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Extended states in interacting disordered polyacetylenelike chains

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In spite of the enormous amount of theoretical and experimental work on conducting polymers, the actual mechanism involved in the transition to a metallic regime is still an open and polemical question. Recently, Galvão *et al.* have proposed, based on the study of long, disordered, one-dimensional chains, that disorder is in the origin of the metallic transition in conducting polymers. They suggest that disorder induces the appearance of extended (conducting) states near the Fermi level. Since in actual samples there are interactions among chains, one important question is whether this kind of state could survive when interactions among chains are taken into account in the calculations. In this work we show that extended states can exist even when the interaction among chains is taken implicitly into account. These results strongly support disorder as the physical mechanism behind the metallic transition in conducting polymers. The density of states of long chains was obtained through the use of the negative factor counting technique coupled to a tight-binding Hamiltonian. [S0163-1829(97)05524-0]

I. INTRODUCTION

Conducting organic polymers are a new class of electronic materials with unusual properties.[1] Among these compounds polyacetylene (PA) is the most studied. The discovery that PA doped by charge-transfer reactions showed a dramatic increase in conductivity started a great number of theoretical and experimental works on conducting polymers.[1] But in spite of the extraordinary amount of work on these materials, some fundamental aspects of its electronic behavior are still not well understood, for example, the nature of the metallic regime for highly doped samples. It has been suggested that the metallic regime of conducting polymers is associated with the presence of (neutral and/or charged) conformational defects such as solitons, polarons, and bipolarons. However, the presence of localized infrared-active vibrational modes and the deviation from the T^{-1} law of the conductivity indicate that doped conducting polymers are not simple metals.[1] Recently, Galvão *et al.*[2] have proposed, based on a series of molecular-orbital calculations on linear-disordered, one-dimensional polyaniline chains, that disorder is in the origin of the metallic transition. The semiconductor-metal transition arises from the movement of the Fermi level towards conducting (extended) states inside the valence band (p-type metal). These results have been generalized to polyacetylene,[3,4] polythiophene,[5] and substituted polyanilines.[6]

The presence of extended states in disordered one-dimensional chains is a very surprising result that is in contrast to Anderson's localization theorem.[7] The precise origin of these states has been explained by Wu and Phillips[3,8] based on the random dimer model (RDM). The RDM was formulated in terms of a tight-binding Hamiltonian, and both diagonal and off-diagonal types of disorder were considered. The existence of unscattered Bloch states by impurities or bond defects in an otherwise perfect monatomic chain containing N sites was demonstrated, given that the system satisfies the following properties:[8] defects have to occur in pairs (dimers) and have to possess internal symmetry. Solitons and bipolarons usually satisfy those conditions. More recently, Lavarda *et al.*[5] have demonstrated that symmetrical defects are not a requirement for the existence of near-resonant scattering states.

Recently, many papers dealing with the existence and stability of this kind of state have been published.[9–17] Although there is an ongoing debate about the existence and interpretation of these states, more and more experimental evidence support the importance of disorder.[18–22] These results strongly support the idea that disorder is the underlying mechanism involved in the metallic transition in conducting polymers. One important question that we could ask is as follows: Can extended states in one-dimensional disordered chains survive if interactions among chains is taken into account explicitly into the calculations? The objective of the present work is to answer the question.

We present the model Hamiltonian in Sec. II. In Sec. III we present the results and discussions.

II. METHODOLOGY

As the PA structure is the simplest possible for conducting polymers, we have chosen the PA-like structure to perform our study. We have investigated the electronic structure of three long PA chains that can interact with each other, as indicated in Fig. 1. Chain 2 is the reference chain; each atom is chain 2 can interact with its equivalent atoms in chains 1 and 3. This interaction among chains can be turned off or on in ordered or random ways for each atom and its value can be varied. We have considered the cases of ordered and disordered distributions of solitonlike conformational defects with and without ordered and random interactions between chains for chains containing up to 10 000 atoms.

Since optical, electrical, and magnetic properties for planar conjugated systems are dominated by π electrons, we treat the polymeric chains as a π system with one orbital per site and represent the electronic Hamiltonian for the $2p_z$ orbitals through a tight-binding model with first neighbor interactions only (interchains and intrachains). The matrix ele-

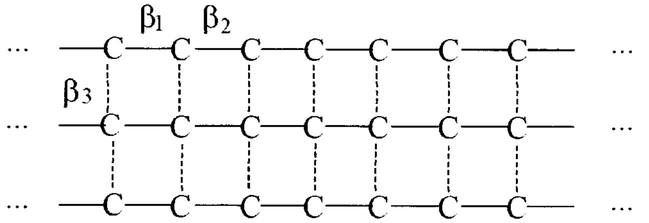

FIG. 1. Scheme of the three interacting PA-like chains. The β_1 and β_2 parameters refer to the resonance integrals related to single, double, or solitoniclike carbon-carbon bonds. The β_3 parameter refers to the resonance integral associated with the bonding among chains. This parameter can be turned on or off according to a probability rate, i.e., the interactions among atoms in different chains is present or absent according to a determined probability value, which can be varied, simulating many different configurations.

ments are obtained from extended Hückel theory[23] with Clementi's parametrization and with geometry from Austin method one[24] oligomer calculations: 1.36 and 1.44 Å,[25] respectively, for single and double bonds and the solitonic bond lengths were taken as an average between single and double bonds. This corresponds to Hamiltonian matrix element values of −5.76, −4.93, and −5.29 eV, respectively. The element describing the interaction between atoms in different chains was taken for the cases presented here as equal to −0.5 eV (~10% of the resonant integral associated with the single bond).

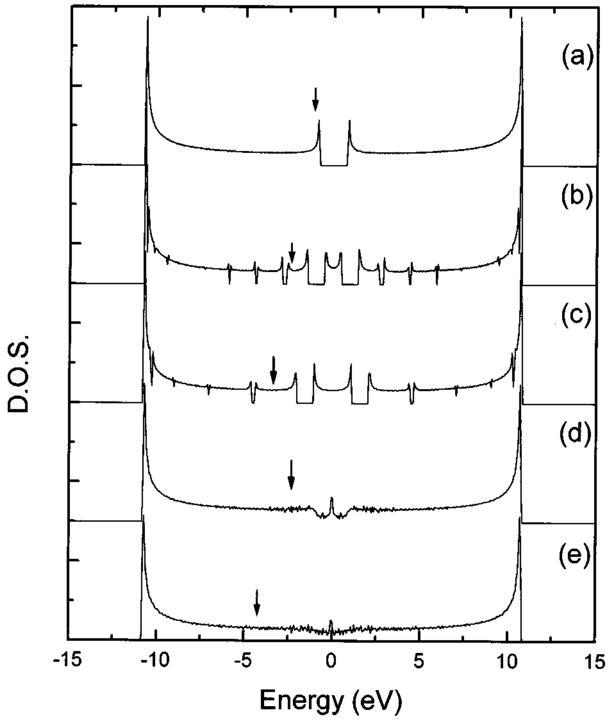

FIG. 2. Density of states (DOS) in arbitrary units of an isolated PA-like chain. The arrow indicates the energy position of the highest occupied molecular orbital (HOMO). (a) Fully dimerized, defectless chain. Curves (b) and (c) and curves (d) and (e) refer to 5% and 10% solitonlike defect distributions (p-type doping), orderly and disorderly distributed, respectively.

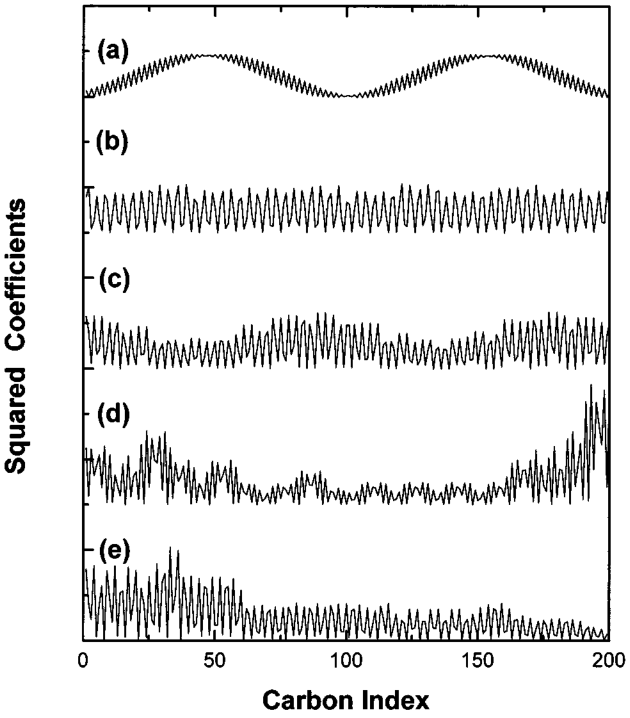

FIG. 3. Squared expansion coefficients of the HOMO states, corresponding to the DOS cases shown in Fig. 2.

The chains are built using two unit cells, one for the fully dimerized PA and the other for the solitonlike defect. We have chosen to model the interaction among chains using a parameter that can be turned on or off depending on a probability rate in order to simulate relative displacement among chains. For the cases discussed below we have considered this probability as equal to 25%, i.e., the probability of an atom in chain 2 interacting (parameter turned on) with the equivalent atom in the neighboring chains is 1 out of 4. The density of states (DOS) of long ordered and disordered interacting and noninteracting chains is obtained using the negative factor counting technique,[26,27] which is a powerful method to treat aperiodic systems. The eigenvectors associated with the eigenvalues of interest are obtained through the inverse iteration method.[27] These techniques allow access to the wave function and length localization patterns.

III. RESULTS AND DISCUSSION

In order to verify the reliability of the methodology described above and for comparison reasons we start by analyzing the DOS [Fig. 2, curve (a)] and the spatial eigenvector distribution of the highest occupied molecular orbital (HOMO) [Fig. 3, curve (a)] of a fully dimerized, defectless PA isolated chain containing 10 000 carbon atoms. As we can see from Fig. 2 curve (a), the DOS is very similar to the DOS of infinite (in the Bloch limit) chains reported in the literature,[4,25] and the calculated gap value is 1.6 eV, in very good agreement with the optical-absorption measurements with the onset at 1.4 eV and a peak at 1.8 eV.[28]

In Fig. 2 curves (b) and (c) and curves (d) and (e) we show the DOS for a chain containing 5% and 10% solitonlike defect concentrations, orderly and disorderly distributed,

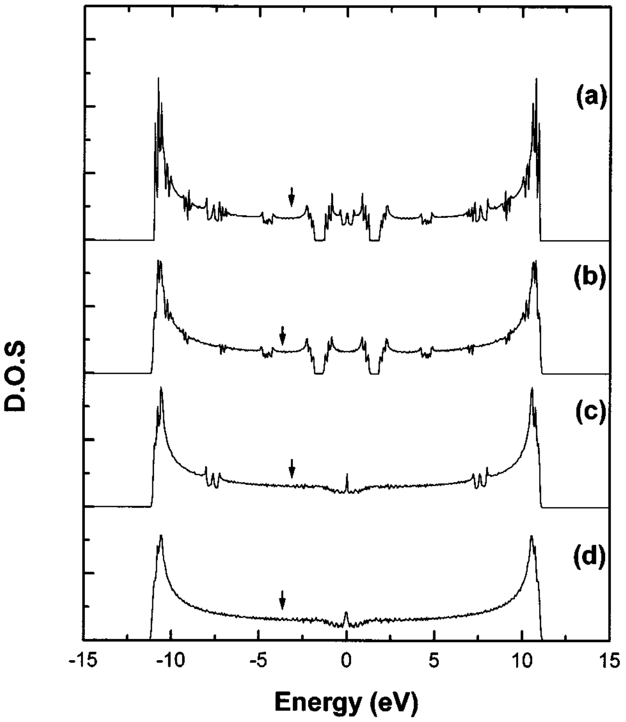

FIG. 4. Total DOS in arbitrary units of three interacting PA-like chains with a 10% solitonlike defect (p-type doping) distribution and with a bonding probability among chains equal to 25%. The arrow indicates the energy position of the HOMO. Curves (a), (b), (c), and (d) correspond to the four possible cases O/O, O/D, D/O, and D/D, respectively, where the first letter refers to the defect distribution [ordered (O) or disordered (D)] and the second letter to the kind of bonding interaction among chains [(O) or (D)].

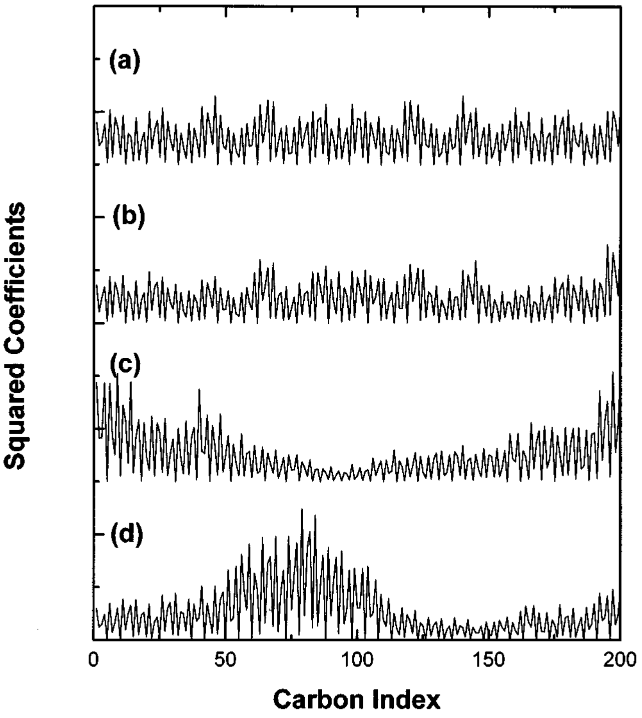

FIG. 5. Squared expansion coefficients of the HOMO states, corresponding to the DOS cases shown in Fig. 4.

respectively. As we increase the defect concentration a defect band is built up and band tailing and antiresonances are clearly seen. However, in terms of DOS the closing of the gap among bands is observed only with a disordered distribution of defects. The finite value of the DOS at the Fermi level is a necessary but not a sufficient condition to ensure a semiconductor-to-metal transition since these states could be localized. It is necessary to analyze the spatial extension of these states. The extensions of the wave functions are inferred from the plot of the square of the coefficients of the expansion of the eigenfunctions in the $2p_z$ basis versus the carbon-atom positions. In Fig. 3 we show this pattern for the equivalent cases indicated in Fig. 2 for chains with 200 atoms. We can see from the figure that, at defect the concentrations considered here, the eigenfunctions are delocalized for the ordered and disordered cases, i.e., a metallic regime can be attained with a disordered defect distribution since the DOS is infinite at the Fermi level and the eigenfunctions are delocalized, thus characterizing a true metal. However, although ordered and disordered defect distributions could lead to metallic regimes, there is strong evidence against an ordered distribution, especially when the dopants are explicitly considered.[29,30]

In Figs. 4 and 5 we show the DOS and the corresponding localization pattern when the interaction among chains is turned on with a 10% defect concentration and with a bonding probability among chains equal to 25%. Figure 4 curve (a) shows the DOS for the case of an ordered distribution of defects and ordered interaction. As we can see from the figure, the gap structures are present and compared to the equivalent case for the isolated chain [Fig. 2, curve (a)] this is a richer structure, with well-resolved antiresonances. When the interaction among chains is random [Fig. 4, curve (b)] this finer structure is destroyed, but the gaps among the valence/conduction and defect band survive. A disordered defect distribution with ordered interchain interactions induces gap closing, but some antiresonance structures survive [Fig. 4, curve (c)]. Similarly to Fig. 4, curve (b) disordered interchain interactions destroy these structures.

Figure 5 shows the corresponding localization patterns for cases shown in Fig. 4. This spatial pattern provides an answer to the question we are interested in. It is very clear from Fig. 5 that, even considering explicitly the interactions among chains, the extended states observed for isolated chains can survive with no significant modifications. These results add to the increasing amount of evidence that disorder plays a crucial role in the transition to a metallic regime in conducting polymers. As demonstrated before,[6] these results are not limited to PA-like structures, but hold for every polymeric system that can be mapped, by means of renormalization procedures, into a one-dimensional AB chain.

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