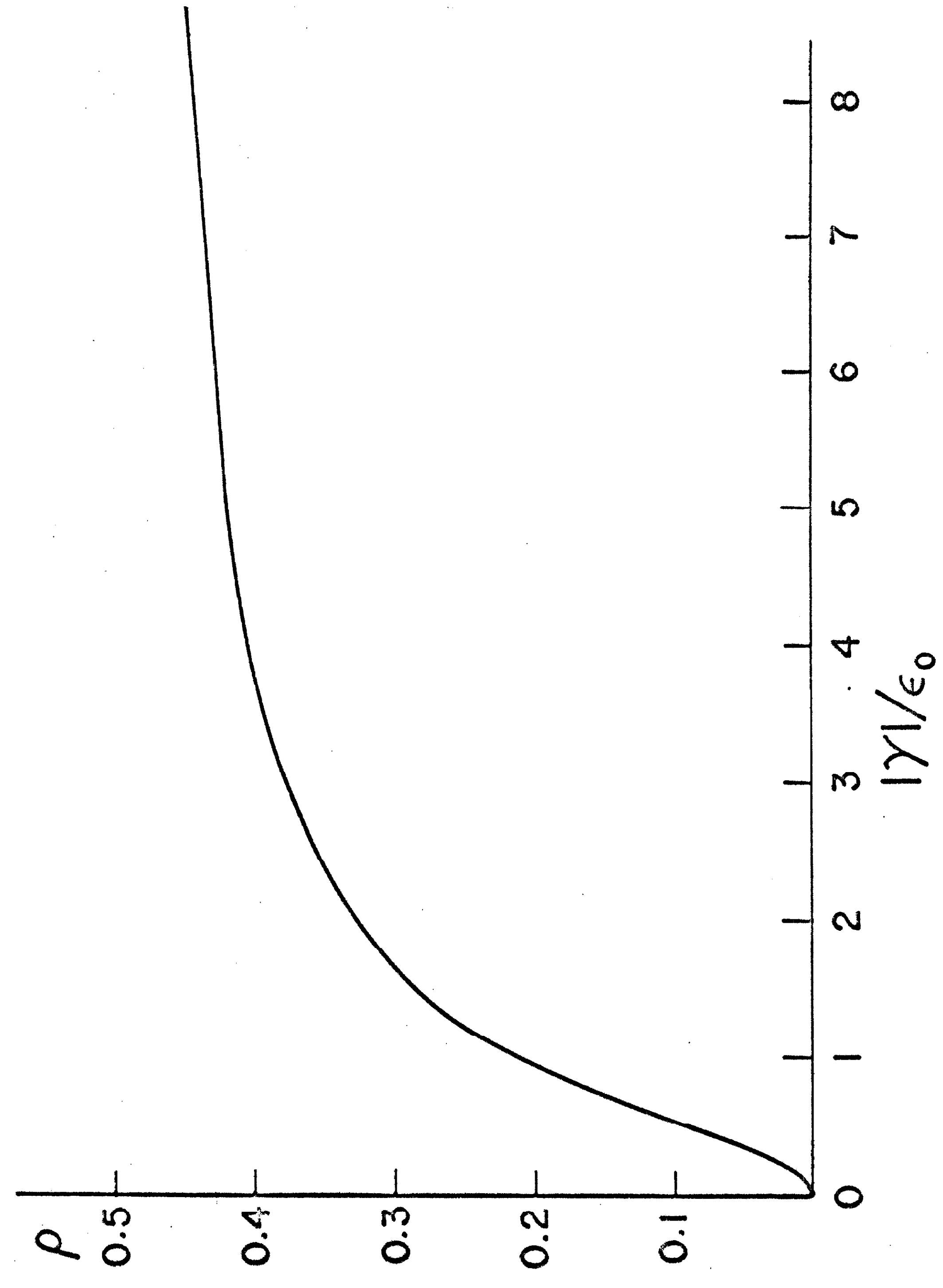

Figure 5