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DYNAMICAL EFFECTS IN THE CONTINUUM TRANS-POLYACETYLENE MODEL

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The theoretical description of the physical properties of the trans-polyacetylene molecule, trans-$(CH)_x$, is essentially based on the soliton conception. In our leotures /1/ we presented a different aspects of polyacetylene physics as well as a some alternative ideas. The soliton excitations in trans-$(CH)_x$ can be described on the basis of the discrete Peierls model where the π-electrons are treated in a tight-binding (Debye - Huckel) approximation. Su, Schrieffer and Heeger derived the one-dimensional lattice Hamiltonian which has the form

$$H = \sum C_n^+ \left(i \frac{\partial}{\partial t} - \mu \right) C_n - \sum_n \left(t_{n,n+1} C_n^+ C_{n+1} + h.c. \right) + \frac{M}{2} \sum \dot{y}_n^2 + \frac{K}{2} \sum_n (y_{n+1} - y_n)^2, \quad (1)$$

where C_n is an annihilation operator of an π-electron on the n-th (CH) group (the spin index σ in (1) is droped), $y_n(t)$(t) is the displacement field of the n-th (CH) group from the equilibrium state, μ is a chemical potential of electrons, M is the mass of the (CH) group and K is the spring constant. The hopping matrix elements $t_{n,n+1}$ in the linear approximation take the form $t_{n,n+1} = t_0 - \alpha (y_{n+1} - y_n)$ where α is an electron-phonon coupling constant.

Brazovskii and Jakayama, Lin-Liu and Maki independently introduced the continuum version of the polyacetylene model which admits an exact analytical solutions. It was shown that the stationary excited states of this system are amplitude solitons. However, these authors used the adiabatical approximation neglecting the real phonon dynamics. In this case the investigation of the effects due to the soliton motion lies without the self-oonsistent approach.

We have been studying the dynamical version of the primary polyacetylene model (1) in the continuum limit. The equations of motion have the form

$$i u_t(x,t) = - i v_F u_x(x,t) + v(x,t) \Delta(x,t) + \frac{a_0^2}{2} \left[v_{xx} \cdot \Delta + v_x \Delta_x + \frac{v}{2} \Delta_{xx} \right], \quad (2a)$$

$$i v_t(x,t) = i v_F v_x(x,t) + u(x,t) \Delta(x,t) + \frac{a_0^2}{2} \left[u_{xx} \cdot \Delta + v_x \Delta_x + \frac{u}{2} \Delta_{xx} \right]$$

together with the self-consistent gap equation

$$M\,\Delta_{tt}(x,t) + Ka_0^2\Delta_{xx}(x,t) = -4K\Delta(x,t) - 16\alpha^2 a_0^2\,\Sigma'(u^*v+v^*u) + O(a_0^3 k) \qquad (2b)$$

where $\Delta(x,t) = 4\alpha y(x,t)$ is a gap parameter, $u(x,t)$ and $v(x,t)$ are the single-particle electronic wave functions, $v_F = 2a_0 t_0$ is the Fermi velocity, a_0 is a lattice constant. The summation in (2b) is assumed over all occupied states up to the Fermi level chosen to be zero. Excluding in (2b) the electronic subsystem ($\alpha = 0$) we obtain the well known optical phonon branch. The acoustic phonon mode can be introduced by analogous manner. On the basis of the acoustic phonon interaction effects the "quasirealistic" model of trans-$(CH)_x$ has been constructed which possesses a moving soliton solution /2/.

An exact nontrivial solutions of the system (2) are unknown at the present time. However we can see that the derivative coupling terms in (2) are smaller than the nonderivative coupling term by the order of $(a_0/\ell)^2$ where ℓ is a soliton width. For the kinks in trans-$(CH)_x$ we have $\ell \simeq 7a_0$ and terms with a_0^2 can be omitted. In the case of the slowly moving solitons we obtain from (2) the following system

$$i u_t(x,t) = -i v_F\, u_x(x,t) + v(x,t)\cdot\Delta \qquad (3a)$$

$$i v_t(x,t) = i v_F\, v_x(x,t) + u(x,t)\cdot\Delta$$

and

$$\Delta = -\frac{4\alpha^2 a_0}{K}\,\Sigma'(u^*v + v^*u). \qquad (3b)$$

It should be noted that all phonon dynamics in (3) is connected with the dynamics of the π-electronic subsystem. Moreover, the system (3) is fully equivalent to the integrable $N = 2$ Gross-Neveu model which is actively investigated in the quantum field theory (see, for review [1]). It is very important for our analysis that the system (3) is invariant under the Lorentz transformations with the characteristic velocity v_F. Hence a moving soliton solutions are related to the known static solutions in a simple way, and we can exactly calculate all physical characteristics of moving solitons /3/.

The kink solution has the form

$$\Delta(\xi) = \Delta_0 \tanh \xi/\xi_s\,, \qquad (4)$$

where $\xi = x - v_s t + x_0$, v_s is the kink velocity, $\xi_s = \xi_0\sqrt{1-\beta^2}$,

$\beta = v_s/v_F$, $\xi_0 = v_F/\Delta_0$ is the width of the statical kink. In the case of the uniformly dimerized trans-$(CH)_x$ chain we obtain from (3) the constant band gap $\Delta_0 \simeq 0.7$ eV. The electronic wave functions in the presence of the kink are given in /1,3/.

The electronic energy spectrum is essentially modified. The valence band electronic states have the same dispersion $E = -\sqrt{\Delta_0^2 + v_F^2 k^2}$ as in the uniform system but suffer phase shifts. It is important when we calculate the soliton creation energy. Moreover the discrete zero energy band state appears kn the presence of the kink.

The polaronic solution is found to be

$$\Delta(x,t) = \Delta_0 - K_0 v_F\left[\tanh K_p \xi_+ + \tanh K_p \xi_-\right], \qquad (5)$$

where $\xi_\pm = x - v_p t \pm x_0$, v_p is a polaron velocity, $K_p = K_0(1-\beta^2)^{-1/2}$ and $K_0 v_F = \sqrt{\Delta_0^2 - \omega_0^2}$. A polaron deformation gives rise to the appearance of the two local levels symmetric with respect to the gap centre ($E = \pm\omega_0$) in the electronic spectrum. It is connected with the symmetry of the Hamiltonian (1) under charge conjugation. In the case of the kink deformation the two electronic states are degenerate in energy, and as a consequence, the unusual charge-spin relation takes place: charged solitons are spinless and neutral solitons carry spin 1/2. In the trans-$(CH)_x$ model the level ω_0 is determined and has a value $\omega_0 = \Delta_0/\sqrt{2}$.

We calculate now the electric charge of solitons. The total change in the local electronic density in the presence of the kink deformation is given by /3/

$$\delta\rho(\xi) = \left[n_0 - \frac{2}{\pi}\,\mathrm{arctg}\,\frac{W\sqrt{1-\beta^2}}{2\Delta_0}\right]\frac{1}{2\xi_s}\,\mathrm{sech}^2\frac{\xi}{\xi_s}\,, \qquad (6)$$

where W is a full band-width ($W \simeq 10$ eV), $n_0 = 0,1,2$ is an occupation number of the discrete local at $E = 0$. The situation with $n_0 = 1$ can be realized in the undoped trans-$(CH)_x$ as a derivation in a pure bond alternated conformation and kink carry unpaired spin 1/2. The charge of the kink is zero because the common charge of the trans-$(CH)_x$ chain is conserved. The cases $n_0 = 0,2$ take place in the doped trans-$(CH)_x$. We obtain an additional charge $Q = \pm e$ but a spin is compensated.

From (6) we have

$$Q = e\left[n_0 - \frac{2}{\pi}\,\mathrm{arctg}\,\frac{W\sqrt{1-\beta^2}}{2\Delta_0}\right]. \qquad (7)$$

In the limit $W \gg \Delta_0$ the all above results are reproduced. However it is followed from (7) that a small contribution to the charge of the kink appears due to the finite value of W. Note that the effect of the soliton motion is additionally reduced by the small parameter $\varepsilon = \Delta_0/W \ll 1$.

Contrary to the kink case the polaron has an additional contribution to the value of charge which is not reduced by the small parameter ε. The polaronic deformation can arise in the trans-$(CH)_x$ chain by doping. Polaron-like excitation has a usual spin-charge relation: $Q = \pm e$ and S = 1/2. The change in the local density has the form

$$\delta\rho(\xi) = \frac{k_p}{4}\left(\mathrm{sech}^2 k_p\xi_+ + \mathrm{sech}^2 k_p\xi_-\right)\Big\{(n_0+2) - \frac{4(1-\beta^2)^{1/2}}{\pi}\cdot \mathrm{arctg}\,\frac{W}{2K_0v_F} + \beta^2\frac{4K_0^2v_F^2}{\pi\left[K_0^2v_F^2(1-\beta^2)-\Delta_0^2\right]}\left[\frac{\Delta_0}{K_0v_F}\,\mathrm{arctg}\,\frac{W(1-\beta^2)^{1/2}}{2\Delta_0} - (1-\beta^2)^{1/2}\,\mathrm{arctg}\,\frac{W}{2K_0v_F}\right]\Big\}, \qquad (8)$$

where we propose that the level $E = -\omega_0$ is occupied as the valence band states and n_0 is an occupation number of the level $E = \omega_0$. For polaron we have $n_0 = 1$. In the limit $W \gg \Delta_0$ at $\beta = 0$ we obtain from (8) an exact result, that the polaronic charge $Q = e$. At $\beta \neq 0$ the correction to the charge appears

$$\delta Q = e\beta^2\,\frac{\Delta_0 - K_0v_F}{\Delta_0 + K_0v_F}. \qquad (9)$$

At $\omega_0 \to 0$ the value of $\delta Q \to 0$ in accordance with the result for the kink case. In trans-$(CH)_x$ we obtain $\omega_0 = \Delta_0/\sqrt{2}$ and $\delta Q \simeq 0.17\,e\beta^2$. It is a sufficiently small correction but very important that the reduction by the small parameter ε is absent.

Using (6) and (8) we can calculate the electrical moment $P_m = e\int \xi^m\,\delta\rho(\xi)\,d\xi$ of solutions. It is easily shown that $\delta\rho(\xi)$ is an even function of ξ for both deformations. Hence, all the odd electrical moments turn to be zero. In the limit $\varepsilon \ll 1$ the quadrupole moment of the kink is

$$P_2^K = \frac{ea_0^2}{12\varepsilon^2}\cdot\left[(n_0-1)(1-\beta^2) + \frac{4}{\pi}\varepsilon\right]. \qquad (10)$$

Taking into account the value of ε we obtain for $(CH)_x$ $P_2^0 \simeq 1.5\,ea_0^2$, $P_2^{\pm} \simeq 17\,ea_0^2$, where P_2^0 and $P_2^{\pm}$ are the quadrupole moments of neutral and charged solitons, respectively.

The quadrupole moment of polaron has the form

$$P_2^P = \frac{ea_0^2}{\varepsilon^2}\Big\{\left[n_0 + \frac{4\sqrt{2}}{\pi}\varepsilon\right]\cdot\left[\frac{1}{6} + \frac{4}{\pi^2}\,\mathrm{arcth}^2\frac{1}{\sqrt{2}+1}\right] + \beta^2\left[(3-2\sqrt{2})\left(\frac{1}{6} + \frac{4}{\pi^2}\,\mathrm{arcth}^2\frac{1}{\sqrt{2}+1}\right) - \frac{n_0}{6}\right]\Big\} \qquad (11)$$

and the main contribution gives $P_2^P \simeq 33\,ea_0^2$.

The soliton creation energy is expressed in terms of the solutions of (3) in the following way

$$E^S = \sum_i{}'\left(E_i^+ - E_i^-\right) + (2\lambda\pi v_F)^{-1}\int d\xi\left[\Delta^2(\xi) - \Delta_0^2\right] + \frac{M}{32\alpha^2 a_0}\int \dot{\Delta}^2(\xi)\,d\xi, \qquad (12)$$

where $\lambda = 4\alpha^2 a_0/\pi K v_F$. The first term in (12) determines the contribution from the electronic subsystem due to the phase shifts in the electronic wave functions in the valence band. In the case of polaron an additional correction from the discrete levels $E = \pm\omega_0$ is appeared. The other two terms in (12) determine the lattice contribution to the creation energy of solitons. If the soliton motion the first two forms in (12) give the contribution the kinetic energy of solitons and the soliton mass renormalization takes place.

The kink creation energy has the form

$$E_K = \frac{2\Delta_0}{\pi} + \beta^2\left(\frac{\Delta_0}{\lambda\pi} + \frac{M\Delta_0^3}{6\lambda\pi K}\right). \qquad (13)$$

At $\beta = 0$ we obtain the well known result for the static kink E_K^0: $E_K^0 = 2\Delta_0/\pi$ /1/. The second term in the brackets determines the contribution from the kinetical term in (12) and we calculate the kink mass $M_K = 6\,m_e$, where m_e is an electronic mass. The first term determines the correction to the kink mass and we obtain

$$\delta M_K = 2\Delta_0/\pi\lambda v_F^2 \simeq 0.09\,M_K.$$

By an analogous manner we obtain the polaronic creation energy /3/

$$E^P = \frac{4}{\pi}\left[K_0v_F + \omega_0\,\mathrm{arctg}\,\frac{\omega_0}{K_0v_F}\right] + (n_0-2)\,\omega_0 +$$

$$+\beta^2\left\{\frac{2K_0 v_F}{\lambda\pi}+\frac{2K_0 v_F}{\pi}\left[1-3\left(\frac{\omega_0}{K_0 v_F}\right)\mathrm{arctg}\left(\frac{\omega_0}{K_0 v_F}\right)\right]+\right. \tag{14}$$

$$\left.+\frac{M\Delta_0^3 v_F}{32\alpha^2 a_0}\left[\frac{8}{3}x^3-4(1-x^2)\left(\ln\frac{1+x}{1-x}-2x\right)\right]\right\},$$

where $x = K_0 v_F/\Delta_0$. In the trans-$(CH)_x$ model we have $\omega_0 = K_0 v_F = \Delta_0/\sqrt{2}$. At $\beta = 0$ we obtain from (14) the result $E_p = 2\sqrt{2}\Delta_0/\pi$ in accordance with that for the statical polaron. The polaronic mass is determined by the kinetical term in (12) and has the value $M_p \simeq 1{,}3 m_e$ (the latter term in (14)). The other term at β^2 in (14) determines the correction to the polaronic mass which is very essential $\Gamma M_p \simeq 0.37 M_p$. Note that contrary to the kink case in (14) there is a contribution to the kinetical energy of polaron due to the electron subsystem.

In conclusion we note that the use of the small parameter $(a_0/\ell)^2$ in (2) may be correct only at small soliton densities. In the highly doped trans-$(CH)_x$ the soliton width decreases, and as a consequence we must take into account the droped terms in (2). It is important in a study of the soliton lattice formation at high soliton densities. One should, however, keep in mind that the continuum approximation may not be applicable at high soliton densities. The quasistatic approximation for moving solitons is applicable because in the real system the highest velocity of the soliton is governed by the lattice and for the kinks its value is $v_s \lesssim v_{sound} \ll v_F$. However, the investigation of the real soliton dynamics in the model (1) is still an open problem. The results may be relevant to the Gross - Neveu model where the dynamical mass of solitons appears when the dynamical effects are taken into account.

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Динамические эффекты в континуальной
модели транс-полиацетилена

Обсуждаются динамические свойства континуальной модели транс-полиацетилена. В рамках самосогласованной схемы вычислены физические характеристики движущихся солитонов /кинк, поляров/.

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Dynamical Effects in the Continuum
Trans-Polyacetylene Model

The dynamical properties of the continuum trans-polyacetylene model are discussed. In the self-consistent scheme the physical characteristics of the moving solitons (kink, polaron) are calculated.

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

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