Lattice Relaxation of Even-Parity Singlet Excited States in Polyacetylene and Four-Soliton Bound State

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We have carried out a theoretical study of the lattice relaxation of some low-lying even-parity singlet excited states in polyacetylene. Both degenerate perturbation and strong coupling calculations give very similar results which indicate the relaxed configuration of the lowest singlet A_g excited state is a novel four-soliton bound state, with a binding energy of about 0.05 eV against dissociation into four free neutral solitons. Experimental implications of the theoretical findings are discussed.

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Polyacetylene is the simplest conjugated polymer. It is generally accepted that solitons and polarons [1] are the dominant elementary excitations in such a system. One particularly interesting example is the relaxation of photogenerated electron-hole pairs into soliton-antisoliton pairs. It was predicted in a noninteracting theory [2]. There has been a substantial amount of experimental data on this issue in recent years. While it is confirmed that charged soliton-antisoliton pairs are photogenerated on a subpicosecond time scale [3] as predicted by theory [4], the simultaneous presence of photoinduced neutral solitons [5] on the same time scale [6,7] has not been well understood [8]. More broadly speaking, due to the variety of spin and charge states of the final solitonic products, there are usually several possible relaxation pathways following each photoexcitation. It is important to determine which pathway is actually followed.

In a noninteracting model, charged solitons are degenerate with neutral solitons. Electron-electron (*e-e*) interactions can lift the degeneracy and are required for any quantitative treatment. Several workers including Hayden and Mele [9], Tavan and Schulten [10], Campbell, and others [11] have studied interacting models, but the results on the relaxation of even-parity states have been at odds with each other. In this Letter we employ degenerate perturbation theory and strong coupling model to study this problem. The results converge to a consistent picture of the relaxation pathways of low-lying excited states of polyacetylene.

We first present calculations done with the following Hamiltonian:

$$H = \sum_{\langle i,j\rangle}\left\{-(t - \alpha\delta r_{ij})\sum_{\sigma}[c^{\dagger}_{i,\sigma}c_{j,\sigma} + \text{H.c.}] + \frac{K}{2}(\delta r_{ij})^2\right\} + U\sum_{n}\rho_{n\uparrow}\rho_{n\downarrow}, \quad (1)$$

which is the Su-Schrieffer-Heeger [12] model supplemented by a Hubbard term (SSHH). Figure 1 depicts the potential energy curves for the following one parameter set of soliton-antisoliton configurations [13],

$$\Delta_n = \Delta\left\{1 + \tanh\left(\frac{2x_0}{\xi}\right)\left[\tanh\left(\frac{na - x_0}{\xi}\right) - \tanh\left(\frac{na + x_0}{\xi}\right)\right]\right\}. \quad (2)$$

In the energy calculation, the Hubbard term in (1) is treated as a perturbation. As we have alluded to above, for large soliton-antisoliton ($S\bar{S}$) separation the various gap state configurations are degenerate. Therefore we treat those states with degenerate perturbation theory. The dimensionless coupling constant is chosen to be $\alpha^2/Kt = 0.37$, which implies a coherence length ξ is about 4 lattice spacings in the uniformly dimerized ground state. The repulsion strength U of the Hubbard term is taken to be $2.5t$, where t is the average hopping integral in Eq. (1).

The lowest curve in Fig. 1 represents the ground state energy in the presence of a soliton-antisoliton pair. The one above it is the lowest triplet excitation curve. For large $S\bar{S}$ separation, the two curves converge to two neutral solitons in the singlet and triplet states. Our calculation is more reliable for large $S\bar{S}$ separation. For shorter $S\bar{S}$ distance the triplet curve should be lower than

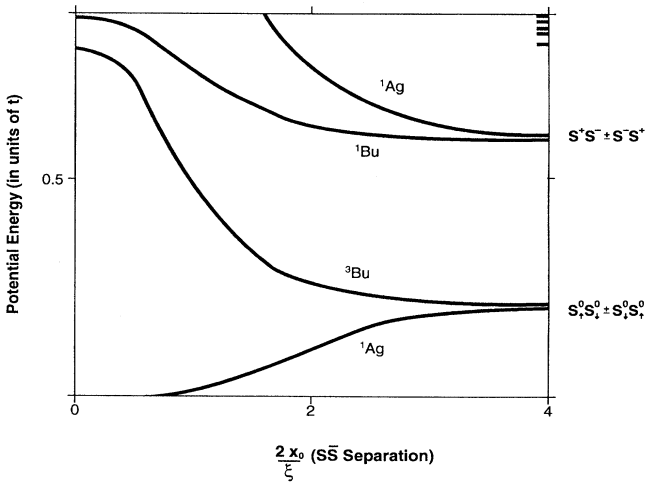

FIG. 1. Potential energy curves in the two-soliton sector calculated in a degenerate perturbation theory.

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Fig. 1 shows in a more complete calculation, a point which becomes clearer as we describe the strong coupling calculation later. In any case, the triplet curve describes the relaxation of a triplet excited state into two neutral solitons.

The two upper curves in Fig. 1 correspond to two charged solitons in the odd- and even-parity states. Kivelson and Wu [14] have used the degeneracy of these two states at large $S\bar{S}$ separation to argue for charge separation in the photogeneration of solitons. The gap value is about $0.8t$. For large $S\bar{S}$ separation, there is an onset of continuum slightly below the gap value. From the energy differences between the curves, one can see that a charged soliton absorbs light at about 0.5 eV and a neutral soliton absorbs at about 1.5 eV provided we choose $t = 2.5$ eV. The U value has been chosen to reproduce these experimentally observed absorption energies of the charged and neutral solitons. We would like to emphasize here that, although more complete calculations are likely to alter the shape of those curves in Fig. 1, the features at large $S\bar{S}$ separation should stay the same. We have exhausted the four possible states of two well separated solitons, and their relative energies are fixed by absorption experiment. Another important feature is that the creation energy of a neutral soliton pair is only about 0.5 eV. This small value of the creation energy is actually consistent with the measurement of triplet energy in polyenes [15]. By comparing the energy of the neutral and charged solitons, it is obvious that the energy to create four neutral solitons is less than that for creating two charged solitons. Therefore one would expect to see an even-parity state relaxes into four neutral solitons (Fig. 2) as being more favorable than the relaxation into two charged solitons.

To confirm the above idea, we have calculated the energies of the ground state as well as the lowest even-parity singlet excited state in the following two parameter set of four-soliton configurations,

$$\Delta_n = \Delta\Big\{1 + \tanh\Big(\frac{2x_0}{\xi}\Big)\Big[\tanh\Big(\frac{na - x_d - x_0}{\xi}\Big) - \tanh\Big(\frac{na - x_d + x_0}{\xi}\Big) + \tanh\Big(\frac{na + x_d - x_0}{\xi}\Big) - \tanh\Big(\frac{na + x_d + x_0}{\xi}\Big)\Big]\Big\}. \quad (3)$$

By minimizing the energy of the lowest even-parity excited state, we find the four-soliton bound state configuration shown as curve (a) in Fig. 3 corresponding to $x_0 = 1.375\xi$ and $x_d = 2.5\xi$. The potential energy curves in Fig. 2 refer to the one parameter family of configurations connecting the uniformly dimerized ground state and the four-soliton bound state we just mentioned, i.e., by keeping a fixed ratio $x_d/x_0 = 1.818$ in (3). At the other end of this family of configurations (for $x_0 = 2\xi$), we have four nearly free solitons as shown in curve (b) in Fig. 3. In calculating the energy of four solitons, we again treat all the gap state configurations by degenerate perturbation theory. Despite the finite binding energy of the four-soliton state (0.05 eV), it is likely that the relaxation of the even-parity state would lead to the production of four neutral solitons. The fact that we are getting four neutral solitons and not four-charged solitons is clear from energetics considerations.

To provide an independent check of the above results, we have considered the following spin-lattice Hamiltonian:

$$H = \sum_{\langle i,j\rangle}\Big\{J[1 + \beta\delta r_{ij}]\vec{S}_i \cdot \vec{S}_j + \frac{K}{2}(\delta r_{ij})^2\Big\}, \quad (4)$$

which can be regarded as the strong coupling limit of the SSHH Hamiltonian (1). The average exchanged coupling is of the order t^2/U. Following Hashimoto [16], the spin-lattice Hamiltonian is first transformed into a fermion-phonon model by a Jordan-Wigner transformation, and the resultant model is solved by perturbation theory. Takimoto and Sasai [17] have employed this approach in comparing the creation energy for four-soliton versus two-soliton configurations in the excited singlet Ag manifold. They found

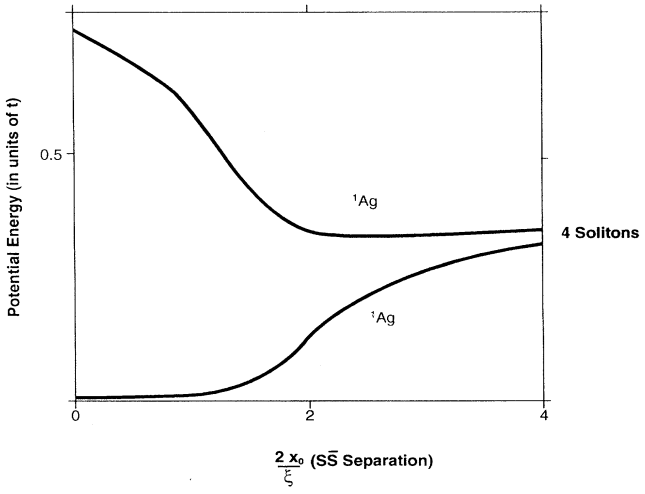

FIG. 2. Potential energy curves in the four-soliton sector calculated in a degenerate perturbation theory.

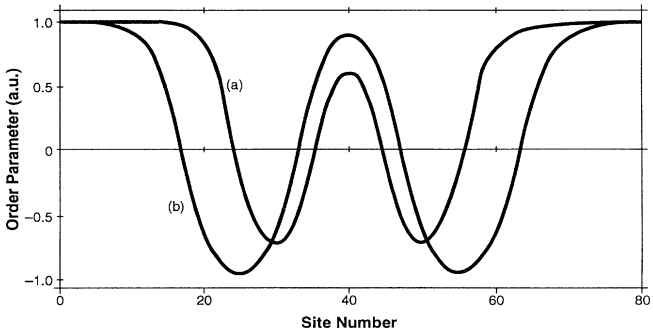

FIG. 3. Two four-soliton configurations.

indeed the four soliton has lower energy than the two soliton. We have carried out a more extensive minimization of the excited state energy within the family of configurations (3). We find that a four-soliton bound state has the lowest excited energy. Upon further relaxation of the bound state configuration with respect to variation of Δ_n for all sites n, we find very little change in shape and energy indicating that the four-soliton bound state is a truly relaxed state in the complete phase space of which Eq. (3) describes only a small subspace.

A plot similar to Fig. 2 is given in Fig. 4 with the dimensionless coupling constant taken to be $J\beta^2/K = 0.654$. The qualitative features are rather similar to Fig. 2. A choice of J comparable to t would allow the two A_g state curves and ground state curves to match each other except for small $S\bar{S}$ separation. Such a value of J is compatible with the intermediate value of U we are adopting.

In Fig. 4 we have also plotted the potential curves of the lowest triplet state and the ground state in the two-soliton sector. Except at small $S\bar{S}$ separation, the shape of the curves is again very similar to those in Fig. 1. In both cases the triplet potential is repulsive. We do not detect any long-range interaction between two neutral solitons as reported by Soos and Ramasesha [18].

The similarity of the results obtained from two independent approaches is encouraging. In addition, a small size exact diagonalization study of the A_g state made by Gammel and Campbell [19] has revealed close resemblance to our results. They have chosen large gap to match the small size; still they were not sure whether they had finite size effects or not. Our calculations are essentially bulk calculations (80 sites). It is rather amazing that all results converge. The convergence gives us confidence that our results will survive more precise calculations.

Within the theoretical picture obtained so far, let us try to make more connections with experiment. The A_g state, once excited optically, would lead quickly to the production of neutral solitons. That could explain the subpicosecond photogeneration of neutral solitons as observed by Shank *et al.* [6] provided that the even-parity state is accessible optically. Two-photon absorption is a possibility. The other possibility is through parity violation. Impurities or structural imperfections can easily be the sources of parity violation, which is also needed to explain the separation of charged solitons [14]. Yet another possibility is the phonon-assisted absorption proposed by Hayden and Mele [9]. All those mechanisms should be further examined theoretically and experimentally.

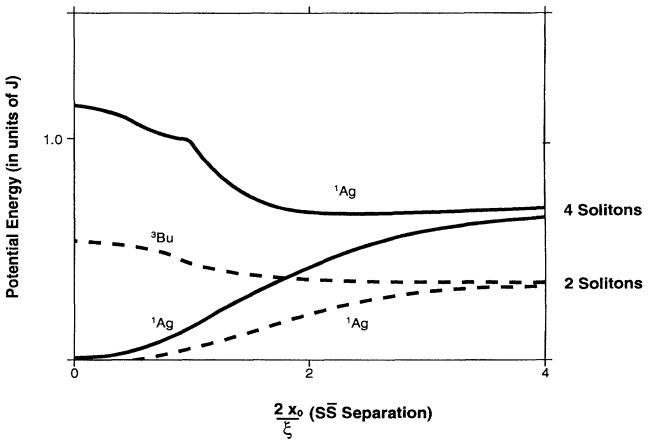

FIG. 4. Potential energy curves in the four-soliton and two-soliton sector calculated in a strong coupling theory.

It has been well known that in short polyenes the lowest excited state has the A_g symmetry. Moreover, its energy decreases with increasing chain length. Based on a simple extrapolation, it has inferred [20] that it should be about 1.0 eV in polyacetylene. This viewpoint was questioned by Fann *et al.* With their third harmonic generation data [21], they have argued that the A_g excited state lies very close to the B_u state.

Recently Halvorson and Heeger [22] have measured the two-photon absorption spectrum of oriented trans-polyacetylene, from which they were able to locate two A_g states. The lowest A_g state was placed at 1.1 eV and a higher one at 1.6 eV. The former is only slightly higher than the four-soliton bound state energy. That could imply that significant four-soliton type quantum lattice fluctuations are present in the ground state. It could also imply a somewhat smaller creation energy of the neutral soliton than we have assumed, placing polyacetylene in the more correlated regime [23]. Similar remarks apply to the even-parity two charged soliton state.

Although our calculations have been done for polyacetylene exclusively, they can be extended to other nondegenerate polymers. Because of the confinement potential, the four-soliton configurations may become less favorable compared to two-soliton configurations depending on the degree of confinement. However, as long as the four-soliton energy is less than the gap, then the fission of an even-parity state into two neutral triplet polarons [24] is quite possible. Because of confinement, the four neutral solitons cannot be indefinitely separated, but they can form two polarons in the triplet states and be separated. Calculations are underway for some nondegenerate polymers.

In summary, we have studied the lattice relaxation of even-parity singlet excited states in polyacetylene. A four-soliton bound state is the lowest energy configuration, which can easily dissociate into four well separated neutral solitons. Our model calculations have provided a consistent picture of the relaxation of important low-lying excited states in polyacetylene.

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