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Solitons, polarons, and phonons in the infinite polyyne chain

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The infinite polyyne chain, $+C\equiv C+_{\infty}$, or polyyne, is interpreted as a Peierls distorted one-dimensional metal with strong intrinsic electron-phonon coupling at the half-filled band level. Because there are two degenerate π-electron bands in polyyne the effective internal degeneracy (N) of the electrons is 4, rather than 2 as in the model of polyacetylene. This leads to a rich variety of kink-soliton and polaron states and, in the limit of a continuum description, to the interesting result that polyyne is an approximate physical realization of an $N=4$ Gross-Neveu model relativistic field theory. The low-lying electronic excitations of the polymer are kink-solitons with charges 0, $\pm e$, and $\pm 2e$. The lowest-lying ionization states are a polaron, a bipolaron, and a tripolaron, with charges $\pm e$, $\pm 2e$, and $\pm 3e$, respectively. Photoexcitation of the polymer leads to a *neutral* polaron consisting of an electron and a hole bound by lattice distortion ("polarexciton"). Both the soliton and the polarons involve the appearance of localized intragap levels that are *not* present in the ground state. Moreover, a localized *excited* state exists for the polaron, while photoexcitation of the bipolaron and the tripolaron result in soliton-antisoliton pair production. Photoinduced absorption measurements on long *finite* polyynes in solution should be able to confirm the photogeneration of the polarexciton. Formation of the polaron states can be expected if doping with strong electron withdrawing species is possible. An *odd*-membered polyyne is predicted to contain a soliton in its ground-state configuration, the doubly ionized closed-shell chain being particularly stable. Soliton- or polaron-bearing acetylenic chains might be of relevance in astrophysics. The ground-state acoustic and optical branches of the phonon spectrum of the discrete chain are also calculated and an expression derived for the reduction of the speed of sound due to the electron-phonon coupling.

I. INTRODUCTION AND SYNOPSIS

Linear chains of carbon atoms with alternating single and triple bonds, i.e., $+C\equiv C+_{n}$, are known as polyynes. Finite polyynes, with a variety of end groups, have been synthesized in the laboratory[1–4] and a value of n as high as 16 has been reported.[3] The observations of small neutral carbon aggregates in the vapor with $n \lesssim 8$, and of similarly small ionized carbon aggregates from secondary ionic emission, have been interpreted in terms of linear chain structures.[5,6] Finite polyynes have also been discovered to exist in the molecular clouds of the Milky Way and therefore are of astrophysical significance.[7,8] Very long-chain, i.e., effectively infinite, polyynes are thought to be the constituents of carbyne,[1,2,9] a proposed crystalline quasi-one-dimensional allotrope of carbon. It has been suggested that carbyne is the thermodynamically stable phase of carbon over a wide range of pressures in the approximate temperature range 2600–3800 K.[1,9] Moreover, the possibility that carbyne is a constituent of interstellar dust and responsible for a number of its hitherto unassigned absorption and radio emission features has also been suggested.[10] Long linear chains of carbon have also been proposed to be the constituents of liquid carbon.[6]

The *infinite* linear chain of carbon atoms has been of theoretical interest for many years and is the subject of the present paper. Early calculations by Longuet-Higgens and Birkitt,[11] employing Hückel theory, and by Hoffman,[12] using extended Hückel theory, found the alternating polyyne configuration to be preferred energetically to the uniform-bond-length cumulene structure $+C=C+_{\infty}$. A similar conclusion has been found by Stankevich and Tomlin[13] on the basis of a CNDO/2 (complete neglect of differential overlap) molecular-orbital calculation. On the other hand, Pitzer and Clementi,[6] Shustorovich,[14] Shustorovich and Popov,[15] and, in particular, Ovchinnikov *et al.*,[16] apparently have found, or have argued, that bond alternation in the infinite chain would, at best, be very small as a consequence of strong electron-electron interactions. The latter, so it is argued, essentially render the chain a Mott-Hubbard insulator[17] with a uniform cumulene structure. However, these arguments are not supported by a series of recent calculations[18–20] initiated by Mazumdar and Dixit,[18] on finite linear tight-binding Hubbard and "extended Hubbard" model chains. These carry one electron per atom and include adiabatic electron-phonon coupling. Interestingly, it is found that provided the (Hubbard) on-site Coulomb repulsion is not excessively larger than the one-electron tight-binding bandwidth, electron-electron interactions *enhance*, rather than inhibit, bond alternation. Moreover, *ab initio* Hartree-Fock calculations performed specifically for the infinite linear carbon chain by Kertesz *et al.*,[21] and by Karpfen,[22] confirm the favorability of the polyyne configuration. Both authors have calculated the electronic band structure while Karpfen has, in addition, presented numerical results for the electronic density of states, force constants, and phonon dispersion curves.

In what follows and throughout this paper we shall refer to the infinite linear chain of carbon atoms as polyyne. In this paper we consider polyyne as a Peierls insulator[23–25] at the half-filled band level and investigate in some detail its microscopic properties as such a system. While this theoretical description of polyyne neglects explicit effects of electron-electron interactions, it does rigorously treat the response of the linear carbon lattice to the presence of the π electrons: the eigenstates of the Peierls insulator are eigenstates of the *coupled* electron-lattice system.[26] The latter effect is large for a quasi-one-dimensional fermion system and cannot be neglected even if electron-electron interactions are taken into account. The microscopic properties which we shall investigate will be the ground-state electronic structure, the phonon spectrum, and the low-lying electronic excitations and ionization states.

We note that, interpreted as a Peierls insulator, polyyne differs in one important respect from the half-filled band Peierls insulator commonly encountered—and whose soliton properties[26,27] have made it such a fascinating system to study, particularly in the context of polyacetylene.[28–32] This difference arises in the effective degeneracy of the π electrons. In polyyne, the latter half-fill two degenerate bands which are derived from the two degenerate atomic carbon p orbitals (p_x,p_y) that are available in the sp σ-bonding configuration of the linear carbon chain. By symmetry, these couple to the instantaneous positions of the carbon nuclei *in an identical manner*. It follows, therefore, that the linear lattice in polyyne couples to a π-electron system whose effective degeneracy N is 4 (in arriving at $N=4$, account has been taken of the twofold degeneracy of the electron spin). By contrast, $N=2$ for the usual one-band Peierls insulator. We find that this effective doubling of N for the polyyne system has several interesting consequences.

First, it leads to an unusually rich spectrum of kink-soliton and polaron states. Both types of states involve the appearance of localized intragap levels that are *not present in the ground state*. The kink excitations, which are the lowest-lying electronic excitations of the chain, arise with charges 0, $\pm e$, and $\pm 2e$ and appropriate states of spin and internal degeneracy. On the other hand, the polaron states, which are the chain's lowest-lying ionization states, arise with charges $\pm e$, $\pm 2e$ and $\pm 3e$. Thus, the first three electrons (or holes) added to polyyne are trapped in intrinsic *localized* states. In addition to these six polaron states, a seventh polaronlike state with *zero* charge is found. This state is actually an excitation and consists of an electron and a hole bound by lattice distortion. It may be photogenerated in polyyne and since its formation is a consequence of lattice distortion only we name it a "polarexciton". (In actual polyyne, and, presumably, also in finite polyyne chains, the presence of the Coulomb interaction will lead to an even more tightly bound exciton.) A preliminary account of these results has been given in a recent Letter.[33]

Second, the degeneracy of four leads to the result that polyyne is—in the limit of a continuum description of the discrete chain—an approximate physical realization of a model relativistic field theory: namely, the static, semiclassical, $N=4$ Gross-Neveu model.[34] The continuum description of polyyne is quantitatively accurate for weak intrinsic electron-phonon interaction. In the Gross-Neveu model, the chiral symmetry of a field of massless relativistic fermions with internal degeneracy (or "flavor") N in $1+1$ dimensions is dynamically broken by coupling to a scaler field. Exact analytical solutions of this model are known[35] (for arbitrary N) and enable us to calculate, in detail, the previously described kink and polaron eigenstates of polyyne. Since solutions of both the $N=2$ and $N=1$ field theories have already found application in linear chain models of polyacetylene[30–32] and the highly correlated 1:2 tetracyanoquinodimethane (TCNQ) charge-transfer salts,[36] respectively, the present application of the $N=4$ case to polyyne is particularly interesting.

Third, the doubling of the number of π electrons relative to the sp^2 σ-bonded case of polyacetylene leads to a large value of the dimensionless electron-phonon coupling constant, $\lambda_{e\text{-ph}}=(8\gamma^2/\pi K t_0)\sim 1$. Here, t_0 denotes the π-electron nearest-neighbor tight-binding hopping integral characteristic of the uniform chain, $-\gamma$ its derivative with respect to the interatomic separation, and K a harmonic spring constant determining the elastic deformation energy of the sp σ bond. This implies strong intrinsic electron-phonon interaction in polyyne, and is indicative of a large Peierls gap $(2\Delta_0)$ and strongly localized kink and polaron states. Thus, although qualitatively correct, the analytic results which we obtain in the limit of a continuum description, are likely of semiquantitative accuracy only. In a sequel to the present paper we shall numerically investigate the exact properties of the discrete chain and, in particular, study the adiabatic (and highly nonlinear) dynamics following photoexcitation.[37]

The existence in nature of the quasi-one-dimensional allotrope of carbon is uncertain. However, our results are relevant to long *finite* polyynes. Indeed, an odd-membered polyyne would be expected to contain a kink soliton in its ground-state configuration—the closed-shell doubly ionized chain being particularly stable. Experimentally, photoinduced absorption measurements on finite polyynes in solution (or, possibly, in solid form) should, in principle, be able to identify the intragap states of the photogenerated polaronic exciton. Possible doping with strong electron-withdrawing atomic or molecular species would be expected to lead to the formation of either of the polaron states. Also, kink- or polaron-bearing polyynes might be of relevance in astrophysics.

The layout of our paper is as follows. In Sec. II we present the underlying model of the polyyne chain, namely a nearest-neighbor tight-binding description of its π electrons and their coupling to the carbon nuclear displacements. The insulating Peierls ground state is derived. In Sec. III the acoustic and optical branches of the phonon spectrum are calculated. The latter is necessarily done taking into account the adiabatic polarization of the π electrons to second order in γ. The physics of the phonon spectrum is discussed and an expression derived for the velocity of sound. In Secs. IV and V the continuum limit of the discrete polyyne chain is taken and the resulting system of equations found to be equivalent to those of the $N=4$ Gross-Neveu field theory. The soliton-kink and "bag" (i.e., polaron) solutions of the latter are transcribed to compute the analogous eigenstates of the polyyne system in detail. Finally, in Sec. VI a discussion of the implications and limitations of our results for polyyne is given.

II. MODEL AND GROUND STATE

We describe the π electrons in polyyne *and* their coupling to the instantaneous positions of the carbon nuclei within the framework of a nearest-neighbor tight-binding model. Specifically, the model is defined by the following Hamiltonian:

$$H = H_L - \sum_{j,\sigma,\lambda} (t_{j+1,j} c^{\dagger}_{j+1,\sigma,\lambda} c_{j,\sigma,\lambda} + \text{H.c.}) . \qquad (2.1)$$

The polyyne chain, which is taken to lie along the z axis, consists of N_0 ($N_0 \rightarrow \infty$) sp^1-hybridized carbon atoms labeled by j ($j=1,2,\ldots,N_0$). Each carbon atom, of mass M, has two degenerate atomic p orbitals (p_x,p_y) and are labeled by λ ($\lambda=1,2$). In (2.1), $c^{\dagger}_{j,\sigma,\lambda}$ 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. The electronic energy is measured relative to the total atomic p-orbital energy and there is one electron per p orbital. To allow for the dependence of the hopping integral $t_{j=1j}$ on the atomic locations, we adopt the linear form

$$t_{j+1,j} = t_0 - \gamma(u_{j+1} - u_j) . \qquad (2.2)$$

Here, u_j denotes the displacement of the jth atom from its position in a uniformly spaced carbon chain of lattice constant 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. We shall see later that the adoption of the linear development (2.2) will place an upper bound on the strength of the intrinsic electron-lattice interaction that may be used in the present model. H_L describes the lattice energy,

$$H_L = \tfrac{1}{2} M \sum_j \dot{u}_j^2 + \tfrac{1}{2} K \sum_j (u_{j+1} - u_j - a_0 + a)^2 , \qquad (2.3)$$

in which K is a harmonic spring constant determining the potential energy of the sp σ bond for small changes in its length relative to its equilibrium length a_0. The latter bond length is defined in the *absence* of overlap of the atomic p_x and p_y orbitals and is, therefore, different from the uniform bond length a which we now identify as the lattice constant of the *cumulene* chain. The latter is obtained by minimizing the total energy of the cumulene chain. We shall assume that a has been found in this way and since the potential energy term in (2.3) differs from

$$\tfrac{1}{2} K \sum_j (u_{j+1} - u_j)^2 , \qquad (2.4)$$

merely by a constant and a term that will average to zero in all our subsequent investigations, we shall retain (2.4) only in (2.3).

The Hamiltonian (2.1), which describes a one-dimensional metal, has been extensively discussed in the literature[25] and, more recently, in connection with polyacetylene.[28,29] As is well known, the uniform metallic phase of the chain is unstable with respect to a periodic distortion of the lattice that renders the chain an insulator. At the half-filled band level, this insulating Peierls phase is achieved by a spontaneous dimerization of the chain. The dimerization opens up an energy gap precisely at the Fermi level of the metallic phase. In the limit of weak intrinsic electron-lattice coupling ($\lambda_{e\text{-ph}} \ll 1$) the lowering of the electronic energy varies as $u^2 \ln(A/|u|)$ while the increase in the lattice energy is proportional to u^2, where u denotes the amplitude of dimerization and A is a positive constant. Thus, a value of u that lowers the total energy of the chain can *always* be found. The driving force of the transition is the intrinsic instability of the one-dimensional electron gas to quasistatic density fluctuations of wave vector $2k_F$, where k_F denotes the Fermi wave vector. Importantly, these discussions treat the nuclear displacements $\{u_j\}$ as a classical field.

In the present case the Hamiltonian (2.1) 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, the ground state of H is a half-filled Peierls insulator in which the electrons possess an effective internal degeneracy N equal to 4, rather than 2 as ordinarily encountered. With the lattice displacements regarded as classical quantities, the ground-state displacement field is

$$u_j = \pm(-1)^j u_0 , \qquad (2.5)$$

where u_0, a positive constant, is the amplitude of the dimerization and the choice of signs in (2.5) correspond to the two possible and *entirely equivalent* senses of the dimerization field. The latter property of the ground state will play a crucial role in determining the elementary excitations of the chain. The resulting ground-state energy spectrum of the electronic π states is

$$\epsilon_{k,\xi} = \pm[\epsilon_k^2 + \Delta^2 \sin^2(ka)]^{1/2} \equiv \pm E_k , \qquad (2.6)$$

where, in the limit $N_0 \rightarrow \infty$, k denotes the allowed wave vectors, $(-\pi/2a) \leq k < (\pi/2a)$, $\epsilon_{k,\xi} = \epsilon_k = -2t_0 \cos(ka)$ is the electronic spectrum of the uniform metallic phase, and $2\Delta = 8\gamma u_0$ is the magnitude of the insulating Peierls gap. The index ξ combines the electronic spin σ and the 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 energy gap 2Δ separates a completely filled lower band from a completely empty upper band. These bands may be referred to as valence and conduction bands, respectively. However, as we shall see in Sec. III, the excitations from and the ionization states of these bands will be quite different from those of a conventional semiconductor. The magnitude of Δ is obtained by minimizing the total ground-state energy,

$$E=(N_0/2)(K/4\gamma^2)\Delta^2-\sum_{k,\xi}E_k\,, \tag{2.7}$$

with respect to Δ. This yields

$$1=(4\gamma^2/KN_0)\sum_{k,\xi}\sin^2(ka)E_k^{-1}\,, \tag{2.8}$$

as the equation determining the equilibrium value, Δ_0, of Δ. The physical content of this equation is as follows. In the dimerized ground state the electronic density is not uniform (as it is in the metallic phase) but sinusoidal with wave vector $2k_F=(\pi/a)$. Equation (2.8) states that the periodic force exerted on the lattice by this electron charge-density wave (CDW) is balanced by the elastic restoring forces of the alternating *sp* σ bonds. Equations of the type (2.8) and (2.9) below were first derived by Fröhlich.[24]

For $(\Delta_0/2t_0)$ small, Eq. (2.8) may be solved analytically to give

$$\Delta_0=(8t_0/2.718)\exp(-1/\lambda_{e\text{-ph}})\,, \tag{2.9}$$

in which $\lambda_{e\text{-ph}}=(8\gamma^2/\pi K t_0)$ is the dimensionless electron-phonon coupling constant. We note that $\lambda_{e\text{-ph}}$ is *twice* that of the case for which $N=2$. If we take as *representative* values for polyyne the values $t_0=3$ eV, $K=68$ eV Å^{-2}, and $\gamma=8$ eV Å^{-1}, which have been employed in the model of polyacetylene,[28] we obtain $\lambda_{e\text{-ph}}\simeq 0.8$ so that $2\Delta_0\simeq 5.0$ eV. Clearly, the condition of weak intrinsic electron-lattice coupling, i.e., $\Delta_0/2t_0 \ll 1$, is not well satisfied, implying strong electron-lattice coupling in polyyne. However, an exact solution of (2.8) is obtained as

$$\lambda_{e\text{-ph}}^{-1}=\int_0^{\pi/2}dx\left[\frac{\sin^2 x}{(1-\beta^2\sin^2 x)^{1/2}}\right] \tag{2.10}$$

$$=\beta^{-2}[K(\beta)-E(\beta)]\quad\text{for }\beta^2<1\,, \tag{2.11}$$

in which $\beta^2=[1-(\Delta_0/2t_0)^2]$ and $K(\beta)$ and $E(\beta)$ are the complete elliptic integrals of the first and second kind, respectively. With $\lambda_{e\text{-ph}}=0.8$ and $t_0=3$ eV, (2.11) yields $2\Delta_0=5.88$ eV. Thus, the weak-coupling limit, although quantitatively inadequate, is not a prohibitively bad approximation for the ground state.

It should be noted that there are no physically meaningful solutions of (2.10), i.e., the gap equation (2.8), for $\beta^2<0$, that is $\Delta_0>2t_0$. The latter would require that the hopping integral for the longer of the two ground-state carbon spacings, $t_0-(\Delta_0/2)$, has become negative, which is impossible. The pathology is a consequence of the inadequacy of the linear development (2.2) for large nuclear displacements and effectively places an upper limit, λ_c, on the value which may be used for $\lambda_{e\text{-ph}}$. Setting $\beta^2=0$ in (2.10) yields $\lambda_c=(4\pi/3)\simeq 1.27$. Also, no particular significance should be given to our choice of the parameters t_0, K, and γ for polyyne other than that they aid comparison with analogous properties calculated in the model of polyacetylene. Other reasonable choices of these parameter sets may be arrived at on the bases of a variety of arguments.

III. THE PHONON SPECTRUM

Another pertinent equilibrium property that reflects the unusual nature of the ground state of the Peierls insulator is the phonon spectrum. It has been investigated by a number of authors[39] and in calculating the phonon self-energy it is essential to take into account the polarization of the π electrons to second order in γ.[40] This gives rise to coupling between lattice displacements of widely separated carbon atoms, i.e., to long-range interactions.

Specifically, the phonon frequency with wave vector $q,\Omega(q)$, is determined by the solution of[41]

$$|\underline{D}(q)-\underline{I}\,\Omega^2(q)|=0\,, \tag{3.1}$$

in which the 2×2 dynamical matrix is

$$D_{ij}=M^{-1}\{\delta_{ij}[2K-8\gamma^2\chi_1(q)]+(1-\delta_{ij})[2K\cos(qa)-8\gamma^2\chi_2(q)]\}\,. \tag{3.2}$$

$\underline{I}$ denotes the unit matrix and δ_{ij} the Kronicker δ function. The functions $\chi_i(q)$ describe the adiabatic density response of the π electrons and are

$$\chi_i(q)=(2N_0)^{-1}\times\sum_{k,\xi}S_i(k,k+q)F(k,k+q)/(E_k+E_{k+q})\,, \tag{3.3}$$

with,

$$S_1(k',k)=\sin^2(ka)+\sin^2(k'a)\,, \tag{3.4}$$

$$S_2(k',k)=2\sin(k'a)\sin(ka)\,, \tag{3.5}$$

and

$$F(k,k')=1+[\epsilon_k\epsilon_{k'}-\Delta^2\sin(ka)\sin(k'a)]/(E_kE_{k'})\,. \tag{3.6}$$

The wave vector lies in the range $-(\pi/2a)\le q<(\pi/2a)$. It immediately follows from (3.1) and (3.2) that the acoustic- and optical-phonon branches, $\Omega_-(q)$ and $\Omega_+(q)$, respectively, are given by

$$M\Omega_\pm^2(q)=2K\{[1\pm\cos(qa)]-8\gamma^2[\chi_1(q)\pm\chi_2(q)]\}\,. \tag{3.7}$$

These two branches are plotted in Fig. 1 where the values of the parameters introduced in the preceding section have been employed. The corresponding phonon branches cal-

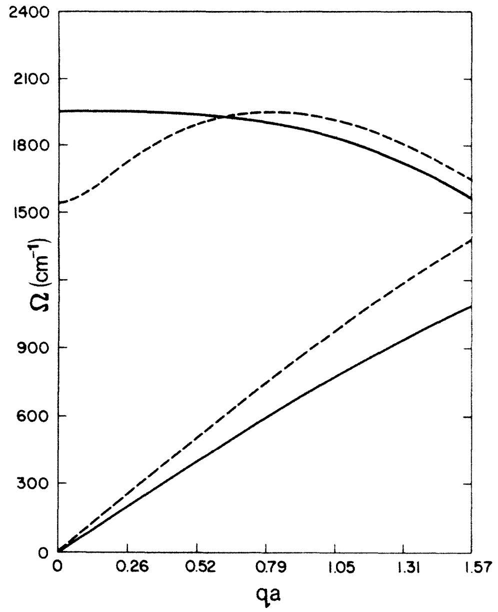


FIG. 1. Phonon spectra of the discrete chain. Solid curve, polyyne ($\lambda_{e\text{-ph}} \simeq 0.8$), dashed curve, polyacetylene model ($\lambda_{e\text{-ph}} \simeq 0.4$).

culated in the ($N=2$) model of polyacetylene are also included in Fig. 1 for comparison. The latter are obtained by employment of the CH mass in Eq. (3.2) for M and a degeneracy of 2 in Eq. (3.2) rather than 4. There are several features worthy of comment.

First, an interesting cancellation occurs in Eq. (2.13) for the long-wavelength ($qa \rightarrow 0$) optical-phonon frequency, $\Omega_+(0)$. The latter is

$$M\Omega_+^2(0) = 4K - (16\gamma^2/N_0) \times \sum_{k,\xi} \sin^2(ka) E_k^{-1} [1 - \Delta^2 \sin^2(ka) E_k^{-2}] \, . \tag{3.8}$$

The second term in (3.8) which, in view of (2.8), is essentially the periodic force acting on the lattice at equilibrium due to the π-electron CDW, is exactly canceled by the first term in (3.8), which is the lattice restoring force at equilibrium. Thus,

$$\Omega_+^2(0) = (16\gamma^2 \Delta_0^2 / M N_0) \sum_{k,\xi} \sin^4(ka) E_k^{-3} \, . \tag{3.9}$$

The restoring force for long-wavelength optical displacements is, therefore, *purely electronic* in origin. In the weak-coupling limit, (2.16) may be evaluated to give

$$\Omega_+^2(0) \simeq 32\gamma^2 / \pi t_0 M \, . \tag{3.10}$$

This formula provides a means of empirically estimating the important parameter γ if Ω_+ is known experimentally and t_0 approximately known theoretically. With our choice of parameter values (3.10) yields $\Omega_+(0) = 2200$ cm^{-1} while an exact evaluation of (3.9) yields 1950 cm^{-1}.

Second, the initial dispersion ($qa \ll 1$) arising from the electronic contribution to $\Omega_+(q)$ is always positive.[40] This reflects the fundamental behavior of the one-dimensional electron gas, namely, that its density response is greatest at the wave vector that corresponds to $2k_F$ in the metallic phase. This positive dispersion ordinarily dominates the behavior of $\Omega_+(q)$ for $qa \ll 1$. This is clearly seen in Fig. 1 for the model polyacetylene calculations. For weak intrinsic electron-lattice coupling (3.7) may be expanded for $qa \ll 1$ to give

$$\Omega_+^2(q) = \omega_0^2 \{ \lambda_{e\text{-ph}} + (qa/2)^2 [(\lambda_{e\text{-ph}}/3)(2t_0/\Delta_0)^2 - 1] \} \, . \tag{3.11}$$

The term of unity in (3.11) is the (usual) negative dispersion arising from the σ-band force constant and $\omega_0^2 = (4K/M)$. Equation (3.11) suggests that the latter dispersion will be dominant if $\lambda_{e\text{-ph}}$ is sufficiently large that $(\lambda_{e\text{-ph}}/3)(2t_0/\Delta_0)^2 > 1$. This indeed has occurred for the calculated polyyne optical branch shown in Fig. 1.

Finally, we note that the sound velocity,

$$S = [d\Omega_-(q)/dq]_{q \rightarrow 0} \, , \tag{3.12}$$

can be significantly reduced by the electron-lattice coupling. Equations (3.7) and (3.12) lead to the result

$$S^2 = S_0^2 [1 - \lambda F(\lambda)] \, , \tag{3.13}$$

in which $S_0 = a(K/M)^{1/2}$ is the sound speed in the absence of electron-lattice coupling, $\lambda = \lambda_{e\text{-ph}}$ and

$$F(\lambda) = \int_0^{\pi/2} dx \left[\frac{\cos x}{(1 + \alpha^2 \tan^2 x)^{3/2}} \right] , \tag{3.14}$$

depends on λ through its dependence on $\alpha = (2t_0/\Delta_0)$. $F(\lambda)$ may be evaluated in terms of elliptic integrals and for $\lambda = 0.8$, yields $S = 0.62 S_0$. Thus the reduction in sound velocity due to the electron-lattice coupling is considerable. Since, according to the preceding section, λ is restricted to values satisfying $\lambda < \lambda_c = (4\pi/3)$, and we find $\lambda_c F(\lambda_c) < 1$, then an instability of the Peierls insulator, corresponding to $\lambda F(\lambda) > 1$ in Eq. (3.13), does not arise in the present model.

The calculated frequencies of the spectrum for polyyne shown in Fig. 1 are smaller but generally consistent with those of Karpfen.[22]

IV. THE CONTINUUM THEORY

By analogy with the model of polyacetylene we anticipate that the low-lying excitations and ionization states of the present model of polyyne[28–32] will be kink solitons and polarons, respectively. Such states will involve spatial inhomogeneities in the dimerization amplitude u_0 and important qualitative changes in the local π-electron spectrum. We require, therefore, a description of the inhomogeneous Peierls insulator. In the limit where the inhomogeneities vary slowly over microscopic distances ($\sim a$), i.e., in the limit of a continuum description of the discrete chain, an elegant system of equations describing the inhomogeneous Peierls insulator may be derived and solved.

As we shall see, the characteristic length scale of the inhomogeneities is $\xi_0 = v_F\Delta_0 = (2t_0/\Delta_0)a$ ($\hbar = 1$). Thus the requirement that ξ_0/a be large is that the intrinsic electron-lattice interaction be weak ($\lambda_{e\text{-ph}} \ll 1$). As we have seen, however, the latter condition is not well satisfied for polyyne. Indeed, with $\Delta_0 \simeq 2.5$ eV and $t_0 = 3$ eV, we have $\xi_0 \simeq 2.4a$. Nevertheless, while the continuum description will provide only semiquantitative results, we do expect it to yield accurately the polymer's spectrum of soliton and polaron states.

In order to take the continuum limit of the discrete chain Hamiltonian (2.1) we express the electron site amplitudes in the form

$$a^{-1/2}c_{j,\sigma,\lambda} = u_\xi(j)\exp(ik_F ja) - iv_\xi(j)\exp(-ik_F ja) \qquad (4.1)$$

and the lattice displacement field as

$$4\gamma u_j = (-1)^j\Delta(j) , \qquad (4.2)$$

where $u_\xi(j)$, $v_\xi(j)$, and $\Delta(j)$ are slowly varying functions of j. In general, they may also depend on time. $\Delta(j)$ is the amplitude of the local dimerization at the site j expressed in units of energy. For the homogeneous system $\Delta(j) = \Delta_0$, a constant, which is equal to one-half of the ground-state Peierls gap. $k_F = (\pi/2a)$. Substituting (4.1) and (4.2) into (2.1), expanding the electron amplitudes up to first order in the lattice spacing a and neglecting rapidly varying terms of the form $(-1)^j$, we obtain, on introducing the spatial continuum location $x = ja$, the continuum Hamiltonian

$$H = (K/4\gamma^2)\int \left[\frac{dx}{2a}\right][\omega_0^{-2}\dot{\Delta}^2(x) + \Delta^2(x)] + \sum_\xi \int dx\, \Psi_\xi^\dagger(x)[-iv_F\underset{\sim}{\sigma}_3\nabla_x + \Delta(x)\underset{\sim}{\sigma}_1]\Psi_\xi(x) . \qquad (4.3)$$

In (4.3) we have introduced the two-component wave functions

$$\Psi_\xi^\dagger = \begin{bmatrix} u_\xi^* \\ v_\xi^* \end{bmatrix} \text{ and } \Psi_\xi = (u_\xi \;\; v_\xi) , \qquad (4.4)$$

and the frequency $\omega_0 = 2(K/M)^{1/2}$. Also, σ_i denote the Pauli matrices

$$\underset{\sim}{\sigma}_0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \underset{\sim}{\sigma}_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} ,$$

$$\underset{\sim}{\sigma}_2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \underset{\sim}{\sigma}_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} ,$$

and $v_F = 2t_0a$ denotes the Fermi velocity. ∇_x denotes differentiation with respect to x while the overdot in (4.3) denotes differentiation with respect to time. The equations of motion of the coupled electron and lattice fields follow immediately from (4.3) and are

$$i\dot{\Psi}_\xi = (-iv_F\nabla_x\underset{\sim}{\sigma}_3 + \Delta\underset{\sim}{\sigma}_1)\Psi_\xi , \qquad (4.5)$$

$$\omega_0^{-2}\ddot{\Delta} + \Delta = (4\gamma^2 a/K)\sum_\xi \Psi_\xi^\dagger\underset{\sim}{\sigma}_1\Psi_\xi , \qquad (4.6)$$

where, for the moment, we have dropped the arguments of Ψ_ξ and Δ, and where the prime attached to the summation symbol in (4.6) indicates summation over occupied states. Equation (4.5) is of the form of a relativistic Dirac equation (in 1 + 1 dimensions) in which v_F is analogous to the velocity of light and Δ^2/v_F^2 analogous to the fermion mass. Equation (4.6), however, shows that the latter has its origin in an independent field which couples to the local off-diagonal fermion density.

We shall be chiefly interested in quasistatic solutions of (4.5) and (4.6) of the form $\Psi_\xi(x,t) = \exp(-i\epsilon_{n,\xi}t)\Psi_{n\xi}(x)$ with $\dot{\Delta} = 0$ and $\Delta = \Delta(x)$. In these cases, (4.5) and (4.6) reduce to the following system of equations:

$$\epsilon_{n,\xi}\begin{bmatrix} u_{n,\xi} \\ v_{n,\xi} \end{bmatrix} = \begin{bmatrix} -iv_F\nabla_x & \Delta(x) \\ \Delta(x) & iv_F\nabla_x \end{bmatrix}\begin{bmatrix} u_{n,\xi} \\ v_{n,\xi} \end{bmatrix} , \qquad \begin{matrix} (4.7\text{a}) \\ (4.7\text{b}) \end{matrix}$$

$$\Delta(x) = -(4\gamma^2 a/K)\sum_{n,\xi}{}'(u_{n,\xi}^* v_{n,\xi} + \text{c.c.}) . \qquad (4.7\text{c})$$

The wave functions are normalized according to

$$\int_{-L/2}^{L/2} dx(\,|u_{n,\xi}|^2 + |v_{n,\xi}|^2) = 1 , \qquad (4.8)$$

where the integration extends over the length L of the polymer ($L = N_0 a \to \infty$). The total energy of the polymer is

$$E = (K/4\gamma^2)\int_{-L/2}^{L/2}(dx/2a)\Delta^2(x) + \sum_{n,\xi}{}'\epsilon_{n,\xi} . \qquad (4.9)$$

In attempts to find solutions of Eqs. (4.7), it is useful to introduce the linear combinations

$$f_{n,\xi}^\pm = u_{n,\xi} \pm iv_{n,\xi} ,$$

in which case (4.7a) and (4.7b) reduce to

$$(v_F^2\nabla_x^2 - \Delta^2(x) - v_F\nabla_x\Delta(x) + \epsilon_{n,\xi}^2)f_{n,\xi}^- = 0 , \qquad (4.10)$$

$$f_{n,\xi}^+ = (-i/\epsilon_{n,\xi})[v_F\nabla_x - \Delta(x)]f_{n,\xi}^- = 0 , \qquad (4.11)$$

so that it is necessary to solve only one wave equation for nonvanishing eigenvalues $\epsilon_{n,\xi}$.

For the ground state $\Delta(x) = \Delta_0$ the solutions of (4.7) or (4.9) are plane waves of the form $\exp(-ikx)$ and yield

$$\epsilon_{n,\xi} = \pm E_k = \pm(\Delta_0^2 + v_F^2k^2)^{1/2} .$$

Here, in view of the development (4.1), the wave vector k is measured relative to $(\pi/2a)$.

V. SOLITONS AND POLARONS

The system of Eqs. (4.7) and the problem of their solution are identical to those of the static, semiclassical $N=4$ Gross-Neveu Model relativistic field theory. In the semiclassical limit of this field theory, initially massless Dirac fermions, possessing chiral symmetry and internal degeneracy N in 1 + 1 dimensions, acquire mass via coupling to a scalar field which dynamically breaks the initial chiral symmetry. Exact analytical solutions of the equations of the field theory model are known for arbitrary N and hence may be transcribed to the present case for which $N=4$. There are two types of solutions. These are kink-soliton solutions and polaron (or bag) solutions. Explicit expressions for the wave functions $\psi_{n,\xi}(x)$ corresponding to these solutions may be found in the papers of Brazovskii[31] and of Campbell and Bishop.[32]

The soliton-kink solutions involve an inhomogeneous dimerization of the form

$$\Delta(x)=\pm\Delta_0\tanh(x/\xi_0)\ , \tag{5.1}$$

in which the kink half-width is $\xi_0=(v_F/\Delta_0)a\simeq 2.4a$ for polyyne. They interpolate between the two possible senses of dimerization described by Eq. (2.4) and thus have the character of domain walls. The corresponding electron spectrum consists of a localized state with energy $\epsilon_{0,\xi}=0$, lying precisely at the middle of the Peierls gap, and a continuum of plane-wave conduction-band and valence-band states with energies $\epsilon_{n,\xi}=\pm E_k(k\neq 0)$, respectively. Although the energies of the continuum state are similar to those of the ground state they are, however, phase shifted as they pass through the region of the kink. The phase shifting collectively removes exactly one-half of a state (*per* spin *per* atomic p orbital) from the filled valence band and the same fraction from the empty conduction band. Thus, a total of exactly one state ($k=0$) is effectively removed from the ground-state spectrum and the charge on the soliton contributed by the *deficit* in the valence band is $-(\frac{1}{2}\times 4)e=-2e$, where e denotes the charge on an electron. Since the mid-gap state can accommodate up to four electrons, it follows that there are five possible charge states for the soliton, namely, $\pm 2e$, $\pm e$, and 0. 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. The valence-band charge deficit of two electrons may be said to "screen" the charge due to the occupancy of the localized midgap state.

Clearly, topological constraints imply that the soliton kinks can be created from the ground state only in the form of kink-antikink ($K\overline{K}$) *pairs*. From Eq. (4.8) we find the minimum energy of such a pair (corresponding to infinite separation) to be

$$2E_s=2(4\Delta_0/\pi)\ . \tag{5.2}$$

The creation of the pair involves the excitation of four electrons from the ground-state valence band. Thus, the formal energy cost per excited electron hole is $(2\Delta_0/\pi)$, which is *smaller* than the insulating gap $2\Delta_0$. That the $K\overline{K}$ pairs are the system's lowest-lying electronic excitations will be seen following our description of the polaron states.

TABLE I. Characteristics of soliton states of polyyne.

Charge	Gap-state occupancy[a]	Spin states	Internal degeneracy
$2e$	●●●●	$S=0$	1
e	●●●—	$S=\frac{1}{2}$	4
0	●●—	$S=1,0$	6
$-e$	●—	$S=\frac{1}{2}$	4
$-2e$	—	$S=0$	1

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

It is interesting to note that the internal degeneracy associated with the (thermal) excitation of a $K\overline{K}$ pair—equal to the number of ways of distributing four fermions over eight degenerate (mid-gap) states—is 70. At finite temperature this high degeneracy enhances the population of thermally excited solitons compared to the case $N=2$ where the corresponding degeneracy factor is only 6.

The *polaron* solutions of (4.7) involve a local inhomogeneity in the dimerization amplitude of the form

$$\Delta_\theta(x)=\Delta_0-K_\theta v_F\{\tanh[K_\theta(x+y_\theta)] - \tanh[K_\theta(x-y_\theta)]\}\ . \tag{5.3}$$

They described indentations in the ground-state dimerization amplitude and, interestingly, may be viewed as kink-antikink bound states. The depth of an indentation is

$$\delta\Delta=\Delta_0-2K_\theta v_F\tanh(K_\theta y_\theta)$$

and its half-width is of order $2y_\theta$. The constants entering these quantities are given by

$$K_\theta=\xi_0^{-1}\sin\theta\ , \tag{5.4}$$

$$y_\theta=(\xi_0/\sin\theta)\tanh^{-1}[\tan(\theta/2)]\ . \tag{5.5}$$

The angle θ is defined in the range $0<\theta<(\pi/2)$ and for arbitrary N is determined by

$$\theta=[(n+h)/N](\pi/2)\ , \tag{5.6}$$

where $N=4$ for the present study. The physical significance of n and h is as follows. The polaron distortion (5.3) 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 indentation. 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 found to be

$$E_p(\theta)=2E_s\sin\theta\ . \tag{5.7}$$

The charges, gap-state configurations, spin states, and internal degeneracies of the polaron solutions admitted by (5.6) are exhibited in Table II. The principal polaron states are as follows

(a) A *polaron* with charges $\pm e$ and spin $\frac{1}{2}$. The intragap levels are at $\epsilon_{\pm}=\pm 0.92\Delta_0$ while the half-width is $2y=1.07\xi_0$. The formation energy is $E_p=0.38\times 2E_s=0.974\Delta_0$, indicating a binding energy (BE) relative to the bottom (top) of the conduction (valence) band of $-0.026\Delta_0$. The polaron indentation is $\delta\Delta=0.16\Delta_0$ and is, therefore, shallow. As indicated in Table II, a *stable* excited state, involving the promotion of an electron from the lower to the upper intragap level, exists for the polaron. This excitation is accompanied by a large increase in width to $2y=1.76\xi_0$ and a lowering of the intragap levels to $\epsilon_{\pm}=\pm 0.38\Delta_0$. The indentation becomes $\delta\Delta=1.24\Delta_0$ and is, therefore, deep.

(b) A *bipolaron* with charge states $\pm 2e$ and the spin and parity states of two electrons distributed over two physically distinct levels that are degenerate in energy. The half-width is $2y=1.23\xi_0$ and the intragap levels lie at $\epsilon_{\pm}=0.71\Delta_0$. The formation energy is $E_p=0.71\times 2E_s=1.81\Delta_0$, leading to a BE of $E_p-2\Delta_0=-0.19\Delta_0$. The depth of the bipolaron indentation is $\delta\Delta=0.59\Delta_0$.

(c) A *tripolaron* with charge states $\pm 3e$ and spin $\frac{1}{2}$. The tripolaron half-width is $2y=1.76\xi_0$ and its intragap levels are $\epsilon_{\pm}=\pm 0.38\Delta_0$. The formation energy is $E_p=0.92\times 2E_s=2.34\Delta_0$. Its BE, $E_p-3\Delta_0$, is, therefore, $-0.66\Delta_0$ and is the most bound of the principal polaron types. The tripolaron indentation is $1.24\Delta_0$.

These six polaron charge states constitute the lowest-lying ionization states of the polyyne system. It is evident from Eqs. (5.6) and (5.7) that a *fourth* electron or hole added to the polyyne ground state will lead to a spontaneous formation of two (eventually widely separated doubly charged kink solitons. We also note that photoexcitation of the bipolaron or tripolaron will lead to their spontaneous decay into charged soliton pairs. The decay is spin conserving. For the bipolaron, the soliton products are singly charged. For the tripolaron, they consist of a singly charged spin-$\frac{1}{2}$ soliton and a doubly charged spin-zero soliton. This behavior exemplifies the interpretation of the polaron states as $K\bar{K}$ bound pairs.

Table II indicates that there is a seventh polaronlike solution with *zero* charge. The intragap occupation is $n=1$, $h=1$. It actually corresponds to an *excitation* from the ground state in which an electron and a hole are effectively bound by lattice distortion. We name this excitation a polarexciton since in the present model its formation is due solely to lattice distortion. The width and intragap levels are the same as the bipolaron, i.e., $2y=1.23\xi_0$ and $\epsilon_{\pm}=0.71\Delta_0$. Its excitation energy is $E_p^0=2E_s\sin(\pi/4)=\sqrt{2}E_s$ and is, therefore, the lowest-lying *individual* electronic excitation of the polymer. However, we note that two polarexcitons are unstable with respect to decay into a soliton pair since $2E_p^0=2\sqrt{2}E_s>2E_s$. Indeed, the difference between the two latter energies, $2(E_p^0-E_s)=1.05\Delta_0$, indicates a strong attractive interaction between polarexcitons. 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. Also, we note that the *photoexcited* polarexciton involves the excitation of an electron-hole pair in *only one* of the two degenerate π bands.

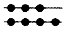
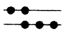
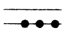
The existence of the neutral polarexciton and the special stability of the polaron with respect to photoexcitation are unique properties of the $N=4$ internal degeneracy.

Finally, we calculate the translational (inertial) masses of the kink and the polarons. This is done by boosting the kink and polaron solutions, (5.1) and (5.2), according to $x\rightarrow x-vt$ for sufficiently small velocities v. For v small by comparison to $\sim 4\xi_0\omega_0$, the motion is adiabatic and the kinetic energy of translation may be calculated from the first term of (4.3) to yield the formula

$$M=(K/4\gamma^2\omega_0^2a)\int_{-\infty}^{\infty}dx[\nabla_x\Delta(x)]^2\ , \qquad (5.8)$$

connecting the translational mass M with the static solution $\Delta(x)$. Inserting the latter into (5.8) leads to[32]

TABLE II. Characteristics of polaron states of polyyne.

Charge	Gap-state occupancy[a]	Spin states	Internal degeneracy	Stable excited state
$3e$		$S=\frac{1}{2}$	4	
$2e$		$S=1,0$	6	
e		$S=\frac{1}{2}$	4	
0		$S=1,0$	16	
$-e$		$S=\frac{1}{2}$	4	
$-2e$		$S=1,0$	6	
$-3e$		$S=\frac{1}{2}$	4	

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

TABLE III. Translational masses of the polarons.

Polaron type	$M_p/2M_k$
polaron	0.109
bipolaron	0.615
tripolaron	1.092
polarexciton	0.615

$$M_p(\theta)=2M_k\sin^3\theta\{1+3\,\mathrm{csch}^2(F_\theta)[F_\theta\coth(F_\theta)-1]\} \tag{5.9}$$

for the polaron masses, where $M_k=(4u_0^2M/3a\xi_0)$ is the kink mass and $F_\theta=2K_\theta y_\theta$. Table III lists the polaron masses (in units of $2M_k$) as calculated from (5.9). It is seen that the mass of the (singly charged) polaron is small by comparison to $2M_k$, whereas the mass of the tripolaron is approximately the same as $2M_k$. With our choice of parameters for polyyne we find the kink mass to be $M_k\simeq 58m$, where m denotes the mass of an electron. These masses are large compared to the case of polyacetylene. However, it should be noted that since $M_k\propto u_0^3$ and u_0 is a sensitive function of $\lambda_{e\text{-ph}}$, the latter value quoted for M_k should not be taken seriously.

VI. LIMITATIONS AND IMPLICATIONS

Two obvious limitations of our treatment of polyyne are, (1) the absence of electron-electron interactions in our model of the π-electron system, and (2) the neglect of quantum fluctuation effects (QFE) in the lattice displacement field $\{u_j\}$. Another limitation is the use of only a harmonic description of the σ-bond potential energy. This is easily treated by the employment of a more general function for the potential energy.

Inclusion of (1) will lead to the lifting of some of the degeneracies of the kink-soliton and polaron states. This is most clearly seen by adding a Hubbard intraorbital Coulomb repulsion U to the Hamiltonian (2.1). To lowest order, this affects electrons occupying the same suborbitals only and splits the degeneracy of the intragap kink and polaron states, including those with the same charge but different suborbital distributions. A more general cataloging of the lifting of the various degeneracies is provided by a straightforward configuration interaction scheme. The lifting of the degeneracies, if eventually observed experimentally, could provide important insight into the relative magnitudes of electron-electron and electron-lattice interactions. The inclusion of electron-electron interactions in the present treatment of polyyne, e.g., within the framework of a Pariser-Parr-Popel model,[16,42] would be an interesting and valuable sequel to the present study, which has sought to underline the importance of the electron-lattice interaction.

The effect on our results of QFE in the lattice displacement field can be ascertained with the use of arguments previously applied to the $N=2$ case of the model of polyacetylene. First, if the carbon mass $M\rightarrow\infty$, the QFE vanish, and the mean-field-theory results we have derived become exact.[32] Second, for $M\rightarrow 0$, H (in the continuum limit) becomes identical to the $N=4$ Gross-Neveu model at the full quantum level.[43] The spectrum of this quantum field theory is known exactly[44,45] 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.

Effectively infinite polyyne chains have been supposed to be the constituents of *carbyne*, a proposed quasi-one-dimensional allotrope of carbon.[1,2,9] The intriguing suggestion that carbyne is present in the interstellar medium has been made by Webster[10] who argues that carbyne would account for many unassigned features in the medium's extinction and radio emission. However, reports of neither a definitive demonstration of carbyne's existence in nature, nor of its successful synthesis in the laboratory, can be found in the current literature.

Nevertheless, our results should be relevant to finite polyynes and related acetylenic chains that are sufficiently long to be able to contain a kink soliton or one of the principal polarons *well within* its length. Such chains have been synthesized in the laboratory by Eastmond, Johnson, and Walton[3] and long linear cyanoacetylene chains have been described by Thaddeus[7] as having been discovered to exist in the interstellar medium. Indeed, Thaddeus stresses that ring structures—e.g., pyrrol—and branched chains appear to be missing in the interstellar medium.[7,46] It is possible, therefore, that molecules with linear carbon backbones are responsible for at least some of the interstellar absorption and radio-emission features which Webster has attempted to assign to carbyne. The intragap levels associated with the soliton and polaron states found in the present paper may further aid the identification of such linear chains.

The long polyyne chains synthesized by Eastmond *et al.* have chemical formula $E(\text{C}\equiv\text{C})_nR$, with n as large as 12 for $R=\text{H}$ and n as large as 16 for $R=(\text{C}_2\text{H}_5)_3\text{Si}$ (triethylsilyl). In terms of the local bond picture of organic chemistry the positive principle polaron states may be thought of as the removal of one electron, two electrons, and three electrons from a carbon triple bond. Similarly, the three principal polaron states with negative charge may be viewed as the addition of one, two, and three electrons to a carbon single bond. On the other hand, the neutral polaronic exciton may be considered to be the excitation in which an electron is removed from a triple bond and added to one of the two neighboring single bonds. The thermal excitation of a neutral kink-antikink pair is depicted in Fig. 2 for a polyyne chain consisting of an even number of carbon atoms. Fig. 2(a) shows the ground-state configuration, Fig. 2(b) the initial excitation of four electrons from a triple bond (i.e., the filled valence band) and Fig. 2(c) the separated $K\bar{K}$ pair.

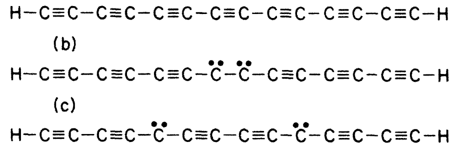
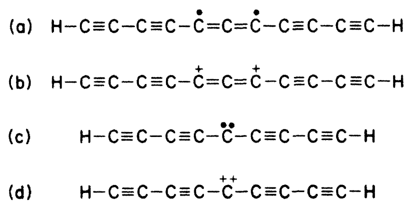


FIG. 2. Soliton-antisoliton pair excitation in an even polyyne: (a) ground state, (b) excitation of four valence electrons, (c) separated soliton and antisoliton.

Interestingly, we note that it is possible for a soliton kink to occur in the *ground-state* configuration of a finite polyyne if it has an odd number of carbon atoms. For these chains, the end groups R enforce conflicting senses of bond alternation. A kink soliton centered at the middle carbon atom, however, allows a smooth interpolation from one sense of alternation to the other. Some aspects of this situation deserve comment. The odd number of carbon atoms may be written as $N_0 = 2n + 1$ in which n may be an even or odd integer. In Sec. V it was seen that the kink soliton arises either with a positive or negative sign. If n is odd the interpolating soliton assumes the positive sign and the carbon atoms neighboring the middle carbon atom are drawn toward the latter. Conversely, if n is even the soliton assumes the negative sign and the neighboring carbon atoms are drawn away from the central carbon atom. This situation is depicted in Fig. 3 for an 11 (n, odd) and a 9 (n, even) carbon atom polyyne. The soliton with positive sign may be viewed as the sequence of two *double* bonds in Fig. 3(a) while the soliton with negative sign may be viewed as the sequence of the *single* bonds in Fig. 3(c). Both kinks are charge neutral (biradicals). If the two (radical) electrons are removed from the soliton intragap levels, the charge on the soliton becomes $2e$ and the odd-membered polyyne is transformed to a doubly charged *closed-shell* ion with markedly increased stability. These are shown in Figs. 3(b) and Fig. 3(d).



(a) $\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}\dot{C}{=}C{=}\dot{C}{-}C{\equiv}C{-}C{\equiv}C{-}H}$

(b) $\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}\overset{+}{C}{=}C{=}\overset{+}{C}{-}C{\equiv}C{-}C{\equiv}C{-}H}$

(c) $\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}\ddot{C}{-}C{\equiv}C{-}C{\equiv}C{-}H}$

(d) $\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}\overset{++}{C}{-}C{\equiv}C{-}C{\equiv}C{-}H}$

FIG. 3. Odd polyynes with positively [(a) and (b)] and negatively [(c) and (d)] sensed solitons. (b) and (d) depict the particularly stable doubly charged closed-shell ions.

Long finite polyynes can be produced in solution[3] and probably also in the form of solid deposits. Comparative photoinduced absorption experiments should be able to detect the intragap levels of the polarexciton following its photoexcitation. Introduction to either solute or solid of strong electron-withdrawing molecular species could be expected to produce either of the principal polarons. Their presence on the (finite) polyyne chains would give rise to electron spin resonance (ESR), intragap optical absorption, and strong infrared vibrational activity. The latter would be associated not only with the translation of the polaron but also with an internal oscillation.[47] Finally, we note that photoexcitation of the system of finite polyynes may lead to a novel mechanism of photoconductivity. If a sufficiently large equilibrium density of polarexcitons is generated by a source of constant illumination an electron occupying the upper level of a polarexciton may hop to a similar level of a polarexciton on a different chain. A similar hop between different polarexcitons may also be made by the hole occupying the lower intragap level. Thus, in this process both the transport site and the electronic carriers are generated by the light source. Clearly, however, the rate of photodecay of the polarexciton would have to be less than the electron or hole-hopping rate.

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