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LATTICE RELAXATION OF EVEN-PARITY SINGLET EXCITED STATES IN POLYACETYLENE

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Abstract We have carried out a theoretical study of the lattice relaxation of some low-lying even-parity singlet exited states in polyacetyelene. Both degenerate perturbation and strong coupling calcualtions give very similar results which indicate the relaxed configuration of the lowest A_g state is a 4-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.

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]. As such it calls for a reexamination of the relaxation pathways of photoexcited states.

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 Mele and Hayden[9], Taven 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 paper 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,

$$H = \sum_{<i,j>} \{-(t_0 - \alpha\delta r_{ij}) \sum_{\sigma} [c^{\dagger}_{i,\sigma} c_{j,\sigma} + H.c.] + \frac{K}{2}(\delta r_{ij})^2\} + U \sum_{n} \rho_{n\uparrow}\rho_{n\downarrow}, \qquad (1)$$

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

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

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 parameters are chosen so that the coherence length ξ is about 4 lattice spacings in the uniformly dimerized ground state.

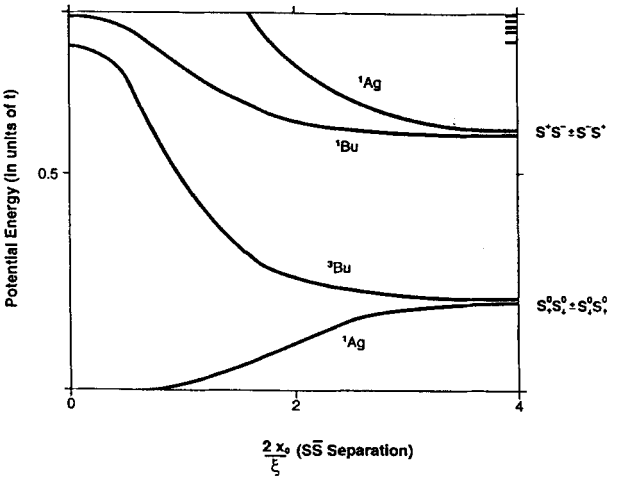

Figure 1. Potential energy curves in the two soliton sector calculated in a degenerate perturbation theory.

The repulsion strength U of the Hubbard term is taken to be 2.5 t, where t is the average hopping integral.

The lowest curve in Figure 1 represents the ground state energy in the presence of s 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 Figure 1 shows in a more complete calculation. In any case, the triplet curve describes the relaxation of a triplet excited state into two neutral solitons.

The two upper curves in Figure 1 correspond to two charged solitons in the odd and even parity states. Kivelson and Wu[13] 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 0.8 t. 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 absorb light at about 0.5 eV and a neutral soliton absorb 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 Figure 1,

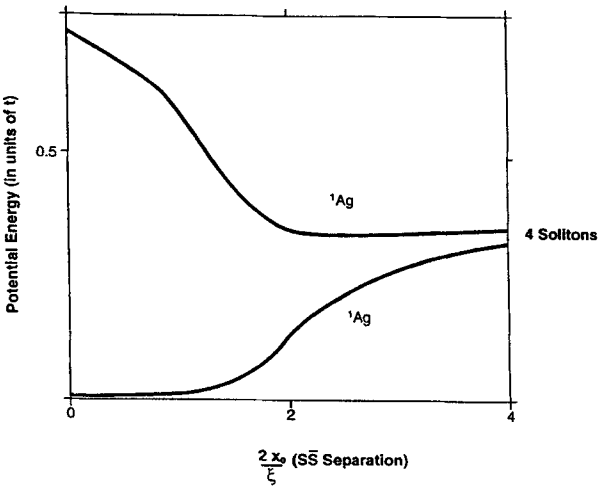

Figure 2. Potential energy curves in the four soliton sector calculated in a degenerate perturbation theory.

the feautures 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 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[14]. By comparing the energy of the neutral and charged solitons, it is obvious that the energy to create 4 neutral solitons is less than that for creating two charged solitons. Therefore one would expect to see an even parity state relaxes into 4 neutral solitons as being more favorable than the relaxation into two charged solitons.

To test the above reasoning, 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 4-soliton configurations,

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

By minimizing the energy of the lowest even-parity excited state, we find the 4-soliton bound state configuration shown as curve (a) in Figure 3 corresponding to $x_0 = 1.375\xi$ and $x_d = 2.5\xi$. We then plot the energy of the ground state and excited state in the one parameter family of configurations connecting the uniformly

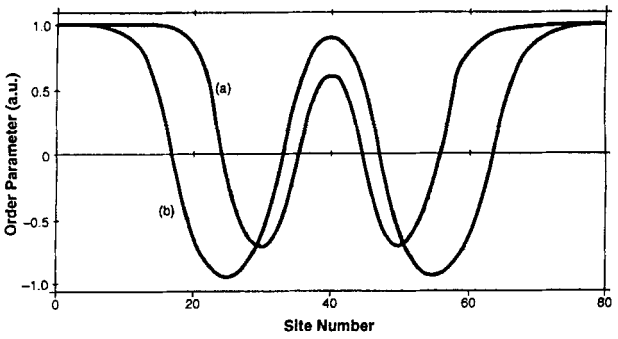

Figure 3. Two 4-soliton configurations.

dimerized ground state and the 4-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 free solitons as shown in curve (b) in Figure 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 4-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 4 neutral solitons and not 4-charged solitons is clear from energetics considerations.

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

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

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[15], the spin-lattice Hamiltonian is first transformed into a fermion-phonon model by a Jordan-Wigner transformation and the resultant model is solved by single particle perturbation theory. Takimoto and Sasai[16] have employed this approach in comparing the creation energy for 4-soliton versus 2-soliton configurations. They found indeed 4-soliton has lower energy than 2-soliton. We have carried out a more extensive minimization of the excited state energy within the family of configurations (3). We find again that a 4-soliton bound state has the lowest excited energy. A plot similar to Figure 2 is given in Figure 4. The qualitative features are rather similar to Figure 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.

The similarity of the results obtained from two independent approaches is encouraging. In addition, small size exact diagonalization study made by Campbell and Gammel[17] 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.

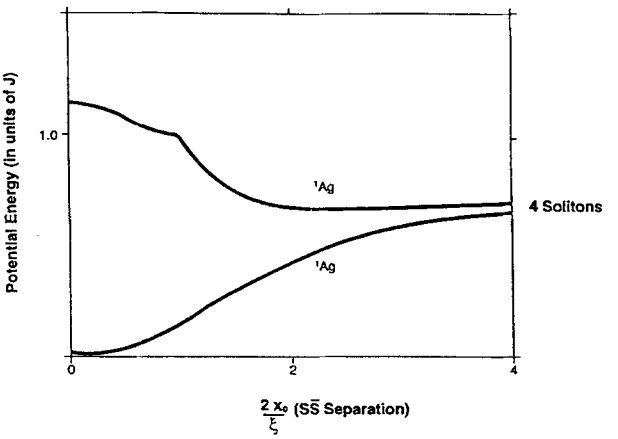

Figure 4. Potential energy curves in the 4-soliton sector calculated in a strong coupling theory.

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. Yet another possibility is the phonon-assisted absorption proposed by Mele and Hayden[9]. All those mechanisms should be further examined theoretically and experimentally.

Recently Halvorson and Heeger[18] 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 4-soliton bound state energy. That could imply that significant 4-soliton type quantum lattice fluctuations are present in the ground state. It could also imply a smaller creation energy of the neutral soliton than we have assumed, placing polyacetylene in the more correlated regime[19]. Similar remarks apply to the even parity two charged soliton state.

Although our calculations have been done for polyacetylene exclusively, they can be repeated for other nondegnerate polymers. Because of the confinement potential, the 4-soliton configurations may become less favorable compared to two-soliton configurations depending on the degree of confinement. However, as long as the 4-soliton energy is less than the gap, then the fission of an even-parity state into two neutral triplet polarons[20] is quite possible. Due to confinement, the 4 neutral solitons can not 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 4-soliton bound state is the lowest energy configuratuon, which can easily dissociate into four well separated neutral solitons. Higher even-parity excited states can decay into two charged solitons, but not neutral ones.

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