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**POLARONS IN TRANS-POLYACETYLENE
AND POLYNYNE CHAINS**

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1. Introduction

It has been first shown by numerical study in [1] that the electron (hole) injection in the trans-polyacetylene chain (trans-(CH)_x) leads to the polaron formation. This state involves an inhomogeneous lattice distortion with the characteristic length $\xi_p \propto 10a$ and an important reconstruction of the local π -electron spectrum. Namely, two localized intragap levels with energies $E = \pm \omega_0$ are formed that are not present in the uniformly dimerized state. The charge of the polaron is obtained to be $\mp|e|$ and spin $\sigma = 1/2$. In a continuum model of trans-(CH)_x an exact analytical solution for a static polaron deformation has been obtained in [2,3]. The continuum theory results were shown to be in a good agreement with discrete calculations. The solution for a slowly moving polaron has been derived in [4]. In the last few years the polaron distortions in trans-(CH)_x have been investigated by many authors both analytically [2 to 6] and numerically [7 to 9].

Of particular theoretical interest is the study of nonlinear excitations in the linear polyene chain $(-C=C-)_x$. The π -electron system in polyene involves two degenerate atomic carbon p orbitals thus leading to the effective internal degeneracy of electrons $N=4$ instead of $N=2$ in trans-(CH)_x. As a result, a rich variety of polaron states arises in polyene which has been described first in [10]. It has been shown in [10] that the lowest-lying ionization states of the polyene chain are a polaron, a bipolaron, and a tri-polaron, with charges $\mp|e|$, $\mp 2|e|$, and $\mp 3|e|$, respectively.



Photoexcitation of the polymer must lead to a neutral polaron consisting of an electron and a hole bound by lattice distortion (named as the polarexciton in [10]). It is of interest that the characteristic lengths of polarons in polyynes are expected to be sufficiently short. In this case the finite-band scheme introduced firstly in [11] for the trans-(CH)_x model should be used for the continuum description. We have shown in [12] that the finite-band scheme describes short kinks in the diatomic polymer model quite well in accordance with the results of the discrete model calculations whereas the linearized continuum scheme doesn't work so well.

In the present work we investigate the statical polaron states in the trans-(CH)_x and polyynes models in the framework of the finite-band continuum scheme. The basic physical properties of polarons (spin, charge, width, formation energy, binding energy) are calculated. We have also carried out numerical calculations on periodic chains using the self-consistent discrete method. The limitation for the continuum description is established.

2. The Model and Solutions: Ground State and Polarons

Formally, the polyyne model proposed in [10] differs from the well known trans-(CH)_x model only in the effective degeneracy of the π -electrons (N=2 for the trans-(CH)_x and N=4 for polyyne model). The lattice Hamiltonian is written as [10]

$$H = -\sum_{n,\sigma,\lambda} (t_{n,n+1} C_{n+1,\sigma,\lambda}^{\dagger} C_{n,\sigma,\lambda} + \text{h.c.}) + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2, \quad (1)$$

where $t_{n,n+1}$ denotes electron transfers between nearest neighbours, $C_{n,\sigma,\lambda}^{\dagger}$ ($C_{n,\sigma,\lambda}$) are the creation (annihilation) operators

of π -electrons with spin σ in the λ th orbital of the n th atom. We label two degenerate atomic p-orbitals (p_x, p_y) by λ ($\lambda=1,2$). For trans-(CH)_x one has only one p-orbital and $\lambda \equiv 1$. The elastic interactions in (1) are restricted to the harmonic terms, K is a spring constant. We consider here the adiabatic limit so that an ion kinetic term is absent in (1) and lattice displacements u_n are static. As usual, we adopt the linear form for the hopping integral $t_{n,n+1}$, $t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n)$, where t_0 is the hopping integral characteristic of the uniformly spaced chain and α is the electron-phonon coupling constant.

The finite-band continuum model can be derived from (1) in the same manner as shown in [11] (see, for details, also [13] where the diatomic polymer model is investigated in the framework of the finite-band scheme). We shall use here the stationary equations for the one-particle electronic states in the form obtained in [13] where another representation for the electronic wave functions as compared to [10] is chosen

$$\begin{aligned} E_k A_k(x) &= -iv_{Fk} \frac{\partial B_k(x)}{\partial x} - (\epsilon_k - i\Delta_k(x)) B_k(x), \\ E_k B_k(x) &= -iv_{Fk} \frac{\partial A_k(x)}{\partial x} - (\epsilon_k + i\Delta_k(x)) A_k(x), \end{aligned} \quad (2)$$

with the self-consistent gap equation in the form

$$\Delta(x) = -\frac{14\alpha^2 a}{K} \sum_{k,\sigma,\lambda}^{\text{occ}} (A_k^*(x) B_k(x) - \text{c.c.}) \cos ka. \quad (3)$$

Here $A_k(x)$ and $B_k(x)$ are eigenstate amplitudes and the eigenvector

corresponding to the eigenvalue E_k is the spinor

$$\psi_k(x) = (\psi_k^A(x), \psi_k^B(x)) \equiv (A_k(x)e^{-ikx}, B_k(x)e^{-ikx}) \text{ normalized by the}$$

condition $\int_{-L/2}^{L/2} dx (|\psi_k^A(x)|^2 + |\psi_k^B(x)|^2) = 1$, $L = N_0 a$ is the chain length, $\Delta(x)$ is the gap parameter, $\Delta_k(x) = \Delta(x) \cos ka$, $\epsilon_k = 2t_0 \sin ka$, $v_{FK} = v_F \cos ka$, where v_F denotes the Fermi velocity $v_F = 2t_0 a$. The wave vector k in (2,3) is measured relative to $k_F = \pi/2a$.

It should be noted that known equations of the linearized continuum scheme [3,10] may be obtained from (2,3) in the limit $\sin ka \ll ka$ and $\cos ka \approx 1$. The ground-state solutions of (2,3) are the plane-wave states with

$$A_k = (2L)^{-1/2} \frac{-\epsilon_k + i\Delta_k}{E_k}, \quad B_k = (2L)^{-1/2}, \quad (4)$$

where the energy spectrum has the form $E_k = \pm (\epsilon_k^2 + \Delta_k^2)^{1/2}$. The gap parameter $\Delta(x) = \Delta_0 = \text{const}$ is determined from (3) which takes the form

$$1 = \frac{4N\alpha^2}{\pi K} \int_0^{\pi/2} dt \frac{\cos^2 t}{(\epsilon_t^2 + \Delta_t^2)^{1/2}}. \quad (5)$$

We recall that $N=2$ for trans-(CH)_x and $N=4$ for polyynes. Performing the integration in (5) one obtains

$$1/\lambda_{\text{eff}} = (K(m) - E(m))/m^2, \quad (6)$$

where $K(m)$ and $E(m)$ are complete elliptic integrals of the first and second kind, respectively; $\lambda_{\text{eff}} = 2N\alpha^2/\pi K t_0$, $m^2 = (1-z^2)$ and $z = (\Delta_0/2t_0)$. For $z^2 \ll 1$ one can reduce (6) to $\Delta_0 = (8t_0/e) \exp(-1/\lambda_{\text{eff}})$, where $e = 2.718\dots$

Let us consider the polaron solutions of (2,3). The gap parameter $\Delta(x)$ is found to have usual form [10]

$$\Delta_\theta(x) = \Delta_0 - K_\theta v_F [\tanh K_\theta(x+x_\theta) - \tanh K_\theta(x-x_\theta)] \quad (7)$$

The polaron distortion (7) leads to an eigenspectrum which is symmetric around $E=0$ and contains two localized intragap levels with energies $E = \pm \omega_\theta$ and two branches of conduction and valence-band states with energies $E = \pm \omega_k$. Note that in the general case quantities marked by θ in (7) depend on the occupation numbers (ν_\pm) of the discrete levels ($E = \pm \omega_\theta$). We shall find this connection below. For $E = +\omega_\theta$ the amplitudes of a localized state read as

$$A_+(x) = N_\theta(1+i) \text{sech} K_\theta(x-x_\theta), \quad B_+(x) = N_\theta(1-i) \text{sech} K_\theta(x+x_\theta), \quad (8)$$

where $N_\theta = (K_\theta/\delta)^{1/2}$, $\tanh K_\theta x_\theta = (\Delta_0 - \omega_\theta)/K_\theta v_F$, and $K_\theta v_F = (\Delta_0^2 - \omega_\theta^2)^{1/2}$. For a state with $E = -\omega_\theta$ one obtains that $A_-(x) = A_+(x)$ and $B_-(x) = -B_+(x)$.

The amplitudes of continuum states are obtained to be

$$A_k(x) = N_k [(\omega_k + \Delta_k + \epsilon_k) - i(\omega_k + \Delta_k - \epsilon_k) + 2\delta(1-i) \tanh K_\theta(x-x_\theta)], \quad (9)$$

$$B_k(x) = N_k [(\omega_k + \Delta_k + \epsilon_k) + i(\omega_k + \Delta_k - \epsilon_k) - 2\gamma(1+i) \tanh K_\theta(x+x_\theta)],$$

where $N_k = (2L)^{-1/2} \{ (\omega_k - \Delta_k) / [(\epsilon_k^2 + K_\theta^2 v_F^2) - 2K_\theta^2 v_F^2 / L K_\theta] 4\omega_k \}^{1/2}$,

$$\delta = \frac{1}{2} K_\theta v_F \left(1 - \frac{i\epsilon_k}{\omega_k - \Delta_k}\right), \quad \text{and} \quad \gamma = \frac{1}{2} K_\theta v_F \left(1 + \frac{i\epsilon_k}{\omega_k - \Delta_k}\right).$$

The continuum states have similar energies $\omega_k = \pm(\epsilon_k^2 + \Delta_k^2)^{1/2}$ as those in the ground state but they are phase shifted by $\delta(k) = -2\text{arctg} \frac{K_\theta v_F k}{\epsilon_k}$ in the region of the polaron location.

The self-consistent condition (7) takes the form

$$\Delta(x) = -\frac{4i\alpha^2 a}{K} \{ \nu_+ (A_+^* B_+ - B_+^* A_+) + \nu_- (A_-^* B_- - B_-^* A_-) + \pi/2a + N \int_{-\pi/2a}^{\pi/2a} dk (A_k^*(x) B_k(x) - B_k^*(x) A_k(x)) \cos ka \} \quad (10)$$

Inserting into (10) exact solutions (8,9) and performing straightforward calculations which are similar to those in [3], we derive the following condition

$$[\pi/2 - K(m)E(\theta, m') - E(m)F(\theta, m') + K(m)F(\theta, m')] = \pi(\nu_- - \nu_+) (1 - z^2 \sin^2 \theta)^{1/2} / 2N, \quad (11)$$

where $F(\theta, m')$ and $E(\theta, m')$ are incomplete elliptic integrals of the first and second kind, respectively, $m' = (1 - m^2)^{1/2}$, the parameters m and z are introduced in (6), and the angle θ is defined as $K_\theta v_F = \Delta_0 \sin \theta$, $\omega_\theta = \Delta_0 \cos \theta$, so that $\text{tg} \theta = K_\theta v_F / \omega_\theta$. Note that in the limit $z^2 \ll 1$ we obtain from (11) the known result of the linearized continuum scheme [10]

$$\theta = (\pi/2) [(N - \nu_- + \nu_+) / N]. \quad (12)$$

Here $0 \leq \nu_\pm \leq N$. We next use (11) to calculate θ .

3. The Physical Characteristics of Polarons

We shall consider here only the principal polaron states. For $\text{trans}-(\text{CH})_x$ there are usual polaron state with $\nu_- = N = 2$ and $\nu_+ = 1$ so that $\theta \propto \pi/4$ (we leave here out of account the antipolaron states which have been investigated in [6,7]) and a bipolaron state with $\nu_+ = 2$ and $\theta \propto \pi/2$. In this case ω_θ tends to zero. As was shown in [2], the bipolaron state in $\text{trans}-(\text{CH})_x$ is absolutely unstable and decays into the charged widely separated kink-antikink pair. In polyene we obtain a rich variety of polaron states (see Table 1).

Table 1. The principal polaron states of polyene

Polaron states	Gap-state occupancy	Spin states	Charge
Polaron minus		$S = 1/2$	e
Polaron plus		$S = 1/2$	$-e$
Bipolaron minus		$S = 1, 0$	$2e$
Bipolaron plus		$S = 1, 0$	$-2e$
Tripolaron minus		$S = 1/2$	$3e$
Tripolaron plus		$S = 1/2$	$-3e$
Polarexciton		$S = 1, 0$	0
Polaron minus*		$S = 1/2$	e
Polaron plus*		$S = 1/2$	$-e$

* denotes stable excited states.

Let us define the polaron width. According to (7) the polaron distortion may be viewed as a kink-antikink bound state. The characteristic width of polaron depends on the value of θ and is obtained in the form

$$\xi_p = 2x_\theta = (2\xi_s/\sin\theta)\operatorname{arcth}[\operatorname{tg}(\theta/2)], \quad (13)$$

where $\xi_s = v_F/\Delta_0$ is the width of a single kink.

Consider now the change in the local electronic density due to the presence of the polaron state in the chain

$$\Delta\rho^p(x) = \nu_+\rho^p(x) + \nu_-\rho^p(x) + \sum_{k,\sigma,\lambda} [\rho_k^p(x) - \rho_k^0(x)], \quad (14)$$

where $\rho_\pm^p(x) = |A_\pm(x)|^2 + |B_\pm(x)|^2 = (K_\theta/4)[\operatorname{sech}^2 K_\theta(x+x_\theta) + \operatorname{sech}^2 K_\theta(x-x_\theta)]$,

$$\rho_k^p(x) = [\epsilon_k^2 + K_\theta^2 v_{FK}^2 - 2K_\theta v_{FK}^2 \rho_+^p(x)] / [L(\epsilon_k^2 + K_\theta^2 v_{FK}^2) - 2K_\theta v_{FK}^2], \quad \rho_k^0 = 1/L.$$

The global charge of a polaron is defined as

$$Q = \int_{-L/2}^{L/2} dx \Delta\rho^p(x) = (N - \nu_+ - \nu_-) |e|. \quad (15)$$

Note that the terms of an order of $O(1/L)$ are absent in (15). Taking into account the results obtained in the linearized scheme [4] we have proposed in our previous paper [13] that a chain relaxation must occur in the presence of a polaron distortion. However, a careful calculation of the last term in (14) performed in the framework of the finite-band scheme shows that an exact compensation of the finite-band correction of an order of $O(z)$ takes place. Such a situation is analogous to the one in the case of a kink-antikink pair in a chain when an exact compensation of local charges occurs without any chain relaxation.

Finally, the formation energy of polarons is defined as

$$E_p = \sum_k \omega_k - \sum_k E_k + \delta E_{\text{lat}}, \quad (16)$$

where $\delta E_{\text{lat}} = (K/8\alpha^2 a) \int dx [\Delta^2(x) - \Delta_0^2]$ and

$$\sum_k \omega_k - \sum_k E_k \rightarrow \omega_\theta(\nu_+ - \nu_-) - \frac{N}{2\pi} E_k \delta(k) \Big|_{-k_F}^{k_F} + \frac{N}{2\pi} \int_{-k_F}^{k_F} E_k \frac{d\delta(k)}{dk} dk, \quad (17)$$

As a result, we obtain

$$E_p(\theta) = 2E_s \sin\theta. \quad (18)$$

Here $2E_s = (2N\Delta_0/\pi)[E(m) - (1-m^2)K(m)]/m^2$ is a creation energy of a kink-antikink pair and the angle θ should be found from (11). For small z (18) is reduced to the result obtained firstly in the linearized scheme [10] with $2E_s = (2N\Delta_0/\pi)$ and θ is defined from (12). It follows immediately from (12) and (18) that for $\nu_- = \nu_+$ ($\theta \propto \pi/2$) the polaron energy approaches one of two kinks. Such states are in fact identical with a kink-antikink pair infinitely far apart. Tables 2 and 3 list the basic physical characteristics of polarons which have been calculated in the framework of the finite-band continuum scheme. We have used the parameter sets for $\text{trans}-(\text{CH})_x$ from [1] and [7] whereas for polyene from [10].

We derive more precise results by the direct numerical calculation on periodic chains where the effects caused by the discreteness of the lattice are taken into account. We have used the self-consistent discrete method proposed in [14,15] and applied with success in [12,16,17] where the details can be found. The numerical calculations are performed on the rings of $N=100$ and 120 atoms with the same parameters as in the continuum investigation. The results are given in Tables 2 and 3.

Table 2. The physical characteristics of polarons in trans-(CH)_x.

The two parameter sets are used: a) $t_0 = 2.5\text{eV}$, $\alpha = 41\text{eV/nm}$,

$K = 21 \times 10^2 \text{eV/nm}^2$ [1] and b) $t_0 = 3.2\text{eV}$, $\alpha = 80.97\text{eV/nm}$,

$K = 61 \times 10^2 \text{eV/nm}^2$ [7].

Model	Parameter set	Δ_0 (eV)	ω_0 (eV)	$2x_0$ (a)	E_p (eV)	E_b (eV)
discrete	a	0.650	0.449	9.726	0.580	-0.070
continuum	a	0.651	0.464	9.531	0.571	-0.080
discrete	b	0.938	0.643	8.664	0.835	-0.103
continuum	b	0.938	0.669	8.460	0.820	-0.118

Table 3. The physical characteristics of the polaron states in polyene.

The parameter set from [12] is used: $t_0 = 3\text{eV}$, $\alpha = 80\text{eV/nm}$,

$K = 68 \times 10^2 \text{eV/nm}^2$. The binding energy E_b is calculated only for the lowest-lying ionization states, i.e. for polaron, bipolaron, and tripolaron, respectively.

Polaron states	Model	Δ_0 (eV)	ω_0 (eV)	$2x_0$ (a)	E_p (eV)	E_b^* (eV)
Polaron(\pm) [*]	discrete	3.0347	2.595	2.190	2.872	-0.162
	continuum	3.0355	2.852	2.060	2.364	-0.671
Bipolaron(\pm)	discrete	3.0347	1.818	2.718	5.088	-0.981
	continuum	3.0355	2.255	2.390	4.626	-1.445
Tripolaron(\pm)	discrete	3.0347	0.964	3.782	6.483	-2.621
	continuum	3.0355	1.283	3.285	6.266	-2.840

4. Conclusion

First of all we note that the finite-band continuum scheme has a remarkable advantage over the widely used linearized scheme. Namely, the linearization of the electron dispersion removes the true lower energy cut-off of the band. If we choose, for example, a momentum cut-off $\Lambda = k_F = \pi/2a$, then we obtain the full band width $W = 2nt_0$ instead of $4t_0$ in the discrete model. Thus, in fact, the linearized scheme contains an additional free parameter, Λ , which should be identified with the actual value of W . That

identification is carried out by the self-consistent condition (3). In the finite-band scheme we have dealt with the real electron spectrum where $\Lambda = \pi/2a$ and $W = 4t_0$. There is no need to introduce additional free parameters and all values can be determined by using the initial parameters of the discrete Hamiltonian (1). So, the self-consistent condition (6) is employed now to calculate the value of Δ_0 . The noted difference between the finite-band and linearized schemes should be taken into account when we want to compare the results obtained in the continuum and discrete investigations.

Moreover, the linearized continuum scheme gives false results in the case of very short characteristic lengths of inhomogeneities [12]. For example, the gap parameter for trans-(CH)_x calculated in the framework of the linearized scheme (we have used (6) at $z \ll 1$) takes the values $\Delta_0 = 0.633\text{eV}$ and $\Delta_0 = 0.909\text{eV}$, respectively, which are well conformed to the discrete calculations. However, in polyene where the characteristic length ξ_0 is small we obtain that $\Delta_0 = 2.525\text{eV}$ far away from the discrete value while the finite-band scheme still works well (see value of Δ_0 in Table 3).

As it follows immediately from our results, the finite-band scheme for polarons in polyene gives a satisfactory agreement only for $\xi_0 \geq 3a$. Note that for kinks in the diatomic polymer we have derived the lower limit as $\xi_0 \propto 2a$ [12]. For such values of ξ_0 the terms of an order of $(a/\xi_0)^2$ should be taken into account in (3). To investigate the polaron states in polyene in more detail one needs to perform the discrete calculations.

Finally, the investigation of the polaron state in a linear diatomic polymer in the framework of the finite-band scheme is of interest. The work in this direction is now in progress.

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Полярны в цепочках транс-полиацетилена и полиена

В рамках конечнозонной континуальной схемы исследовано формирование полярных состояний в моделях транс-полиацетилена и полиена. Вычислены основные физические характеристики полярнов: спин, заряд, энергия рождения, ширина, энергия связи. Рассмотрены биполярное, триполярное и полярэкситонное состояния в модели полиена. Проведен численный самосогласованный расчет полярнов в дискретных цепочках. Дано сравнение результатов, полученных в рамках конечнозонной континуальной схемы, с результатами дискретного расчета.

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Polarons in Trans-Polyacetylene and Polyyne Chains

The polaron formation in trans-polyacetylene as well as polyyne chains is investigated in the framework of the finite-band scheme. The physical characteristics of polarons (spin, charge, formation energy, width, binding energy) are calculated. The bipolaron, tripolaron, and polarexciton states in polyyne are considered. The self-consistent discrete analysis of polaron states is presented. Comparison between the finite-band and discrete calculations is done.

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

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