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Neutral and charged soliton defects in polyacetylene

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Self-consistent-field calculations have been applied to the study of defect geometries in finite-chain models of polyacetylene. The extent of the disruption of the normal bond-length pattern is less than previously expected and varies with the charge state. It is shown that the charged (neutral) defects induce a spatially damped, charge- (spin-) density wave of extent greater than that of the lattice kink itself.

Considerable theoretical effort has recently been expended in search of a model for conduction in one-dimensional metals.[1–6] Polyacetylene (all *trans*) has been the target of most of this work because it appears in many respects to be prototypical of the other systems and because of its elegant simplicity combined with subtle physical effects. It has been possible to correlate some of the more unusual properties of doped polyacetylene (e.g., spinless charge carriers) with defects in the pattern of carbon-carbon bond lengths. It has long been known[7] that infinite polyenes should show a pattern of bond-length alternation: $\cdots \mathrm{C{-}C{=}C{-}C{=}C{-}C{=}C{-}C} \cdots$, and that creation of a kink in this sequence ($\cdots \mathrm{C{-}C{=}C{-}C{-}C{=}C{-}C} \cdots$) requires little energy.[8] Such defects, referred to as "solitons" in recent literature,[2] can explain many of the physical observations in doped polyacetylene, including spinless conduction.

Calculations of the properties of chains containing solitons have been based on fairly simple Hamiltonians but have produced tantalizing suggestions.[1–6] The underlying principle of this work is a simple adaptation of Hückel theory. The Hamiltonian is constructed assuming that there are only two types of matrix elements: the diagonal elements are the orbital binding energies and the only nonzero off-diagonal elements are between bonded orbitals. The values of the matrix elements are adjusted to fit known properties of simple molecules and are transferred to other molecules. In the studies of defects in polyenes the parameters are usually assumed to have an exponential dependence on the length of the bond between atoms, thus coupling the lattice to the electron states. While the electron-lattice interactions are treated self-consistently (and give rise to the Peierls distortion), it is important to note that such schemes are not self-consistent with respect to electron-electron interactions. Thus dependence on orbital occupancy is not included and no distinction between charged and uncharged defects can be made except via perturbation treatments.[9]

In order to remove some of the deficiencies of the earlier approaches, we have carried out fully self-consistent-field calculations on varying length polyenes containing soliton defects. Our calculations are aimed at quantifying the geometries of isolated defects and exploring the differences between positive, negative, and neutral defects. The scheme we used, known as MNDO[10] (modified neglect of differential overlap), involves a semiempirical Hamiltonian which includes both electron-lattice and electron-electron coupling. All valence electrons are included, s and p states being treated on equal footings; previous work considered only p_z orbitals. The method finds that lattice structure (atomic geometry) which corresponds to the minimum total energy; for each trial geometry a self-consistent solution is used to compute the energy. Indeed, self-consistent treatment of all valence electrons is probably the most important missing ingredient in previous work and makes possible the recognition of differences between charged and uncharged species. With Hückel theory, where only π electrons are treated, there is an exact symmetry between the states at the valence- and conduction-band edges, forcing results for positive and negative defects to be identical. While the MNDO method used is approximate and subject to possible quantitative error, we are convinced that our predictions are sound consequences of the basic physics of the systems studied. It should also be noted that, with regard to the geometric considerations, the MNDO method has been widely tested and has an excellent track record.[11]

The neutral defects simulated are radicals located at the site of the topological kink in the bond-length alternation pattern. We have made calculations on varying length chains with the radical constrained to the center by imposition of a symmetry plane. In each case the entire molecule is allowed to relax to an equilibrium (planar) geometry. Results are shown in Fig. 1 and compared with earlier expectations.[1,6] Here the difference between adjacent bond lengths for a given carbon atom is plotted versus the distance of that atom from the defect site. The solid line is a hyperbolic tangent curve representing a particular form of soliton solution which has been shown[1] to have minimum energy by the earlier calculations. The asterisks show the results of our calculations on a chain containing 41 carbon atoms, which is easily of sufficient length to eliminate end effects. Thus our MNDO results suggest that the defect is more localized than previously expected (width $=2l\sim6$ vs 14 from Hückel theory). A spatially damped spin-density wave (SDW) is associated with the radical. It is to be stressed that this SDW, having a width $2l\sim10$, extends further than the lattice kink. Recent ESR results[12] have been interpreted as requiring widths between 10 and 17 in agreement with our calculations since the ESR experiment specifically probes the SDW rather than the lattice kink. Note that Hückel theory does not allow for distinction between SDW and lattice kink widths.

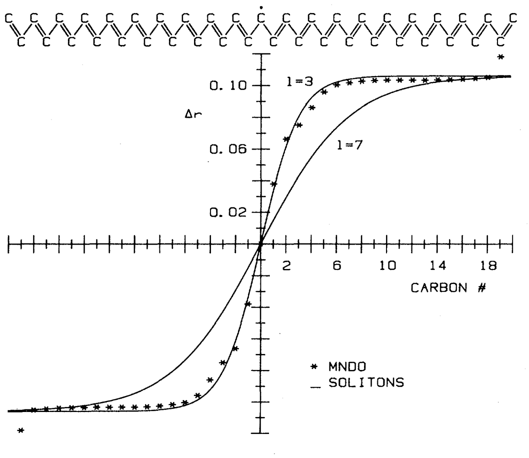

FIG. 1. Summary of MNDO results for 41-carbon-atom polyene shown schematically at the top of the figure. The difference between lengths of adjacent bonds Δr is plotted vs carbon position. The $l=7$ curve is a hyperbolic tangent function predicted by Su, Schrieffer, and Heeger (Ref. 1). According to MNDO, the neutral soliton defect is more localized ($l\sim3$) then previously expected.

The eigenvalue spectrum has, as expected, a half-filled orbital near the center of the energy gap. The charged defects are created by filling or emptying this midgap level and permitting further geometric relaxation. We find that the positive defect is more extended ($2l\sim10$) than the neutral. The negative defect is more compact than the positive, but not well represented with the tanh function.

Perhaps the most striking result of our calculations is the form taken by the screening charge. Screening is accomplished by polarization of alternate π bonds via charge transfer between contributing p_z orbitals. This in turn yields a marked oscillation of charge from site to site which decreases in magnitude as one gets farther from the defect site. This damped charge-density wave (CDW), illustrated in Fig. 2 for the positive defect, is a direct consequence of the self-consistency and has not previously been considered.[13] Just as for the SDW in the neutral defect, the width of the CDW ($2l\sim16$) is larger than that of the lattice kink itself. The CDW causes a periodicity on the backbone which would yield a significant band gap even if the bond alternation were to disappear. In addition, the vibrational intensities associated with backbone carbons should exhibit a large enhancement, consistent with experiment.[13] Finally, we note that the resultant dipole moment of the oscillation (all + charge on one side and all − charge on the other) could have significant impact on the motion of similar defects on neighboring chains[12,14]; therefore the charged defects intrinsically lead to strong coupling between the conducting chains of the polyacetylene. Results for the negatively charged defect are virtually identical to those in Fig. 2 (with reversed sign) even though the negative defect is more spatially compact than the positive.

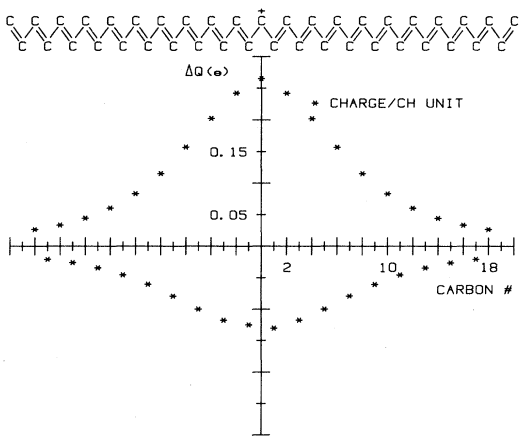

FIG. 2. Net charge (ΔQ) per CH unit along the chain as a function of distance from a positively charged defect, illustrating the damped CDW.

Recently, Fukutome and Sasai[15] have examined the electronic and geometric structure of the neutral and charged solitons with the use of a UHF method based on the Parriser-Parr-Pople Hamiltonian which includes *e*-*e* repulsions. Their results support ours and indicate that simple Hückel theory does not completely describe these systems.

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