On the possibility of a metal-dielectric transition in one-dimensional systems with noninteger number of electrons per unit

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A one-dimensional lattice electron gas is considered with a noninteger number of electrons per unit cell. It is shown that for certain values of the electron interaction constants the system undergoes a metal—dielectric transition and charge alternation occurs in the dielectric phase.

The appearance of organic one-dimensional semiconductors on the basis of the salts of tetracyanoquinonedimethane (TCNQ)[1] has raised a number of problems in the theory of one-dimensional systems. These semiconductors vary greatly, both in physical properties and in their structure. There is a number of complexes with charge transfer based on TCNQ, in which the electronic structure and the properties are similar to the electronic structure of organic semiconductors with conjugated bonds. The latter contain as a rule a single electron per cell and are Mott dielectrics at all possible values of the electronic parameters.[2,3] The entire complex of their physical properties can be described on the basis of the one-dimensional Hubbard Hamiltonian:[4]

$$\hat{H}_x = \beta \sum_{n\sigma} (a_{n\sigma}^{+} a_{n+1,\sigma} + a_{n+1,\sigma}^{+} a_{n\sigma}) + \frac{\gamma}{2} \sum_{n\sigma} a_{n\sigma}^{+} a_{n\sigma} a_{n-\sigma}^{+} a_{n-\sigma}. \quad (1)$$

Here $a_{n\sigma}^{+}$ and $a_{n\sigma}$ are the Fermi operators of creation and annihilation of electrons at the center n with spin σ. The parameters γ and β are determined by experiment. Thus, for example, for the system TCNQ-MNP (N-methyl-phenazine), Epstein et al.[4] obtained the values $\gamma = 0.17$ eV and $\beta = 0.021$ eV.

However, there exist complexes with charge transfer on the basis of TCNQ for which the number of electrons per unit center (or per unit cell) is not equal to unity. For example, for the salt $TCNQ_3Cs_2$, there is $^2/_3$ electron per molecule of TCNQ, for the salt $TCNQ_2$-quinoline, $^1/_2$ electron, and so on. It turns out that in all these cases an analysis of the system on the basis of the Hamiltonian (1) is inadequate and one must take into account the interaction of electrons in more detail. The purpose of the present note is to point out the possibility of a Mott metal-dielectric transition for certain definite values of the electronic parameters for systems of such a type.

We consider the Hamiltonian (1), but assume that the total number of electrons M is less than the number of centers N (i.e., $\rho = M/N < 1$). We investigate the energy of the ground state and the spectrum of the system in the limit as $\gamma \to \infty$. In this limit, the electrons are each located at its center, the total energy of the system is equal to zero and the ground state is strongly degenerate. For $\rho < 1$ there is added to the spin degeneracy of the system a degeneracy connected with the possibility of distributing the electrons over the different centers. This latter degeneracy is removed with the help of the kinetic-energy operator in (1). It is essential that the operator eigenstates considered here do not contain ionic configurations. Thus a condition is satisfied, for example, by a one-determinant function (in the n-representation) made up of single-electron eigenfunctions of the kinetic energy Hamiltonian with all the different quasimomenta. The spin part of this function should be so chosen that it satisfies the condition of antisymmetry upon simultaneous permutation of the coordinate and spin of two particles (the total spin of the system equal to zero). Obviously, a function constructed in this fashion has no ionic terms.

In other words, the eigenstates of the system are identical in the limit as $\gamma \to \infty$ with the states of the Hamiltonian

$$\hat{H}_1 = \beta \sum_n (c_n^{+} c_{n+1} + c_{n+1} c_n), \quad (2)$$

where c_n^{+} and c_n are the Fermi creation and annihilation operators of the electron (but without spin). By changing the statistics of the particles, we take into account their strong repulsion at a single center. Similar considerations were used by Girardeau[5] in the theory of one-dimensional Bose gas of impenetrable particles. The total number of electrons is equal to $N\rho$. The contribution to the energy of the ground state is equal here to

$$\frac{E_1}{N|\beta|} = -\frac{2}{\pi} \sin \pi\rho. \quad (3)$$

It is difficult to obtain the next term of the expansion in β/γ in the energy by such a method; however, it can be obtained by starting from the exact equations for this Hamiltonian.[2,3] The corresponding calculations give

$$\frac{E}{N|\beta|} = -\frac{2}{\pi} \sin \pi\rho - \frac{4 \ln 2|\beta|}{\gamma} \left(\rho^2 - \frac{\rho}{2\pi} \sin 2\pi\rho\right) + \ldots$$

The last term in (4) is connected with the lifting of the spin degeneracy. At $\rho = 1$, Eq. (4) transforms into an expression for the energy of the ground state of the Heisenberg antiferromagnetic Hamiltonian.

The study of the spectrum of excited states can be carried out in the same way. In particular, at large γ/β the excitation spectrum (1) is identical with the excitation spectrum of the Hamiltonian (6), i.e., with the spectrum of an ideal lattice gas without spin. This spectrum begins with zero:

$$\varepsilon(k) = 2|\beta|\,|\cos k - \cos \pi\rho|, \quad \pi < k < \pi\rho, \quad (5)$$

and consequently the system is a metal.

The situation can change if we take into account the repulsion of the electrons not only at a single center. We now consider the following Hamiltonian:

$$\hat{H} = \hat{H}_x + \frac{\gamma_{12}}{2} \sum_{n\sigma_1\sigma_2} a_{n\sigma_1}^{+} a_{n\sigma_1} a_{n+1,\sigma_2}^{+} a_{n+1,\sigma_2}. \quad (6)$$

The second term in (6) describes the repulsion of elec-

trons located at neighboring centers. For definiteness, we consider the case $\rho = {}^1/_2$, which is characteristic for the system $TCNQ_2^- - M^+$ (M^+ is any donor).

For the study of the properties of the ground state and the spectrum of excitations, we make γ very large ($\gamma/\beta, \gamma/\gamma_{12} \to \infty$). According to considerations developed above, the first-approximation Hamiltonian will take the form

$$\hat{H}_1 = \beta \sum_{n=1}^{N} (c_n^+ c_{n+1} + c_{n+1}^+ c_n) + \gamma_{12} \sum_{n=1}^{N} c_n^+ c_n c_{n+1}^+ c_{n+1}. \qquad (7)$$

The operators c_n and c_n^+ have the same meaning as in (2). The Hamiltonian (7) was studied in detail by exact methods.[6,7] It is most important for us here that at $\gamma_{12} = 2/|\beta|$ the system characterized by (7) changes from a metal to a dielectric ($\gamma_{12} < 2|\beta|$—metal, $\gamma_{12} > 2|\beta|$—dielectric). The gap in the dielectric phase is equal to[7]

$$\Delta E = \frac{\pi \operatorname{sh}\theta}{\theta} \sum_{-\infty}^{\infty} \operatorname{ch}^{-1} \frac{(2n+1)\pi^2}{2\theta}, \quad \operatorname{ch}\theta = \frac{\gamma_{12}}{2|\beta|}. \qquad (8)$$

As $\theta \to 0$, the gap ΔE rapidly approaches zero.[7] Thus, we see that a one-dimensional system described by (6) can undergo a metal-dielectric transition, depending on ρ, γ_{12}/β, and γ/β. In the dielectric phase there is an alternation of electron density. Such an alternation has evidently been observed in the system $TCNQ_2^-$-ditoluolchromium$^+$ in[8]. The detailed theory of the transition at finite γ has not been constructed and is a thing of the future. The same can be said of the possibility of Peierls distortion of the lattice in such systems.

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