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THEORY OF NON-UNIFORM ANTIFERROMAGNETIC SPIN CHAINS

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A linear system of spins with antiferromagnetic interaction between nearest neighbors is considered, the interaction constants between each spin and its left and right neighbors being different. A system with such a non-uniform interaction may serve as a model for π-electrons of linear molecules with alternating bonds. The transformation of spin operators to operators of the Fermi type and the Hartree-Fock approximation are used. It is shown that in a system with non-uniform interaction an excitation gap exists for any number of spins. In a linear chain the gap disappears only in the case of uniform exchange interaction of an infinite number of spins. The method of calculation can be extended to more complex structures.

IN the preceding paper [1] a linear chain of spins having the same exchange interaction for all neighboring pairs of spins was investigated. It was pointed out that such a system could serve as a model for long molecules with conjugated bonds. Ginzburg and Faĭn [2] raised the question of the character of the excitation spectrum for a linear system of spins of a more complicated type.

In the present paper we consider a chain of spins $s = 1/2$, shown schematically in Fig. 1, in which the circles represent the positions of the spins and the dashes the interactions between them. This chain consists of N links, two spins per link; within the link the spins interact with constant J_1; the interaction between the nearest spins of neighboring links is specified by the constant J_2. The Hamiltonian of the system has the form

$$\mathcal{H} = \sum_{j=1}^{N} J_1 \left(\mathbf{S}_{j1}\mathbf{S}_{j2} - \tfrac{1}{4}\right) + J_2 \left(\mathbf{S}_{j2}\mathbf{S}_{j+1,1} - \tfrac{1}{4}\right), \qquad (1)$$

where S_{j1} is the operator of the first spin of the j-th link and S_{j2} is the operator for the second spin of the same link.

According to Bogolyubov, [3] a spin exchange Hamiltonian can be written down for a system of electrons interacting with ions and among themselves, with the following restrictions:

a) the many-electron wave function is made up only of atomic wave functions of the valence electron φ_f, where the atomic wave function φ_f corresponds to the lowest energy state of the valence electron;

b) if the expansion is over the smallness parameter $\epsilon \approx \varphi_{f_1}\varphi_{f_2}$ with $f_1 \neq f_2$ (the product of the wave functions enters in integrals of the Coulomb, exchange, and overlap types, etc.), then higher order terms in ϵ, beginning with ϵ^4, are neglected.

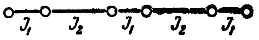

FIG. 1

In order to obtain the Hamiltonian (1), it is necessary to make still another approximation, namely to neglect all integrals with atomic wave functions φ_{f_1} and φ_{f_2} for which $|f_1 - f_2| \geq 2$. If it is necessary to keep integrals with $|f_1 - f_2| \leq n$, then the interactions between each spin and its n neighbors must be taken into account in the spin exchange Hamiltonian.

From what has been said, it is clear that the Hamiltonian (1) with the assumptions mentioned describes π-electrons in linear and cyclic polyene molecules with alternating bonds, if one takes as the atomic wave function φ_f the appropriate linear combination of s- and p-orbitals of the carbon atoms.

Polyene molecules with alternating bonds have been considered by Longuet-Higgins and Salem [4] and by Ooshika [5] using the linear combination of atomic orbital-molecular orbital (LCAO-MO) method.

In the Hamiltonian (1) it is convenient to change to dimensionless parameters by exchanging J_1 by unity (thus expressing all energy magnitudes in units of J_1) and J_2 by the quantity $\gamma = J_2/J_1$ which characterizes the non-uniformity of the exchange interaction. For $\gamma = 1$, the system is completely uniform, and one can introduce the period of the chain, which is half as great as in the case $0 \leq \gamma < 1$.

It was shown in [1] that in a system with uniform interaction, the gap $\epsilon_{\min}$ between the ground state of the system (total spin S = 0) and the first excited state with S = 1 decreases with increasing number of spins according to the law $\epsilon_{\min} \approx 1/N$ and disappears in the limit of infinite N. In the investigation the spin operators were transformed to operators of the Fermi type, and the resulting Hamiltonian with four-Fermion interaction was solved in the Hartree-Fock approximation. In the present paper the same method is used, and it is shown that the gap $\epsilon_{\min}$ of order $1 - \gamma$ remains for arbitrary N.

1. TRANSFORMATION OF THE SPIN HAMILTONIAN

For spins s = 1/2 the Fermi operators ψ_{j1}^{-}, ψ_{j2}^{-} and their Hermitian conjugate operators ψ_{j1}^{+} and ψ_{j2}^{+} can be introduced:

$$\psi_{j1}^{\pm} = (2)^{2j-2} S_{11}^z S_{12}^z \ldots S_{j-1,1}^z\, S_{j-1,2}^z\, S_{j1}^{\pm},$$

$$\psi_{j2}^{\pm} = (2)^{2j-1} S_{11}^z S_{12}^z \ldots S_{j-1,1}^z\, S_{j-1,2}^z\, S_{j1}^z S_{j2}^{\pm}, \qquad (2)$$

where $S^{\pm} = S^x \pm iS^y$. [1)]

We introduce a momentum k characterizing the distribution of field over the chain and analogous to the wave momentum of electrons in crystals. From the periodicity conditions $\psi_{j1} = \psi_{j+N,1}$ and $\psi_{j2} = \psi_{j+N,2}$, it follows that $k = 2\pi n/N$, n = 1, 2, . . . , N. The transition to the momentum representation

$$\psi_{j1} = \frac{1}{\sqrt{N}} \sum_k a_k e^{-ikj}, \qquad \psi_{j2} = \frac{1}{\sqrt{N}} \sum_k b_k e^{-ikj} \qquad (3)$$

together with the canonical transformation

$$a_k = 2^{-1/2} (\alpha_k + \beta_k)\, e^{-i\varphi_k}, \qquad b_k = 2^{-1/2} (\alpha_k - \beta_k)\, e^{i\varphi_k}; \qquad (4)$$
$$\tan\, 2\varphi_k = -\gamma \sin k/(1 + \gamma \cos k)$$

brings the Hamiltonian (1) into the form

$$\mathcal{H} = \sum_k (\omega_k^\alpha \alpha_k^+ \alpha_k + \omega_k^\beta \beta_k^+ \beta_k)$$
$$+ \frac{1}{2N} \sum_{k_1+k_2=k_3+k_4} V(k_1k_2k_3k_4)\, (\alpha_{k_1}^+ - \beta_{k_1}^+)\, (\alpha_{k_2}^+ + \beta_{k_2}^+)$$
$$\times (\alpha_{k_3} + \beta_{k_3})\, (\alpha_{k_4} - \beta_{k_4});$$
$$V(k_1k_2k_3k_4) = {}^1/_2\, [1 + \gamma e^{i(k_4-k_1)}]$$
$$\times \exp\{-i(\varphi_{k_1} - \varphi_{k_2} + \varphi_{k_3} - \varphi_{k_4})\},$$
$$\omega_k^{\alpha,\beta} = -{}^1/_2 (1 + \gamma) \pm {}^1/_2 \sqrt{1 + \gamma^2 + 2\gamma \cos k}. \qquad (5)$$

In the operators α_k, β_k the value of the z component of the total spin S_z is written in the form

$$S_z = N - \sum_k (\alpha_k^+ \alpha_k + \beta_k^+ \beta_k). \qquad (6)$$

The Hamiltonian (5) describes a system of two kinds (α and β) of Fermi-particles with a four-Fermion interaction; S_z is expressed through the operator for the total number of particles.

2. HARTREE-FOCK APPROXIMATION AT ABSOLUTE ZERO

Replacing the mean value of the four operators by an average in pairs, we obtain the Hartree-Fock approximation

$$E = \langle \mathcal{H} \rangle = \sum_k \left[\omega_k^\alpha n_k^\alpha + \omega_k^\beta n_k^\beta \right]$$
$$+ \frac{1}{2} \sum_{k_1 k_2} [V(k_1k_2k_2k_1)\, (n_{k_1}^\alpha n_{k_2}^\alpha + n_{k_1}^\beta n_{k_2}^\beta + n_{k_1}^\alpha n_{k_2}^\beta + n_{k_1}^\beta n_{k_2}^\alpha)$$
$$+ V(k_1k_2k_1k_2)\, (-n_{k_1}^\alpha n_{k_2}^\alpha - n_{k_1}^\beta n_{k_2}^\beta + n_{k_1}^\alpha n_{k_2}^\beta + n_{k_1}^\beta n_{k_2}^\alpha)]. \qquad (7)$$

Here $n_k^\alpha = \langle \alpha_k^+ \alpha_k \rangle$, $n_k^\beta = \langle \beta_k^+ \beta_k \rangle$, and the average is to be understood in the quantum-mechanical and statistical sense. In Eq. (7) and henceforth, we set N = 1, i.e., the energy and other thermodynamic quantities are calculated for one link.

We determine the occupation numbers n_k^α and n_k^β from the condition for minimum free energy $F = E - T\sigma$, where T is a dimensionless temperature and the entropy σ is expressed through the occupation numbers

$$\sigma = -\sum_k [n_k^\alpha \ln n_k^\alpha + (1 - n_k^\alpha) \ln (1 - n_k^\alpha) + n_k^\beta \ln n_k^\beta$$
$$+ (1 - n_k^\beta) \ln (1 - n_k^\beta)]. \qquad (8)$$

The system of equations for determining the occupation number has the form

$$n_k^{\alpha,\beta} = [1 + \exp(\varepsilon_k^{\alpha,\beta}/T)]^{-1},$$
$$\varepsilon_k^{\alpha,\beta} = \omega_k^{\alpha,\beta} + V(0) \sum_{k'} (n_{k'}^\alpha + n_{k'}^\beta) \pm \sum_{k'} V(k, k')\, (n_{k'}^\beta - n_{k'}^\alpha),$$
$$V(k_1k_2) = \operatorname{Re} V(k_1k_2k_1k_2) = {}^1/_2 \cos 2(\varphi_{k_1} - \varphi_{k_2})$$
$$+ {}^1/_2 \gamma \cos (k_2 - k_1 - 2\varphi_{k_1} + 2\varphi_{k_2}),$$
$$V(0) = \operatorname{Re} V(k_1k_2k_2k_1) = {}^1/_2 (1 + \gamma). \qquad (9)$$

The solution of this system of equations for T = 0 is easily obtained:

$$n_k^\alpha = 0, \quad n_k^\beta = 1,$$
$$\varepsilon_k^\alpha = -\varepsilon_k^\beta = {}^1/_2 \sqrt{1 + \gamma^2 + 2\gamma \cos k} + {}^1/_2 \cos 2\varphi_k \sum_{k'} \cos 2\varphi_{k'}$$
$$+ {}^1/_2 \gamma \cos (k + 2\varphi_k) \sum_{k'} \cos (k' + 2\varphi_{k'}). \qquad (10)$$

[1)] The transformation to Fermi operators is possible for any half-integral spin.[11]

For large N it is possible to replace the summation over momenta by an integration; then

$$\varepsilon_k^\alpha = \frac{1}{2}\sqrt{1+\gamma^2+2\gamma\cos k} + \frac{(c_1+\gamma c_2)+(\gamma c_1+c_2)\cos k}{\sqrt{1+\gamma^2+2\gamma\cos k}};$$

$$c_1 = \frac{1}{2\pi}(1+\gamma)E\left(\frac{2\sqrt{\gamma}}{1+\gamma}\right) + \frac{1}{2\pi}(1-\gamma)K\left(\frac{2\sqrt{\gamma}}{1+\gamma}\right),$$

$$c_2 = \frac{1}{2\pi}(1+\gamma)E\left(\frac{2\sqrt{\gamma}}{1+\gamma}\right) - \frac{1}{2\pi}(1-\gamma)K\left(\frac{2\sqrt{\gamma}}{1+\gamma}\right), \tag{11}$$

where K(x) and E(x) are complete elliptical integrals.

The energy of the ground state for large N is

$$E_0 = -{}^1/_4(1+\gamma) - (c_1+c_2) - c_1^2 - c_2^2/\gamma. \tag{12}$$

The energy spectrum of the system is shown schematically in Fig. 2. The energy of the quasiparticles is distributed in two bands; the width of each band is $\gamma + 2c_2$. The upper level contains the N levels of α-quasiparticles with positive values of energy, the lower, N levels of β-quasiparticles with negative values of energy. In the ground state the band for the α-particles is filled in accordance with the Fermi distribution and the upper band for the β-particles is empty. The state with one excess α-particle corresponds to a level of the system with $S_z = -1$; an energy of $\epsilon_k = \epsilon_k^\alpha$ is necessary for its excitation. The state without one β-particle (β-hole) gives $S_z = +1$, and the energy excitation of this level is $\epsilon_k = -\epsilon_k^\beta = \epsilon_k^\alpha$.

There is an energy gap $\epsilon_{\min}$ for excitation:

$$\varepsilon_{min} = {}^1/_2(1-\gamma) + c_1 - c_2. \tag{13}$$

The gap vanishes only for $\gamma = 1$. In this case, we have for the ground-state and excitation energies

$$E_0 = -{}^1/_2 p^2, \qquad \varepsilon_k = p\,|\cos(k/2)|,$$

$$p = 1 + \frac{1}{N}\sum_k\left|\cos\frac{k}{2}\right|, \qquad k = \frac{2\pi}{N}n, \quad n = 1, 2, \ldots, N. \tag{14}$$

For large N we go over to integration, and $\rho = 1 + 2/\pi$, $\epsilon_{\min} = (\pi + 2)/N$ for N odd and $E_0 = -1.338$. These results agree with those obtained previously [1].

The contribution of the correlation forces to the energy of the ground state for $\gamma = 1$ is easily specified by the methods of quantum field theory [6]. The calculation of the diagrams shown in Fig. 3, where all the unbroken lines are taken in the Hartree-Fock approximation and the interaction lines in the lower approximation $D_0(k) = 2\cos k$, gives $E_0 = -1.370$. An accurate value for the energy of the ground state for an infinite uniform chain was obtained by Orbach; [7] it is $E_0 = -1.386$.

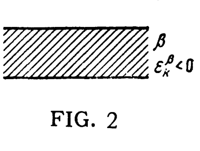

FIG. 2

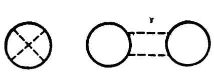

FIG. 3

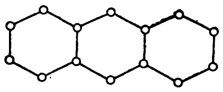

FIG. 4

Note that for N even (polymers of the type $C_{4n}H_{4n}$) the ground state of a uniform chain turns out to be four-fold degenerate. In fact, from Eq. (14) $\epsilon_k^\alpha = -\epsilon_k^\beta = 0$, if $k = \pi/2$. Correspondingly, the states with $N/2 + 1$ ($S_z = -1$), $N/2 - 1$ ($S_z = +1$) particles and the two states with N/2 particles have the same energy. The three states with $S_z = 0, \pm 1$ belong to $S = 1$, and the level with $S_z = 0$ to $S = 0$. This result contradicts the demonstrations by Marshall [8] and by Karayianis, Morrison, and Wortman [9] that the ground state of spins with antiferromagnetic interaction is nondegenerate. Obviously, the degeneracy is lifted by the correlation forces, the level $S = 0$ becoming the ground level, and $S = 1$ the first excited state.

It is interesting to compare the accurate data of Orbach for finite uniform chains [10] with N = 3.5 with the results of the Hartree-Fock approximation. For this, it is necessary to consider that the terms $S_{N2}^+ S_{1,1}^-$ and $S_{N2}^- S_{1,1}^+$ in the Hamiltonian (1) are replaced by $\psi_{N2}^+\psi_{1,1}$ and $\psi_{1,1}^+\psi_{N2}$, respectively, even though their equality does not follow from the transformation (2). For $\epsilon_{\min}$ Orbach obtained 0.68 for N = 3 and 0.43 for N = 5. Calculation by the Hartree-Fock approximation gives respectively 0.81 and 0.51. The Hartree-Fock approximation is found to be accurate for $\gamma = 0$. From Eqs. (11) and (12) we obtain $E_0 = -1$ and $\epsilon_k = 1$.

Ginzburg and Faĭn [2] assumed that in the excitation spectrum of a nonuniform linear chain $\epsilon_{\min} \to 0$ as $N \to \infty$. This assumption was based on results of spin-wave theory, which gives $\epsilon_k \approx \sqrt{\gamma}\sin k$ for the excitation spectrum. As the authors themselves emphasized, [2] the absence of a gap for large N could not possibly be assumed, since the applicability of spin-wave theory to a linear chain is doubtful. The results of this work show that when $\gamma < 1$ the spin-wave theory gives incorrect results. This is explained by the fact that the spin-wave approximation assumes degeneracy of the ground state (sublattice "+ −" and "− +") even for $\gamma = 0$, when the system degenerates into spin pairs and the interaction is only within a pair. But the ground state of a system of two spins with antiferromagnetic interaction is not degenerate; it has $S = 0$. The excited states of two spins are separated from the ground state by the gap $\epsilon_{min} = 1$; they have $S = 1$. It should be mentioned that a similar conclusion about the inapplicability of spin-wave theory cannot be made in the case of two- and three-dimensional antiferromagnetic substances.

In the ferromagnetic case ($J_1, J_2 < 0$), the ground state has $E_0 = 0$ and total spin $S = N$, according to Eq. (9). For the "one-particle" excitation spectrum (excitation of the level with $S = N - 1$) we have

$$\varepsilon_k^{\alpha,\beta} = {}^1/_2(1+\gamma) \pm {}^1/_2\sqrt{1+\gamma^2+2\gamma\cos k}. \quad (15)$$

For small values of k, Eq. (15) gives $\epsilon_k^\beta \approx k^2\gamma/2(1+\gamma)$ and $\epsilon_{min} \approx 1/N^2$ for sufficiently large N. The branch ϵ_k^β also gives $\epsilon_k^\beta \to 0$ as $\gamma \to 0$. This property of a nonuniform ferromagnetic chain and the absence of an excitation gap for $N \to \infty$ are results of the degeneracy of the ground state of two spins with ferromagnetic interaction.

The expression for the heat capacity of a linear chain with antiferromagnetic interaction will contain a factor $\exp(-\epsilon_{min}/T)$. At room temperatures and $\gamma < 1$ this factor is exponentially small. The magnetic permeability in fields $H < J_1/\mu$ will have the same property, since under usual conditions paramagnetism is not exhibited by a system with nonuniform interaction.

In comparing this work with that of Longuet-Higgins and Salem [4] and of Ooshika, [5] it is necessary to note that the LCAO-MO method without electronic interactions in the molecular orbitals gives the same result for the spectrum of single-electron excitations as the spin exchange Hamiltonian without terms in the z-components of the spin operators. Thus it is assumed that if integrals with single-particle wave functions φ_{f_1} and φ_{f_2} for which $|f_1 - f_2| > n$ are neglected in the LCAO-MO method, then in the spin Hamiltonian one considers the interactions of each spin with only its n neighbors. The resemblances and differences between the two methods become clearer if it is kept in mind that the terms containing the z components of the spin operators describe the interaction of the α- and β-fermions.

The transformation of the spin operators to Fermi-type operators together with the Hartree-Fock approximation for the Hamiltonian obtained permits consideration of spin structures of a more complicated type than is illustrated in Fig. 1. Without complicating the calculations too much linear chains with next-nearest neighbor interactions can be handled. A four-fermion interaction Hamiltonian is obtained in the Fermi operator representation. Such a Hamiltonian will also describe the structure represented schematically in Fig. 4.

Hamiltonians with four- and six-fermion interactions can be used to describe more complicated structures, and only in the case of structures that are infinite in two or three dimensions do terms representing the interaction of an infinite number of fermions appear in the Hamiltonian.

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