Unusual Soliton Properties of the Infinite Polyyne Chain

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Within a Peierls continuum description of the infinite polyyne chain $-(C\equiv C)-$ it is found that the polymer possesses soliton excitations with charges $\pm 2e$, $\pm e$, and 0 and polaron states with charges $\pm e$, $\pm 2e$, and $\pm 3e$. An excitation ("polarexciton") consisting of an electron and a hole bound by lattice distortion is also found and may be photogenerated in the polymer.

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Linear chains of carbon atoms with alternating single and triple bonds, i.e., $-(C\equiv C)-_x$, are known as polyynes. Experimentally, finite polyynes, with a variety of terminal groups, have been available for some time[1-3] and very long-chain (i.e., effectively infinite) polyynes are thought to be constituents of *carbyne,* a crystalline quasi-one-dimensional allotrope of carbon.[1-4] Carbyne has been of interest in astrophysics,[5] where it is thought to be a constitutent of interstellar dust, and has been proposed as the thermodynamically stable phase of carbon over a wide range of pressures in the approximate temperature range 2600–3800 K.[1,4] Theoretically, *ab initio* Hartree-Fock calculations[1,6-8] have suggested that, in the linear carbon chain, the alternating polyyne configuration $-(C\equiv C)-_x$ is preferred energetically to the uniform-bond-length *cumulene* structure $=(C=C)=_x$. In this Letter, we point out that, within a simple one-electron description of its electronic π states, the infinite polyyne chain is a half-filled Peierls insulator[9] in which the electrons possess an *effective* internal degeneracy (N) equal to 4. This leads to an unusual variety of soliton and polaron states and, in the continuum limit, to the remarkable result that the infinite polyyne chain is an approximate physical realization of the $N=4$ Gross-Neveu model relativistic field theory.[10]

Within the framework of a one-electron tight-binding description,[11] the π-electron states of polyyne are determined by the linear-chain Hamiltonian

$$H=H_L-\sum_{j,\sigma,\lambda}\{t_{j+1,j}c_{j+1,\sigma,\lambda}^{\dagger}c_{j,\sigma,\lambda}+\text{H.c.}\}. \tag{1}$$

The chain consists of N_0 ($N_0\to\infty$) sp^1-hybridized carbon atoms labeled by j ($j=1,2,\ldots,N_0$). Each carbon atom has two degenerate, orthogonal, atomic p orbitals transverse to the chain axis. The latter two orbitals are labeled by λ ($\lambda=1,2$). In (1), $c_{j,\sigma,\lambda}{}^{\dagger}$ and $c_{j,\sigma,\lambda}$ are fermion operators which create or destroy, respectively, an electron with spin σ in the λth orbital of the jth carbon atom. To allow for the dependence of the hopping integral $t_{j+1,j}$ on the atomic locations, we adopt the form[12]

$$t_{j+1,j}=t_0-\gamma(u_{j+1}-u_j). \tag{2}$$

In (2) u_j denotes the displacement of the jth atom from its position in a uniformly spaced carbon chain of lattice constant $\vec{a}$, while t_0 is the hopping integral characteristic of the uniformly spaced chain and $-\gamma$ is the derivative of $t_{j+1,j}$ with respect to the interatomic separation. H_L describes the lattice energy in the absence of the overlap of the atomic p orbitals,

$$H_L=\tfrac{1}{2}M\sum_j\dot{u}_j{}^2+\tfrac{1}{2}K\sum_j(u_{j+1}-u_j)^2, \tag{3}$$

in which M denotes the mass of the carbon atom and K a harmonic spring constant characteristic of the linear sp^1 sigma bonding. In (1) the electronic energy is measured relative to the total atomic p-orbital energy and there is one electron per p orbital.

The linear chain Hamiltonian (1) describes two degenerate half-filled π bands which couple to the instantaneous positions of the carbon nuclei *in an identical manner.* It follows, therefore, that if allowance is made for the twofold degeneracy of the electronic spin and we treat the atomic displacements $\{u_j\}$ as a classical field, the ground state of H is a half-filled Peierls insulator[9] in which the electrons possess an effective internal degeneracy N equal to 4. For the half-filled Peierls insulator ordinarily encountered, e.g., polyacetylene,[12,13] $N=2$.

The ground-state displacement field is $u_j = \pm(-1)^j u_0$ (all j), where u_0 is a positive constant, while the energy spectrum of the π states is

$$\mathcal{E}_{k,\xi} = \pm[\epsilon_k^2 + \Delta^2 \sin^2(ka)]^{1/2} \equiv \pm E_k.$$

In the latter, k denotes the allowed wave vectors, $-(\pi/2a) \leqslant k < (\pi/2a)$, $\epsilon_k = 2t_0\cos(ka)$, and $2\Delta = 8\gamma u_0$ is the magnitude of the Peierls gap. The index ξ combines the electronic spin σ and band index λ and may be assigned the values $\xi = 1$, 2, 3, and 4 corresponding to the four possible configurations, $(\downarrow,1)$, $(\uparrow,1)$, $(\downarrow,2)$, and $(\uparrow,2)$, of the subscript (σ,λ). Within this scheme the one-electron energy level with wave vector k may formally contain up to four electrons. The total ground-state energy is

$$E = (N_0/2)(K/4\gamma^2)\Delta^2 - \sum_{k,\xi} E_k,$$

which on minimizing with respect to Δ leads to the equation

$$1 = (4\gamma^2/KN_0)\sum_{k,\xi} \sin^2(ka) E_k^{-1} \tag{4}$$

for the equilibrium gap parameter Δ. For $\Delta/2t_0 \ll 1$, which is the criterion for the validity of a continuum description[14] of (1), (4) may be evaluated analytically to yield $\Delta = (8t_0/2.718)\exp(-1/\lambda_{\mathrm{ep}})$. Note that the dimensionless electron-phonon coupling constant $\lambda_{\mathrm{ep}} = 8\gamma^2/\pi K t_0$ is *twice* that of the case $N=2$. If we take as representative values for polyyne the values $t_0 = 3$ eV, $K = 68.6$ eV Å^{-2}, and $\gamma = 8$ eV Å^{-1} employed for polyacetylene,[15] we obtain $2\Delta = 5.0$ eV. Clearly the condition $\Delta/2t_0 \ll 1$ is not well satisfied, implying strong electron-phonon interaction for polyyne. However, the exact solution of (4), obtained numerically, is $2\Delta = 5.88$ eV, indicating that the weak-coupling limit is not a prohibitively bad approximation. Another important physical property of the Peierls insulator is the long-wavelength optical-phonon frequency[16] Ω_+. For the present model of polyyne it immediately follows from a related calculation by Rice and Mele[17] that

$$\Omega_+^2 = (16\gamma^2\Delta^2/MN_0)\sum_{k,\xi} \sin^4(ka) E_k^{-3} \tag{5}$$

$$\simeq (32\gamma^2/\pi t_0 M) \quad \text{for} \quad (\Delta/2t_0) \ll 1. \tag{6}$$

Evaluations of (5) and (6) with the representative values introduced above yield $\Omega_+ = 1941$ cm^{-1} and $\Omega_+ = 2200$ cm^{-1}, respectively. A definitive experimental value of Ω_+ for polyyne is, to our knowledge, unknown, but the latter calculated values of Ω_+ together with our estimates of 2Δ are consistent with the results of *ab initio* calculations performed by Karpfen.[8]

We now focus on the main topic of this Letter. Although we expect that the continuum limit[14] of the discrete model (1) will provide only a semiquantitative description of polyyne, we can, however, expect it to yield accurately the polymer's spectrum of soliton and polaron states. In the continuum limit of (1) the one-electron eigenvalues $\epsilon_{n,\xi}$ and the local gap parameter $\Delta(x)$ are determined by the coupled equations[14] ($\hbar \equiv 1$)

$$\epsilon_{n,\xi} u_{n,\xi}(x) = -iv_{\mathrm{F}}\nabla_x u_{n,\xi}(x) + \Delta(x) v_{n,\xi}(x), \tag{7a}$$

$$\epsilon_{n,\xi} v_{n,\xi}(x) = iv_{\mathrm{F}}\nabla_x v_{n,\xi}(x) + \Delta(x) u_{n,\xi}(x), \tag{7b}$$

$$\Delta(x) = -(4\gamma^2/K)\sum\nolimits'_{n,\xi}[u_{n,\xi}^*(x) v_{n,\xi}(x) + \mathrm{c.c.}], \tag{7c}$$

where $v_{\mathrm{F}} = 2t_0 a$ and the eigenstate correspondto $\epsilon_{n,\xi}$ is the two-component spinor $\psi_{n,\xi} = (u_{n,\xi}\, v_{n,\xi})$, normalized according to $\int dx\, \psi_{n,\xi}^* \psi_{n,\xi} = 1$, where the integration extends over the length of the polymer $L = N_0 a \to \infty$. The total energy of the polymer is

$$E = \sum_{n,\xi}{}' \epsilon_{n,\xi} + \frac{K}{4\gamma^2}\int_{-L/2}^{L/2} \frac{dx}{2a}\Delta^2(x). \tag{8}$$

The prime on the summation symbol in Eqs. 7(c) and (8) denotes summation over occupied states. These equations apply for the case of a *static* inhomogeneity. The ground-state solutions of Eqs. (7) are plane waves with $\epsilon_{n,\xi} = \pm\epsilon_k = \pm(\Delta_0^2 + v_{\mathrm{F}}^2 k^2)^{1/2}$ where, here, the wave vector k is measured relative to the zone edge $\pi/2a$ and $2\Delta_0$ denotes the (homogeneous) ground-state dimerization gap.

By established techniques,[18] Eqs. (7) can be shown to be identical to the static, semiclassical equations for the $N=4$ Gross-Neveu model relativistic field theory.[10] Hence, all the exact solitary-wave solutions can be readily cataloged. First, there are the "kink" soliton solutions for which $\Delta(x) = \pm\Delta_0\tanh(x/\xi_0)$, where the soliton halfwidth $\xi_0 = v_{\mathrm{F}}/\Delta_0$ ($\simeq 2.5a$ for polyyne, versus $\simeq 8.5a$ for polyacetylene). The corresponding eigenspectrum consists of a localized midgap state $\epsilon_{0,\xi} = 0$ and a continuum of phase-shifted plane-wave conduction-band and valence-band states with energies $\epsilon_{n,\xi} = \pm\epsilon_k$ ($k \neq 0$). However, since $N=4$, the presence of the soliton removes a total of $2 = 4 \times \frac{1}{2}$ states from the filled valence band.[19] Consequently the charge associated with the occupation of the midgap state will always be "screened" by a charge deficit of precisely two electrons. Since the midgap state may accommodate up to four electrons it follows that the solitons arise with the charges $\pm 2e$, $\pm e$, and 0, where e denotes the charge on an electron. The formation of these charge states is depicted in Table I. The variety of spin states and internal degeneracies with which they arise is also indicated in Table I. Topological constraints imply that solitons can be created from the ground state only in $K\bar{K}$ pairs, and from Eq. (8) we find the minimum energy of such a pair to be $2E_s = 2(4\Delta/\pi)$. The creation of the pair involves the excitation of four electrons from the valence band.

Second, there are the polaron solutions, for which $\Delta(x)$ has the form

$$\Delta_\theta(x) = \Delta_0 - K_\theta v_F\{\tanh[K_\theta(x+y_\theta)] - \tanh[K_\theta(x-y_\theta)]\}, \tag{9}$$

in which $K_\theta = \xi_0^{-1}\sin\theta$,

$$y_\theta = (\xi_0/\sin\theta)\tanh^{-1}[\tan(\theta/2)],$$

and θ is an angle defined in the range $0 \leq \theta < (\pi/2)$ and determined by

$$\theta = [(n+h)/4](\pi/2). \tag{10}$$

The physical significance of n and h is as follows. The polaron distortion (9) leads to an eigenspectrum consisting of two localized intragap states with energies $\epsilon_{\pm,\xi} = \pm\Delta_0\cos\theta$ and a spectrum of conduction and valence-band states with energies $\epsilon_{n,\xi} = \pm\epsilon_k$ $(k \neq 0)$ that are phase shifted in the region of the polaron distortion. The occupation of the upper gap state ϵ_+ is denoted by n $(0 \leq n \leq 4)$ while the number of *holes* in the lower gap state ϵ_- is denoted by h $(0 \leq h \leq 4)$. The phase-shifted valence-band states give rise to a local charge deficit of precisely four electrons and the net charge on the polaron is $Q = (n-h)e$. The formation energy of the polaron state is

$$E_p(\theta) = 2E_s\sin\theta. \tag{11}$$

The charges, gap-state configurations, spin states, and internal degeneracies of the polaron solutions admitted by (10) are exhibited in Table II. The principal polaron states are a polaron $(Q = \pm e)$, a bipolaron $(Q = \pm 2e)$, and a tripolaron $(Q = \pm 3e)$. These constitute the lowest-lying ionization states of the polymer. Their respective gap states lie at $\pm 0.92\Delta_0$, $\pm 0.71\Delta_0$, and $\pm 0.38\Delta_0$, while their corresponding widths $2y_\theta$ are $1.07\xi_0$, $1.23\xi_0$, and $1.76\xi_0$. It is evident from Eqs. (10) and (11) that a *fourth* electron or hole added to the polymer leads to the spontaneous formation of two (widely separated) doubly charged solitons. It is noteworthy, in contrast to the case $N = 2$, that an exact solution for an excited state, involving the promotion of an electron from the lower to the upper gap state (so $n = 2$, $h = 1$ or $n = 1$, $h = 2$), exists for the singly charged polaron.

We note from Table II that there also exists a *neutral* polaron solution $(n = h = 1)$. This corre-

TABLE I. Characteristics of soliton states of polyyne.

charge	gap-state occupancy[a]	spin states	internal degeneracy
2e	●●●●	S = 0	1
e	●●●—	S = 1/2	4
0	●●——	S = 1, 0	6
− e	●———	S = 1/2	4
− 2e	————	S = 0	1

[a] Each solid circle denotes an electron. The gap states are screened by a valence-band charge deficit of two electrons.

TABLE II. Characteristics of polaron states of polyyne.

charge	gap-state occupancy[a]	spin states	internal degeneracy	stable excited state
3e	●●●— ●●●●	S = 1/2	4	
2e	●●—— ●●●●	S = 1, 0	6	
e	●——— ●●●●	S = 1/2	4	●●—— —●●●
0	●——— —●●●	S = 1, 0	16	
− e	———— —●●●	S = 1/2	4	●——— ——●●
− 2e	———— ——●●	S = 1, 0	6	
− 3e	———— ———●	S = 1/2	4	

[a] Each solid circle denotes an electron. The gap states are screened by a valence-band charge deficit of four electrons.

sponds to an excitation in which an electron and a hole are bound by lattice distortion, i.e., a "polarexciton." Since its excitation energy is $E_p{}^0 = 2E_s \sin(\pi/4) = \sqrt{2}E_s < 2\Delta_0$, it is the lowest-lying *individual* electronic excitation of the polymer (i.e., a relaxed electron-hole pair excited in one of the two degenerate π bands). However, we note that two polarexcitons are unstable with respect to decay into a soliton pair since $2E_p{}^0 = 2\sqrt{2}E_s > 2E_s$. Thus, the lowest-lying thermal excitations of the polymer will be solitons. We expect, however, that the *photoexcitations* of the polymer at low temperature will be polarexcitons. An electron-hole pair photogenerated in the polymer will initially relax into a polarexciton. The latter will remain the dominant photogenerated species provided that the electron-hole recombination rate for the polarexciton proceeds much faster than the rate for the thermal decay of the polarexcitons into solitons.

Finally, let us comment on two obvious limitations of our treatment of the infinite polyyne chain: (1) the absence of electron-electron interactions in H and (2) the neglect of quantum fluctuation effects (QFE) in $\{u_j\}$. First, if we imagine treating (1) by adding a Hubbard U term to H we see that physically the interaction should, to lowest order, affect only electrons in the same orbital. Thus, it will split the degeneracy of the kink soliton states, even those with the same charge but *different* orbital distributions. This effect, if eventually observed experimentally, could provide important insight into the relative importance of electron-electron and electron-phonon interactions in quasi one-dimensional conjugated polymers. Second, with use of arguments previously applied to polyacetylene (i.e., $N=2$),[18,20] the QFE can be "bracketed" by considering the $M \to \infty$ and $M \to 0$ limits of H. For $M \to \infty$, the QFE vanish, and the mean-field-theory results we have derived become exact.[18] For $M \to 0$, H (in the continuum limit) becomes identical to the $N=4$ Gross-Neveu model at *the full quantum level.*[20] The spectrum of this *quantum* field theory is known exactly[21] and is, in fact, the same as the mean-field-theory result for $N=3$. Hence we know that even for $M=0$, QFE will not destroy either the dimerization or the rich variety of soliton and polaron states.

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