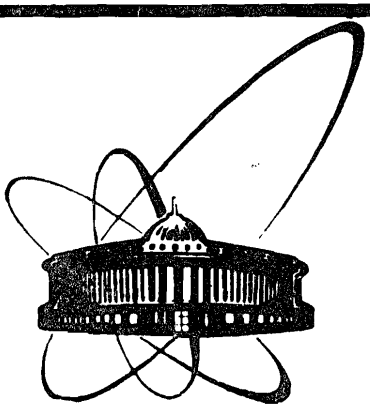

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KINKS WITH NON-INTEGRAL CHARGE IN TRANS-POLYACETYLENE

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It has been obtained in [1,2] within the continuum trans-polyacetylene, $(CH)_x$, model that a charge of a kink excitation differs from an integer value $Q = 0, \pm e$ by the amount $\delta Q = \pm \gamma e$, where e is the electron charge and γ characterizes a finite-band correction ($\gamma = \Delta/2t_0$, Δ is the gap parameter and $2t_0$ is the band half-width). This result was interpreted in [1] as a difficulty of a continuum theory and was attributed with the local failure of the completeness relation. It is of interest to study this problem using the finite-band scheme[3] that conserves the basic properties of a discrete model and correctly includes the finite-band corrections. We perform all calculations up to an order of $O(1/L)$ where L is a chain length, neglecting the terms of an order of $O[(a/\xi_s)^2]$, where a is the lattice constant and ξ_s is the width of excitation. We assume also that the polymer is sufficiently long $L \gg \xi_s$.

We start from the stationary equations for the one-particle electronic states in the form

$$E_k A_k(x) = -i v_{fk} \frac{\partial B_k(x)}{\partial x} - (\epsilon_k - i\Delta_k(x)) B_k(x), \qquad (1a)$$

$$E_k B_k(x) = -i v_{fk} \frac{\partial A_k(x)}{\partial x} - (\epsilon_k + i\Delta_k(x)) A_k(x), \qquad (1b)$$

where another representation for the electronic wave functions $A_k(x)$ and $B_k(x)$, as compared to [3], is used; $A_k(x)$ and $B_k(x)$ are slowly varying functions of x, $\epsilon_k = 2t_0 \sin ka$, $\Delta_k(x) = \Delta(x)\cos ka$, $v_{fk} = v_f \cos ka$, $v_f = 2t_0 a$. The wave vector k $(-\pi/2a \le k \le \pi/2a)$ is measured relative to $(\pi/2a)$.

A self-consisten condition is obtained in the form

$$\Delta(x) = -\frac{4i\gamma^2 a}{K} \sum_{k,\sigma}{}' \left(A_k^*(x) B_k(x) - B_k^*(x) A_k(x)\right) \cos ka, \qquad (2)$$

where K and γ are the parameters of a discrete trans-$(CH)_x$ model [4], and the sum is over the energy levels below the Fermi level; σ labels an electronic spin. The wave functions are normalized according to $\int_{-L/2}^{L/2} dx \left(|A_k(x)|^2 + |B_k(x)|^2\right) = 1$.

Consider now two types of solutions of (1,2):

(a) In the case of uniform dimerization $\Delta(x) = \Delta_0 = \text{const}$ the solutions of (1,2) are plane waves of the form $\exp(-ikx)$: $B_k = (N_k L)^{-1/2}$, $A_k = B_k(-\epsilon_k + i\Delta_k)/E_k$, where $N_k = 2$ and $E_k = \pm\sqrt{\epsilon_k^2 + \Delta_k^2}$. The local electronic density in the valence band is $\rho_k^0 = 1/L$.

(b) The kink solution involves an inhomogeneous dimerization in the form $\Delta(x) = \pm\Delta_0 \tanh k_0 x$. The corresponding electron spectrum contains a localized state with energy $E = 0$ lying precisely at the middle of the gap. It follows from (1) that two possibilities arize: (1) $B(x) = 0$ and (2) $A(x) = 0$ which correspond to the kink (K) and antikink ($\bar{K}$) states, respectively.

Let us consider the case (1). From (1b) one obtains that $A(x) = N_0 \operatorname{sech} k_0 x$, where $k_0 = \Delta_0/v_f = 1/\xi_s$ and $N_0 = \sqrt{(k_0/2)\operatorname{cth}(L/2\xi_s)}$.

The valence band electronic states are

$$A_q(x) = B_q(-\epsilon_q + i\Delta_q \tanh k_0 x)/E_q, \quad B_q = (N_q L)^{-1/2} \qquad (3)$$

and $N_q = 2\left[E_q - (\Delta_q^2/Lk_0 E_q)\right]/E_q$. The electron energy spectrum in the valence (conduction) band is similar to that of the dimerized state $E_q = \mp\sqrt{\epsilon_q^2 + \Delta_q^2}$. However, the continuum states suffer a phase shift $\delta(q) = -\operatorname{arctg}(\Delta_q/\epsilon_q)$. The allowed values of k and q are connected by $kL = qL + \delta(q)$.

The local electronic density in the presence of a kink deformation is found to be in the valence band $\rho_k^S(x) = \frac{1}{L} - \frac{\Delta_q^2}{2LE_q^2}\operatorname{sech}^2 k_0 x + \frac{\Delta_q^2}{k_0 E_q^2 L^2} + O\left(\frac{1}{L^3}, \frac{\gamma^2}{L^2}\right)$ whereas for the discrete level $\rho_0^S(x) = \frac{k_0}{2}\operatorname{sech}^2 k_0 x$. The total change in the local density is obtained in the form

$$\Delta\rho(x) = (\nu_0 - \nu I)\rho_0^S(x) + \frac{\nu I}{L} + \frac{\Delta N}{L}, \qquad (4)$$

where $I = \sum_q \left(\Delta_q^2/k_0 L E_q^2\right)$, $\nu_0\ (= 0,1,2)$ is an occupation number of a discrete level at $E = 0$; $\nu = 2$; $\Delta N = \nu\left(\sum_q 1 - \sum_k 1\right)$ defines the change in the number of states in the valence band. We can see from (4) that $\Delta\rho(x)$ consists of the inhomogeneous part and the homogeneous "background". It was proposed in [5] that the homogeneous background would be compensated by the removal of exactly one state from the valence band $(\Delta N = -1)$. The direct calculation shows, however, that for the kink excitatinn $I_K = \frac{1}{2} - \frac{\gamma}{2} + O(\gamma^2)$. Thus, the full compensation does not occur as much as the finite-band correction is present. As a result, we conclude that a single kink cannot be created in the trans-$(CH)_x$ chain. It is remarkable that for an antikink state one obtains $I_{\bar{K}} = \frac{1}{2} + \frac{\gamma}{2} - O(\gamma^2)$, so that in the sum

we derive $I_k + I_{\bar{k}} = 1$. At $\Delta N = -2$ the background charge is fully compensated. Thus, the soliton kinks in the undoped trans-$(CH)_x$ chain must be created from the ground state only in the form of $K\bar{K}$ pairs. The kinks have charges $Q_{k,\bar{k}} = \pm 2e$ and spins $\sigma_{k,\bar{k}} = \pm 1/2$. In the sum one obtains $Q_k + Q_{\bar{k}} = 0$ and $\sigma_k + \sigma_{\bar{k}} = 0$. This result agrees with a topological requirement as well as with Kramer's theorem. Note that an analogous situation has arisen in analysing the continuum states in the diatomic polymer model[6] (see, also[7]).

In the discrete model [4] the local compensation sum rule for both the dimerized and soliton states has been defined in the form $\int_{-\infty}^{0} \rho_{nn}^{0}(E)dE = \int_{-\infty}^{\infty} \rho_{nn}^{s}(E)dE + |\Phi_0(n)|^2$. As immediately follows from this relation, one kink with charge $Q = 0$ can be formed as opposed to the statement of Kramer's theorem. According to our analysis, the above mentioned equality takes place, strictly speaking, only for the ($K\bar{K}$) pair.

In the general case the full compensation of the background charge may be obtained if we take into account the change in the density of states due to the chain relaxation. In [8] the ground state of a dimerized trans-$(CH)_x$ chain with an odd number of atoms has been investigated. This chain always contains one unpaired π - electron at the end (CH) group. It is assumed that a chain has a free boundary. It was shown in[8] that kink excitation occured in the ground state configuration of such a chain. On this basis the interpretation of a remarkably high value of unpaired spins in the trans-$(CH)_x$ chain was given.

Let us consider a continuum model of a chain with one unpaired π -electron. Since the boundary is suggested to be free, we admit in the general case that the length L' of the dimerized chain can differ from the length L of the chain with a kink. In this case the allowed values of k and q are connected by

$$kL' = qL + \delta(q) . \tag{5}$$

Using (5) we can rewrite (4) in the form

$$\Delta\rho'(x) = \Delta\rho(x) - \nu N(\Delta L/L) , \tag{6}$$

where $\Delta L = L - L'$. Thus, the compensation of the homogeneous background takes place if $\Delta L = -2a$. It means that the creation of a single kink in the odd-membered dimerized trans-$(CH)_x$ chain

should be accompanied by the change in the chain length by the value ΔL . One obtains that exactly one state is removed from the valence band in this case ($\Delta N = -1$). For the antikink we derive $\Delta L = 2a$.

The total energy of the dimerized chain containing one unpaired π -electron increases by the value $E^{\pi} = 2\Delta_0$ needed to create an electron-hole pair by this electron. We determine now the energy of the chain with the single kink as compared to the dimerized state

$$E^{S} = \sum_q E_q - \sum_k E_k + E_{lat} ,$$

$$\text{where } E_{lat} = \frac{K}{8\gamma^2 a}\left[\int_{-L/2}^{L/2} dx\,(\Delta_0 \tanh k_0 x)^2 - \int_{-L/2}^{L/2} dx\,\Delta_0^2\right] = -\frac{K t_0 \Delta_0}{2\gamma^2} + O(z^2). \tag{7}$$

Taking into account (5) we can rewrite the electronic energy in the form

$$\sum_q E_q - \sum_k E_k = -\frac{\nu}{2\pi}\left(\delta(q) + q\Delta L\right)E_q\Big|_{-\pi/a}^{\pi/a} + \frac{\nu}{2\pi}\int \frac{d\delta(q)}{dq} E_q\,dq + \frac{\nu\Delta L}{2\pi}\int E_q\,dq . \tag{8}$$

Performing the integration in (8), we obtain

$$E^{S} = \frac{2\Delta_0}{\pi}\frac{1}{m^2}\left[E(m) - (1-m^2)K(m)\right] + \frac{2\nu t_0}{\pi a}\Delta L\left[E(m) - \frac{\pi}{2}\right] , \tag{9}$$

where $K(m)$ and $E(m)$ are the complete elliptic integrals of the first and second kind, respectively, $m^2 = 1 - z^2$. It stands to reason that for the $K\bar{K}$ pair the value of ΔL is $\Delta L = \Delta L_k + \Delta L_{\bar{k}} = 0$ and $2E^{S} = (4\Delta_0/\pi m^2)\left[E(m) - (1-m^2)K(m)\right]$ in accordance with the result of [3].

Using the value of ΔL for a single soliton, one obtains

$$E^{S} = \frac{2\Delta_0}{\pi}\frac{(1-m^2)}{m^2}\left(E(m) - K(m)\right) + \Delta_0 . \tag{10}$$

At $z^2 \ll 1$ ($m^2 \to 1$) we derive that $E^{S} = \Delta_0$. Since $E^{S} < E^{\pi}$, one obtains that the kink always occurs in the ground state configuration. The unpaired π -electron occupies the discrete level with $E = 0$ and has a local charge $Q_k = 2e$ and spin $\sigma_k = 1/2$. Note that Kramer's theorem is also valid in this case.

We conclude that the local compensation sum rule defined in[4] is destroyed in the order of $O(z/N)$ and should be rewritten for a

single soliton in the form

$$\int_{-\infty}^{\infty} dE_k \rho^0_{nn}(E_k) = \int_{-\infty}^{\infty} dE_q \rho^S_{nn}(E_q) + |\phi_0(n)|^2 \quad \text{or using} \quad (5)$$

$$\int_{-\infty}^{0} \left[\rho^S_{nn}(E) - \rho^0_{nn}(E)\right] dE = -\frac{1}{2}|\phi_0(n)|^2 + \left(\Delta L/2L\right), \quad (11)$$

where $\Delta L = \mp 2a$ for a kink (antikink), respectively.

Thus, the investigation performed in the finite-band continuum trans-$(CH)_x$ model shows that in the chain where all π-electrons are paired the $K\bar{K}$ pair is created as lower-lying excitation without the contradiction with Kramer's theorem. However, each kink carries a local non-integral charge which is fully compensated in the pair. In the chain with an unpaired π-electron the single kink occurs in the ground state configurations in conformity with the result of /8/. The nonintegral charge of this kink is compensated due to the change of the chain length.

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Кинки с нецелочисленным зарядом
в транс-полиацетилене

В конечнозонной континуальной модели транс-полиацетилена установлено нарушение локальной компенсации правила сумм. В результате низколежащими возбуждениями полимера должны быть кинк-антикинковые пары, где каждый кинк имеет нецелый локальный заряд. В димеризованной цепочке с одним неспаренным π-электроном формируется кинк в основном состоянии. В этом случае локальный заряд кинка компенсируется изменением длины цепочки.

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Kinks with Non-Integral Charge
in Trans-Polyacetylene

The violation of a local compensation sum rule in the finite-band continuum model of trans-polyacetylene is established. As a result, the low-lying excitations of the polymer should be kink-antikink pairs where each kink has a non-integral local charge. In the dimerized chain with one unpaired π-electron the single kink is formed in the ground state configuration. In this case the local charge of a kink is compensated due to the change of a chain length.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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