Photoproduction of neutral soliton pairs in *trans*-$(CH)_x$

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Despite the many successes of the soliton theory of $(CH)_x$, the identity of the defect species responsible for the high-energy peak (~ 1.4 eV) in the photoinduced absorption spectrum has remained unexplained, and has provided reason to doubt the validity of the simple independent-electron model on which the theory was based. Here we show that (1) the presence of even *weak* interactions which break the charge-conjugation symmetry of the continuum model permit the photogeneration of neutral soliton pairs in polyacetylene, (2) these pairs attract to form a bound state which, in the presence of disorder, can be highly metastable, and (3) these pairs provide a natural explanation for the high-energy peak and several other heretofore unexplained experimental observations.

I. INTRODUCTION

The properties of polyacetylene $(CH)_x$ have been extensively studied in the last few years, in part because it is the simplest of conducting polymers, and hence most amenable to theoretical understanding.[1-11] In particular, it was suggested that the lowest-lying electronic excitations are topological defects, solitons, with unusual quantum numbers: The charged soliton ($Q^*=\pm e$) has spin 0 and the neutral soliton ($Q^*=0$) has spin $\frac{1}{2}$. These conclusions are based on studies of simple models, such as the Su-Schrieffer-Heeger (SSH) model, which consists of a single one-dimensional electron π-band interacting with a one-dimensional phonon band. The model was originally treated in a mean-field approximation, but the conclusions have been shown to be mostly unchanged by quantum fluctuations of the lattice.[8] Similarly, the original model ignored all direct electron-electron interactions; it has been shown that weak interactions, while they have important effects where they lift degeneracies of the noninteracting model, can be treated perturbatively and hence do not fundamentally alter the nature of the excitation spectrum.[8-11]

Since single crystals of $(CH)_x$ have not been made, it has been difficult to measure the intrinsic nature of the excitations unambiguously. Thus, a wide variety of experimental probes have been used and compared in some detail with the prediction of the theory. This has led to a large number of successes and collectively produced very strong evidence for the validity of the soliton theory in general, and especially of the reverse charge-spin relations of the solitons. Some of the most dramatic evidence of the existence of solitons has come from a series of experiments[12-16] which explore the nature of the photogenerated excitations of the system. This has allowed the identification of a highly metastable photogenerated excitation with a lifetime at room temperature of order 10^{-3} sec. The excitation is known to be charged and spinless and to induce features in the optical-absorption spectrum in one-to-one correspondence with those induced by doping. Moreover, the fact that it does not occur in *cis*-rich $(CH)_x$ suggests that it is topological in character. When the effect of multiple-phonon bands[5] and weak electron-electron interactions are taken into account,[8-11] the various spectroscopic features are found to agree semiquantitatively with those expected from a charged soliton.

Despite the successes of the simple soliton theory, it has repeatedly been argued that the simple one-electron picture adopted in the standard models is simply inadequate for understanding $(CH)_x$. One of the major reasons for adopting this view is the seeming inability of the standard models to account for the other prominent feature in the photoinduced absorption spectrum of $(CH)_x$, the so-called high-energy peak.[13] This has led people[17] to postulate that it is due to an exciton of some sort, perhaps analogous to the A_g^1 mode observed in short polymers. If this were true, it would, in turn, imply strong, nonperturbative effects of electron-electron interactions.

In this paper we shall show that photoproduction of *neutral,* bound soliton-antisoliton pairs is expected to occur in $(CH)_x$ with quantum efficiency of order one, and that further the presence of these pairs provides a detailed explanation of the properties of the high-energy peak and several other related phenomena. This discussion expands the original suggestion of a similar mechanism proposed by Vardeny, Ehrenfreund, and Brafman in Ref. 16. Su and Schrieffer[6] have shown, in the context of the noninteracting electron model, that an electron-hole pair rapidly ($t \lesssim 10^{-13}$ sec) decays into a soliton-antisoliton pair which separate at a velocity of order the speed of sound. Ball, Su, and Schrieffer[7] (BSS) have further shown that the same model predicts that the branching ratio of neutral to charged solitons is zero in the adiabatic approximation and vanishes at least to second order in the nonadiabatic electron-phonon interaction. In Sec. II we show that the Su-Schrieffer mechanism persists in the presence of electron-electron interactions but that even quite weak interactions which break charge-conjugation symmetry lead to a catastrophic breakdown of the BSS theorem resulting in a rapid ($t \sim 10^{-13}$ sec) conversion of many (probably most) photogenerated charged solitons into bound neutral soliton pairs. These soliton pairs can be thought of as highly excited breathers. In Sec. III we discuss the dynamics of recombination, and describe a mechanism

whereby a neutral soliton pair can be rendered highly metastable at low temperatures by a defect, such as a short *cis*-$(CH)_x$ segment in a *trans*-$(CH)_x$ chain. Section IV is a brief summary of the information concerning the nature of the defect that gives rise to the high-energy peak which can be derived from experiment without direct reference to any theoretical model. Finally, in Sec. V we discuss a possible scenario for the return to equilibrium following photoexcitation, and identify the neutral soliton pair as the species responsible for the high-energy peak.

II. NEUTRAL SOLITON-PAIR GENERATION

In this section we demonstrate the following results: (i) In the adiabatic approximation, charged solitons are photogenerated by the Su-Schrieffer mechanism, even in the presence of electron-electron interactions. (ii) For a noninteracting model, such as the SSH model, a charge soliton pair cannot decay into a neutral soliton pair to any order in the nonadiabaticity parameter. (This extends the proof of Ball, Su, and Schrieffer to all orders in perturbation theory. A similar but somewhat less general extension of the BSS result has been derived by Danielson and Ball.[18]) (iii) The presence of weak charge-conjugation breaking interactions results in a catastrophic breakdown of the BSS theorem and leads to a nonradiative decay rate of order $10^{12}\sim 10^{13}$ sec^{-1}. These results follow from very general symmetry considerations.

The general derivation is based on two sets of properties that are shared by all the models that have been used to study the properties of $(CH)_x$: (i) There exist soliton excitations with reversed charge-spin relations. The creation energy of a charged soliton $E_{s\pm}$ is less than the particle (hole) creation energy Δ, and the neutral soliton creation energy E_{s0} is less than or equal to $E_{s\pm}$. (The soliton creation energy is independent of its charge in noninteracting models.) (ii) The Hamiltonian is symmetric under spin rotation (spin-orbit coupling being negligible) and under charge conjugation. By charge-conjugation symmetry we mean that there exists a unitary charge-conjugation operator Λ such that if $|\psi\rangle$ is a (many-electron) eigenstate of the Hamiltonian H, then $\Lambda|\psi\rangle$ is also an eigenstate with the same energy but with charge density $\langle\psi|\Lambda^\dagger\rho(x)\Lambda|\psi\rangle=-\langle\psi|\rho(x)|\psi\rangle$. In Appendix A we explicitly construct this operator for the SSH-extended Hubbard model. Similar operators can be found for the various continuum models as well. Since $\Lambda^2=1$, there are only two irreducible representations of the charge-conjugation group, the even and odd representations, $\Lambda|\psi_\pm\rangle=\pm|\psi_\pm\rangle$. The ground state is easily seen to be even. Since the current operator is odd, the excited state produced by the absorption of a single photon is necessarily in the odd representation, and therefore *cannot decay nonradiatively into the ground state.*

Figure 1(a) shows schematically the adiabatic potential energy of a soliton-antisoliton pair in the electronic ground state (curve E_0) and first and second excited spin-singlet states (curve E_1,E_2) as a function of the soliton-pair separation R. The solid lines are appropriate to a noninteracting model, the dashed and broken lines include the effect of weak electron-electron interactions.

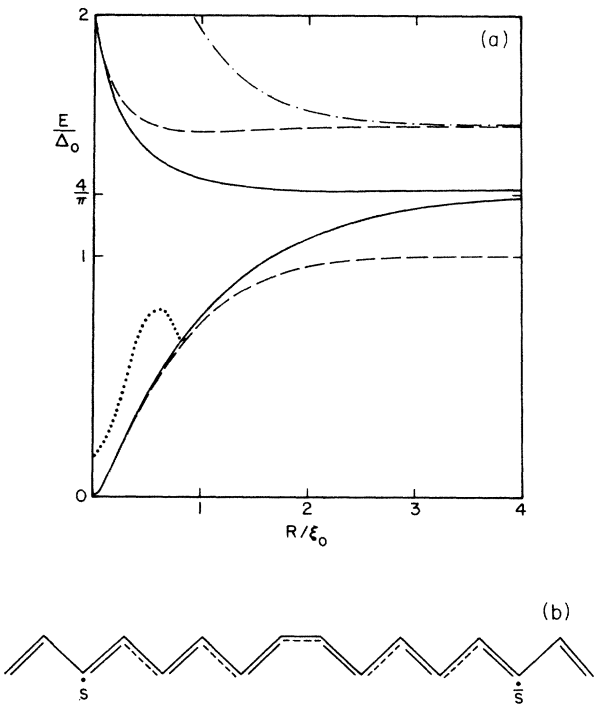

FIG. 1. (a) Adiabatic potential energy curves for the ground (E_0), first and second excited (E_1,E_2) electronic states as a function of the soliton-pair separation R (Appendix B). Solid curves are for the noninteracting model. Dashed curves include the effects of weak electron-electron interactions. Dotted curve shows the effect of a putative defect on the $(CH)_x$ chain (such as the (b)] on the ground-state adiabatic potential. (b) Schematic example of the sort of defect that could stabilize a neutral soliton pair. Solid lines indicate the bond order in the ground-state configuration; dashed lines in the metastable soliton-pair configuration.

The important qualitative features of these curves can be extracted by the following simple arguments. At $R=0$, the solitons are coincident, and hence the lattice is perfectly dimerized. Thus, the ground state is separated from the first excited state by an energy gap of twice the particle (or hole) creation energy, 2Δ. (Note, this differs only in a matter of definition from the family of soliton-pair configurations discussed in Ref. 19 where $R=\xi_0$ corresponds to the perfectly dimerized lattice.) For $R\gg\xi_0$, where $\xi_0=\hbar V_F/\Delta$ is the electronic correlation length, the curves asymptote to twice the soliton creation energy. For the noninteracting model this implies that the two adiabatic potentials become degenerate for $R\gg\xi_0$. In the presence of interactions there are two possible asymptotic values of the adiabatic potential energy corresponding, respectively, to a far separated pair of neutral solitons (the lower curve) and charged solitons (the upper curves). The neutral pair state has the same quantum numbers as the ground state from which it evolves adiabatically. Thus, it is charge conjugation even and a spin singlet. Since the first excited state is optically accessible, it must be

charge-conjugation odd. Since charge conjugation simply changes the sign of the soliton charge, as $R \rightarrow \infty$ this state becomes asymptotically the antisymmetric combination of a charged soliton and an antisoliton, $|\psi_1\rangle \rightarrow [|S^+S^-\rangle - |S^-S^+\rangle]/\sqrt{2}$, where $|S^+S^-\rangle$ is the *many-electron state* in which the soliton is positively charged and the antisoliton is negatively charged, and $|S^-S^+\rangle = \Lambda |S^+S^-\rangle$ has the opposite charges. We shall see that it is important to include the second excited spin-singlet state $|\psi_2\rangle$ in our discussion. This state has the same quantum numbers as the ground state $|\psi_0\rangle$, in particular, it is charge-conjugation even. As $R \rightarrow \infty$, $|\psi_2\rangle$ tends asymptotically to the symmetric combination of a charged soliton and antisoliton, $|\psi_2\rangle \rightarrow [|S^+S^-\rangle + |S^-S^+\rangle]/\sqrt{2}$. At large R, the separation between the ground-state energy, $E_0(R)$, and the energy $E_1(R)$ of $|\psi_1\rangle$ tends to twice the energy difference between a charged and neutral soliton, $E_1 - E_0 \rightarrow U^{\text{eff}}$ as $R \rightarrow \infty$. However, the splitting between $|\psi_2\rangle$ and $|\psi_1\rangle$ tends exponentially to zero,

$$E_2 - E_1 \rightarrow (8e^{-2}\Delta_0^2/U^{\text{eff}})e^{-2R/\xi_0}$$

for $R \gg \xi_0$ [see Fig. 1(a) and Appendix B].

Let us begin by treating the optical-absorption process in the same simple fashion as Su and Schrieffer in which the lattice motion is treated classically. Thus, we trace the lattice dynamics following an optically induced electronic transition. At $t=0$ the lattice is perfectly dimerized ($R=0$ configuration) and an electron and hole are produced at the band edges. This electronic state ($|\psi_1\rangle$) is necessarily spin-singlet and charge-conjugation odd. Su and Schrieffer computed the evolution of the lattice by numerically integrating the classical equations of motion corresponding to the SSH model. Their most important results can be understood qualitatively by considering the equations of motion for the collective coordinate R alone in the adiabatic potential illustrated in Fig. 1(a). The time T_s required for the system to evolve from perfectly dimerized ($R=0$) to a fully formed soliton pair ($R \geq \xi_0$) can be estimated from the value of the soliton mass and the typical magnitude of the repulsive force between solitons ($F \sim \Delta/\xi_0$) to be of order $T_s \sim 2\pi\omega_0^{-1}$, where ω_0 is the zone-center optical-phonon frequency $T_s \sim 2\times 10^{-14}$ sec (see Refs. 1 and 8). From the figure, it is clear that this continues to be true in the interacting model as well, since the adiabatic force at $R=0$ remains nonzero.

The fact that the lattice dynamics are actually quantum mechanical can have a profound effect on the low-energy tail of the soliton-pair *excitation* spectrum,[20,21] but the quantum fluctuations of the lattice do not effect the branching ratio between charged and neutral solitons, which is zero in any charge-conjugation symmetric model.

It is important to note that because $|\psi_2\rangle$ and $|\psi_1\rangle$ become so nearly degenerate for large R, even *very weak* interactions which break charge-conjugation symmetry will cause strong mixing between $|\psi_2\rangle$ and $|\psi_1\rangle$. Although $|\psi_1\rangle$ cannot decay nonradiatively, $|\psi_2\rangle$ *can* since it has the same quantum numbers as the ground state, $|\psi_0\rangle$ (see Appendix B). Thus, the presence of arbitrarily small terms in the Hamiltonian which break charge-conjugation symmetry will profoundly affect the excited-state lifetime.

While the simplest lattice models and all models in the continuum limit are charge-conjugation symmetric, $(CH)_x$ itself is not. Many terms can be considered which break charge-conjugation symmetry, three of which have been examined previously.[8,9] The simplest such term, and the one we expect is largest, is a second nearest-neighbor hopping term

$$H_2 = -\sum_{n,s} t_2 (C_{ns}^{\dagger} C_{n+2s} + \text{H.c.}) \tag{1}$$

which in Ref. 9 we estimated by comparing the widths of the valence and conduction bands of $(CH)_x$ to be $t_2 \sim 0.25$ eV.

Notice the fact that charge-conjugation breaking terms are much smaller than other terms in the Hamiltonian. Within the accuracy of the simple models, these terms play a minor role in determining most properties of the system. However, when the decay channels of a soliton-antisoliton pair are considered, the very existence of charge-conjugation breaking terms in *trans*-$(CH)_x$ changes the picture completely. Under the influence of even a very weak charge-conjugation breaking term, the system will lose its (phase) memory of its charge-conjugation parity. The charge soliton pair can therefore decay into a neutral soliton pair via intersoliton hopping of an electron, e.g., $S^+S^- \rightarrow S^0S^0$. The reaction is exothermic, due to the electron-electron repulsion in the soliton $(E_{s+} + E_{s-} - 2E_{s0}) \equiv U^{\text{eff}}$, where U^{eff} was estimated by Wu and Kivelson to be $U^{\text{eff}} \sim 0.45$ eV.[11] Since the solitons are weakly coupled to the phonons, the transition rate is expected to have the form

$$\nu(R) = \nu_0 \exp(-2R/\xi_0) . \tag{2a}$$

Engelman and Jortner[22] have obtained an expression for the nonradiative transition rate for large molecules, which yields for ν_0 in the weak coupling limit

$$\nu_0(R) = \frac{4e^{-2}\Delta^2\sqrt{2\pi}}{\hbar[\hbar\omega_0 U^{\text{eff}}(R)]^{1/2}} \exp\left[-\frac{\lambda U^{\text{eff}}(R)}{\hbar\omega_0}\right], \tag{2b}$$

where ω_0 is the optical-phonon frequency, and λ is a number of order one and depends weakly upon the strength of the coupling to the phonon modes. For *trans*-$(CH)_x$, we estimate $\nu_0 \sim 2\times 10^{14}$ Hz. Therefore we conclude that for solitons within about ξ_0 of each other, the hopping rate is of order 10^{13}–10^{12} Hz. For comparison, we note that the radiative transition rate calculated by Rice and Howard[23] under the same circumstances is $\nu_{\text{rad}} \sim 10^8$ Hz, much slower than the nonradiative transition. We further note that since U^{eff} is lost to the heat bath in the transition, the product neutral soliton pair will typically be in a bound, or breather state. This state is a spin singlet, has vanishing charge density everywhere, but nonvanishing spin density which is a superposition of the spin density due to the soliton and the antisoliton.

Finally, we conclude this section with a remark. Direct photoexcitation into the second excited state $|\psi_2\rangle$ is possible by a two-photon process. For $|\psi_2\rangle$, the Su-Schrieffer mechanism is inoperable; the repulsive force between solitons vanishes as $R \rightarrow 0$ for this state. Thus, we expect the two-photon absorption edge to be much sharper than the single-photon absorption edge.[24]

III. RECOMBINATION DYNAMICS

Once a charged soliton pair is formed, the process by which the pairs recombine to form a breather is one-dimensional diffusion-limited recombination. Imagine a soliton pair is created at time 0. Then the probability of finding a charged soliton pair at time t a distance $R>0$ apart is $P(R,t)$, which satisfies a one-dimensional diffusion equation, and the probability of finding that they have formed a breather is $Q(t)$. Since the only decay mechanism for charged solitons is via breather formation, the breather population satisfies the equation

$$\dot{Q}(t)+\gamma Q(t)=\int dR\, \nu(R)P[R(t)]=-\dot{P}(t)\,, \tag{3}$$

where γ^{-1} is the breather lifetime, $\nu(R)$ is the recombination rate defined in Eq. (2), and $P(t)=\int dR\, P(R,t)$ is the total survival probability of finding a charged soliton pair. (Note, it is possible that there is a substantial population, Q_0, of breathers photogenerated within the first 10^{-13} sec by processes other than charge soliton recombination, as discussed in Ref. 25.) The total number of neutral solitons is proportional to $Q(t)$, which could be measured spectroscopically while the number of surviving charged solitons is proportional to $P(t)$ and can be measured either spectroscopically or in transient photoconductivity experiments.

In the simplest approximation, where the effects of deep trapping are ignored, we expect that

$$P(t)\sim A(\nu t)^{-1/2} \quad \text{for } \nu t\gg 1 \tag{4}$$

and

$$Q(t)=\begin{cases} Q_0 e^{-\gamma t}+1-P(t) & \text{for } \gamma t\ll 1 \\ -\dot{P}(t)/\gamma & \text{for } \gamma t\gg 1 \end{cases} \tag{5}$$

where

$$\nu=\left[\int dR\, \nu(R)\right]^2/\pi D \tag{6}$$

and D is the soliton diffusion constant.

We do not have an accurate estimate of γ. Breathers have been shown to be stable classically for long times, but quantum effects, disorder, interchain effects, etc., are all likely to reduce their lifetimes dramatically. From Eq. (6) we see that $\nu=\nu_0(\nu_0\xi_0^2/4\pi D)$. To estimate ν we take $\nu_0=10^{13}-10^{14}$ Hz and $D=2\times 10^{-2}$ cm^2/sec, from which we find that $\nu=2\times 10^{11}$ to 2×10^9 Hz. Beyond 10^{-9} sec, we would expect few remaining excitations in the absence of disorder.

Disorder can produce long-lived excitations in many ways. A likely candidate for a metastable neutral soliton pair is illustrated in Fig. 1(b). Here we imagine that there is a defect on the chain, in this case a short segment of *cis*-$(CH)_x$. This segment produces a barrier which must be surmounted for the pair to recombine, as shown by the dotted curve in Fig. 1(a). The presence of such defects will produce long-lived neutral soliton pairs at low temperature, with a lifetime that tends exponentially to infinity with decreasing temperature.

IV. REVIEW OF EXPERIMENTAL INFORMATION

The experiments which lead to the identification of the low-energy peak in the photoinduced absorption with the charged soliton are briefly summarized in Sec. I. It is important to note that these solitons are always the most long-lived photoexcitation, but that they are generated with a quantum efficiency of order 10^{-2}. In some samples,[17] which seem to be relatively disordered, it has been found they are largely generated by an extrinsic process involving interchain diffusion of charged polarons and conversion of intrinsic neutral solitons into charged solitons. This has made it possible to identify a bleaching peak in the room-temperature photoinduced absorption with the absorption due to an isolated neutral soliton. This peak occurs within 0.05 eV of the high-energy peak. In less disordered samples, it has been suggested[26] that the long-lived charged solitons are generated when two polarons of like charge recombine on a given chain to form a charged soliton pair. A similar process has been observed in polythiophene.

Many features of the excitation which produces the high-energy peak are known from experiment: (i) It is produced with quantum efficiency near 1, but within the first 10^{-9} sec all but of order 10^{-2} have decayed into something else (probably phonons). The remaining excitations have a broad distribution of lifetimes (dispersive decay) with a typical lifetime in excess of 10^{-3} sec below about 150°K, and of order 10^{-5} sec at room temperature. The broad distribution of lifetimes and the rapid temperature dependence suggesting that the long-lived few are stabilized by some sort of defect which produces a barrier to recombination. (ii) At least for times short compared to 10^{-9} sec, it is highly mobile and highly one dimensional, which suggests that it is primarily an intrachain excitation. (iii) It is known to be neutral and spinless, at least on moderately long times scales (typically $\sim 10^{-5}$ sec). (iv) It can be produced in *cis*-rich samples, where it is thought to be associated with *trans*-segments. From this it can be concluded that it is topologically trivial.

V. SCENARIO FOR RETURN TO EQUILIBRIUM

The theoretical considerations in Secs. II and III, and the experimental considerations in Sec. IV, suggest the multipartate scenario for the return to equilibrium, illustrated in Fig. 2. Following photoproduction of an e^+e^- pair at $t=0$, we identify the following time domains: (i) $t\lesssim 10^{-13}$ sec: Most of the e^+e^- pairs form S^+S^- pairs by the Su-Schrieffer mechanism. Some small fraction (dependent on the excitation energy) separates onto different chains and form polarons which diffuse apart (3D diffusion). (ii) $t<10^{-9}$ sec: The charged soliton pairs are confined to a given chain and hence, in the way of all one-dimensional diffusion, have frequent encounters. The result is a rapid conversion of charged soliton pairs into neutral soliton pairs. These neutral pairs are dynamically stable for moderate times. The dominant species in this time interval are mobile-neutral soliton pairs with a small

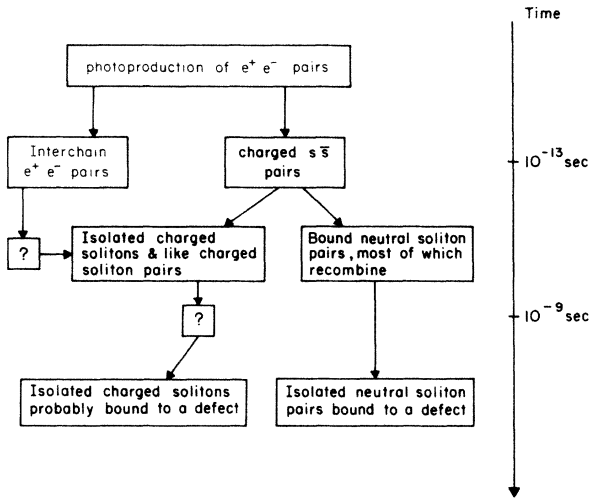

FIG. 2. Scenario for the return to equilibrium following photoexcitation. See discussion in Sec. V.

component of mobile charged solitons. By $t \sim 10^{-9}$ sec all the soliton pairs have recombined save those few, at low temperatures, that are rendered metastable by a defect on the chain. The polaron pairs have all recombined or formed stable charged solitons, probably via one of the two mechanisms described in Sec. IV. (iii) $t > 10^{-9}$ sec: The properties of the relaxation to equilibrium at long times are almost certainly disorder dominated. The neutral soliton pairs recombine via a thermally activated barrier crossing. The charged solitons, which are likely also bound to defects, must relax via intersoliton hopping.[27] Both processes are expected to be highly dispersive and very slow at low temperatures.

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APPENDIX A: CHARGE-CONJUGATION OPERATOR FOR THE SSH-EXTENDED-HUBBARD MODEL

The electronic part of the Hamiltonian for the most general form of the SSH-extended-Hubbard model is

$$H = -\sum_{n,s} t_n (C^\dagger_{n,s} C_{n+1,s} + \text{H.c.}) + \sum_{\substack{s,s' \\ n,n'}} V_{ss'}(n,n') \rho_s(n) \rho_{s'}(n') , \tag{A1}$$

where $C^\dagger_{ns}$ creates an electron of spin s on site n, $\rho_s(n)$ is the density operator

$$\rho_s(n) = (C^\dagger_{ns} C_{ns} - \tfrac{1}{2}) , \tag{A2}$$

and the nearest-neighbor hopping matrix element t_n and the Coulomb matrix elements $V_{ss'}(n,n')$ are, in general, dependent on the pattern of lattice distortion. We have included a $-\frac{1}{2}$ in the definition of $\rho_s(n)$ so that the expectation value of $\rho_s(n)$ in the undistorted (metallic) state is zero corresponding to charge neutrality. The charge-conjugation operator Λ for any model of this form is

$$\Lambda = KS , \tag{A3}$$

where

$$S = \exp\left[i \sum_{n,s} \pi n C^\dagger_{n,s} C_{n,s} \right] \tag{A4}$$

and K is particle-antiparticle conjugation operator which has the property

$$K^\dagger C_{ns} K = C^\dagger_{ns} . \tag{A5}$$

It is easy to verify that

$$\Lambda^\dagger H \Lambda = H \tag{A6}$$

and that

$$\Lambda^\dagger \rho(n) \Lambda = -\rho(n) , \tag{A7}$$

where

$$\rho(n) = \sum_s \rho_s(n) .$$

APPENDIX B: INTERACTION EFFECTS ON THE SOLITON-PAIR ENERGY

There are two gap states associated with a soliton-antisoliton pair, a bonding state $|\psi_+\rangle$ and an antibonding state $|\psi_-\rangle$. We can define a localized state associated with each soliton according to $|S_1\rangle = 1/\sqrt{2}[|\psi_+\rangle + |\psi_-\rangle]$ and $|S_2\rangle = 1/\sqrt{2}[|\psi_+\rangle - |\psi_-\rangle]$. When the separation R between two solitons is finite, these two gap states overlap producing a nonzero energy splitting $2\varepsilon(R)$ between the bonding and antibonding states. The potential energy for a soliton-antisoliton pair in the presence of weak electron-electron interactions can be obtained from a truncated Hamiltonian H_t,

$$H_t = U^{\text{eff}}(R) \sum_{n=1}^{2} (C^\dagger_{n\uparrow} C_{n\uparrow} - \tfrac{1}{2})(C^\dagger_{n\downarrow} C_{n\downarrow} - \tfrac{1}{2}) + \varepsilon(R) \sum_s (C^\dagger_{2s} C_{1s} + C^\dagger_{1s} C_{2s}) + V(R) , \tag{B1}$$

where $C^\dagger_{ns}$ $(n=1,2)$ creates an electron in state $|S_n\rangle$; $V(R)$ is an effective adiabatic potential energy, and U^{eff} is the effective electron-electron interaction. According to Ref. 19

$$\varepsilon(R)=\Delta_0[1-(\xi_0/\xi)^2]^{1/2}\ , \tag{B2}$$

$$V(R)=\frac{4}{\hbar}\Delta_0\left\{\frac{\xi_0}{\xi}+\left[1-\left[\frac{\xi_0}{\xi}\right]^2\right]^{1/2}\cos^{-1}\left[\frac{\xi_0}{\xi}\right]\right\}, \tag{B3}$$

where the soliton width ξ is an implicit function of soliton separation R in terms of free soliton width ξ_0 by equation

$$\frac{\xi_0}{\xi}=\tanh\left[\frac{R+\xi_0}{\xi}\right]. \tag{B4}$$

The $U^{\rm eff}$ was obtained by Wu and Kivelson,[11]

$$U^{\rm eff}(R)=0.56\Delta_0\left\{\frac{\xi_0}{\xi}-3\left[\frac{\xi}{\xi_0}\frac{\varepsilon(R)}{\Delta_0}\right]^2\times\left[\tanh^{-1}\left[\frac{\xi_0}{\xi}\right]-\frac{\xi_0}{\xi}\right]\right\}. \tag{B5}$$

Now we can diagonalize H_t in the charge-neutral spin-singlet sector. There are three states in that sector. Namely,

$$\begin{aligned}|\phi_0\rangle&=\frac{1}{\sqrt{2}}(C^\dagger_{1\uparrow}C^\dagger_{2\downarrow}+C^\dagger_{2\uparrow}C^\dagger_{1\downarrow})|0\rangle\ ,\\ |\phi_1\rangle&=C^\dagger_{1\uparrow}C^\dagger_{1\downarrow}|0\rangle\ ,\\ |\phi_2\rangle&=C^\dagger_{2\uparrow}C^\dagger_{2\downarrow}|0\rangle\ .\end{aligned} \tag{B6}$$

In this basis, H_t has the matrix representation

$$H_t(R)=\begin{bmatrix} V(R)-\frac{1}{2}U^{\rm eff}(R) & \sqrt{2}\varepsilon(R) & \sqrt{2}\varepsilon(R)\\ \sqrt{2}\varepsilon(R) & V(R)+\frac{1}{2}U^{\rm eff}(R) & 0\\ \sqrt{2}\varepsilon(R) & 0 & V(R)+\frac{1}{2}U^{\rm eff}(R)\end{bmatrix}. \tag{B7}$$

When we diagonalize this matrix, we get the eigenvalues and eigenstates

$$\begin{aligned}E_0(R)&=V(R)-\{[\tfrac{1}{2}U^{\rm eff}(R)]^2+[2\varepsilon(R)]^2\}^{1/2}\ ,\\ |\psi_0\rangle&=N_+\left[(\tfrac{1}{2}U^{\rm eff}(R)+\{[\tfrac{1}{2}U^{\rm eff}(R)]^2+[2\varepsilon(R)]^2\}^{1/2})|\phi_0\rangle-2\varepsilon(R)\frac{1}{\sqrt{2}}(|\phi_1\rangle+|\phi_2\rangle)\right],\end{aligned} \tag{B8}$$

$$\begin{aligned}E_1(R)&=V(R)+\tfrac{1}{2}U^{\rm eff}(R)\ ,\\ |\psi_1\rangle&=\frac{1}{\sqrt{2}}(|\phi_1\rangle-|\phi_2\rangle)\ ,\end{aligned} \tag{B9}$$

$$\begin{aligned}E_2(R)&=V(R)+\{[\tfrac{1}{2}U^{\rm eff}(R)]^2+[2\varepsilon(R)]^2\}^{1/2}\ ,\\ |\psi_2\rangle&=N_-\left[(\tfrac{1}{2}U^{\rm eff}(R)-\{[\tfrac{1}{2}U^{\rm eff}(R)]^2+[2\varepsilon(R)]^2\}^{1/2})|\phi_0\rangle-2\varepsilon(R)\frac{1}{\sqrt{2}}(|\phi_1\rangle+|\phi_2\rangle)\right],\end{aligned} \tag{B10}$$

where

$$N_\pm=[4\varepsilon^2(R)+(\tfrac{1}{2}U^{\rm eff}(R)\pm\{[\tfrac{1}{2}U^{\rm eff}(R)^2]+[2\varepsilon(R)]^2\}^{1/2})^2]^{-1/2}\ . \tag{B11}$$

Since

$$\begin{aligned}\Lambda|\phi_0\rangle&=|\phi_0\rangle\ ,\\ \Lambda|\phi_1\rangle&=|\phi_2\rangle\ ,\\ \Lambda|\phi_2\rangle&=|\phi_1\rangle\ ,\end{aligned} \tag{B12}$$

it is clear that $|\psi_0\rangle\,|\psi_2\rangle$ are charge-conjugation even states and $|\psi_1\rangle$ is charge-conjugation odd.

The condition for the truncation approximations to be valid is

$$\frac{U^{\rm eff}(R)/2}{\Delta_0-\varepsilon(R)}<1\ . \tag{B13}$$

It is easy to see that Eq. (B13) is satisfied for any value of R. The $E(R)$'s are plotted in Fig. 1(a). Notice there is a shallow minimum in $E_1(R)$ which is consistent with the results in Ref. 28.

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