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THEORY OF ONE-DIMENSIONAL MOTT SEMICONDUCTORS AND THE ELECTRONIC STRUCTURE OF LONG MOLECULES HAVING CONJUGATED BONDS

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The current status of the theory of the electronic structure of polymers containing conjugated bonds is reviewed. Compounds having conjugated bonds have a number of remarkable physical properties, and they occupy a central point in quantum-mechanical studies. The energy of the first optical transition as a function of the molecular length shows unusual behavior. As the molecule is lengthened, the energy of the first transition approaches a finite value called the gap. Hence such a polymer is a semiconductor. A first attempt to explain the gap was based on the hypothesis of spontaneous alternation of bond lengths. The review presents this hypothesis and subjects it to a thorough critique. It has recently been shown that the mechanism that gives rise to the gap in these systems is interaction of electrons and an associated Mott metal-dielectric transition. This conclusion was first based on the unrestricted Hartree-Fock method, and later upon exact solutions for the one-dimensional problem. The article reviews these studies. Polymers with conjugated bonds also show non-trivial magnetic properties, in spite of their lack of d and f electrons. The magnetic properties of these compounds can be described on the basis of the one-dimensional Hamiltonian of Hubbard. Here an exact solution of the wave functions of the ground and excited states is found and the exact excitation spectrum is analyzed. The ground state of these polymers proves to be antiferromagnetic at absolute zero. The spin-wave spectrum begins at zero. Hence these systems show appreciable paramagnetism at finite temperatures. This review analyzes the relation of the paramagnetic susceptibility and the intensity of the EPR signal to the temperature and the polymer length. In conclusion, the review lists problems and questions in the theory of the electronic structure of conjugated polymers that await solution.

CONTENTS

1. INTRODUCTION

THE problem of the electronic structure of long conjugated chains already has a rather substantial history. Beginning with the first theoretical studies,[1] research in this field has continued more or less intensively for more than thirty years. We shall briefly describe the chemical structure and types of conjugated molecules. The most widespread element of these systems is the polyene chain


(1)
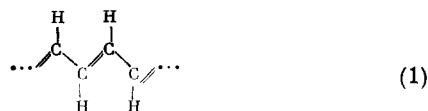
In terms of classical organic chemistry, a polyene chain is characterized by a large number of unsaturated (multiple) C = C bonds. From the standpoint of electronic structure, this means the following. A carbon atom has four valence electrons. Three of them are in hybridized sp^2 orbitals, and form saturated bonds (or σ bonds) with the neighboring carbon atoms and the hydrogen atom. Since we are dealing with a long molecule, we can say that the saturated bonds form a low-lying completely-filled band. The wave function of the fourth electron (π electron) has the symmetry of the $2p_z$ function of the carbon atom (the z axis lies perpendicular to the plane of the drawing; see (1)), and the corresponding band is called the π band. The CH fragment contains an odd number of electrons, and in this sense the chain in (1) is analogous to a chain of sodium or hydrogen atoms. Various groups can occur at the ends of such a chain: hydrogen atoms, CH_3 groups, benzene rings; in addition, some of the hydrogen atoms in the main chain can also be substituted by CH_3 groups and

other saturated radicals. It turns out that the electronic properties of the π electron system proper change rather weakly upon such a substitution. For example, this can be seen by comparing the optical spectra of conjugated molecules having different substituents.[1] Hence, we shall characterize polyene molecules only by the number N of π electrons in the main chain, and shall state whether the chain is open or closed.

There are also long conjugated systems that differ from polyene chains, e.g., the polyacenes (a linear system made of benzene rings in which neighboring benzene rings have one bond in common), the polyphenylacetylenes (a polyene chain in which H atoms alternate with C_6H_5 benzene rings), etc. We note that graphite is also a system with conjugated bonds. Finally we note the peculiar compounds recently synthesized by Sladkov, Kasatochkin, et al (see[2]), which consist only of carbon. The chemical structure of these compounds, called the cumulenes, is reflected by the formula

$$H_2C = \ldots = C = C = C = \ldots = CH_2.$$
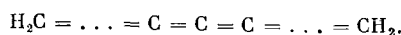
The cumulenes are strictly linear, and have two degenerate π bands that are characterized by a projection of the angular momentum on the axis of the molecule of m = ± 1. Of course, this degeneracy is removed in the crystal field, but the corresponding splitting is small, and it does not affect the optical properties of the molecules. The length of these molecules in the crystallite is as much as 1000—1500 links. More detailed information on the chemical and physical properties of polymers having conjugated bonds can be found in the monographs[3-6].

The scientific interest in these systems primarily involves practical demands. As we know, molecules with conjugated bonds occur as constituent parts in a number of biologically active molecules (vitamin A, chlorophyll, etc.). It has recently been found possible to use polymers with conjugated bonds in practice as semiconductors with good working properties and also as catalysts for a number of very important reactions.[3,7]

In the physics literature, interest in such systems has arisen in line with Little's[8] suggestion of using long molecules having conjugated bonds to create superconductors having high critical temperatures. This idea has stimulated experimental study of such interesting one-dimensional systems as highly conductive complexes based on tetracyanoquinodimethane (TCNQ)[9] and organic chains containing regularly incorporated atoms of the metals Pt and Ir[7] (Fig. 1). A very large number of studies in quantum chemistry have been concerned with systems having conjugated bonds. Moreover, the very birth of quantum chemistry involved the appearance of the first studies on the electronic structure of benzene. Thenceforth all the theoretical methods have been worked out on systems having conjugated bonds. However, only recently has the use of the most rigorous methods of many-body theory made it possible to elucidate a number of fundamental problems of the electronic structure of large conjugated systems.

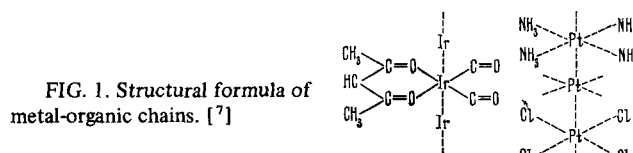In speaking of the factors that have stimulated theor-

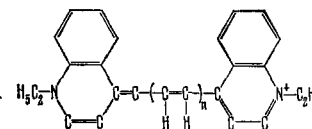FIG. 1. Structural formula of metal-organic chains. [7]

FIG. 2. Skeleton of a symmetrical cyanine dye.

etical studies of the electronic structure of polymers having conjugated bonds, we cannot but note the following.

One-dimensional models have been rather widely used in the theory of the condensed state of matter as a "testing range" for testing various theoretical constructions whose mathematical treatment proves too complex in the three-dimensional case. It suffices to mention the studies of Van Hove, Kac, etc.[10,11] to find the equation of state of one-dimensional gases, Dyson's study[12] on the vibrational spectrum of a disordered chain, and the studies of Bethe,[13] Hulten,[14] and others[15] on determining the properties of a one-dimensional antiferromagnetic chain, etc.[2] However, the one-dimensional model usually permits one to analyze only the mathematical structure of a theory. Its physical adequacy to a real situation remains in question, since the lack of one-dimensional objects hinders comparison of experiment with mathematically exact (or almost exact) one-dimensional solutions. Polyene and cumulene chains were until recently the only actually-existing one-dimensional objects. In principle, studying them can help in selecting physically correct theories that describe not only their own structures, but also, e.g., the metal-dielectric transition, the antiferromagnetic state, and phase transitions in three-dimensional crystals. Hence, the problem of the electronic state of long conjugated chains is of general scientific importance.

We shall note the relation of the problem of the Mott metal-dielectric transition to the electronic structure of polymers having conjugated bonds. As we have mentioned, each CH fragment in a polyene chain has an odd number of electrons. That is, a polyene should be a metal from the standpoint of its band system. However, experiment has shown that conjugated polymers of the polyene type are semiconductors.

Mott[17] has given qualitative arguments favoring the idea that any condensed substance (implying polymer chains as well) must undergo a metal-dielectric transition as the atoms are separated. However, these arguments are too general, and they do not answer the question why graphite is a conductor (albeit a poor one), while conjugated polymers are semiconductors, given the same electronic parameters. We shall spell out these arguments below, and this will make it possible to explain the experimental data on the electronic structure and physical properties of these compounds.

A series of studies by Brooker and his assoc-

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[1] We should say that the complete chemical names of the molecules undergo considerable changes upon substitution.

[2] In order to get a picture of the large scope of studies with one-dimensional models, it suffices to become acquainted with the collected volume of articles [16] (which is indeed already out of date).

iates[18,19] have established the experimental facts that the theory must explain, and they can be formulated as follows:[20]

a) The wavelength of the first electronic transition in the spectra of symmetrical cyanine dyes (Fig. 2), which contain an odd number of carbon atoms in the main chain, increases by $\lambda_c = 1000 \pm 50$ Å upon addition of each additional HC = HC group. This "red shift" does not decline when we go to longer chains. In other words, this means that the energy ΔE of the first optical transition approaches zero as the number N of atoms increases to infinity.

b) In the molecules of polyenes (and also those of unsymmetrical dyes), the band of the first transition lies in a region of shorter wavelength than this rule implies, and its energy approaches a finite limit different from zero as N → ∞. This limiting value has been termed the energy gap ΔE_∞. Its value as obtained by extrapolation of frequencies from N = 30 is 2.25 eV[22] (see[21] for a summary).

The behavior of the energy of the first transition in the symmetrical dyes (point a) can be explained within the framework of very simple one-electron methods: the "free electron" method and the molecular orbital (MO) method.

The free-electron model gives the following formula for ΔE:[23,24]

$$\Delta E = h^2 (8md^2)^{-1} (N + 1)/N^2$$

(d = cos 30° · 1.40 Å for a polyene chain[19]). Consequently the wavelength of the first transition is proportional to N, and $\lambda_c \approx 900$ Å.[3] Considering the crudeness of the model, this agrees satisfactorily with Brooker's data. In the simplest variant of the MO method,

$$\Delta E = - 4\beta \sin [\pi/2 (N + 1)],$$

so that $\Delta \lambda \sim N$, $\lambda_c = hc/\beta$. If we take $\beta = 4.0$ eV, as has been obtained by analyzing the spectra of short polyenes, we also get agreement with Brooker's results. However, these simple formulas, which give a zero value for ΔE_∞, do not reflect the situation in the polyenes (which ought to be described better by the simple methods, since they do not contain heteroatoms). As Mulliken has shown, the result is also the same in the refined variants of the MO method. We note that the difference in behavior of ΔE_∞ between the symmetrical dyes and the polyenes is remarkable in general, regardless of the results given by the simple methods, since these chains differ only in their end groups. When we increase the number of atoms, so that we can neglect end effects, their "bulk" characteristics (including ΔE_∞) should coincide. Thus, optical experimentation has posed two problems for the theory: 1) to elucidate the reasons for appearance of a gap in the spectra of the polyenes; 2) to elucidate the reasons for the difference in properties of the symmetrical dyes and the polyenes.

We note immediately that the overwhelming majority of the theoretical studies have been concerned with solving the first problem. This has happened for the following reasons. Polyene chains and symmetrical dyes differ in the same way that an ideal crystal and a

crystal containing an impurity do. Hence, whereas use of the translational symmetry allows one to derive for the polyenes a set of rigorous results (and sometimes even exact; see below), this cannot be done with the symmetrical dyes. Furthermore, theoretical description within the framework of model Hamiltonians requires considerably fewer undefined parameters (to be determined by comparison with experiment) for the polyenes than for the dyes. Naturally, this also increases the reliability of the obtained results. Finally, interpretation of the optical data themselves is more unequivocal for the polyenes than for the dyes. Hence, this article will also discuss mainly the first problem. We shall treat briefly at the end of the review the possible reasons for the differences between the spectra of the polyenes and the dyes.

2. THE HYPOTHESIS OF ALTERNATION OF BONDS IN LONG POLYENE CHAINS

In this chapter, we shall examine the hypothesis that the reason for existence of the gap in the electronic spectra of the polyenes is instability of the ground (metallic) state of a chain of equal bonds with respect to nuclear shifts that create a configuration having alternating bond lengths. This hypothesis is now apparently only of historic interest in the problem of the electronic state of long molecules having conjugated bonds. Nevertheless, it served until recently as the only explanation for the gap in the optical spectrum of the polyenes. Moreover, this viewpoint impresses chemists studying the properties of polymers having conjugated bonds, since the difference between double and single bonds has been established experimentally for short chains. Apparently this is the very fact that explains the great tenacity of this hypothesis. For example, several recent monographs devoted to organic semiconductors present this hypothesis as being an established fact.[3-5] Along this line, we shall give a rather well developed presentation and detailed critique of these notions.

The qualitative side of the problem is fully contained in the statement known as the "Peierls theorem"[26] that a one-dimensional metal cannot exist. We shall present its content for the case of interest to us.[27]

Let there be a one-dimensional homoatomic chain of equal bonds, each atom of which contributes one electron to the system. We shall assume that the adiabatic approximation is satisfied. The electronic levels of such a system in the one-electron approximation form a single band that is half-filled in the ground state. Let us consider a perturbation V that amounts to an infinitesimally small shift of every other atom in a given direction (alternation). Then the band splits into two bands separated by an energy gap. Only the lower band is filled in the ground state. Such a perturbation mixes levels that are symmetric with respect to the Fermi level. Since states whose energies are close to the Fermi level are almost degenerate, the correction to the levels calculated by the perturbation theory is linear in V, and it is negative for levels in the lower band. At the same time, the correction for the rest of the levels and also the increase in the potential energy of the skeleton are quadratic in V. Consequently, the total energy of the chain declines. That is, the configuration of

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[3] N increases by two upon addition of each link.

an infinite equal-bonded homoatomic chain proves to be unstable.

In concluding the discussion of the Peierls theorem, we emphasize that its proof is substantially based on the assumption that the one-electron system is at least qualitatively true. In other words, the mechanism of creation of the gap described by the Peierls theorem is necessarily realized whenever no other mechanism to create one exists (electron-phonon interaction to create a superconducting gap, interelectronic interaction leading to a metal-dielectric transition, etc.).

Before we proceed to a quantitative description of the alternation, let us introduce the Hamiltonian of the discussed π system:

$$\mathcal{H} = \sum_{n, m, \sigma} \hat{c}^+_{n\sigma} \hat{c}_{m\sigma} \beta_{mn} + \sum_{n, m, \sigma, \sigma'} \gamma_{nm} \hat{c}^+_{n\sigma} \hat{c}_{n\sigma} \hat{c}^+_{m\sigma'} \hat{c}_{m\sigma'} + \mathcal{H}_\sigma; \quad (2)$$

Here $\hat{c}^+_{n\sigma}$ and $\hat{c}_{m\sigma}$ are the operators for creation and annihilation of electrons of spin σ at the nodes n and m, respectively, and β_{nm} is the resonance integral of the bond between atoms n and m. It is usually considered to be a certain standard function of the bond length R_{mn} between the atoms n and m:

$$\beta_{mn} = \beta \, (R_{mn}) < 0. \quad (3)$$

Since the length of the C = C bond in different conjugated molecules differs little from its mean value 1.40 Å (the length of the C = C bond in benzene), we can replace the function (3) with its expansion in the vicinity of the mean distance:

$$\beta_{mn} = \beta \, (R_0) + \beta' \, (R_0) \delta R_{mn}. \quad (4)$$

The second term in (2) describes the Coulomb repulsion of electrons, and γ_{mn} is the Coulomb integral. Finally, $\mathcal{H}_0$ is the energy of the σ electrons, which we can consider accurately enough to be equal to the sum of σ energies of their bonds in the molecule:

$$\mathcal{H}_\sigma = \sum_{m, n} E_\sigma \, (R_{mn}), \quad E_\sigma (R_{mn}) = E_\sigma (R_0) + (k_{mn}/2) \, (\delta R_{mn})^2. \quad (5)$$

The possibility of alternation of bond lengths in infinite polyene chains has been studied in[1], even before the existence of a gap in their energy spectrum had been shown. These authors wanted to answer the question whether the alternation that is observed in short polyenes persists as we go to longer chains (for example, it amounts to 0.14 Å in butadiene (N = 4)[28] and 0.10—0.12 Å in tetraene (N = 8)[29]). They treated the problem by the simple MO method (i.e., with $\gamma_{mn} = 0$ in Eq. (2)), and used different values of the resonance integrals ($|\beta_1| > |\beta_2|$) for the bonds differing in length ($r_1 < r_2$).

Although the final conclusion of these studies that alternation in the one-electron approximation is energetically unfavorable later proved to be wrong, the expressions for the one-electron energy levels derived therein

$$\varepsilon_k = \pm \, (\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k)^{1/2} \quad (6)$$

were correct. They showed that a gap arises in the one-electron spectrum of a chain when alternation ex-

ists. Kuhn[23,30,31] first advanced the hypothesis of alternation as the reason for appearance of a gap. In these studies he calculated the spectrum of eigenvalues of the one-electron Hamiltonian with a potential whose shape is shown in Fig. 3. The equation was solved numerically with this potential function, but the obtained values of the energies of the transitions are satisfactorily described by the formula

$$\Delta E = (h^2/8mL^2) \, (N + 1) + V_0 \, (1 - N^{-1}),$$

Here N is the number of atoms in the chain and L is its length. One can get satisfactory agreement with experiment by setting $V_0 \approx 2$ eV. However, it remained unclear here how the alternation of the bond lengths arose.

A more rigorous proof of the energy advantage of alternation was required to make the treatment more convincing. The first proofs of this type were given in[20,29,32] by direct calculation in the MO approximation and comparison of the electronic energies of configurations having different degrees of alternation. A favorable distinction of the study by Longuet-Higgins and Salem[33] consists in the fact that their proof that alternation is necessary in the MO approximation was separate from their numerical estimates, and they carried it out for a well defined simple model.

Let us calculate E_π for a cyclic polyene containing 4n + 2 atoms under the assumption that consecutive bonds and the corresponding β_{mn} values alternate. The equations of the simple MO method lead to the expression (6) for the one-electron energies with the quasi-momentum $k = 2\pi j/(2n + 1)$, where $j = 0, \pm 1, \pm 2, ..., \pm n$. The one-electron levels form two bands: a filled one $(\beta_1 + \beta_2 \le \epsilon_k \le -|\beta_1 - \beta_2|)$, and a vacant one $(|\beta_1 - \beta_2| \le \epsilon_k \le |\beta_1 + \beta_2|)$, which are separated by a forbidden band of width $2(|\beta_1 - \beta_2|)$. Hence the π-electron part of the energy of the ground state is:

$$E_\pi = -2 \sum_{k=-n}^{n} \varepsilon_k. \quad (7)$$

Let the chain be brought in any way whatever into a state having equalized bonds, and then let a small change in the nuclear coordinates occur such that one of each two consecutive bonds lengthens by δR, while the other shortens also by δR. Upon applying (4)—(7), we can derive in the limit N $\rightarrow \infty$ the following formula for the energy change $\Delta E(x)$ for such a shift:[34]

$$\Delta E \, (x) = ax^2 + bx^2 \ln \, (x_0/x), \quad (8)$$

$$a = (k/2) + [(\beta')^2/\pi \, | \beta \, ||, \, b = 2 \, (\beta')^2/\pi \, | \beta \, |, \, x_0 = 4 \, |\beta/\beta'|,$$

$$x = \delta R/R,$$

Here k is the force constant of the hypothetical σ bond and R is the bond length in the equal-bonded chain. Since the second term on the right-hand side is always larger than the first for small x, $\Delta E(x)$ has a maximum at x = 0. If we minimize (8) with respect to x, we can determine the equilibrium distance, and consequently, the width of the gap.

In order to make quantitative estimates, we must know the parameters k and β that enter into Eq. (8). Within the framework of the semiempirical approach that we have applied, it seems most consistent to determine them by comparison with experimental data on the vibrational frequencies and geometries of the organic molecules. Such a method has been developed in[35]. The essence of the method amounts to the following.

If we assume that the presence of the π electrons causes a small change in the bond lengths by δR_m, and
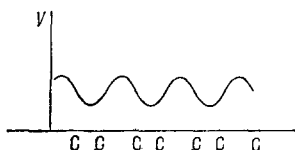

FIG. 3. Form of the one-electron potential. [30,31]

in the angles by $\delta\varphi_l$, as compared with their values in a hypothetical molecule without the π electrons, then in the MO approximation the energy of the molecule has the form

$$E = E_\sigma^{(0)} + 2\sum_i \beta_i P_i + \sum_m (1/2)\, k_{1m}\delta R_m^2 + \sum_l (1/2)\,(k_2 R^2)\,\delta\varphi_l^2, \quad (9)$$

Here the β_i are the resonance integrals for consecutive atoms, and the P_i are the corresponding elements of the density matrix. If we vary the total energy in (9) with respect to independent δR_m and $\delta\varphi_l$ with (4) taken into account), we get the values of δR_m and $\delta\varphi_l$ that minimize it. The found values of δR_m and $\delta\varphi_l$ depend in a complex way on the elements of the density matrix. They must be substituted into the expression for E, and then (9) is transformed into a nonlinear equation for finding P_i. We must again substitute the solution of this equation into the formulas for δR_m and $\delta\varphi_l$, etc., until this iteration procedure leads to self-consistency. For a molecule that does not contain closed rings, the variation of (9) with respect to δR_i gives

$$\delta R_i = -2\beta_i' P_i/(k_i + 2\beta_i'' P_i), \quad R_i = R_{0i} + \delta R_i. \quad (10)$$

This formula contains four parameters (R_{0i}, β_i', k_i, and β''). To determine them, we can use the fact that P_i is fixed by symmetry properties alone for four substances (graphite, benzene, ethylene, and acetylene), and the equilibrium distances have been measured by x-ray diffraction. Then the obtained parameter values can be tested by calculation and comparison with experimental data on the bond lengths for a large number of organic molecules. Moreover, when the equilibrium distances have been determined, Eq. (9) is converted to quadratic form with respect to small shifts of the nuclei from the equilibrium positions. This permits us to construct in the usual way the equations of motion for the vibrational coordinates of the molecule and to find the corresponding frequencies of the normal vibrations, which can also be compared with experimentally determined frequencies in the infrared absorption spectra of the molecules. This provides another independent way of determining semiempirically the parameters k, β', and β''. This procedure has been carried out in[35], and values were found for these parameters that satisfy a large number of the experimental data, and which are hence quite reliable.

Using these parameters gives a gap width ΔE_∞ $\approx 0.1–0.3$ eV. This is an order of magnitude smaller than the value $\Delta E_{exp} = 2.25$ eV[22] obtained by extrapolating the experimental data. We note that the authors of[33], who used another method of determining the parameters, likewise got $\Delta E_\infty = 0.25$ eV. This disagreement between the experimental data on the size of the gap and the theoretical calculations from the alternation hypothesis served as the first clue that the latter was false. We should also point out an experimental proof[4] of lack of alternation in the cyclic molecule $C_{18}H_{18}$ (Fig. 4).

A further development of studies along this line was a series of studies by Shustorovich and Popov.[4,27] They used a semiempirical variant of the self-consistent field method for calculating the band structure of polyene chains. Upon accounting for interelectronic interaction, these authors got a gap width close to the experimental value. However, the parameters that they
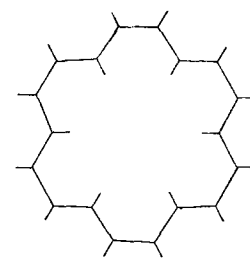

FIG. 4. Skeleton of 18-annulene ($C_{18}H_{18}$).

used were not fitted correctly to the experimental data on the geometry and vibrational spectra of small molecules having conjugated bonds. Hence, the agreement found in these studies of the gap width with experiment cannot serve as a proof of the alternation hypothesis.

We should mention one inconsistency in[28]. In order to determine the equilibrium distances in an infinitely long polyene, they used a formula[36] similar to (10) that was derived in[31], whereas a general analysis of the applicability of this formula implies that it is inapplicable when the energy depends on x as $x^2 \ln x$.

We note that, although Longuet-Higgins and Salem's result on the instability of an equal-bonded configuration of a polyene in the MO approximation with respect to alternation directly stems from the Peierls theorem, we cannot consider it to be trivial in this sense and extend it without concrete analysis to any extended conjugated system. One of the conditions for satisfaction of this theorem is that the appropriate nuclear displacement can mix the states of the upper and lower halves of the band. The question of whether alternation of bonds satisfies this criterion must be elucidated separately in each concrete case. Thus, the treatment in[37] of the situation in the polyacenes showed that alternation cannot occur here, since the adjoining bands have a symmetry such that interaction with an antisymmetric vibration does not mix the states belonging to them.

Let us briefly discuss another attempt to explain the existence of a gap in the optical spectrum of the polyenes that involved adducing notions of plasma oscillations. Plasma oscillations in polyene chains were first treated in[38]. Just as in the three-dimensional case, its authors found that the plasmon spectrum in an equal-bonded chain begins at some finite frequency (i.e., $\lim_{k \to 0} \omega_p(k) = \omega_{op} \neq 0$). They also expressed the idea that the first optical transition in the polyenes involves excitation of a plasmon. Thus the experimentally-observed dependence of the frequency of the transition on the number of atoms is explained by the fact that the limiting plasma frequency differs from zero. However, it has later been shown[39] that the authors of[38] were too much fascinated with the analogy with the three-dimensional problem, and they estimated incorrectly a number of matrix elements for interelectronic interaction. A more correct treatment[39] showed that the plasmon spectra in an equal-bonded polyene chain (more exactly, in a chain having a metallic-type one-electron spectrum) begins at zero (for small k, $\omega(k) \sim k \ln^{1/2}(k_0/k)$).[4] This result refuted the interpretation

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[4] In the cumulenes, as the study by Shustorovich and Popov [27] implies, another plasma branch exists in addition to this one, and it also begins at zero.

of the optical data proposed in[38].

The studies[41-43] have treated plasma oscillations of a polyene chain under the assumption that its one-electron spectrum has a gap. They showed that the limiting value of the plasma frequency is 5—6 eV for a gap of $\Delta E_\infty \approx 2.5$ eV. Thus, the plasma-wave spectrum lies considerably higher that the spectrum of one-particle excitations, and it does not appreciably affect the observed optical absorption.

It was shown in[42] that another branch of collective excitations can exist in polyene chains besides the plasma oscillations: Wannier-Mott excitons. They should give rise to a hydrogen-like series in the absorption spectrum (possibly lacking the first line) lying near the fundamental interband transition. Such a spectrum has not yet been detected experimentally.

3. CORRELATION OF ELECTRONS AND THE ENERGY SPECTRUM OF POLYENE CHAINS

As we have pointed out, the first impulse that struck investigators with the idea that bond alternation is the reason for the gap in the electronic spectrum of the polyenes was the experimentally-observed alternation of bond lengths in short chains. Then supported by the Peierls theorem on the instability of a one-dimensional metal with respect to electron-phonon interaction, this explanation began to seem the only one possible. At the same time, the very statement that an equal-bonded chain is a metal in its electronic structure (i.e., a substance having a partly-filled valence band) is based on the assumption that the band system (and in particular, that of the ordinary MO method) is always suitable for describing the ground and lowest excited states of a system of this type. However, as we have mentioned in the Introduction (Chap. 1), Mott (see[17,44]) has given a qualitative explanation for the necessity of a metal-dielectric transition as the lattice constant a increases in substances having partly-filled bands (e.g., the hypothetical crystal of hydrogen atoms), even when one neglects electron-phonon interaction. In terms of formulas, this means that the ground state for some substances (metals) is correctly described by a wave function in the form of a Slater determinant constructed of Bloch functions (the LCAO method). In this case we get a partly-filled band and metallic conductivity. For other substances (in spite of the fact that they are made of atoms having incompletely filled shells), the ground state is correctly described by a Slater determinant whose elements are atomic functions or Wannier functions (the Heitler-London (HL) or valence-bond (VB) method). Most naturally, this second method leads to an arrangement of spins characteristic of an antiferromagnet. Here the lowest excited states, which are not separated from the ground state by a gap, are spin waves, and they are not accompanied by charge transport. The latter becomes possible only for excited states involving migration of an electron from one atom to another, and these are separated from the ground state by a gap, ~ I − A. We should expect that we must use an expansion to describe the metal-dielectric transition within the framework of the band model (MO) that is an intermediate variant between the MO and VB methods.

In searching for the golden mean, Löwdin[45] has de-

veloped a method of calculating the electronic wave functions of crystals and molecules that amounts to a synthesis of the two fundamental approximations. This method has been called the alternating molecular orbital (AMO) method, or in the more general case, the method of different orbitals for different spins (MDODS). The ideas that Löwdin used here were first applied by Hylleraas[46] for calculating the helium atom and by Weinbaum[47] to calculate the hydrogen molecule. Other names are also used for the AMO method that concretize the system of calculation used. Thus, if the variation of the energy is performed on a component of the wave function with a definite multiplicity by the AMO method, the corresponding method is called the extended Hartree-Fock method (EHFM). However, if one does not isolate the stated component, the method is called the unrestricted Hartree-Fock method (UHFM). There is also the term "generalized HF method", which denotes in different studies either the EHFM or the UHFM. Hence we shall not use it.

Mott's ideas were first adduced to explain the finite value of the first electronic transition in long polyene chains by Misurkin and one of the present authors.[48] We discussed the nontrivial solutions of the self-consistent field (SCF) equation for the π electrons of a polyene chain. The one-dimensional Hamiltonian of Hubbard[49] was used to describe the polyene chain in[48]:

$$\mathscr{H} = \beta \sum_{v, \sigma} \hat{C}_{v\sigma}^+ (\hat{C}_{v+1,\sigma} + \hat{C}_{v-1,\sigma}) + \gamma \sum_{v,\sigma} \hat{n}_{v\sigma}\hat{n}_{v,-\sigma}, \qquad (11)$$

Here $\beta < 0$ is the resonance integral, $\gamma > 0$ is the Coulomb-interaction parameter per atom, α_0 is the Coulomb integral, and $\hat{C}_{v\sigma}^+$ and $\hat{C}_{v\sigma}$ are the operators for creation and annihilation of an electron having a spin respectively of $\sigma = \uparrow, \downarrow$.

Hubbard[49] proposed the Hamiltonian of (11) to describe the d and f electrons in the transition metals and rare earths. The suitability of this approximation for describing a polyene chain will be discussed below.

In the applied approximation, the Hartree-Fock equations have the form

$$E_l C_{v\sigma}^l = \alpha_0 C_{v\sigma}^l + \beta (C_{v+1,\sigma}^l + C_{v-1,\sigma}^l) + \gamma n_{v,-\sigma} C_{v\sigma}^l, \qquad (12)$$

Here the $C_{v\sigma}^l$ are the coefficients of the expansion of the molecular orbital $\Psi_{l\sigma}$ in terms of the atomic $\varphi_{v\sigma}$, and the $n_{v\sigma} = \sum_l |C_{v\sigma}^l|^2 n_{l\sigma}$ are the averages over the sought state.

Equations (12) have the solution

$$E_l = \alpha_0 + 0.5\gamma \pm [(\gamma\delta)^2 + 4\beta^2 \cos^2 (\pi l/N)]^{1/2}, \qquad (13)$$

where 2N is the number of atoms in the chain.

If $N = 2p + 1$, then the levels that are filled in the ground state are those that have a minus sign before the square-root term in (13), and that have $-p \leq l \leq p$. The excited states have a plus sign before the square root in (13). The levels that are filled in the ground state correspond to the following values of the coefficients:

$$C_{v\sigma}^l = [\cos \theta_l (2N)^{-1/2}] e^{i\pi vl/N} + \tau_\sigma [\sin \theta_l (2N)^{-1/2}] e^{i\pi v(l+N)/N}, \qquad (14)$$

where $-p \leq l \leq p$. The wave functions of the vacant molecular orbitals have the form

$$C_{v\sigma}^l = -\tau_\sigma [\sin \theta_l (2N)^{-1/2}] e^{i\pi vl/N} + [\cos \theta_l (2N)^{-1/2}] e^{i\pi v(l+N)/N}, \qquad (15)$$

where

$$\sin 2\theta_l = \gamma\delta \left[(\gamma\delta)^2 + 4\beta^2 \cos^2 (\pi l/N)\right]^{-1/2},$$

$$\tau_\sigma = \begin{cases} +1 & (\sigma = \uparrow), \\ -1 & (\sigma = \downarrow). \end{cases} \tag{16}$$

The parameter δ is determined from the equation

$$(2N)^{-1}(\gamma/2\,|\beta\,|) \sum_{l=-p}^{p} \left[(\gamma^2\delta^2/4\beta^2) + \cos^2 (\pi l/N)\right]^{-1/2} = 1. \tag{17}$$

Equation (17) has two solutions. The first solution $\delta = 0$ corresponds to the ordinary Hartree-Fock method, with

$$C_{v\uparrow}^l = C_{v\downarrow}^l, \quad E_l = 2\beta \cos (\pi l/N).$$

When $\delta \neq 0$, the energy of the ground state of a polyene chain is lower than when $\delta = 0$ for $N \to \infty$. The ground state of the system for $\delta \neq 0$ is separated from the excited states by a gap equal to

$$\Delta E = 2\gamma\delta, \tag{18}$$

where $\delta > 0$ is determined from (17). As calculated per electron, the UHFM gives the following expression for the energy $E(N)/N$ ($N \to \infty$)[48]:

$$\varepsilon(\delta) = \alpha_0 + (4\beta/\pi) \int_0^{\pi/2} \left[(\delta^2\gamma^2/4\beta^2) + \cos^2 k\right]^{1/2} dk + \gamma(0.25 + \delta^2).$$

This expression implies that $\epsilon(\delta) < \epsilon(0)$. We note that $\epsilon(\delta)$ shows the proper asymptotic behavior (apart from the coefficient) as the nuclei are separated, i.e., as $\beta/\gamma \to 0$:[48]

$$\varepsilon(\delta) \approx \alpha_0 - (2\beta^2/\gamma) + \cdots,$$

whereas the exact energy here behaves as $\epsilon = \alpha_0 - 2.76\,\beta^2/\gamma + \cdots,$[13] while the energy given by the ordinary MO method $\epsilon(0) = \alpha_0 + (4\beta/\pi) + 0.25\gamma$ behaves incorrectly.

We can explain the correct asymptotic behavior of $\epsilon(\delta)$ by the existence in the UHFM wave function of a component arising from the VB method, which permits us to account for a considerable part of the correlation energy of the polyene chain.

We should mention the very important asymptotic behavior of ΔE as $(\gamma/\beta) \to 0$. Here

$$\Delta E = 16\beta e^{-2\pi\,|\beta\,|/\gamma}.$$

Equations (13) and (17) permit one to estimate the energy of the first electronic transition as a function of N. For the parameter values $\beta = -2.4$ eV, $\gamma = 5.42$ eV, which are apparently close to their actual values in a polyene chain,[50] numerical analysis has shown that the theoretical values of $\Delta E(N)$[48] agree well with the experimental values (Fig. 5). Thus, the features of the optical spectrum of the polyenes can be explained by correctly taking account of interelectronic interaction without resorting to the hypothesis of alternating bond lengths.

Bychkov, Gor'kov, and Dzyaloshinskiĭ[51] and Popov[52] have shown that if one assumes that the energy gap in long one-dimensional systems stems from
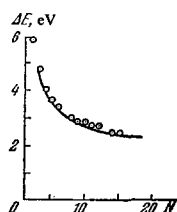
the joint effect of alternation and interelectronic correlation, then $\Delta = (\Delta_{corr}^2 + \Delta_{al}^2)^{1/2}$.

However, as we see from the results of[33-35,48], $\Delta_{al} \approx 0.1\Delta_{exp}$, and $\Delta_{exp} \approx \Delta_{corr}$ for the real parameters characteristic of polyene chains. Hence, even if alternation is energetically advantageous, it can contribute no more than one percent to the experimental value of the observed optical gap. The problem of the energetic advantage of alternation becomes more complicated when we take account of interaction of electrons. In particular, the simple qualitative ideas that lead to the Peierls theorem and the necessity of alternation are inapplicable when there is a correlational gap, since now all the corrections to the energy due to alternation are of the second order in terms of the perturbation that they introduce, and they have differing signs. Consequently, the problem of existence of alternation can be solved only by numerical calculations of its energy advantage. Popov was the first to perform such a calculation.[50] His fundamental system was the same as that used in deriving Eq. (8). However, instead of using Eq. (6) for the one-electron levels ϵ_k, he used the formula

$$\varepsilon_k = \pm \left((\gamma\delta)^2 + \beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k\right)^{1/2},$$

The latter differs from (13) in that the assumed alternation has been introduced; the energy of the σ skeleton was taken into account as it was in[28]. As we should expect, the final result depends on the numerical values of γ and β; the estimate of the parameters in[50] leads to the conclusion that the equal-bonded configuration is energetically favorable. The authors of[53] came to the same conclusion.[5]

Thus, a new hypothesis has appeared for the source of the gap in the optical spectrum of a long polyene chain. Within the framework of this hypothesis, this gap is explained by interaction of electrons. Accounting for electronic interaction within the framework of the UHFM suffices here for obtaining the gap in the spectrum of a polyene chain.

The properties of other polymers with conjugated bonds for which experimental data on the optical spectra exist were studied in[55] by the same method.

As we know, the first electronic transition in a cumulene chain of N carbon atoms has a frequency of the order of 1.0 eV as $N \to \infty$.[56] Thus the cumulenes are dielectrics, whereas graphite shows metallic conductivity (albeit small in comparison with typical metals).

The results of the calculations show that the UHFM gives a finite value for ΔE of the first electronic transition in a long cumulene chain for any $\gamma > 0$. Here the value of ΔE agrees well with experiment for the actual parameter values. For graphite, there is a gap in the one-particle spectrum only when $\gamma/2|\beta| > 1.13$. However, the actual values give $\gamma/2|\beta| \approx 1.13$. Thus, the results of the UHFM correctly describe the optical properties of the cumulenes, and they do not contradict experiment for graphite.

ΔE, eV

FIG. 5. Theoretical and experimental values of ΔE (N). [48]

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[5]The opposite result was obtained in [54], and an alternating configuration proved to be energetically more favorable than the equal-bonded one within the framework of the EHFM. However, the extremely small energy gain from alternation (~0.04 eV per atom) and the use of parameters that had not been calibrated against the vibrational spectra render the conclusions of [54] not very convincing.

We note also that the experimentally-studied proper-
ties of one-dimensional chains of complexes based on
TCNQ (the position and size of the gap in the one-elec-
tron spectrum and the charge distribution along the
stack of molecules) are described well within the frame-
work of the correlation model without adducing the hypo-
thesis of alternation. The same conclusion has been
drawn from a study of organic chains containing incor-
porated Pt and Ir atoms, for which, in particular, relia-
ble X-ray data exist.[57]

Here we must also mention the approximation in
which one assumes that $\gamma_{\mu\nu} = \delta_{\mu\nu}\gamma$. At first glance,
this approximation seems inconsistent, since it ignores
the long-range nature of the Coulombic interaction.
However, as Ruedenberg has shown, as well as Murrell
and Salem,[58] the effect of $\gamma_{\mu\nu}$ ($\mu \neq \nu$) on the electronic
spectrum can be partially taken into account by renorm-
alizing the parameters γ and β, at least in the SCF ap-
proximation. Since the parameters are chosen em-
pirically, taking account of $\gamma_{\mu\nu}$ ($\mu \neq \nu$) is not important
qualitatively. This viewpoint was directly confirmed in
a study by Fukutome,[59] who also found nontrivial solu-
tions of the SCF equations for a polyene chain. However,
in contrast to[48], all of the $\gamma_{\mu\nu}$ were accounted for
in[59]. Here he obtained a nontrivial solution of the SCF
equations whose properties are fully analogous to those
of the solution described by Eqs. (13)—(16) for $\delta > 0$.

Let us examine another aspect involved in the non-
trivial solution of (12). We recall that Eqs. (12) have
two solutions: trivial ($\delta = 0$) and nontrivial ($\delta \neq 0$). The
question arises: what type of perturbation can convert
the system from the unstable state described by the
trivial solution to a state described by the nontrivial
solution $\delta \neq 0$?[6] This question is answered in[60]. It
turns out that the trivial solution is unstable with res-
pect to an arbitrarily small perturbation caused by spin
polarization of the electron clouds of the polyene. For
example, such a perturbation might be the addition of an
electron to the chain. In the Hartree-Fock approxima-
tion, the Hamiltonian of (11), apart from a constant, has
the following form for a system of 2N electrons:

$$\mathcal{H}_0 = \sum_{k\sigma} \epsilon_0(k)\, \hat{a}_{k\sigma}^+ \hat{a}_{k\sigma}, \qquad (19)$$

Here $\epsilon_0(k) = 2\beta \cos k$, and $a_{k\sigma}^+$ and $a_{k\sigma}$ are the operators
for creation and annihilation of an electron in the band
state $\Phi_k = (N)^{-1/2}\Sigma$ $(\sin k\nu)/\varphi_{\mu\nu}$. Such a choice of band
functions made it possible to take explicit account of
end effects. As we shall see, this has proved to be im-
portant in applications. Addition of an electron to the
chain leads to a small change in the Hamiltonian of (19):

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \sum_k \Delta_{-\sigma}\hat{a}_{k\sigma}^+ \hat{a}_{\bar{k}\sigma}, \qquad (20)$$

Here $\bar{k} = \pi - k$, and we assume that the added electron
has entered the lowest vacant orbital with $k = \pi/2$ and
$\sigma = \uparrow$. Transformation to the new operators

$$\hat{b}_{k\sigma}^{(1)} = (\hat{a}_{k\sigma} - \tau_\sigma\xi_k\hat{a}_{\bar{k}\sigma})(1 + \xi_k^2)^{-1/2},$$

$$\hat{b}_{k\sigma}^{(2)} = (\hat{a}_{\bar{k}\sigma} + \tau_\sigma\xi_k\hat{a}_{k\sigma})(1 + \xi_k^2)^{-1/2}$$

diagonalizes the Hamiltonian of (20). In order to satisfy

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[6] As we mentioned above, the state described by the trivial solution
of the SCF equations ($\delta = 0$) is unstable with respect to vibrations of
the chain involving alternating bonds.

self-consistency, the value of Δ_σ calculated from the
new ground-state function

$$\Psi(n) = \hat{b}_{\pi/2,\uparrow}^{(1)+} \prod_{k < \frac{\pi}{2}} \hat{b}_{k\uparrow}^{(1)+}\hat{b}_{k\downarrow}^{(1)+} |0\rangle,$$

where n = 2N + 1, must coincide with the original value.
This gives an equation for Δ_σ:

$$\Delta_\uparrow = -\Delta_\downarrow = \Delta, \quad (\gamma/\pi)\int_0^{\pi/2} dk\,[4\beta^2\cos^2 k + \Delta^2]^{-1/2} = 1,$$

which agrees with (17). The expression for the energies
of the filled and vacant levels also agrees with (13). An
exception is the level for $k = \pi/2$: $\epsilon_{\pi/2,\sigma} = -\tau_\sigma\Delta$.

Thus, the authors of[60] have extended the UHFM
solution to long polyene chains having an odd number of
electrons, or neutral polyene radicals.

As Berggren and Johansson[61,62] have shown, the
gap in the spectrum of one-particle excited states can
be obtained not only by the UHFM, but also by the spin-
density wave method (SDWM) proposed by
Overhauser[63]. The Hamiltonian used in[48] has the
form

$$\hat{\mathcal{H}} = \sum \epsilon_0(k)\,\hat{n}_{k\sigma} +$$

$$+ \left(\frac{\gamma}{2N}\right)\sum_{k_1,\,k_1',\,k_2,\,k_2',\,\sigma} \hat{a}_{k_2,-\sigma}^+ \hat{a}_{k_1\sigma}^+ \hat{a}_{k_1'\sigma}\hat{a}_{k_2'}, -\sigma\delta(k_1+k_2-k_1'-k_2'+n\cdot2\pi) \qquad (21)$$

Here $\hat{a}_{k\sigma}^+$ and $\hat{a}_{k\sigma}$ are the operators for creation and
annihilation of an electron in the band state

$$\psi_{k\sigma} = (N)^{-1/2}\sum_{\nu=1}\varphi_{\nu\sigma}e^{ik\nu} \qquad (-\pi \leqslant k \leqslant \pi).$$

The ground state of a system having the Hamiltonian
of (21) is described in the UHFM by the wave function

$$\Psi_1(N) = \prod_k \hat{A}_{k\uparrow}^+ \hat{A}_{k\downarrow}^+ |0\rangle, \qquad (22)$$

where the $\hat{A}_{k\sigma}$ are defined by Eq. (14), provided that we
make the following replacement in the latter:
$(2N)^{-1/2}e^{ik\nu} \to \hat{a}_{k\sigma}$.

If we introduce new operators according to the ex-
pressions

$$\hat{\alpha}_k = \cos\theta_k\hat{a}_{k\uparrow} + \sin\theta_k\hat{a}_{k+Q,\downarrow},$$

$$\hat{\beta}_k = \sin\theta_k\hat{a}_{k\uparrow} + \cos\theta_k\hat{a}_{k+Q,\downarrow} \qquad \left(-\frac{\pi}{2}-\frac{Q}{2} < k < \frac{\pi}{2}+\frac{Q}{2}\right)$$

and choose the wave function of the ground state in the
form

$$\hat{\mathcal{H}} = \sum_k [\epsilon_1(k)\hat{\alpha}_k^+\hat{\alpha}_k + \epsilon_2(k)\hat{\beta}_k^+\hat{\beta}_k], \qquad (23)$$

then the effective self-consistent Hamiltonian has the
form

$$\Psi_2(N) = \prod_k \hat{\alpha}_k^+ |0\rangle,$$

where $\epsilon_{1,2}(k)$ is determined by (13).

The wave function of (23) is a function of the Over-
hauser type.[63] From the energetic standpoint, it is
equivalent to (22), since they both describe states of the
same energy and the same spectrum. Moreover, the
functions can be obtained from (22) by a certain unitary
transformation in spin-variable space.[64] Thus, the
UHFM and the SDWM are equivalent in treating a poly-
ene chain. This fact is all the more remarkable, since
there is no such equivalence in the one-dimensional case
of a free Fermi gas.[62,63]

The difference between the functions (22) and (23)

consists only in the following. In the state described by (22), the spin density at the atoms alternates according to the law

$$\langle \Psi_1 | \hat{S}_\nu^{(z)} | \Psi_1 \rangle = (-1)^\nu \delta, \quad \langle \Psi_1 | \hat{S}_\nu^{(x, \, y)} | \Psi_1 \rangle = 0, \qquad (24)$$

in contrast to the state described by (23), for which

$$\langle \Psi_2 | \hat{S}_\nu^{(z, \, y)} | \Psi_2 \rangle = 0, \quad \langle \Psi_2 | \hat{S}_\nu^{(x)} | \Psi_2 \rangle = (-1)^\nu \delta. \qquad (25)$$

The authors of[60] calculated the spin density in a long polyene radical for the UHFM wave function and its doublet component. Here it turned out that the alternation of spin density along the chain with finite amplitude persists, even after projection:

$$\rho_\mu = \langle 2S_\mu^{(z)} \rangle = (-1)^{\mu+1} \, (4\Delta/3\pi) \int_0^{\pi/2} \sin^2 \mu x \, (4\beta^2 \cos^2 x + \Delta^2)^{-1/2} \, dx.$$

Thus, both methods lead to alternation of spin density in the chain. Still, the possible existence of such magnetic structures is fundamentally dubious. Actually, as Lieb and Mattis[65] have shown, the ground state of polyene-type chains having an even number of electrons must be a singlet, and alternation of spin density cannot exist in a singlet state as it does in (24) and (25). The latter fact has been established by Fock[66] and independently by Vonsovskiĭ and Svirskiĭ.[67] Alternation of spin density in the singlet state arises from the circumstance that the UHFM function (22) and the SDWM function (23) are not eigenvectors of the operator S^2, but mixtures of multiplets having the values S = 0, 1, 2, ..., N/2.

However, a series of studies[68,69] on conjugated systems has recently appeared in which the UHFM wave function was projected onto a state of definite multiplicity, and then the energy was varied. That is, the EHFM was used. The projection procedure can be carried out as follows.[68]

Let a finite-rotation operator

$$e^{-i\hat{S}^{(y)}\alpha} e^{-i\hat{S}^{(y)}\beta} e^{-i\hat{S}^{(z)}\gamma} = \hat{T}(\alpha, \, \beta, \, \gamma)$$

act on the UHFM wave function $\Psi_1(N)$;[22] here $\hat{S}^{(y)}$ is the operator for the yth component of the total spin $\hat{S}$:

$$\hat{S}^{(y)} = -(1/2)i \sum_k (\hat{a}_{k\uparrow}^+ \hat{a}_{k\downarrow} - \hat{a}_{k\downarrow}^+ \hat{a}_{k\uparrow}), \qquad (26)$$

$\hat{S}^{(z)}$ is the operator for the zth component of the total spin:

$$\hat{S}^{(z)} = (1/2) \sum_k (\hat{a}_{k\uparrow}^+ \hat{a}_{k\uparrow} - \hat{a}_{k\downarrow}^+ \hat{a}_{k\downarrow}),$$

and α, β, and γ are the Eulerian angles of the rotation. If in addition we take an integral of the type

$$\Psi^{(S)} = [(2S+1)/8\pi^2] \int\int\int D^{(S)}(\alpha, \, \beta, \, \gamma) \, \hat{T}(\alpha, \, \beta, \, \gamma) \, \Psi_1 \, d\alpha \, d\beta \, d\gamma,$$

where $D^S(\alpha, \, \beta, \, \gamma)$ is the matrix of the irreducible representation of the three-dimensional rotation group, then we can easily see that $\Psi^{(S)}$ will be a function having the definite multiplicity 2S + 1. Upon projection onto the singlet state, $D^{(0)}(\alpha, \, \beta, \, \gamma) = 1$. Such a projection in operator form permits us to write an overall expression for the energy in the EHFM approximation.

Another projection method based on Löwdin's studies[45] was used in[69].

Let us present the conclusions from[68,69] of interest to us here.

1. The difference between the ground state energies

as calculated in the UHFM and EHFM approximations approaches zero with increasing N (as 1/N). Thus, one can use the simple one-determinant UHFM function in order to get the self-consistent wave functions and energy spectrum within the framework of the EHFM for a system having a large number of electrons.

2. The spin density $\langle 2S_\mu^{(z)} \rangle$ in the EHFM differs from the corresponding value in the UHFM by a factor S/(S + 1), where 2S + 1 is the multiplicity of the ground state:

$$\langle \Psi^{(\mathrm{PMX}\Phi)} | S_\mu^{(z)} | \Psi^{(\mathrm{PMX}\Phi)} \rangle = S \, (S+1)^{-1} \langle \Psi^{(\mathrm{HMX}\Phi)} | S_\mu^{(z)} | \Psi^{(\mathrm{HMX}\Phi)} \rangle. \quad (27)$$

Consequently, the spin density alternates in the state $\Psi^{(S)}$ if S $\neq$ 0 and $\langle S^{(z)} \rangle \neq 0$.

3. The correlation function

$$K(\nu) = (-1)^\nu \delta^2, \qquad (28)$$

approaches the following finite value as $\nu \to \infty$:

$$K(\nu) = \langle \Psi^{(S)} | \hat{S}_0^{(z)} \hat{S}_\nu^{(z)} | \Psi^{(S)} \rangle \qquad (29)$$

which coincides for infinite N with its value for the function $\Psi_1(N)$ of (20).

4. The spectra of excited states, and hence also the width of the gap, agree for long chains within the frameworks of the EHFM and the UHFM.

Equation (29) implies that an infinitely long polyene chain in the ground state will have long-range magnetic order amounting to antiferromagnetism. If the ground state is not a singlet (e.g., a doublet for radicals), an antiferromagnetic alternation of the mean values $\langle S_\mu^{(z)} \rangle$ will also be observed with an amplitude given by (24) and (27).

It is of interest to trace the relation between the values of the spin-correlation functions (26) and the spin densities (27) in long polyene chains as obtained within the framework of the UHFM. Without projection, i.e., in the UHFM, there is the simple relation

$$K(\mu) = |\rho_\mu/2|^2 \, (-1)^{\mu+1}.$$

Bonner and Fisher[70] have obtained an analogous relation between these quantities for a finite Heisenberg chain upon turning off an alternating magnetic field adiabatically.

However, as we have mentioned above, strictly speaking, the $\langle S_\mu^{(z)} \rangle$ must be identically zero in a singlet state. The EHFM does not contradict this general statement, according to (27). Still, the result is remarkable that as we go from the even polyenes (to a doublet ground state), i.e., as we add one atom to the long chain, then an antiferromagnetic alternation of ρ_μ arises with finite amplitude according to the EHFM. Apparently, this indicates instability of a ground state that is characterized by a spin correlation function (28) that differs from zero and $\rho_\mu \equiv 0$, with respect to appearance of antiferromagnetic alternation of $\langle S_\mu^{(z)} \rangle$.[7] Naturally, this fact requires further study.

4. EXACT RESULTS IN THE THEORY OF ELECTRONIC STRUCTURE OF CONJUGATED SYSTEMS

Application of the UHFM and the EHFM to the problem of the electronic structure of chain-type molecules

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[7] We note that a non-zero value of the correlation function of (28) when $\langle S_\mu^{(z)} \rangle = 0$ and $\langle S^{(z)} \rangle = 0$ had already been obtained by Kurata [71] in calculating spin correlation of paramagnetic impurities in metals.

encounters some difficulties and objections. First, Bychkov, Gor'kov, and Dzyaloshinskiĭ[51] showed in discussing a weakly non-ideal Fermi gas that, in the limit in which the interaction constant for the electrons in the one-dimensional case is small, one must account for not only the Hartree-Fock diagrams (we are speaking of the diagram representation of perturbation theory), but a broader class of diagrams called the parquet diagrams. The authors of[51] concluded that transition to a non-trivial state having a spin structure is impossible.

However, it has recently become understood[72] that this result is true only for a model of a one-dimensional, weakly non-ideal Fermi gas with a repulsion that can be represented by a δ-function. For Hubbard's model,[49] one must also take account of flipping processes. With the latter taken into account, the system proves unstable with respect to transition to an antiferromagnetic state, in agreement with the UHFM.

We should mention also several studies[10,73] in which they prove the impossibility of phase transitions at finite temperatures in one-dimensional systems. On the one hand, this theorem does not forbid a system to have long-range order at absolute zero, and on the other hand, it does not give the degree to which it is violated at non-zero temperatures. A well-known example of this type is the one-dimensional Ising model with a positive exchange integral. At a temperature strictly equal to zero, the system is antiferromagnetic, and it has an infinite spin-correlation distance. However, when $T \neq 0$, the long-range order vanishes, but here the correlation distance depends exponentially on the temperature: $l \approx e^{I/kT}$ (I is the exchange integral). It is practically infinite for $I \approx 1$ eV at room temperature. However, we cannot take this estimate too seriously, since the exact nature of the spin correlation in actual molecules is not known.

The cited difficulties make it necessary to use more exact methods of calculating the energy of the ground state and the excitation spectrum in long molecules having conjugated bonds. The circumstance that makes it possible to get more exact results is the one-dimensionality of the system. For example, let us treat a one-dimensional classical gas made of hard, identical spheres that interact only during collision. Owing to the laws of conservation of energy and momentum, when two spheres in one dimension collide, the spheres can only exchange velocities, but they cannot vary them. This means that the set of velocities of the spheres in this system will not vary in time. That is, the momentum distribution function is an integral of motion. This fact is also manifested in the quantum case.

Recently, in developing the work of Bethe,[13] Gaudin,[74] Yang,[75] and Lieb and Wu[76] have derived an exact expression for the eigenfunction of the Hamiltonian of (18). It has the form

$$\Psi(n_1, n_2, \ldots, n_N) = \sum_P [Q, P] \exp(i \sum_j k_{P_j} n_{Q_j}) \; (n_{Q_1} \leqslant n_{Q_2} \leqslant \ldots \leqslant n_{Q_N}); \quad (30)$$

Here the n_Q are the coordinates of the electrons, $k_1, k_2, \ldots, k_N$ are the set of quasimomenta, which constitute the quantum numbers of the system (in line with the remark about a one-dimensional gas made above), $Q = (Q_1, Q_2, \ldots, Q_N)$, $P = (P_1, P_2, \ldots, P_N)$ are permuta-

tions among the coordinates and the quasimomenta, respectively, and $[Q, P]$ are coefficients that depend simultaneously on Q and P; they must be determined from the Schrödinger equation and requirements of symmetry.

The Schrödinger equation gives the following relation between these coefficients:

$$[Q, P] = \hat{Y}_{nm}^{ab} [Q, P'],$$

Here the operator $\hat{Y}_{nm}^{ab}$ has the form[13]

$$\hat{Y}_{nm}^{ab} = [-(i\gamma/2) + (\sin k_n - \sin k_m) \hat{P}^{ab}] [\sin k_n - \sin k_m + (i\gamma/2)]^{-1},$$
$$Q_i = a = Q'_j, \quad Q_j = b = Q'_i,$$
$$P_i = m = P'_j, \quad P_j = n = P'_i,$$

$Q_k = Q'_k$, $P_k = P'_k$ when $k \neq i, j$, and the operator $\hat{P}^{ab}$ interchanges Q_i and Q_j. Here the energy eigenvalue of the system is expressed in terms of the quasimomenta k_i as follows:

$$E = 2\beta \sum_{j=1}^{N} \cos k_j. \quad (31)$$

If we systematically apply the operator $\hat{Y}_{nm}^{ab}$, we can express any coefficient $[Q, P]$ in terms of (a vector of dimensionality N!) the coefficient $[Q, I]$, where I is the unit permutation between the momenta $k_1, k_2, \ldots, k_N$.

Using the conditions of cyclicity and the symmetry of the wave function leads to a system of equations for the coefficients $[Q, I]$. Omitting the further calculations, which are given in considerable detail by Yang,[75] we shall write out the transcendental equations for the quasimomenta k_i that arise from solving this system:

$$Nk_j = 2\pi I_j + \sum_{\beta=1}^{N/2} \varphi(\beta j), \quad (32)$$

$$\sum_{j=1}^{N} \varphi(j\alpha) = 2\pi J_\alpha + \sum_{\beta=2}^{N/2} \psi(\beta\alpha) + \pi, \quad (33)$$

$$e^{i\varphi(j\beta)} = [\sin k_j - \Lambda_\beta + (ic/2)] [\sin k_j - \Lambda_\beta - (ic/2)]^{-1},$$
$$e^{i\psi(\beta\alpha)} = (\Lambda_\beta - \Lambda_\alpha + ic)(\Lambda_\beta - \Lambda_\alpha - ic)^{-1}, \quad c = \gamma/2|\beta|;$$

Here the Λ_α ($\alpha = 1, 2, \ldots, N/2$) are a set of numbers that are all different from each other, and which generally can be complex. The phases $\psi(\alpha, \beta)$ and $\varphi(j, \beta)$ are defined so that

$$-\pi < \text{Re } \psi(\alpha, \beta), \quad \text{Re } \varphi(j, \beta) < \pi,$$

I_j ($j = 1, 2, \ldots, N$) and J_α ($\alpha = 1, 2, \ldots, N/2$) are integers. They give the numbers of the eigenstates of the system. For example, the total momentum Q of the system is expressed in terms of them as follows:

$$Q = \sum_{j=1}^{N} k_j = 2\pi N^{-1} \left(\sum_{j=1}^{N} I_j + \sum_{\alpha=1}^{N/2} J_\alpha \right).$$

In the ground state of the system, we must select J_α and I_j as follows:

$$J_\alpha = 1, 3, 5, \ldots, N-1,$$
$$I_j = -N/2, -(N/2) + 1, \ldots, (N/2) - 1. \quad (34)$$

For quasi-homopolar levels, all of the k_j are real, and for convenience we can reduce all of them to the interval $(-\pi, \pi)$.

In order to determine the excited triplet states, following[77], we shall choose J_α in the form

$$J_\alpha = 0, 2, 4, \ldots, 2n-2, 2n+1, \ldots, N-1, \quad (35)$$

Here J_α is a certain number that determines the total quasimomentum of the system. Equations (32) and (33)

are solved by transforming to a continuous distribution of the numbers k_j and Λ_α. Here one can use the formal equality $\rho(k) = dj/dk_j$ for the density of the numbers k_j over the segment $(-\pi, \pi)$ and $\sigma(\Lambda) = d\alpha/d\Lambda_\alpha$ for the density of the numbers Λ_α over the entire axis $(-\infty, \infty)$. Upon performing the necessary differentiation in (32) and (33) under the conditions (34) and (35), we get the following system of equations for the ground state:

$$\rho(k) = (2\pi)^{-1} + (\cos k/2\pi) \int\limits_{-\infty}^{\infty} 4c\sigma(\Lambda)\,[c^2 + 4(\Lambda - \sin k)^2]^{-1}\,d\Lambda,$$

$$\int\limits_{-\pi}^{\pi} 4c\rho(k)\,[c^2 + 4(\Lambda - \sin k)^2]^{-1}\,dk = 2\pi\sigma(\Lambda) + \int\limits_{-\infty}^{\infty} 2c\sigma(\Lambda')\,[c^2 + (\Lambda - \Lambda')^2]^{-1}\,d\Lambda,$$

$$E = 2N\beta \int\limits_{-\pi}^{\pi} \rho(k)\cos k\,dk.$$

If we perform a Fourier transformation of the function $\sigma(\Lambda)$, we can easily get expressions for $\rho(k)$ and $\sigma(\Lambda)$. While omitting this calculation, we shall give the answer for the energy of the ground state, which was first determined by Lieb and Wu:[76]

$$E_0 = 4N\beta \int\limits_{0}^{\infty} J_1(\omega)\,J_0(\omega)\,[\omega\,(1 + e^{\omega c})]^{-1}\,d\omega,$$

where $J_0(\omega)$ and $J(\omega)$ are Bessel functions.

It is of interest to compare the results of exact calculation of the energy of the ground state with the results of the UHFM[62] (Fig. 6). The latter gives the energy of the separated atoms (1), the calculations by the Hartree-Fock method (2) and the UHFM (3), and the exact solution (4).

We shall give another result involving the energy of the ground state that Lieb and Wu calculated. Let us consider a series expansion of the energy in terms of the small quantity $\gamma/2\,|\beta| = c$.[78] As $c \to 0$. we have

$$E_0/N\,|\beta| = -(4/\pi) + (c/2) - (c^2/4\pi^3) \sum\limits_{n=0}^{\infty} (c/2\pi)^{2n}$$

$$\times [(2n-1)!!]^3\,(2n+1)\,(2^{3n}n!)^{-1}\,f(n) + O(c^{3/2}e^{-2\pi/c});$$

$$f(n) = (2^{2n+3} - 1)\,\zeta(2n+3),$$

where $\zeta(x)$ is the Riemann zeta function.

It is interesting to note that the series in the small quantity c is asymptotic. The assertion that the expansion of the energy of the ground state in terms of the interaction constant will be asymptotic in nature had been stated long ago. However, the cited expansion is the first rigorous proof of this statement for a non-trivial model in many-body theory.

5. THE ELECTRONIC-EXCITATION SPECTRUM OF A ONE-DIMENSIONAL CHAIN HAVING CONJUGATED BONDS[79,80]

The exactly-solvable Hubbard model permits us to make a complete study of the excitation spectrum of a chain having conjugated bonds. We shall give a qualitative description of the spectrum in the limiting case in which the distance between the CH-fragments is large. All of the eigenstates in this limit are divided into groups of almost degenerate states: homopolar, ionic,
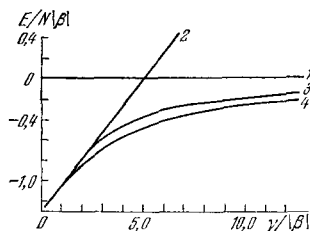

FIG. 6. The energy of a long polyene in the Hubbard approximation. [62]

doubly-ionized, etc. The first group consists of 2^N (where N is the number of identical atoms in the system) homopolar states of almost zero-point energy. The splitting of the energy levels belonging to this group is described by the Heisenberg spin Hamiltonian. We should state that the UHFM does not give the spectrum of homopolar states. In order to determine them, we must use the method of random phases in the ground state of the UHFM. This fact was first pointed out in[81].

Bulaevskiĭ[82] has proposed another method for describing the homopolar states of conjugated molecules. He obtained spin Hamiltonians that best approximate the Hamiltonian of the type of (1) for the homopolar states. Kohn[83] and Bulaevskiĭ[82] showed that an optical transition from the ground state, which is homopolar, to other homopolar states is forbidden or of low intensity.

The second group consists of $N \cdot 2^N$ ionic states having energies of $\sim\gamma$. The lowest excited state of the system to which an optical transition can occur belongs to this group.

The third group consists of $N(N-1) \cdot 2^{N-1}$ states having energy $\sim 2\gamma$, etc. At actual equilibrium distances between the atoms, all the energy levels can also be characterized by belonging to one of these groups. Here one should add the prefix "quasi" to the name of the group.

From the standpoint of exact solutions, the classification into quasi-ionic and homopolar excited states is carried out as follows. An ionic-type excitation involves vacancies in the distribution of numbers I_j, while a quasi-homopolar excitation involves vacancies in the distribution of numbers J_α. In order to create a quasi-ionic state of a system of N particles, we add to the system of N particles in its ground state a $(N+1)$-st particle of quasimomentum k_+, and then remove one of the original particles having quasimomentum k_-. The ex-excitation energy in the quasi-ionic state is given by the expression

$$\Delta E\,(k_+, k_-) = \gamma - \mu\,(k_+) - \mu\,(k_-),$$

Here $\mu(k_-)$ is the amount by which the energy $E(M, M)$ of the ground state of N particles would diminish upon removing a particle of quasimomentum k_- having its spin pointing upward ($M - 1$ particles remain with spin ↑ and M particles with spin ↓):

$$\mu\,(k_-) = E\,(M, M) - E\,(M-1, M)_{k_-}. \tag{36}$$

The quantities $\mu(k_+)$ are found by directly calculating the energies $E(M-1, M)k_+$, using Eqs. (32) and (33).

Removal of one particle from a system of N particles occurring in the ground state can be reflected by a corresponding change in the numbers I_j and J_α in Eqs. (32) and (33). The numbers $I_j^{(N-1)}$ and $J_\alpha^{(N-1)}$ that correspond to the excited state of the system of $N-1$ particles obtained by removing a particle of quasi-momentum k_- from the system of N particles are related to the numbers $I_j^{(N_0)}$ and $J_\alpha^{(N_0)}$ (the ground state of the system of particles) by the relations

$$I_j^{(N-1)} = I_j^{(N_0)} + (1/2)\Theta\,(k_j - k_{\min}) + (1/2)\Theta\,(k_j - k_\pm),$$

$$J_\alpha^{N-1} = J_\alpha^{(N_0)} + \Theta\,(\Lambda - \Lambda_0),$$

Here $\Theta(x)$ is a Θ-function, and when $N \to \infty$, $k_{\min} \to -\pi$, and $k_{\max} \to \pi$. If we know the distribution of the num-

bers $I_j^{(N-1)}$ and $J_\alpha^{(N-1)}$, we can find the density $\rho(k)$ of states over the interval $[-\pi, \pi]$. In Eq. (31), if we transform from summation to integration, then we can determine the necessary energy values. We get for the energy of the system of $N-1$ particles:

$$E(M-1, M)_{k_\pm, \Lambda_0} = E(M, M) + E_1(-\pi) + E_1(k_\pm) + E_2(\Lambda_0),$$

where

$$E_1(k) = \beta \cos k + 2\beta \int_0^\infty J_1(\omega) \, \omega^{-1} \cos(\omega \sin k) \, [1 + \exp(u\omega/2)]^{-1} \, d\omega,$$

$$E_2(\Lambda_0) = 2\beta \int_0^\infty J_1(\omega) \, \omega^{-1} \cos(\omega\Lambda_0) \, [\text{ch}\,(u\omega/4)]^{-1} \, d\omega \qquad (u \equiv \gamma/|\beta|). \tag{37}$$

We must take $\Lambda_0 = \infty$ for a singlet excitation. Then $E_1(\Lambda_0 = \infty) = 0$, and we can find from (36) an expression for the energy of a singlet quasi-ionic excitation

$$\Delta E(k_+, k_-) = \gamma + \varepsilon(k_+) + \varepsilon(k_-),$$

Here $\varepsilon(k_-) = E_1(-\pi) + E_1(k)$ is the excitation energy of a "hole" having the quasimomentum k in the completely filled band of the ground state of the system.

As $N \to \infty$, the width of the gap in the spectrum of optically-observable intense quasi-ionic excitations has the form

$$\Delta E = \Delta E(k_+ = \pi, k_- = \pi) = \gamma - 4\beta + 8\beta \int_0^\infty J_1(\omega) \, \omega^{-1} \, [1 + \exp(u\omega/2)]^{-1} \, d\omega.$$

As was shown in[79], as $\gamma/|\beta| \to 0$,

$$\Delta E \approx 8\,(\gamma\beta)^{1/2}\,\pi^{-1} \exp(-2\,|\beta|\,\pi/\gamma).$$

We note that the exponential part of this expression coincides with the expression for the gap in the UHFM. However, the factor in front of the exponential can vary greatly at small values of $\gamma/2|\beta|$. In particular, this variation makes it necessary to vary the parameter $\gamma/2|\beta|$ in order to match the calculated size of the slit with the experimental value.

Upon taking account of the relation of the parameter Λ_0 to the total momentum of the system

$$Q = (\pi/2) + \int_0^\infty J_0(\omega) \, \omega^{-1} \sin \omega\Lambda_0 \, [\text{ch}\,(\omega u/2)]^{-1} \, d\omega$$

the quantity $E_2(\Lambda_0)$ in (37) gives an expression for the spectrum of triplet quasi-homopolar excited states.

There are quasi-homopolar excitations of more complex structure. Thus, for example, singlet excited states can occur as bound states of two triplet excitations. They also begin at zero (as $N \to \infty$). However, in contrast to the latter, they have an endpoint at some quasi-momentum q_0. Apparently this endpoint of the spectrum is analogous to the endpoint in the excitation spectrum in liquid helium that was found by Pitaevskiĭ.[84] As we know, existence of an endpoint in a spectrum involves instability of excitations with respect to decomposition into two excitations. Figure 7 gives the general form of the spectrum. It shows the singlet (1) and triplet (2)
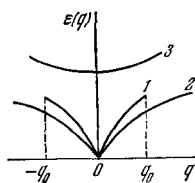
quasi-homopolar excitations and the quasi-ionic excitations (3).

However, the exact methods that have been developed do not permit us unambiguously to solve the problem of the correlational spin properties of these systems, since a wave function of the type of (30) is too complex for calculation of the means. In truth, there are some weak arguments in favor of the idea that the ground state (at $T = 0$) is antiferromagnetic (or in any case, the correlation of two spins declines very slowly, e.g., as $1/n$). For example, these arguments include the double periodicity of the triplet excitation spectrum, which is characteristic of antiferromagnetic systems.

6. PARAMAGNETIC PROPERTIES OF POLYMERS HAVING CONJUGATED BONDS

The quasi-homopolar states are very important in determining the physical and chemical properties of polymers having conjugated bonds. The fact that the triplet excitation spectrum begins at zero for infinitely long chains causes these molecules to be appreciably paramagnetic.[85,86] In this regard, it is interesting to discuss the existing data on the EPR spectra of long carbon-chain polymers.

It was established[86-88] in 1959 that linear polymers whose main-chain structure resembles the polyene chain, e.g.,
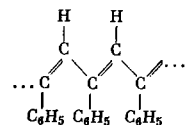
give intense EPR signals. Here the EPR spectrum consists of a rather narrow single line having a g factor close to that of a free electron. The nature of the variation of the spectra under different conditions (solid state or in benzene solution)[86-88] indicates that this EPR spectrum arises from the intramolecular structure of the polymers, rather than intermolecular interactions. The intensity of the EPR signal increases with decreasing temperature. From this fact, the authors of[85-88] concluded that the observed EPR spectrum arises from the ground state of the polymer, rather than from transition to excited states. The signal intensity also increases with increasing length of the polymer chain. Here the equivalent concentration of unpaired electrons is $10^{17}-10^{19}$ per gram of material. That is, it varies by two orders of magnitude as a function of the chain length.

There are currently a number of interpretations of the EPR experiments on carbon-chain polymers. We shall discuss them without adhering to historical sequence. One of the explanations of these experiments, which was based on the results of[76,79,89], was proposed by Berlin, Vinograd, and Ovchinnikov.[90] As was implied by[79], the spectrum of the lowest triplet excitations of a polyene chain has the form

$$E_n^0 = \delta\,|n|/N, \quad \text{где} \quad \delta = 4\pi\beta I_1(2\pi\,|\beta|\,/\gamma)\,[I_0(2\pi\,|\beta|\,/\gamma)]^{-1},$$

Here I_0 and I_1 are Bessel functions of imaginary argument, and $n = \pm 1, \pm 2, ..., p \ll N$. These excitations show the property of additivity: $E^0(n_1, n_2) = E^0(n_1) + E^0(n_2)$, with $n_1 \neq n_2$. The excitation $n = |n|$ corresponds to a z-axis projection of the spin equal to unity, while $n = -|n|$ corresponds to -1. If we apply to the system a

FIG. 7. Energy spectrum of a long polyene chain.

magnetic field along the z axis, then the energy of this excitation can be represented in the form

$$E(n) = (\delta \mid n \mid /N) + (\mid n \mid /n)\, \mu g H,$$

Here μ is the Bohr magneton, and g is the g-factor.

Upon treating the set of such excitations as a Fermi gas having a zero chemical potential (but with a "degenerate" zero level n = 0), the authors of [90] derived the following expression for the partition function:

$$Z = \prod_{n=-\infty}^{\infty} (1 + e^{-E_n/kT}). \tag{38}$$

We get the following from (38) for the statistical magnetic susceptibility χ_0:

$$\chi_0 = -\frac{\partial^2 F}{\partial H^2}\Big|_{H=0} = \frac{\mu^2 g^2}{2kT} \sum_{n=1}^{\infty} \frac{1}{\mathrm{ch}\,(n\delta/2NkT)}, \tag{39}$$

where F is the free energy.

The inequalities [88] $\delta/kT \gg 1$ and $\mu g H/kT \ll 1$ hold under the experimental conditions of [86-88].

If $\delta/NkT \ll 1$, then we get from (39):

$$\chi_0 = \mu^2 g^2 N/\delta. \tag{40}$$

Hence, for an infinite chain as calculated per unit volume, we get $\chi_0 = 10^{-29} n$, where n is the number of π electrons per unit volume.

Equation (40) gives a fully exact value of the paramagnetic susceptibility of an infinite polyene chain in the Hubbard model at absolute zero, as the rigorous calculations of Takahashi [91] imply. The fact that the paramagnetic susceptibility at absolute zero differs from zero for this system relates polymers with conjugated bonds with the metals, whereas in terms of electric conductivity they are semiconductors. This is a distinctive feature of Mott semiconductors in general.

The converse inequality $\delta/NkT \gg 1$ (at T $\lesssim$ 300°) holds for finite values of N (even rather large ones, N $\approx 10^2 \gg 1$). In this case we get from (39)[8)]

$$\chi_0 = (2\mu^2 g^2/kT)\, e^{-\delta/NkT}. \tag{41}$$

As is implied by the theory of dispersion relations, the integral intensity of the EPR signal $\int_0^{\infty} I(\omega)\, d\omega$ is proportional to the paramagnetic susceptibility χ_0.

Since the intensity standard commonly used experimentally is diphenylpicrylhydrazyl, which is a paramagnetic substance, the equivalent spin density is

$$n_{eq} = (4kT/\mu^2 g^2)\, \chi_0, \tag{42}$$

since the spin susceptibility is

$$\chi_{sp} = (\mu^2 g^2/4kT)\, n_{sp}$$

From (40) and (42) we get the equivalent spin concentration for an infinite chain

$$n_{eq}^{\infty} = 4kTn/\delta = 4\cdot10^{-3}.$$

[8)] For polyene chains $\delta \approx 20$ eV, and in accord with (40) and (41), one should observe an appreciable paramagnetism only for rather long chains, since $e^{-\delta/NkT} \approx e^{-20/N\cdot0.03} \approx e^{-30}$ (N = 20). As recent studies have shown, the value of δ can be smaller by a factor of 2–3 for other systems (e.g., the polyphenylacetylenes, so that even chains containing 10–15 links can prove to be paramagnetic.

Since experimentally we are dealing with finite chains, $n_{eq} < n_{eq}^{(\infty)}$. This result agrees with the experimental results [86-88] for conjugated polymers.

Comparison of the experimental and theoretical temperature-dependences of the EPR signal in these molecules is very difficult. It has recently been found that the time for relaxation of the paramagnetic susceptibility of polyphenylacetylene to its equilibrium value for a given T increases greatly with decreasing temperature (below 20°C). However, this time is relatively short above 20°C (minutes), and an increase in the paramagnetic susceptibility with temperature is observed in this temperature range, in agreement with (41). Below 20°C, the susceptibility increases with decreasing temperature for reasonable observation times.

The authors of [90] explain the experimental dependence of the intensity on T in this temperature range by the idea that the triplet excited states have very long lifetimes, and they do not succeed in relaxing to the equilibrium concentration as the specimen is cooled.

In fact, the triplet-singlet relaxation time for the benzene molecule already amounts to several seconds. However, theoretical estimates and further studies of relaxation processes in these systems are needed to confirm this argument.

Another explanation of the EPR experiments on polymer chains involves the concept of charge-transfer complexes.[92] However, as we have said above, the states in which charge transfer can occur (quasi-ionic) are separated from the ground state by a considerable gap. Hence it is hard to explain their origin. There is also another viewpoint [93] which says that the paramagnetism of polymer chains involves stabilization of triplet excitations by conformational change of the molecules. However, it is dubious that a large molecule (N $\gg$ 1) can change its nuclear configuration upon going to the lowest ($\Delta E \sim 1/N$) excited state. The problem of the source of the EPR signal in carbon-chain polymers requires further theoretical and experimental study.

7. LOCAL STATES IN POLYMERS HAVING CONJUGATED BONDS

One of the possible methods of studying the electronic structure of periodic systems is to study the effect on their energy spectrum of defects that have been introduced in special ways. As we know, any violation of the periodicity of an ideal chain can lead to splitting of local levels from the band of allowed states. The local levels can lie either in the forbidden bands or in regions above and below the two allowed bands. Naturally, the levels that lie in the forbidden band are of greatest interest. In [94], the exact conditions for appearance of local states upon very simple perturbations of the ideal polyene chain were obtained by the methods of the theory of local perturbations. [95] It was assumed here that the reason for creation of the gap was alternation of bond lengths. In [95,96], analogous conditions were derived for the case in which the gap is of purely correlational or "combined" nature, and the results for the two models were compared. It turned out that a perturbation (a variation $\Delta\alpha$ of the Coulomb integral) of the nth atom in the alternating-bond model leads to splitting off of a local level in the forbidden band only when $|\Delta\alpha|$

$\geq 4\,\beta_1\beta_2/n\Delta E$, while a change in the resonance integral also generates a pair of local states only when the weaker bond is strengthened, or the stronger bond is weakened. In the correlational-gap model, a perturbation of the even atoms gives approximately the same result as in the alternation case, whereas action on an odd atom splits off a local level even under an infinitesimally small perturbation. In this model, a change in the strength of a bond does not at all give rise to local states in the forbidden band. Thus, in principle, study of local states that arise upon substitutions and conformational changes in the chain can be used for experimental choice between two theories of the electronic structure of the polyenes.

Studying local states also opens up an interesting possibility for detecting band alternation in chains that contain two atoms (A and B) per unit cell (e.g., heterocumulenes). In these systems, a gap already exists in the energy spectrum, owing to the alternation of atoms. Hence, neither alternation of bond lengths nor existence of a correlational contribution to the gap is generally necessary.[52] If bond alternation is actually absent (or very small), then, as was shown in[96], all the possible substituents can be divided into two groups (a and b) in such a way that, e.g., a representative of group a will give a local level only when attached to an atom of type A, but not B, and vice versa. However, if the alternation is substantial, then substituents of either group can generate a local level when attached to any atom of the chain.

Finally, we note that existence of local states can explain the difference noted in the Introduction in the behavior of the frequency of the first electronic transition between the symmetrical dyes and the polyenes. Actually, it is highly probable that the introduction of nitrogen atoms into the chain in the symmetrical dyes (see Fig. 1) gives rise to local states near the band boundary, so that the first electronic transition occurs from a local level into the free band. Since the energy of such a transition for long chains is small, extrapolation of the experimental data must lead to a zero (or almost zero) size of the gap.

8. ONE-DIMENSIONAL SEMICONDUCTORS HAVING NON-INTEGRAL NUMBERS OF ELECTRONS PER CELL

The discovery of organic one-dimensional semiconductors based on TCNQ has posed a number of problems for the theory. These systems are varied both in terms of physical properties and in structure. There are a number of charge-transfer complexes based on TCNQ in which the electronic structure and properties resemble the electronic structure of the components discussed above. They contain one electron per center, and are Mott semiconductors. Here the entire complex of their physical properties can be described on the basis of the ideas developed in the preceding sections.[98] Of course, their concrete electronic parameters differ considerably from those for compounds having conjugated bonds. For example, for the system TCNQ⁻—NMP⁺ (N-methylphenazine), which was studied by Epstein et al.,[98] $\gamma = 0.17$ eV, $\beta = 0.021$ eV, and the gap in the quasi-ionic excitation spectrum is 0.02 eV. The fact that the size of the

gap is comparable to kT at room temperature greatly complicates analysis of the experimental situation. This case requires precise analysis of the partition function using the Hamiltonian of (11). Recently the studies of the Yangs[99] and of Takahashi[100] have provided exact equations for the partition function of the Heisenberg antiferromagnetic Hamiltonian. Takahashi has derived (but not published) exact equations for the partition function with the Hamiltonian of (11). However, the derived equations are nonlinear and too complex, and consequently they have not been solved in any of the studies. We note a recent study by Shiba and Pincus,[101] where they performed a numerical analysis of the thermodynamic quantities of a system having the Hamiltonian of (11) that contained six centers in a ring.[9] Apparently, the difficulties in the temperature generalization of Hubbard's one-dimensional model will very soon be overcome.

However, there are charge-transfer complexes based on TCNQ in which the number of electrons per center (or per cell) is not unity. For example, there is 2/3 electron per TCNQ molecule in the salt Cs_2TCNQ_3, and 1/2 electron in the salt $TCNQ_2^-$ (quinolinium)⁺. Other situations can also occur. In all cases, it turns out that analysis of the system based on Hubbard's Hamiltonian is insufficient, and we must take more detailed account of the interaction of electrons.

Let us consider again the Hamiltonian of (11). However, we shall assume that the total number of electrons is not equal to the number of centers, and hence the electron density $\rho = M/N$ is not equal to unity. We shall study the energy of the ground state of the system in the limit as $\gamma \to \infty$. We can get the zero-order term in the expansion of the energy by keeping in the Hamiltonian of (11) only the part involving interaction of electrons. In this limit, each electron is situated at its center, the total energy is zero, and the ground state is highly degenerate. When $\rho < 1$, a degeneracy is added to the spin degeneracy of the system that involves the possibility of distributing the electrons over different centers. This latter degeneracy is removed by using the kinetic-energy operator in (11). It is essential to consider the eigenstates of this operator that do not contain ionic configurations.

For example, this condition is satisfied by a one-determinant wave function (in the n-representation) composed of one-electron wave eigenfunctions of the kinetic-energy Hamiltonian with all the different quasi-momenta. The spin part of this function must be chosen so as to satisfy the condition that the function should be antisymmetric with respect to simultaneous interchange of the coordinates and spin of two particles (the total spin of the system must be zero). Evidently ionic terms are lacking in a function constructed in this way. In other words, the eigenstates of the system in the limit as $\gamma \to \infty$ coincide with the states of the Hamiltonian

$$\mathscr{H}_1 = \beta \sum_{\nu=1}^{N} (C_\nu^+ C_{\nu+1} + C_{\nu+1}^+ C_\nu), \qquad (43)$$

Here C_ν^+ and C_ν are the Fermi operators for creation

and annihilation of an electron (but without the spin). By varying the statistics of the particles, we take account of their strong repulsion at a given center. Girardeau[102] has used analogous ideas in the theory of a one-dimensional Bose gas of impenetrable particles. The total number of electrons is $N\rho$. The process of antisymmetrizing the obtained wave function with account taken of spin is important in obtaining the energy in the next order of magnitude with respect to β/γ. We can easily see that the contribution to the energy of the ground state here is

$$E_1/N \mid \beta \mid = -(2/\pi) \sin \pi\rho.$$

It is hard to obtain the next term of the expansion in this way. However, we can get it by using the exact equations (32) and (33). Upon performing the appropriate calculations, we have

$$E \mathbin{/} N \mid \beta \mid = -(2/\pi) \sin \pi\rho - (4 \ln 2 \mid \beta \mid/\gamma) [\rho^2 - (\rho/2\pi) \sin 2\pi\rho)] + \ldots \tag{44}$$

The last term in (44) involves removing the spin degeneracy. When $\rho = 1$, Eq. (44) goes over into an expression for the energy of the ground state for the Heisenberg antiferromagnetic Hamiltonian.

We can study the spectrum of the excited states in the same way. In particular, for large γ/β, the excitation spectrum coincides with that of the Hamiltonian of (43), i.e., with the spectrum of an ideal spinless Fermi gas on a lattice. This spectrum begins at zero:

$$\varepsilon\,(k) = 2 \mid \beta \mid \cdot \mid \cos k - \cos \pi\rho \mid, \quad \pi > k > \pi\rho,$$

and the corresponding system is a metal. The situation can change when we take account of the interaction of electrons situated at more than one center. For example, let us consider a Hamiltonian of the following form:

$$\mathcal{H} = \mathcal{H}_{(11)} + (\gamma_{12}/2) \sum_{v,\,\sigma_1,\,\sigma_2} C_{v,\,\sigma_1}^+ C_{v,\,\sigma_1} C_{v+1,\,\sigma_2}^+ C_{v+1,\,\sigma_2}. \tag{45}$$

Here $\mathcal{H}_{(11)}$ is the Hamiltonian given by (11), and the second term is a Hamiltonian describing the repulsion of electrons located at adjacent centers. For the sake of concreteness, we shall treat the case $\rho = 1/2$, which is characteristic of the system $TCNQ_2^- - M^+$ (where M^+ is any donor).

In order to study the properties of the ground state and the excitation spectrum, we shall make γ very large $(\gamma/|\beta|$ and $\gamma/\gamma_{12} \to \infty)$. According to the ideas developed above, the Hamiltonian of the first approximation will have the form

$$\mathcal{H}_1 = \beta \sum_{v=1}^{N} (C_v^+ C_{v+1} + C_{v+1}^+ C_v) + \gamma_{12} \sum_{v=1}^{N} C_v^+ C_v C_{v+1}^+ C_{v+1} \tag{46}$$

(the operators C_v^+ and C_v have the same meanings as in (43)). The Hamiltonian of (46) has been studied in detail by exact methods in a number of studies[103-107] (this is the Hamiltonian of an anisotropic Heisenberg chain of spins). The most essential fact for us here is that the system characterized by (46) transforms at $\gamma_{12} = 2|\beta|$ from a metal to a dielectric (when $\gamma_{12} < 2|\beta|$ it is a metal, but when $\gamma_{12} > 2|\beta|$ it is a dielectric). The size of the gap in the dielectric phase is[106]

$$\Delta E = \frac{\pi \, \mathrm{sh}\, \theta}{\theta} \sum_{n=-\infty}^{\infty} \left(\mathrm{ch}\, \frac{(2n+1)\pi^2}{2\theta}\right)^{-1}, \quad \mathrm{ch}\,\theta = \gamma_{12}/2 \mid \beta \mid.$$

When γ_{12} is close to $2|\beta|$, ΔE is highly non-analytic.

Thus we see that a system described by the Hamiltonian of (45) (or one more complex) can undergo a Mott metal-dielectric transition that depends on ρ, γ/β, and γ_{12}/β. A detailed theory of the transition at finite γ has not been constructed, and is a matter for the future.

The possibility of a Peierls lattice distortion in these systems is also a topic for study.

9. CONCLUSION

As the material presented in this review indicates, we can consider the fundamental features of the electronic structure of simple homoatomic chains having conjugated bonds to have been elucidated. Only the problem of the spin structure of the ground state of these systems and the associated problem of their magnetic properties (antiferromagnetism and ferromagnetism) require further study. The difficulties encountered here are general in nature, and apparently, solving them will make it possible to advance considerably further toward constructing a general theory of cooperative magnetic phenomena.

In the last decade, a large number of polymers with conjugated bonds have been synthesized that have more complicated main-chain structures than the polyenes.[2,5,6] Many of them are used in practice as thermally stable semiconductors, catalysts, etc. (see[6] and Chaps. V and VI). Hence it is important to study the electronic structure and energy spectrum of such chains by using the methods developed in the theory of the polyenes. Evidently, a number of new problems will arise here that involve taking account of possible distortions of their linear structure, calculating the most probable configurations, estimating the effect of intermolecular interaction, etc., since these effects are always important in real polymeric materials. The theoretical explanation of the unusual catalytic properties of conjugated polymers is worthy of especial attention.

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