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TITLE: STATICS AND ADIABATIC DYNAMICS OF NONLINEAR EXCITATIONS IN DEFECTED POLYACETYLENE

AUTHOR(S): S. R. Phillpot
D. Baeriswyl
A. R. Bishop
P. S. Lomdahl

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Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Statics and Adiabatic Dynamics of Nonlinear Excitations in Defected Polyacetylene

S. R. Phillpot,[†] D. Baeriswyl,[††] A. R. Bishop and P. S. Lomdahl

Center for Nonlinear Studies and Theoretical Division
Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)

[†] Also at: Physics Department, University of Florida, Gainesville, FL, 32611 USA. Present Address: Xerox Webster Research Center, Webster, NY, 14580, USA.

[††] Permanent Address: Seminar für Theoritische Physik, ETH-Hönggerberg, CH-8093, Zurich, Switzerland.

Abstract

Within the Su, Schrieffer and Heeger model we have calculated, both analytically and numerically, the effects of model impurities on the electronic structure and lattice distortion of trans-polyacetylene. We find that the electron-phonon coupling may result in a fundamental alteration of the impurity level location.

In simulated photoexcitation experiments on the defected system we find that, in addition to the kinks and breathers produced in the undefected system, "trapped kinks", excitons and polarons may also be produced. We suggest that the polarons produced in this novel way may be unusually stable and play an important role in hopping conduction mechanisms.

I. Introduction

It has become widely advocated that nonlinear excitations play a central role in the understanding of the structural, optical and electronic properties of trans-polyacetylene and related materials. This has been supported by experimental studies and by both analytic and numerical calculations on model systems -- particularly the "SSH" Hamiltonian [1]:

$$H_{SSH} = \frac{M}{2}\sum_n \dot{u}_n^2 + \frac{K}{2}\sum_n (u_n - u_{n-1})^2 + \sum_n [-t_0 + \alpha(u_n - u_{n-1})][c_n^+ c_{n-1} + c_{n-1}^+ c_n] \quad , \qquad (1)$$

where all the variables have their conventional meanings (see e.g. ref. 2). Most previous theoretical work has considered only defect-free systems, although the strong sample dependence of "pristine" samples

suggests that intrinsic defects, e.g. from bends, breaks or cross-links in the polymer backbone are important to a complete understanding of the system. Further, by doping with extrinsic impurties, the electrical conductivity can be varied reversibly and systematically over approximately thirteen orders of magnitude. This not only shows the importance of the role of extrinsic defects in understanding the transport properties of the system, but also suggests that dopant impurities are (typically) non-substitutional and not chemically reactive with the σ electrons of the polymer backbone.

In this paper we consider two model defects. The "site impurity" [3], which may model complex morphological effects, such as cross-linking and hybridization or the bonding of an orbital in a dopant to the π orbital of a single carbon atom, is modeled by the addition of a term to the SSH Hamiltonian, which couples to a single site. The "bond impurity" [4], represented by a local variation in the transfer matrix of the electronic part of the SSH Hamiltonian, may model intrinsic defects, such as chain bends and breaks, or amorphous and cis-like regions within the trans-polyacetylene chain.

In section II we discuss the effects of impurities on the purely dimerized lattice, while in section III we consider some typical photoexcitation experiments. Section IV contain a brief discussion and our conclusions.

II. Impurities in the Uniformaly Dimerized Lattice

The site impurity is represented by the addition to the SSH Hamiltonian of a potential at site m:

$$H_1 = V_0 \, c_m^+ c_m \quad , \tag{2}$$

while a bond impurity acts on a the bond between sites m and m + 1:

$$H_2 = -W_0(c_m^+ c_{m+1} + c_{m+1}^+ c_m) \quad , \tag{3}$$

This bond impurity does not break the electron-hole symmetry of the SSH Hamiltonian and thus any induced impurity levels must appear in pairs symmetrically about midgap. The site impurity, on the other hand, breaks the electron-hole symmetry and the impurity levels need not be paired.

Using, e.g., a continued fraction scheme similar to that used in ref. 5 we find [6] that the site impurity induces localized levels at

$$E_{\pm} = \pm \text{ sgn } (V_0) | (t_A^2 + \tfrac{1}{2}V_0^2)^{1/2} \pm (t_B^2 + \tfrac{1}{2}V_0^2)^{1/2} | \tag{2}$$

where $t_A = t_0 + \Delta_0/2$ and $t_B = t_0 - \Delta_0/2$. For a donor impurity ($V_0 < 0$) a state detaches from the bottom of the valence band into the "ultraband region" and a state moves from the bottom of the conduction band into the "intragap region". For the bond impurity where a single matrix element t_A is replaced by $t_E = t_A + W_0$, there are a pair of intragap states at

$$E = \pm\{t_E^2 + t_A^2 - [(t_E^2 - t_A^2)^2 + 4t_E^2 t_B^2]^{1/2}\}/(2t_E) \tag{5}$$

if the impurity either strengthens a weak bond ($t_A < |t_E|$, $t_A < t_B$) or weakens a strong bond ($t_A > |t_E|$, $t_A > t_B$). Similarly ultraband states are produced at

$$E = \pm \{t_A^2 + t_E^2 + [(t_E^2 - t_A^2)^2 + 4t_E^2 t_B^2]^{1/2}\}/(2t_E) \tag{5}$$

if the impurity strengthens the bond ($t_A < |t_E|$).

Both impurities also induce a localized lattice defect, a linear approximation calculation of which will appear elsewhere [6]. The numerical adiabatic dynamics studies were in good agreement with the analytical calculations and showed that the site impurity induces a localized lattice distortion consisting of a sharp step on the weak bond neighboring the impurity and a tail on the strong bond neighboring the impurity (see fig. 1). For the bond impurity the lattice distortion is symmetric about the defected bond and simply corresponds to a change in the local dimerization of the lattice.

On numerically relaxing to a fully self-consistent coupled electronic structure and lattice distortion, we find for the site impurity that the impurity electronic levels become more localized. For the bond impurity the renormalization of the location of the impurity levels may be qualitatively fundamental with the intragap level becoming less localized. This is partially compensated by the localization of a pair of ultraband levels.

III. Photoexcitation in the Presence of Defects

It has previously been shown in numerical studies of the undefected system [2,7] that photoexcitation of a single electron across the electronic gap leads to the production of a separating kink and antikink and also a localized anharmonic phonon bound state -- a "breather". We have suggested that this may account for the experimentally observed photoinduced photoabsorption spectrum [8]. If this view is valid, it is important to demonstrate that the scenario remains qualitatively unchanged in the defected system.

Here we briefly discuss a few representative photoexcitation experiments -- complete details will be published elsewhere [6]. Consider a charged impurity with a singly occupied intragap level above midgap and a doubly occupied ultraband level below the valence band and a fully consistent electronic-lattice structure. At time t = 0 an electron is excited into (i.e. manually placed in) the intragap level. We find that the intragap impurity level drops to midgap forming a negatively charged antikink around the impurity tail, which is expelled at the maximum free kink velocity. This leaves behind a kink trapped over a single lattice site around the impurity step. This "trapped kink" is not associated with an intragap level but is maintained by the ultraband impurity level. (Other mechanisms for creating these interesting "trapped kinks are dicussed in Ref. [6]). In addition the singly occupied level at the top of the valence band and the empty level at the bottom of the conduction band move into the gap to form a hole polaron. In photoexcitation into the lowest level of the conduction band we find that, rather than a polaron, an "exciton" and a breather are formed. Similar evolutions take place for neutral impurities and for systems with more than one impurity [6].

Now consider a neutral bond impurity, with a pair of intragap impurity levels: the upper empty, the lower doubly occupied. Although photoexcitation adds insufficient energy to produce a $K\bar{K}$ pair, the electronic energy of the system is lowered by the removal of states from the top of the conduction band and the bottom of the valence band, thus providing enough lattice energy for the production of a separating $K\bar{K}$ pair, along with a localized defect on the impurity bond.

IV. Discussion and Conclusions

We have found that both the site and bond model impurities may result in the production of localized electronic levels in the gap and in the ultraband region. In the case of the bond impurity the renormalization due to the electron-phonon coupling may be qualitative and result in the intragap levels becoming less localized [9]. In studies of the kink-impurity interaction, discussed fully elsewhere [6], we found that the mobility of a kink is typically strongly reduced by the presence of impurities. Indeed a single kink may become trapped around a site impurity, allowing the kink to be supported purely by the ultraband impurity level, and letting the midgap level drop into the valence band. These dynamics suggest that the ballistic transport of kinks is unlikely to make a significant contribution to the transport properties of the system.

Contrary to naive expectations the presence of lattice defects strongly enhances the production of nonlinear excitations, including trapped kinks and excitons, which are not stable in the undefected system. Further, breathers are not suppressed and may still be expected to contribute to the subband edge absorption. The observed $K\bar{K}$ production below the direct production threshold ($2\Delta_0$) is additional to quantum and thermal Urbach tail mechanisms.

Finally, polarons may be produced in both kink-impurity interactions and in photoexcitations. As kinks may rapidly trap and decrease the polaron mobility, there may be a strong enhancement of the polaron lifetime in the defected system, which could play an important role in hopping transport mechanisms.

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Figure 1. Staggered lattice displacement for 98 site ring with a neutral (solid line) and a charged (dashed line) impurity at the 50th site. The step is localized around one site and is "kink-like", while the tail is over a larger number of sites and is "antikink-like".

Figure 2. Photoexcitation into the intragap level of a charged site impurity. Note the trapped kink at the center and the rapidly moving free antikink. The polaron forms close to the trapped kink and is expelled by it.

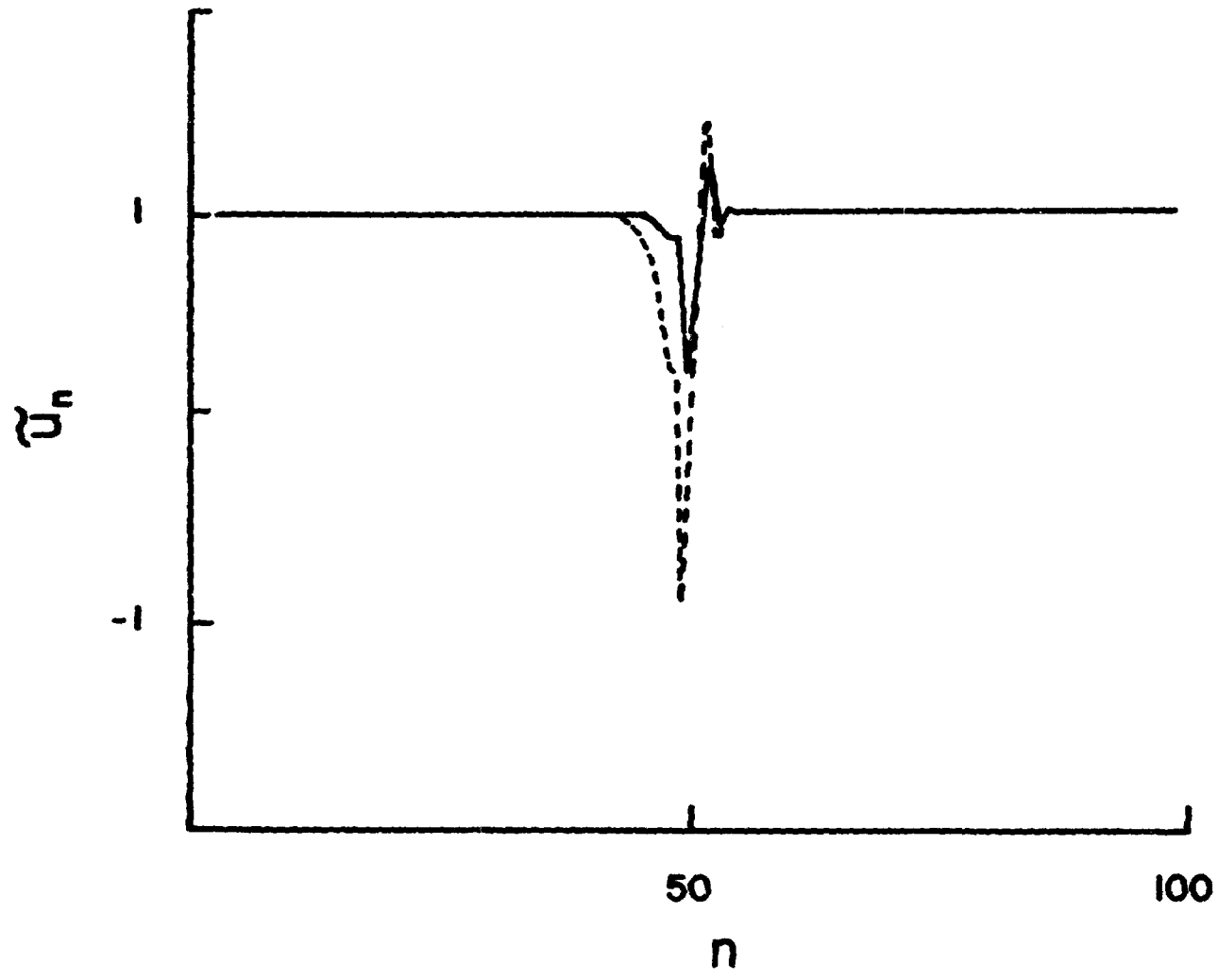
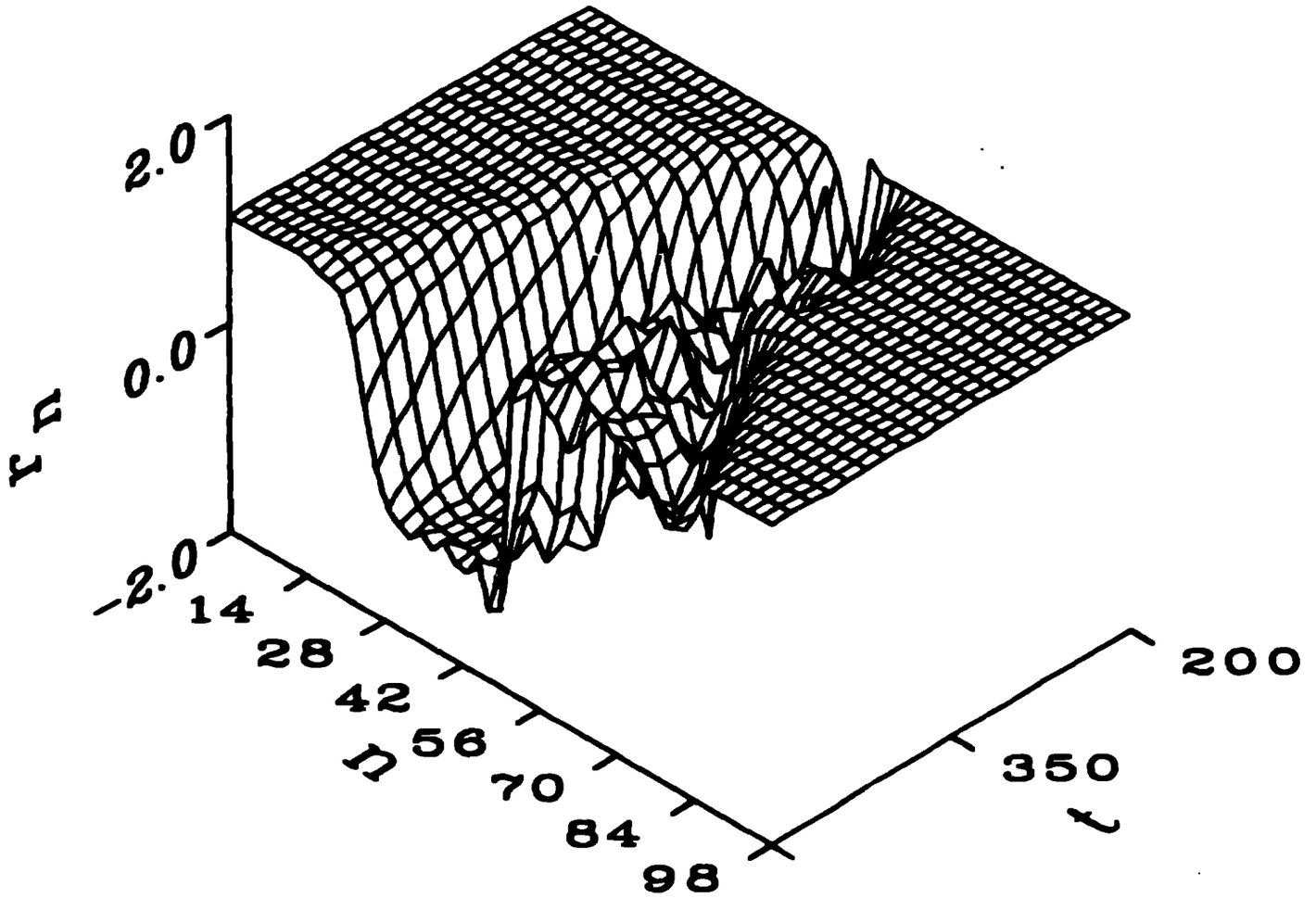


Fig. 2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