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**ON THE THEORY
OF LINEAR DIATOMIC POLYMERS**

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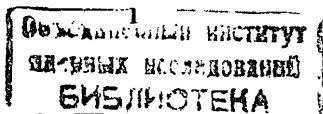
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I. Introduction

The recent progress in the study of linear conjugated organic polymers is based on the extensive investigation of the Su-Schrieffer-Heeger (SSH) model ^{/1/} formulated for the trans-polyacetylene, $(\text{CH})_x$. The tight-binding electron-phonon SSH model contains solitons as elementary excitations. The physical characteristics of solitons evaluated in ^{/1/} are in good agreement with a lot of experimental data (see, for example, a review ^{/2/}). The following evolution of the SSH model includes two main lines: (a) The extension of the SSH Hamiltonian by the electron-electron interaction terms, by including the three-dimensional effects and a more realistic phonon spectrum, etc. (b) The description of the novel types of polymers on the basis of the SSH-like models. In recent years the cis-polyacetylene ^{/3/}, polyynes $(-\text{C} \equiv \text{C}-)_x$ ^{/4/} and polycarbonitrile $(-\text{CH}=\text{N}-)_x$ ^{/5/} models have intensively been studied. The last polymer is an example of a diatomic (AB) system.

The lattice model for an AB polymer proposed in ^{/5/} is a usual extension of the SSH model on the diatomic chain. In ^{/5/} the phonon spectrum, ground state as well as one-particle excitations of the AB system have been investigated. In ^{/6/} the continuum Hamiltonian of the AB polymer has been constructed and a soliton charge has been evaluated. It has been found that the low-lying particle-like excitations of the AB polymer model are the pairs of solitons where each soliton carries spin $\sigma = 0$ (or $\sigma = 1/2$) and non-integral fermion charge. The soliton creation energy is a function of a parameter $2\alpha = E_A - E_B$ which characterizes the difference between the atomic p-orbital energy of the A and B atoms. In ^{/7/} the polaron-like solution of the AB polymer model has been studied. The behaviour of a soliton charge at finite temperature and chemical potential has been investigated in ^{/8/}. In ^{/9/} the possibility of forming a soliton lattice with increasing solitonic pairs in the AB chain has been considered.

In the present paper we study the extended AB polymer model when the next-nearest neighbour hopping processes are taken into account. Both the ground state and the phonon spectrum are investigated and the sound velocity is calculated. We construct the continuum equations of motion using the finite-band scheme introduced for the first time



in ^{/10/} for the trans-(CH)_x model. In this case the basic properties of a discrete model are conserved. We show that the correct description of the one-particle excitations is essentially based on the consideration of the effects of an order of $O(1/L)$, where L is the chain length. The kink solution is obtained and the physical characteristics of kinks are calculated. In conclusion we summarize the obtained results.

2. Hamiltonian, ground state and phonon spectrum

We start with the Hamiltonian in the site representation which takes the form

$$H = H_{\text{lat}} + \alpha \sum_{j,\sigma} a_{j,\sigma}^+ a_{j,\sigma} - t_{2A} \sum_{j,\sigma} (a_{j,\sigma}^+ a_{j+2,\sigma} + \text{h.c.}) - \sum_{j,\sigma} t_{j+1,j} (a_{j,\sigma}^+ b_{j+1,\sigma} + \text{h.c.}) - \alpha \sum_{\ell,\sigma} b_{\ell,\sigma}^+ b_{\ell,\sigma} - t_{2B} \sum_{\ell,\sigma} (b_{\ell,\sigma}^+ b_{\ell+2,\sigma} + \text{h.c.}) - \sum_{\ell,\sigma} t_{\ell+1,\ell} (b_{\ell,\sigma}^+ a_{\ell+1,\sigma} + \text{h.c.}), \quad (1)$$

where H_{lat} describes the lattice energy

$$H_{\text{lat}} = \frac{M_A}{2} \sum_j \dot{u}_j^2 + \frac{K}{2} \sum_j (y_{j+1} - u_j)^2 + \frac{M_B}{2} \sum_\ell \dot{y}_\ell^2 + \frac{K}{2} \sum_\ell (u_{\ell+1} - y_\ell)^2. \quad (2)$$

In (1) $j(\ell)$ labels odd(even) sites, $a_{j,\sigma}^+$ ($a_{j,\sigma}$) and $b_{\ell,\sigma}^+$ ($b_{\ell,\sigma}$) are the creation (annihilation) operators of π -electrons with spin σ ($\pm 1/2$) at the site $j(\ell)$. The π -electrons can be treated in the tight-binding approximation with hopping integrals $t_{j+1,j}$ ($t_{\ell+1,\ell}$) which can be expanded to first order about the undimerized state $t_{j+1,j} = t_0 - \gamma(y_{j+1} - u_j)$, $t_{\ell+1,\ell} = t_0 - \gamma(u_{\ell+1} - y_\ell)$; t_0 is a hopping integral for the undimerized chain and γ is the electron-lattice coupling constant. Additionally to ^{/5/}, we included in (1) the next-nearest neighbour hopping processes with the hopping integrals t_{2A} and t_{2B} . It has been shown in ^{/11/} that these processes are important for the analysis of the electron loss data in trans-(CH)_x. The parameter α is estimated in the introduction. The energy level $(E_A + E_B)/2$ is chosen to be zero. We assume that there is exactly one π -electron per atom. In (2) u_j (y_ℓ) are the lattice displacements from the uniformly distributed atoms, M_A and M_B are the atomic masses. We use the harmonic approximation for the lattice energy, K is a spring constant.

Note that the electron-electron interactions between π -electrons as well as the interchain coupling are neglected in (1). Usually the lattice displacements are treated as classical quantities. The quantum fluctuation effects (QFE) in the lattice displacement fields u_j (y_ℓ) can be considered in such a manner as in the

polyacetylene model ^{/12/}. It is known ^{/12/} that the QFE will not destroy either the dimerization or the soliton states.

The ground state is determined by making an adiabatic (Born-Oppenheimer) approximation where the ground state displacement fields are given by $y_\ell = -u_j = \pm W/2$ for all values of j, ℓ and $W = \text{const}$. The choice of signs here corresponds to the two possible and entirely equivalent senses of the dimerization field. First of all let us note that the difference between the values of M_A and M_B leads to the doubling of the lattice constant $2a$ while the distance between sites is a . Thus, we obtain that the Fermi momentum of the valence electrons is $k_F = \pi/2a$. In the case of one π -electron per atom the valence band is fully occupied while the conduction band is empty. The gap in the electronic spectrum opens at the Fermi level thus leading to the dielectric properties of a diatomic polymer in accordance with the Peierls theorem. At $W = \text{const}$ the electronic energy spectrum is easily calculated and has the form

$$E_{1,2}(k) = -(t_{2A} + t_{2B}) \cos 2ka \pm \sqrt{(2t_0 \cos ka)^2 + (\Delta \sin ka)^2 + \alpha^2 - 2\alpha \delta \cos 2ka + (\delta \cos 2ka)^2}, \quad (3)$$

where in the first Brillouin zone $-\pi/2a \leq k \leq \pi/2a$; $\Delta = 2\gamma W$ and $\delta = t_{2A} - t_{2B}$. The parameter Δ characterizes the dimerization gap. The energy gap at the Fermi level has the value $\Delta(k_F) = \sqrt{\Delta^2 + \alpha^2 + \delta^2 + 2\alpha\delta}$. Note that the terms with $t_{2A,B}$ and α in (1) break the charge conjugation symmetry. This is a qualitatively new effect beyond the primary SSH picture. We can see from (3) that the processes with α are of direct interest because the parameter α determines the value of the gap $\Delta(k_F)$. Conversely, the influence of the next-nearest neighbour hopping processes is reduced only to the shift of a chemical potential of a system. The terms with δ in $\Delta(k_F)$ are much smaller in comparison with α . We shall return to this discussion in the next section. It should be noted that the 1+1 dimensional quantum-field-theory models with broken charge conjugated symmetry have been studied in ^{/13/}.

Consider now the equations of motion $i|\dot{\Psi}\rangle = H|\Psi\rangle$, where H is defined in (1). For the one-particle excitations we obtain the following equations:

$$i\dot{\psi}_j = \alpha \psi_j - t_{2A} (\psi_{j+2} + \psi_{j-2}) - t_0 (\psi_{j+1} + \psi_{j-1}) + \gamma [(y_{j+1} - u_j) \psi_{j+1} + (u_j - y_{j-1}) \psi_{j-1}], \quad (4)$$

$$i\dot{\psi}_\ell = -\alpha \psi_\ell - t_{2B} (\psi_{\ell+2} + \psi_{\ell-2}) - t_0 (\psi_{\ell+1} + \psi_{\ell-1}) + \gamma [(u_{\ell+1} - y_\ell) \psi_{\ell+1} + (y_\ell - u_{\ell-1}) \psi_{\ell-1}],$$

where we determine $|\Psi(t)\rangle = (1/\sqrt{N}) \sum_n (\varphi_{2n+1}(t) a_{2n+1}^\dagger + \varphi_{2n}(t) b_{2n}^\dagger) |0\rangle$,
 $\varphi_{2n+1}(t)$, $\varphi_{2n}(t)$ are the Schrödinger wave functions. The self-consistent condition takes the form

$$M_A \ddot{u}_j = K(y_{j+1} - 2u_j + y_{j-1}) + \gamma \sum_{\sigma} [\varphi_{\sigma}^*(\psi_{j+1} - \psi_{j-1}) + \text{h.c.}] , \quad (5)$$

$$M_B \ddot{y}_l = K(u_{l+1} - 2y_l + u_{l-1}) + \gamma \sum_{\sigma} [\psi_{\sigma}^*(\varphi_{l+1} - \varphi_{l-1}) + \text{h.c.}] .$$

• The sum in (5) is over the occupied states in the valence band. In the ground state the self-consistent condition is written as

$$1 = \frac{4\gamma^2}{KN} \sum_{k,\sigma} E_k^{-1} \sin^2 ka , \quad (6)$$

where $E_k = \sqrt{(2t_0 \cos ka)^2 + (\Delta \sin ka)^2 + \alpha^2 - 2\alpha \delta \cos 2ka + (\delta \cos 2ka)^2}$.
 The expression for the gap parameter in the ground state will be obtained below in the continuum scheme. We note here that $\Delta \neq 0$ and the dimerization of the AB polymer chain takes place.

It has been investigated in ^{15/} that in calculating the phonon spectrum, it is essential to take into account the polarization of the π -electrons to second order in γ . The phonon frequency is determined from (4,5) by the solution of

$$\det \|\hat{D}(q) - \Omega^2(q) \hat{I}\| = 0 , \quad (7)$$

where

$$\hat{D}_{ij}(q) = (M_A M_B)^{-1/2} \{ \delta_{ij} [2K - 8\gamma^2 \chi_1(q)] + (1 - \delta_{ij}) [2K \cos qa - 8\gamma^2 \chi_2(q)] \} , \quad (8)$$

δ_{ij} is the Kronecker δ function, $\hat{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$. The contributions from the π -electrons are determined by ^{15/}

$$\chi_i(q) = (1/N) \sum_{k,\sigma} S_i(k, k+q) F(k, k+q) / (E_k + E_{k+q}) \quad (9)$$

with $S_1(k, k') = z_k^2 + z_{k'}^2$, $S_2(k, k') = 2z_k z_{k'}$, $z_k = \sin ka$ and

$$F(k, k') = 1 + [(2t_0 \cos ka)(2t_0 \cos k'a) - \Delta^2 z_k z_{k'} + \alpha^2] / (E_k E_{k'}) .$$

From (7) and (8) we immediately obtain the acoustic $\Omega_-(q)$ and optical $\Omega_+(q)$ phonon branches

$$\Omega_{\pm}^2(q) = \frac{(M_A + M_B) G(q) \pm \sqrt{(M_A - M_B)^2 G^2(q) + 4M_A M_B P^2(q)}}{2M_A M_B} , \quad (10)$$

where $G(q) = 2K - 8\gamma^2 \chi_1(q)$, $P(q) = 2K \cos qa - 8\gamma^2 \chi_2(q)$, and the wave vector lies in the range $-\pi/2a \leq q \leq \pi/2a$. At $\delta = 0$ these two branches have been plotted in ^{15/}, where the values of the parameters $t_0 = 3$ eV, $K = 68,6$ eV/Å², $\gamma = 8$ eV/Å and M_A and M_B for polycarbonitrile were used. It should be noted that the restoring force for long-wavelength optical displacements ($qa \rightarrow 0$) which is purely electronic in origin, increases with α leading to a giant Kohn anomaly as $\alpha \rightarrow \Delta_0$.

Finally, we obtain the sound velocity in the AB polymer. Neglecting the electron-lattice coupling ($\gamma = 0$) it immediately follows from (10) that

$$\Omega_{\pm}^{\circ 2}(q) = K \left\{ \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \pm \left[\left(\frac{1}{M_A} + \frac{1}{M_B} \right)^2 - \frac{4 \sin^2 qa}{M_A M_B} \right]^{1/2} \right\} \quad \text{and the sound}$$

velocity is determined as $S_0 = (\partial \Omega_{\pm}^{\circ} / \partial q)_{q \rightarrow 0} = a \sqrt{K/M}$, where $2M = M_A + M_B$. At $\gamma \neq 0$ we obtain from (10)

$$\Omega_{-}(q) = \sqrt{\frac{G(q) - P(q)}{M}} + O\left[\left(\frac{\delta M}{2M}\right)^2\right] , \quad (11)$$

where $\delta M = M_A - M_B$. We assume that $|\delta M| \ll M$. The sound velocity is found to be

$$S = S_0 \sqrt{1 - \lambda F(z, y)} \quad (12)$$

with

$$F(z, y) = \frac{1}{(1+y^2)^{3/2}} \left[\int_0^{z/2} \frac{\cos^4 t dt}{(1-m^2 \sin^2 t)^{3/2}} + y^2 \int_0^{z/2} \frac{\cos^2 t dt}{(1-m^2 \sin^2 t)^{3/2}} \right] \quad (13)$$

and with our choice of parameters $\lambda = 4\gamma^2 / \pi K t_0 \approx 0,4$, $z = \Delta / 2t_0$,

$y = \alpha / 2t_0$, $m^2 = (1 - z^2) / (1 + y^2)$. An exact evaluation of (13) leads to the result

$$F(z, y) = \frac{1}{(1+y^2)^{3/2}} \left[\frac{2-m^2}{m^4} E(m) - \frac{2(1-m^2)}{m^4} K(m) + \frac{y^2}{m^2} (K(m) - E(m)) \right] . \quad (14)$$

In the limit $z \ll 1$ and $y \ll 1$ we obtain that $F(z, y) \rightarrow 1$ and $S \rightarrow 0,78 S_0$. When the values of z and y are increased the sound velocity S decreases.

3. The continuum model

The continual variant of the AB polymer model excluding the terms with $t_{2A,B}$ has been considered in ^{5,6}. We shall obtain the continuum equations of motion immediately from (4) and (5) using the finite-band scheme ¹⁰. Namely, the electronic wave functions are expressed in the form $\psi_j = \sqrt{2a} A(j) \exp(ik_j a)$, $\psi_\ell = \sqrt{2a} B(\ell) \exp(i\ell a)$, where the wave vector k is measured relative to $k_F = \pi/2a$ and we assume that $-\pi/2a \leq k \leq \pi/2a$ by analogy with ¹⁰. The lattice displacement fields have the form $4xy(\ell) \exp(iq\ell a) = \Delta(\ell)$, $4xu(j) \exp(iqja) = -\Delta(j)$, where $q = 2k_F$; $A(j)$, $B(\ell)$, $\Delta(j)$ and $\Delta(\ell)$ are slowly varying functions of $j(\ell)$. Introducing the spatial continuum location $x = ma$ ($m = j, \ell$) we obtain from (4) and (5) the following equations of motion:

$$i\dot{A} = (\alpha + t_{2Ak})A - (\epsilon_k - i\Delta_k)B - iV_{Fk}B' - 4iat_{2A} \sin 2ka A' + \frac{a}{2} \sin ka (B\Delta' + 2\Delta B') + \frac{a^2}{2} [i \cos ka (\frac{1}{2} B\Delta'' + \Delta B'' + \Delta' B') - 2\epsilon_k B'' + 4t_{2Ak} A''], \quad (15a)$$

$$i\dot{B} = (-\alpha + t_{2Bk})B - (\epsilon_k + i\Delta_k)A - iV_{Fk}A' - 4iat_{2B} \sin 2ka B' - \frac{a}{2} \sin ka (A\Delta' + 2\Delta A') - \frac{a^2}{2} [i \cos ka (\frac{1}{2} A\Delta'' + \Delta A'' + \Delta' A') - 2\epsilon_k A'' + 4t_{2Bk} B''], \quad (15b)$$

where $A = A(x,t)$, $B = B(x,t)$, $\Delta = \Delta(x,t)$, $\dot{A} = \partial A / \partial t$, $A' = \partial A / \partial x$, $\epsilon_k = 2t_0 \sin ka$, $V_{Fk} = v_F \cos ka$, $v_F = 2t_0 a$, $t_{2A,Bk} = 2t_{2A,B} \cos 2ka$, $\Delta_k = \Delta \cos ka$.

We regard in (15) the terms up to the second order of $(a/f_s)^2$, where f_s is the characteristic length of excitations. Note that the continuum approximation may be applicable at $f_s \gg a$. The electronic fields are normalized according to $\int_{-L/2}^{L/2} dx (|A|^2 + |B|^2) = 1$, where $L = Na$ is the length of the chain. We obtain from (5) the self-consistent condition

$$M\ddot{\Delta} + K\dot{\Delta} = -4K\Delta + 16j^2 a \sum_{\sigma} [B^* (i \cos ka (A + \alpha^2 A'/2) + \sin ka A') + h.c.]. \quad (16)$$

It can be seen that the terms with $\ddot{\Delta}$ and $\dot{\Delta}$ in (16) are of the same order. We must regard both these terms in analysing the soliton dynamics as well as the soliton lattice formation at high soliton densities. For trans-(CH)_x the value of t_1 is

known ¹¹ $t_1 \approx (0.05 \pm 0.1)t_0$. Assuming $t_{2A} \approx t_{2B}$ we obtain that $\delta = 0.01 t_0$. Thus, to lowest order we can neglect the difference between the values of $t_{2A,B}$ in (15).

Consider now the stationary equations of the model (15) in the leading approximation

$$\begin{aligned} (\tilde{E}_n - \alpha - t_{2k})A_n(x) &= -iV_{Fk}B'_n(x) - (\epsilon_k - i\Delta_k(x))B_n(x), \\ (\tilde{E}_n + \alpha - t_{2k})B_n(x) &= -iV_{Fk}A'_n(x) - (\epsilon_k + i\Delta_k(x))A_n(x), \end{aligned} \quad (17)$$

together with the self-consistent gap equation

$$\Delta(x) = -\frac{4ij^2 a}{K} \sum_{n,\sigma} (A_n^*(x)B_n(x) - B_n^*(x)A_n(x)) \cos ka. \quad (18)$$

It is easy to see from (17) that the terms with t_{2k} only renormalize the Fermi energy. In the following calculations we set $E_n = \tilde{E}_n - t_{2k}$. To investigate the influence of the hopping processes with $t_{2A,B}$ on the physical characteristics of solitons, one needs to solve the full system (15,16). The role of the parameter α in (17) is more essential. At $\alpha = 0$ equations (17) are reduced to those in the continuum trans-(CH)_x model. For the case $\alpha = 0$ and $t_{2k} = 0$ the system (15,16) has been obtained for the first time in ¹⁴.

Three classes of solutions for (17,18) are known: ground state, kink and polaron. In the present article we consider the ground state and kink solutions.

a) In the uniformly dimerized phase ($\Delta = \text{const}$) the solutions of (17) are the plane-wave states with

$$A_q = (N_q L)^{-1/2} \frac{-E_q + i\Delta_q}{E_q - \alpha}; \quad B_q = (N_q L)^{-1/2}, \quad (19)$$

where $N_q = 2E_q / (E_q - \alpha)$ and the energy spectrum takes the form

$E_q = \pm \sqrt{\epsilon_q^2 + \Delta_q^2 + \alpha^2}$. The gap parameter Δ is determined from (18)

$$1 = \frac{8j^2}{\pi K} \int_0^{\pi/2} dt \frac{\cos^2 t}{\sqrt{\epsilon_t^2 + \Delta_t^2 + \alpha^2}}. \quad (20)$$

Note that (20) is a continuum analog of (6). In the limit $\alpha \ll 1$ and $y \ll 1$ we obtain from (20)

$$\sqrt{\Delta^2 + \alpha^2} = \Delta_0 = (\delta t_0 / e) \exp(-1/\lambda), \quad (21)$$

where $e = 2.718 \dots$ and λ is introduced in (12). At $\alpha = 0$ we have $\Delta = \Delta_0$. When the value of α is increased the gap parameter Δ decreases and $\Delta = 0$ at $\alpha = \Delta_0$. Thus, the dimerization in the diatomic polymer takes place only at $\alpha < \Delta_0$. At our choice of parameters we obtain $2\Delta_0 = 1.4$ eV.

b) At $\alpha < \Delta_0$ the system (17,18) has the exact kink solution

$$\Delta(x) = \pm \Delta_0 \tanh k_0 x. \quad (22)$$

We determine the state with plus (minus) in (22) as a soliton (anti-soliton), respectively. The electronic energy spectrum consists of a localized state with energy $E = \pm \alpha$, lying in the gap, and a continuum of plane-wave conduction-band and valence-band states with the energies $E_k = \pm \sqrt{\epsilon_k^2 + \Delta_k^2 + \alpha^2}$. At $E = +\alpha$ we obtain from (17) that $B_0 = 0$ and

$$A_0(x) = N_0 \operatorname{sech} k_0 x \quad (23)$$

with $k_0 = \Delta / v_F$ and $N_0 = \sqrt{(k_0/2) \operatorname{ctanh}(Lk_0/2)}$. The continuum states in the presence of a soliton have similar energies as in a uniform system but they allow phase shifts. We obtain

$$A_k(x) = \frac{B_k}{E_k - \alpha} [-\epsilon_k + i \Delta_k \tanh k_0 x]; \quad B_k = (N_k L)^{-1/2}, \quad (24)$$

where

$$N_k = \frac{2}{E_k - \alpha} \left[E_k - \frac{\Delta_k^2}{k_0 L (E_k - \alpha)} \right] \quad (25)$$

and the phase shift $\delta(k)$ is determined by $\delta(k) = -\arctg(\Delta_k / \epsilon_k)$.

4. Physical characteristics of kinks

Let us consider the change in the local electronic density in the presence of an A-kink excitation. We propose that an occupation number of the discrete level $E = \alpha$ is ν_0 ($\nu_0 = 0, 1, 2$) whereas in the valence band is $\nu = 2$. We have

$$\Delta \rho(x) = \nu_0 \rho_0^S(x) + \nu \sum_k \rho_k^S(x) - \nu \sum_q \rho_q^0(x), \quad (26)$$

where $\rho_0^S(x) = (k_0/2) \operatorname{sech}^2 k_0 x$ and

$$\rho_k^S(x) = \frac{1}{L} - \frac{\Delta_k^2 \operatorname{sech}^2 k_0 x}{2E_k(E_k - \alpha)L} + \frac{\Delta_k^2}{E_k(E_k - \alpha)L k_0} - \frac{\Delta_k^4 \operatorname{sech}^4 k_0 x}{2E_k^2(E_k - \alpha)^2 L^2 k_0} + O\left(\frac{1}{L^3}\right).$$

The last term in $\rho_k^S = \int_{-L/2}^{L/2} \rho_k^S(x) dx$ can be omitted because it enters with a factor that is negligible with respect to $O(1/L)$. From (19) we obtain the value $\rho_0^0 = 1/L'$ for the dimerized chain. We admit at this stage that the length L' of the dimerized chain can differ in the general case from the length L of the chain with soliton. Note that this assumption is essential for a detailed analysis of one-particle excitations. Moreover, as it will be shown below the creation of a single soliton in a finite chain leads to a chain relaxation (the effect of "solitonstriction" takes place).

Expression (26) can be written as

$$\Delta \rho(x) = (\nu_0 - \nu I_+) \rho_0^S(x) + \frac{\nu I_+}{L} + \frac{\nu}{L} \sum_k 1 - \frac{\nu}{L'} \sum_q 1 + O\left(\frac{1}{L^2}\right), \quad (27)$$

where $I_{\pm} = \sum_k \Delta_k^2 / E_k(E_k \pm \alpha)L k_0$. We have I_- for a B-soliton. The last two terms in (27) determine the change in the density of states in the valence band in the presence of a soliton. We can rewrite these terms in the form $\delta N / L - N \delta L / L^2$, where $\delta N = N - N'$ and $\delta L = L - L'$; $N(N')$ is a number of states in the valence band in the presence (absence) of a soliton. Expression (27) includes an inhomogeneous term with $\rho_0^S(x)$ and a homogeneous part ("background"). Setting the homogeneous part to be zero, we obtain the following condition

$$\delta N = N \frac{\delta L}{L} - \nu I_+. \quad (28)$$

The value of I_+ may be evaluated in terms of elliptic integrals. In the limit $x^2 \ll 1$ and $y^2 \ll 1$ we obtain that $I_+ = \beta/\pi - z/2$, where $\operatorname{tg} \beta = \Delta/\alpha$. Note that in the general case δN has an unreal irrational value. Thus, there are restricted abilities to create a single soliton in the isolated chain.

Consider now two types of the chains.

1) The chain with fixed boundaries. In this case $\delta L = 0$. It immediately follows from (28) that kinks in a such chain can be created only in AB-pairs where the A-soliton has an energy level $E = \alpha$ whereas for the B-soliton $E = -\alpha$. Note that this result agrees with a topological requirement. The condition (28) for a solitonic pair takes the form $\delta N = -\nu(I_+ + I_-)$, where $I_- = 1 - \beta/\pi + z/2$.

We obtain that $\delta N = -2$ at $\nu = 2$. Thus, exactly two electrons are removed from the valence band when the pair of kinks is created. The kink charge has an irrational value at any occupation number of the levels with $E = \pm \alpha$. At $\nu_0 = 1$ we have the pair of kinks with spins $\sigma = 1/2$ and charges $Q_{A,B} = \pm e^{(2/\pi)} \operatorname{arctg}(\alpha/\Delta)$, where e is an electron charge, and we neglect the contribution terms $\pm \xi e$. At $\nu_0 = 0$ ($\nu_0 = 2$) we have the pair of kinks with spins $\sigma = 0$ and charges $Q_{A,B} = \mp e^{(2/\pi)} \operatorname{arctg}(\Delta/\alpha)$ (for $\nu_0 = 2$ the signs in $Q_{A,B}$ should be reversed). As $\alpha \rightarrow 0$ the known result for a trans-(CH)_x model is obtained. Namely, $Q = 0$ at $\sigma = 1/2$ and $Q = \pm e$ at $\sigma = 0$. However, small corrections $\pm \xi e$ to the kink charge persist (see also ^{15,16}). In ¹⁵ this result has been interpreted as a difficulty of the continuum theory. Conversely, we suppose that the appearance of the small local charge of a soliton is a general property both for the continuum and discrete models. In the AB-pair the charges of the A- and B-solitons are fully compensated.

2) The chain with a free boundary. In this case $\delta L \neq 0$ and one soliton can be created in a chain. Indeed, setting in (28)

$\delta N = -1$ (i.e. exactly one electron is removed from the valence band), we obtain the condition

$$\delta L = a \left[-1 + \frac{2\beta}{\alpha} - \xi \right]. \quad (29)$$

Thus, the creation of one kink should be accompanied by the change in the chain length on the value δL . For the B-kink the value of δL has the sign opposite to (29). It follows from (29) that the value of δL increases with increasing α , which can be energy unfavourable. We calculate now the creation energy of an A-kink relative to the dimerized phase energy:

$$E^s = \sum_k E_k - \sum_q E_q + E_{\text{cat}}, \quad (30)$$

$$\text{where } E_{\text{cat}} = \frac{K}{8\beta^2 a} \left[\int_{-1/2}^{1/2} (\Delta \tanh kx)^2 dx - \int_{-1/2}^{1/2} \Delta^2 dx \right] = -\frac{K t_0 \Delta}{2\beta^2} + O(\xi^2).$$

The allowed magnitudes of a wave vector in the dimerized phase are $q_n L = 2\pi n$ whereas in the presence of a kink we obtain $k_n L + \delta(k_n) = 2\pi n$, where $n = 0, \pm 1, \dots, \pm N/2$ and $\delta(k_n)$ is determined above. By replacing the sum in (30) by an integral, one obtains

$$\begin{aligned} \sum_k E_k - \sum_q E_q &= -\frac{\nu}{2\pi} \int (\delta(k) + k \delta L) dE_k + \alpha \nu_0 = \\ &= -\frac{\nu}{2\pi} (\delta(k) + k \delta L) E_k \Big|_{-k_f}^{k_f} + \frac{\nu}{2\pi} \int \frac{d\delta(k)}{dk} E_k dk + \frac{\nu \delta L}{2\pi} \int E_k dk + \alpha \nu_0, \end{aligned} \quad (31)$$

where $\nu_0 \pm$ characterizes the occupation of discrete levels with $E = \pm \alpha$. Carrying out the integration in (31), we obtain from (30)

$$\begin{aligned} E_A^s &= \alpha \nu_0 + \frac{2\Delta}{\pi} \left\{ \frac{1}{m^2} [E(m) - (1-m^2)K(m)] + \frac{y^2}{\sqrt{1+y^2}} [K(m) + \right. \\ &\quad \left. + \frac{\sqrt{1+y^2}}{2y} \left(\frac{\pi}{2} - \psi \right) \right\} + \frac{2\nu t_0}{\pi a} \delta L \left[\sqrt{1+y^2} E(m) - \frac{\pi}{2} \right], \end{aligned} \quad (32)$$

where $K(m)$ and $E(m)$ are the complete elliptic integrals of the first and second kind, respectively; $\operatorname{tg} \psi = \frac{2\sqrt{1+y^2}}{y\sqrt{1-z^2}}$, $m^2 = \frac{(1-z^2)}{(1+y^2)}$, $z = \Delta/2t_0$, $y = \alpha/2t_0$. For $\delta L = 0$ and $\alpha = 0$ we recover from (32) the known result for the trans-(CH)_x model ¹⁰ when the finite-band corrections are taken into account. It gives rise to a better accordance of the value E^s with the discrete calculations ¹¹. In the limit $\xi \ll 1$ and $y \ll 1$ (32) turns into

$$E_A^s = \alpha(\nu_0 + 1) + \frac{2}{\pi} \left[\Delta - \alpha \operatorname{arctg} \frac{\Delta}{\alpha} \right] + \frac{2\nu t_0}{\pi a} \delta L \left(1 - \frac{\pi}{2} \right). \quad (33)$$

The energy to create a B-soliton can be obtained in an analogous manner. In the case $\delta L = 0$ we obtain from (33) the creation energy of an AB kink pair

$$2E^s(\nu_0, \nu_0) = \alpha(2 + \nu_0 - \nu_0) + \frac{4}{\pi} \left[\Delta - \alpha \operatorname{arctg} \frac{\Delta}{\alpha} \right] \quad (34)$$

in accordance with the result of ¹⁵. Thus, the creation energy of spinless AB solitons is $2E^s(0,2) = (4/\pi) [\Delta - \alpha \operatorname{arctg}(\Delta/\alpha)]$ whereas for solitons with spin $\sigma = 1/2$ we have a larger value $2E^s(1,1) = 2E^s(0,2) + 2\alpha$. It is clear that $2E^s(1,1) = 2E^s(0,2) = 4\Delta_0/\pi$ at $\alpha = 0$. Using (29) we determine from (33) the creation energy of one soliton

$$E^s = \alpha + \Delta + \left[\frac{2\alpha}{\pi} + \frac{8t_0}{\pi^2} \left(\frac{\pi}{2} - 1 \right) \right] \operatorname{arctg} \frac{\alpha}{\Delta}, \quad (35)$$

where we set $\nu_{0+} = 1$ in accordance with our proposal $\delta N = -1$. For $\alpha = 0$ we obtain that $E^S = \Delta_0$. This result should be explained in detail.

First of all note that we have considered in (30) the energy of the dimerized chain with an even number of atoms. Thus, we obtain formally that the energy to create one soliton in such a chain is $E^S = \Delta_0$, where we take into account both the increase of the local energy in the vicinity of the soliton and the shift of the end-effect energy due to the chain relaxation.

The situation is replaced in the chain with an odd number of atoms where one unpaired π -electron is always present. In this case the energy of the dimerized chain increases by the value $2\Delta_0$ needed to create the electron-hole pair by this π -electron. Hence, the creation of one kink is favoured. We obtain that the chain with an odd number of atoms (but, strongly speaking, with an even number of π -bonds) always contains a kink in the ground-state configuration. This result agrees with the analysis by Su¹⁷ within the framework of the discrete trans-(CH)_x model. A more complicated situation emerges in the AB polymer model. As $\alpha \rightarrow 0$ we obtain from (35) that $E^S(\alpha \rightarrow 0) \rightarrow \Delta_0$, whereas as $\alpha \rightarrow \Delta_0$ $E^S(\alpha \rightarrow \Delta_0) = \Delta_0 + \frac{\pi}{2} \left[\frac{2\Delta_0}{\pi} + \frac{8t_0}{\pi^2} (\frac{\pi}{2} - 1) \right] > 2\Delta_0$. Hence, the critical value $\alpha = \alpha_c$ exists when the creation of one soliton is energy unfavourable. At our choice of parameters we solve the equation $E^S(\alpha) = 2\Delta_0$ and obtain that $\alpha_c = 0.23$ eV. Thus, at $\alpha > \alpha_c$ the electron-hole pair will be created in the odd-membered dimerized AB polymer chain. The lattice deformation at $\alpha = \alpha_c$ has a maximal value $\delta L = \mp 0.32a$ for A- and B-soliton, respectively.

5. Summary

In our paper various aspects of a linear diatomic polymer model are considered.

The analysis of the ground state of an AB polymer model shows that the dimerization in such a system occurs only at $\alpha < \Delta_0$. The electronic energy spectrum exhibits the gap $2\Delta_0$ leading to dielectric properties of the AB polymer. The phonon spectrum has both acoustic and optical branches. The optical branch contains the giant Kohn anomaly as $\alpha \rightarrow \Delta_0$. The reduction of the velocity of sound due to electron-phonon coupling takes place. The influence of the next-nearest hopping processes on the solitonic properties arises only in the order $(\alpha/\xi_s)^4$.

Since the characteristic length scale of the inhomogeneities $\xi_s = v_F/\Delta = a/\alpha$ has a minimal value $\xi_s(\alpha=0) \approx 9.5a$, the continuum approximation is correct. The use of the finite-band scheme

gives a better convergence with the results from a discrete model. The correct analysis of one-particle excitations requires the inclusion of the effects of an order of $O(1/L)$. It is shown that the creation of an AB solitonic pair where each soliton has an irrational charge takes place in the chain with the fixed boundaries. The creation of the charged excitations with spin $S=0$ gains an advantage over the magnetic ($S=1/2$) excitations. We have calculated the creation energy of a solitonic pair taking into account the finite-band corrections. In the case of an odd-membered chain the one soliton with an irrational charge and $S=1/2$ ($\nu_{0+}=1$) should be presented in the ground-state configuration. The irrational charge is compensated due to the chain relaxation by the value δL . The critical value of the parameter α is calculated. At $\alpha > \alpha_c$ the electron-hole pair formation in the dimerized odd-membered chain takes place instead of the soliton formation. At $\alpha = 0$ our results are in accordance with¹⁷, where the finite discrete trans-(CH)_x odd-membered chain has been considered. Note that on this basis the interpretation of a remarkably high value of unpaired spins in trans-(CH)_x chains was given in¹⁷. Nevertheless, the situation with one soliton in a trans-(CH)_x chain is rather exotic because the polymerization process most likely adds carbon atoms pairwise. In our opinion of most interest is the investigation of a polaronic state in a chain. It was shown in¹⁶ that the finite band corrections to a polaron charge appears thus leading to the analogous chain relaxation in the presence of a polaron. This investigation is in preparation. Other problems to be solved in the AB-polymer model are the inclusion in (1) of electron-electron interactions and QFF effects as well as an interchain coupling:

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К теории линейных двухатомных полимеров

Рассмотрена модель линейного двухатомного полимера. Исследована структура основного состояния и фоннный спектр. Вычислена величина скорости звука в АВ цепочке с учетом электрон-фононного взаимодействия. Построены континуальные уравнения движения в конечнозонной схеме. Анализируется решение в виде кинка с учетом эффектов порядка $O(1/L)$, L -длина цепочки. Вычислено изменение электронной плотности в присутствии солитона. Показано, что в цепочке с фиксированными граничными атомами всегда рождается солитон-антисолитонная пара, причем каждый солитон имеет дробный фермионный заряд и спин $\sigma = 0$ (или $\sigma = \pm 1/2$). В цепочке с нечетным числом атомов и свободной границей в зависимости от величины параметра α имеет место либо солитон в основном состоянии, либо рождается электрон-дырочная пара в димеризованной фазе. При рождении одного солитона для компенсации нецелочисленного заряда имеет место изменение длины цепочки на величину δL . При этом ровно один электрон уходит из валентной зоны. При $\alpha = 0$ все результаты справедливы для модели транс-полиацетилена.

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On the Theory of Linear Diatomic Polymers

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The model of linear diatomic polymers is considered. Both the ground state and the phonon spectrum of a discrete AB chain are investigated. Taking into account the electron-phonon coupling as well as the finite-band corrections, the expression for the sound velocity is derived. The continuum equations of motion in the finite-band scheme are constructed. The kink solution is analysed when the effects of an order of $O(1/L)$, where L is a chain length, are included. It is shown that the low-lying electronic excitations of an AB chain with fixed end atoms are the kink pairs where each kink has an irrational charge and a spin $\sigma = 0$ (or $\sigma = 1/2$). Depending on the value of the parameter α the odd-membered chain with a free boundary is obtained to contain either a soliton or an electron-hole pair in its ground state. To compensate the irrational charge the creation of one soliton should be accompanied by the chain relaxation. In this case exactly one electron is removed from the valence band. At $\alpha = 0$ the all obtained results are valid for the trans-polyacetylene model.

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