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ELECTRONIC STRUCTURE OF LONG MOLECULES WITH CONJUGATED BONDS

I. A. Misurkin and A. A. Ovchinnikov
L. Ya. Karpov Physico-chemical Research Institute
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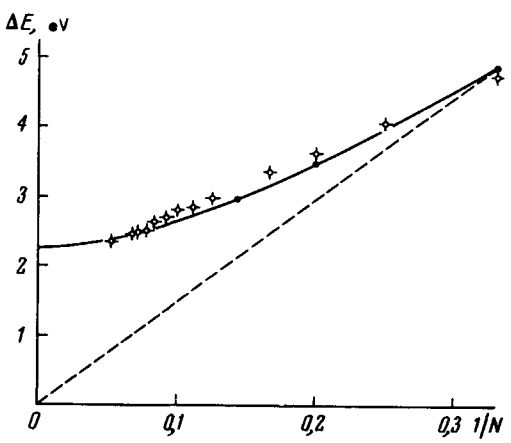
It is usually assumed that when the length of a molecule with conjugated bonds increases (we shall consider molecules of the type of polyene, $(CH)_{2N}$) the distances between the electronic levels vary like 1/N, so that for sufficiently large N the molecule becomes a one-dimensional metal. The experimental data, however, contradict these notions. Indeed, with increase in the length of the polyene chain the magnitude of the first electronic transition tends to a finite value ~2.24 eV [1,2] (see the figure).

The fact that the metal becomes a dielectric at a sufficiently large electron repulsion was noted already by Mott [3]. For polyenes, however, Mott's arguments are not valid, since the repulsion is actually not too large. It is known, in particular, that graphite is a metal at the same electronic parameters. The presence of a gap in the spectrum might be attributed to the transition of the molecule into a state with alternating bond lengths as $N \to \infty$ [4]. For real parameters of the electron-phonon interaction [5], the gap is one order of magnitude smaller than the experimental value. Finally, Langmuir oscillations in a one-dimensional system have an acoustic character, and consequently cannot explain the observed spectrum [6]. We propose below an explanation of the indicated experimental fact, on the basis of an allowance for the electron repulsion.



First electronic transition of the molecule $C_{2N}H_{2N}$ vs. 1/N: -◊- - experiment, -●- - our calculations, --- - electronic transition withoug allowance for electron repulsion.

The Hamiltonian of the electrons of the chain has in Hubbard's approximation [7] the form

$$H = \sum_{mn\sigma} T_{mn} c^{+}_{m\sigma} c_{n\sigma} + \frac{\gamma}{2} \sum_{n\sigma} c^{+}_{n-\sigma} c_{n-\sigma} c^{+}_{n\sigma} c_{n\sigma} , \tag{1}$$

where $c^{+}_{n\sigma}$ and $c_{n\sigma}$ are the operators of creation and annihilation of an electron with spin σ on an atom n, and where all the $T_{mn} = 0$ except $T_{nn} = \alpha$ and $T_{n\pm 1\, n} = \beta$. Allowance for all other terms in the electron interaction merely renormalizes α and β.

The wave function (Φ) is calculated by the generalized method of the Hartree-Fock self-consistent field, in which the electrons with different spins are on different Bloch orbits.

The magnitude of the gap in the spectrum as $N \to \infty$ equals $\Delta E = 2\gamma\delta$ [1]. In the ground state, the spin density at the atom n is

$$\langle \Phi | c^{+}_{n\sigma} c_{n\sigma} | \Phi \rangle = \tfrac{1}{2} + \sigma(-1)^{n}\delta, \tag{2}$$

i.e., this state has an antiferromagnetic spin structure [2].

Let us consider the ground-state function for arbitrary interaction parameters.

When $\gamma/2|\beta| \gg 1$ we can easily find that the ground state is antiferromagnetic with $\delta = 1/2$ and is separated from the excited state by a gap $\Delta E = \gamma$, in accordance with Mott's notions [3]. Further, the ground-state energy calculated in this limit for one particle is $\epsilon \simeq \alpha - 0.5(2\beta)^2/\gamma + \ldots$, whereas the exact solution yields $\epsilon_{exact} \simeq \alpha - 0.69(2\beta)^2/\gamma + \ldots$ [9]. Thus, the density (2) yields a qualitatively correct description of the behavior of the system in this limiting case. Thus there are grounds for expecting that for polyenes, where $\gamma/2|\beta| \sim 1$, the function Φ is a reasonable approximation. In fact, for real values of the electronic parameters, $\beta = -2.4$ eV, and $\gamma = 5.42$ eV [10], the calculated dependence of the first electronic transition $\Delta E(N)$ is in good agreement with experiment (see the figure).

We note that for small N ($N \lesssim 5$) the state with $\delta = 0$ is more favored energywise. For large N we have $\delta \sim 0.2$, i.e., the average magnetic moment per carbon atom is $\sim 0.4\ \mu_B$. Unfortunately no direct experiments have been made to determine the spin structure of polyenes.

For $\gamma/2|\beta| \ll 1$ we have $\Delta E \sim |\beta| \exp(-2\pi|\beta|/\gamma)$. Recently Bychkov, Gor'kov, and Dzyaloshinskii [11] considered a one-dimensional Fermi gas, with repulsion between particles and $\gamma/2|\beta| \equiv g \to 0$, and reached the conclusion that there is no transition to a nontrivial state with spin structure. It must be stated that their conclusion is correct only in the sense that there is no nontrivial state in which ΔE has an asymptotic behavior like $\sim\exp(-\text{const}/g)$. Indeed, using the method of compensation for dangerous diagrams, developed by Bogolyubov et al. [12], we obtain the following equation for u_p and v_p (the spin structure is such that $(uv)_{p\sigma} = -(uv)_{p-\sigma}$):

$$2p(uv)_p = \frac{1}{2\pi}(u_p^2 - v_p^2) \int_{-p_0}^{p_0} dp' S^{-}(\xi)(uv)_{p'} , \tag{3}$$

[3]

where

$$u_p^2 = \tfrac{1}{2}(1 + p[p^2 + \Delta^2(p)]^{-\frac{1}{2}}), \quad v_p^2 = \tfrac{1}{2}(1 - p[p^2 + \Delta^2(p)]^{-\frac{1}{2}}),$$

$$\xi = \frac{g}{\pi} \ln 2p_0(|p| + |p'| + |p + p'|)^{-1} .$$

The function $S^-(\xi)$ was obtained in a logarithmic approximation by Bychkov et al. [11] and is equal to

$$S^-(\xi) = g\left(\frac{3}{8}\frac{\xi}{1+\xi} + \frac{1}{1+\xi} - \frac{\xi}{8} - \frac{1}{4}\ln(1+\xi)\right).$$

For such a function $S^-(\xi)$, Eq. (3) has only a trivial solution $\Delta(p) = 0$. However, terms of order g^2 in $S^-(\xi)$ can change this conclusion. For example, if we add to $S^-(\xi)$ the constant $g^2S_0 > 0$, then Eq. (3) will have a nontrivial solution, and the gap on the Fermi surface will have the asymptotic value $\Delta(p = 0) \sim \exp[(-2\pi/g)\ \ln(1/gS_0)]$. Thus, the question of existence of a state with spin structure for a one-dimensional Fermi gas with repulsion between particles as $g \to 0$ cannot be solved in a logarithmic approximation.

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[1] In the trivial state $\delta = 0$.

[2] A state of this type for one-dimensional Fermi gas with repulsion between particles was considered by Overhauser [8], but he used different variational functions.

[3] $S^-(\xi)$ - Cooper vertex part, coinciding with that in [11].