Solitons in polyacetylene and relativistic-field-theory models

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Using recent results on a model relativistic field theory, we find explicitly a new solitonlike solution, essentially the conventional strong polaron, in the continuum interacting electron-phonon model of a Peierls-dimerized chain such as polyacetylene [$(CH)_x$]. This solution is in good agreement with recent numerical simulations in a discrete model of $(CH)_x$. We discuss further areas in which known field-theory results may apply to $(CH)_x$.

Theoretical models[1] of solitons in polyacetylene have ranged from discrete lattice Hamiltonians[2] through continuum interacting electron-phonon theories[3–6] to phenomenologically motivated ϕ^4 Landau-Ginzburg-like descriptions.[7] Apart from the crucial questions of interpreting observed experimental phenomena in $(CH)_x$ in terms of any of these models,[1,8] it is of clear importance to understand the relations among them. In the present Communication we use the perhaps unexpected source of model relativistic field theories to illustrate a number of links among the various models and thus clarify both the nature of possible soliton excitations in $(CH)_x$ and the relative consistency of models used to describe these excitations. In particular, we establish the existence, within the continuum electron-phonon model, of a localized, solitonlike excitation additional to, and qualitatively different from, the amplitude "kink" solitons previously discussed.[1–7] These additional solitons, which are in essence conventional (strong) polarons, have very recently been seen in numerical studies of lattice models.[9]

In the continuum electron-phonon models,[4,5] a sequence of controlled approximations leads to a set of (adiabatic mean field) equations for the single-particle electron wave functions, Ψ_n, of energy ϵ_n,

$$\epsilon_n \Psi_n(x) = \left[-iv_F\sigma_3\frac{\partial}{\partial x} + \Delta(x)\sigma_1\right]\Psi_n(x) \quad , \tag{1a}$$

and a "self-consistent" equation for the (real) gap parameter $\Delta(x)$—which is directly related to the staggered displacement in the lattice model—

$$\Delta(x) = \frac{-g^2}{2\omega_Q^2}\sum_{n,s}{}' \Psi_n^\dagger \Psi_n \quad . \tag{1b}$$

Here σ_i is the ith Pauli matrix, the two-component (unit-normalized) spinor Ψ_n is defined by $\Psi_n^\dagger \equiv (u_n^*, v_n^*)$, and ω_Q^2/g^2 describes the net effective electron-phonon coupling. The Fermi velocity, v_F, satisfies $v_F = Wa/2$—units $\hbar = 1$—with W the full bandwidth [$\simeq$10 eV for $(CH)_x$] and a, the undistorted lattice spacing ($\simeq$1.22 Å). For undoped $(CH)_x$ the summation in (1b) is over the two spin states—for simplicity, the spin labels have been suppressed on Ψ_n—for each energy level (n) in the valence band, i.e., up to the Fermi level, chosen to be zero. We note that in the continuum Hamiltonian which leads to (1) the kinetic energy of the phonons—a term proportional to $(\partial\Delta/\partial t)^2$—has been dropped.

Two solutions to Eq. (1) have been explicitly discussed[4,5] in connection with $(CH)_x$. First, the constant-band-gap solution has $\Delta(x) = \Delta_0$ [$\simeq$0.7 eV for $(CH)_x$] and leads to a single-electron energy spectrum $\epsilon(k) = \pm(k^2v_F^2 + \Delta_0^2)^{1/2}$.[4,5] This corresponds to the uniformly dimerized ground state of $(CH)_x$. Formally stated, this dimerization reflects the *dynamical* symmetry breaking of the apparent $\Delta \to -\Delta$, $\Psi \to \sigma_3\Psi$ invariance of the original Hamiltonian and equations of motion. The relation between the band gap Δ_0 and the full band width W is $\Delta_0 = W \times \exp(-\pi v_F\omega_Q^2/g^2)$. The second solution, often referred to as *the* soliton in $(CH)_x$, is $\Delta(x) = \Delta_0 \tanh(x/\xi_0)$, with $\xi_0 = v_F/\Delta_0 = Wa/(2\Delta_0)$, describes an amplitude kink or domain wall which connects the two degenerate $\Delta = \pm\Delta_0$ ground states. A crucial feature of this solution is the presence of the "midgap" single-electron state, with $\epsilon \equiv \omega_0 = 0$; this electronic state can be unoccupied, singly occupied, or doubly occupied, correpsonding to solitons of charge $+e$, 0, and $-e$, respectively. Note that the addition of an electron—or the removal of one, to create a hole—to the valence band modifies the summation in Eq. (1b). Equations (1) actually permit a third solution, which has not been previously discussed explicitly.[10] Our knowledge of the existence of this solution comes from the recognition of an *exact* equivalence of (1) with the *static, semiclassical* equations[11] of a recently studied relativistic field-theory model. Although we cannot discuss here the equivalence in detail, we note that the relativistic theory—the "Gross-Neveu" (GN) model[11]—is

described by the Lagrangian density

$$\mathcal{L}(x)=\sum_{\alpha=1}^{N}\bar{\Psi}^{(\alpha)}(x)\left[i\gamma_\mu\frac{\partial}{\partial x_\mu}\right]\Psi^{(\alpha)}(x)$$
$$-g_{\mathrm{GN}}\sigma(x)\sum_{\alpha=1}^{N}\bar{\Psi}^{(\alpha)}(x)\Psi^{(\alpha)}(x)-\tfrac{1}{2}\sigma^2(x) \qquad (2)$$

involving N fermion fields $\Psi^{(\alpha)}(x)$, $\alpha=1,2,\ldots,N$ and an auxiliary boson field $\sigma(x)$. The exact equivalence holds between (1) and the $N=2$ *static, semiclassical* equations[11] which follow from (2). The new solutions to (1) have a single-electron spectrum with two states symmetrically placed in the gap at $\epsilon_\pm\equiv\pm\omega_0$ and exist *only* when there is a single unpaired electron—beyond those in the valence band—occupying the ϵ_+ state (the localized "electron" state) or, equivalently, when the ϵ_- state is only singly, rather than doubly, occupied (the localized "hole" state). Since the electron (hole) is trapped in a structure generated by its coupling to phonons, this excitation is polaronlike.[12] That the continuum model admits both polarons and amplitude kinks should prove useful for studying these particlelike nonlinear excitations (and their interactions) in a unified manner.

The explicit form of the polaron solution has $\Delta(x)$ given by

$$\Delta(x)=\Delta_0-\kappa_0 v_F(t_+-t_-)=\Delta_0-\frac{(\kappa_0 v_F)^2}{\omega_0}s_+s_- \ , \qquad (3)$$

where

$$\kappa_0 v_F=(\Delta_0^2-\omega_0^2)^{1/2}, \quad t_\pm\equiv\tanh\kappa_0(x\pm x_0) \ ,$$
$$s_\pm\equiv\mathrm{sech}\kappa_0(x\pm x_0) \ ,$$

and x_0 is determined by $\tanh\kappa_0 x_0=\kappa_0 v_F/(\Delta_0+\omega_0)$. For the ϵ_+ bound-state wave functions one has, with $N_0=\kappa_0^{1/2}/4$,

$$u_0(x)=N_0[(1-i)s_++(1+i)s_-] \ ,$$
$$v_0(x)=N_0[(1+i)s_++(1-i)s_-] \ . \qquad (4)$$

The negative-energy bound-state wave functions follow from (4) by the transformations $u_{-0}\equiv u|_{\epsilon=-\omega_0}=v_0$ and $v_{-0}\equiv v|_{\epsilon=-\omega_0}=-u_0$. The negative-energy valence-band continuum states are

$$u_-(k;x)=N_k''e^{ikx}[(\omega+\Delta_0-kv_F)-\gamma(1+i)t_++\delta(1-i)t_-] \qquad (5a)$$

and

$$v_-(k;x)=-N_k''e^{ikx}[(\omega+\Delta_0+kv_F)-\gamma(1-i)t_++\delta(1+i)t_-] \ , \qquad (5b)$$

where

$$\omega=(k^2v_F^2+\Delta_0^2)^{1/2} \ ,$$
$$\gamma\equiv\tfrac{1}{2}\kappa_0 v_F\left[1-\frac{ikv_F}{\omega-\Delta_0}\right], \quad \delta=\gamma^* \ ,$$

and

$$N_k''=\frac{1}{2}\frac{1}{2\pi}\left[\frac{\omega-\Delta_0}{\omega(k^2v_F^2+\kappa_0^2v_F^2)}\right]^{1/2} .$$

By direct calculation, one can verify that these forms for u and v satisfy the electron part of the continuum equations (1) for *any* value of ω_0 in $0<\omega_0<\Delta_0$. However, *only for the specific value* $\omega_0=\kappa_0 v_F=\Delta_0/\sqrt{2}$ is the self-consistent gap equation for $\Delta(x)$ also satisfied. A detailed discussion will be given elsewhere. The form of the polaron solution and its comparison[12] with the amplitude kink are shown in Fig. 1. From (3) we deduce the characteristic width of the polaron as

$$2x_0=Wa/(\Delta_0\sqrt{2})\ln(\sqrt{2}+1)\sim 1.24\xi_0 \ ,$$

where ξ_0 is the kink width parameter. The value of $\Delta(x)$ at the central "depression" is $\Delta_{\min}=\Delta(0)=\Delta_0(\sqrt{2}-1)$. Finally, the energy of the polaron is $E=(2\sqrt{2}\Delta_0)/\pi\sim 0.90\Delta_0$, so that its binding energy is $0.10\ \Delta_0$ [$\simeq$0.07 eV for $(CH)_x$]. All these numbers are in good agreement with the very recent numerical results on electron injection in the *lattice* model of $(CH)_x$.[9] Since the lowest level in the dimerized conduction band has $E_{\min}=\Delta_0$ and placing an electron into a kink-antikink $(K\bar{K})$ pair—recall that topological constraints require kinks to be produced in pairs—requires $E_{\min}=2(2\Delta_0)/\pi$, the polaron is the lowest-energy state available to a single electron. Hence such states may play a role in specific types of doping in $(CH)_x$, may provide "doorway" states to $K\bar{K}$ pair production and annihilation (e.g., in photogeneration experiments), and may prove crucial in interpreting tunnel injection experiments. In addition, polaron transport studies should be undertaken.

Elsewhere, we shall pursue these and other physical implications of polaron states in $(CH)_x$. Here we turn now to several other illustrations of implications from field theories for models of polyacetylene. First, consider the relation of the continuum electron-phonon model to the phenomenological ϕ^4 theory, the applicability of which for $(CH)_x$ has been questioned[5] because the ground-state energy's dependence[13] on Δ_0 [$E(\Delta_0)\simeq\Delta_0^2\ln\Delta_0^2$] and strong nonlocality suggest that the Landau-Ginzburg expansion

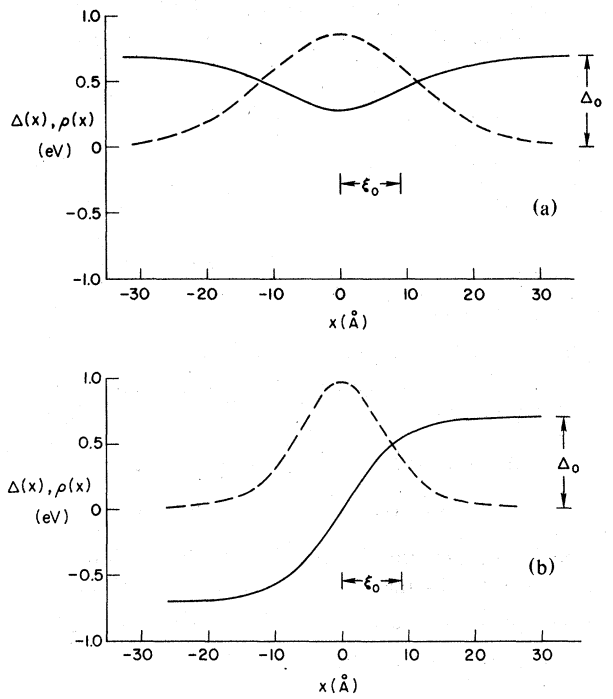

FIG. 1. A comparison in the continuum electron-phonon model of the gap parameter $\Delta(x)$—solid line—for (a) the new "polaron" excitation and (b) the previously known "kink" excitation. The vertical scale is in eV, the horizontal in Å. The dashed lines indicate plots (in arbitrary units) of the electron density $[\rho(x)]$ in (a) the "bound state" ($\omega_0 < \Delta_0$) and (b) the "midgap" state ($\omega_0 = 0$).

motivating the ϕ^4 theory must fail. Yet, the qualitative successes of the ϕ^4 model remain and, in fact, can be somewhat clarified by referring to known qualitative similarities, at the semiclassical level, between the GN model—which is structurally similar to the continuum $(CH)_x$ model—and the ϕ^4 field theory, coupled to fermions, with Lagrangian density (f constant)

$$\mathcal{L}(x) = \tfrac{1}{2}(\partial_\mu\phi)(\partial^\mu\phi) - \tfrac{1}{4}\lambda(\phi^2 - f^2)^2 + \sum_{\alpha=1}^{N} \bar{\Psi}^{(\alpha)}(x)\left(i\gamma_\mu\frac{\partial}{\partial x_\mu} - g\phi\right)\Psi^{(\alpha)}(x) \quad . \quad (6)$$

Among the similarities between the GN and ϕ^4 models which are already known to have counterparts in the $(CH)_x$ comparison are that both GN and ϕ^4 theories have (i) spontaneous symmetry breaking in the ground state, in ϕ^4 from the explicit $\phi = \pm f \neq 0$ minima of the meson potential and in the GN model from the *dynamical* effects of fermions which lead to an effective potential containing the term $V(\sigma) \sim \sigma^2 \ln\sigma^2$,[11] in direct analogy to the full electron-phonon result[13] for $(CH)_x$; and (ii) topological solitons (kinks) and, when fermions are coupled to ϕ^4, "midgap" states ($\omega_0 = 0$) with unusual spin-charge assignments.[14] Further qualitative parallels, not previously noted in the context of $(CH)_x$, are (i) that *both* GN (Ref. 14) and ϕ^4 (Ref. 15) models have "polaronlike" solutions; and (ii) in the limit that N—the number of different fermion fields—approaches infinity, the ϕ^4 (with fermions) and GN models become formally equivalent.[15] An immediate consequence is that the ϕ^4 model in $(CH)_x$, without explicitly including valence-electron effects, *does* contain the polaron we have found in the continuum electron-phonon model. In solid-state language, the ϕ^4 potential is imitating the effects of the valence-band electrons.

Field-theory models also suggest new and possibly important effects in $(CH)_x$. First, $K\bar{K}$ scattering in ϕ^4 theory is known to have a very interesting resonance structure in the intermediate-velocity region.[16] The implications for transport and soliton lifetimes in polyacetylene—and the question of its persistence in more fundamental models of $(CH)_x$—are being studied. Second, analytic studies of the semiclassical GN equations[11] and recent numerical investigations[17] of ϕ^4 have revealed time-periodic, spatially localized "breatherlike" solutions in both theories. It is thus natural to speculate that similar excitations may exist in $(CH)_x$, although these will have to be sought numerically, because of the absence in the GN model of a term comparable to $(\partial\Delta/\partial t)^2$ in the full $(CH)_x$ continuum Hamiltonian. Finally, we note that all the theoretical models we have discussed have been treated in the adiabatic mean-field approximation. The fully quantum theory of $(CH)_x$ is only now beginning to be studied.[18] Here again a comparison to relativistic field theory models, although not conclusive, proves provocative. Recently, the fully quantum GN theory has been (partially) solved. For arbitrary N, the exact quantum S matrix[19] (and hence the particle spectrum) has been found. For $N = 2$, it is known that only kinklike excitations exist[19]; neither polarons nor breathers remain in the fully quantum theory with exact GN dynamics.[4,10] Of course, this result cannot immediately be translated to polyacetylene, because the phonon kinetic energy term $(\partial\Delta/\partial t)^2$ in the full continuum $(CH)_x$ Hamiltonian has no counterpart in the GN model. Nonetheless, this result underscores the importance of the (difficult) task of studying the fully quantum theory of $(CH)_x$ and of continuing the emerging dialogue[6,14] on nonlinear excitations between field theory and solid-state physics.

Note added in proof. Since the submission of our manuscript, work by S. A. Brazovskii and N. N. Kirova describing similar results has appeared [Pis'ma Zh. Eksp. Teor. Fiz. 33, 6 (1981) and (unpublished)]. These authors obtain the polaron solution for both *trans*- and *cis*- polyacetylene. Insofar as the results of our two groups overlap, they are in complete agreement.

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