

Semiconductor-to-metal transition in *trans*-polyacetylene (the role of correlated solitons)

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Abstract

In this study the nature of transition to metallic regime in *trans*-polyacetylene (*trans*-PA) is investigated. Based on Su-Schrieffer-Heeger (SSH) model and the use of Continued - Fraction Representation (CFR) as well as Lanczos algorithm procedure, we studied the effects of some selected soliton distributions on the semiconductor-to-metal transition in *trans*-PA. We found that: *i*) this transition occurs only when there exists a soliton sublattice in *trans*-PA, *ii*) disordered soliton distributions and soliton clustering are the origin of the metallic transition in *trans*-PA, that is consistent with the experimental data. Our results show that in the presence of correlation between solitons, the disorder in accompanying single soliton distributions plays a crucial role in inducing the transition to metallic regime, so that in contrast to Anderson's localization theorem, the electronic states near the Fermi level are extended, that is the most significant criteria for the metallic regime.

Keywords: Lanczos algorithm and continued-fraction representation, polyacetylene, disorder and soliton, semiconductor-to-metal transition

1. Introduction

Much effort has been devoted to the understanding of the conduction properties of π -conjugated polymers [1-5]. These semiconductor systems play an important role in the development of molecular devices for electronic applications [6]. Among these compounds, *trans*-PA is the most studied. This is due to the fact that while, being the simplest π -conjugated polymers, *trans*-PA has considerable potential applications as an alternative conductor. The possibility of the semiconductor-to-metal transition and the capability of becoming a very conductive material have been the reason for the experimental and theoretical investigations on the physical properties of *trans*-PA in comparison with the other conducting polymers [7]. Based on experimental data, the metallic phase in doped *trans*-PA is characterized by a conductivity that is on the order of

10^4 s/cm, a factor of 10^{12} greater than the conductivity in the insulating forms of the polymer [8-13]. However, one should note that the deviation from the T^{-1} law of the conductivity indicates that doped conducting polymers are not simple metals [14]. There is a great number works concerning the study of physical mechanisms behind the metallic transition in *trans*-PA [15-17]. The experimental investigations on the conduction properties of *trans*-PA support the idea that disorder is responsible for insulator to metal transition in *trans*-PA [18-22]. The occurrence of the metallic regime, with the presence of disorder, in *trans*-PA chains is an unexpected result. Because, based on Anderson's localization criteria, disorder induces the electronic localized states in one-dimensional structures [23]. It has been proposed, however, that the metallic regime of doped *trans*-PA (and other conducting polymers) and

existence of extended states near the Fermi level occurs when there is a given concentration of random defects in pairs with an internal structure that is symmetric about some plane [16,24]. In trans-PA, solitons do have this symmetry inherently and provide the necessary conditions. In addition, from the physical point of view, it has been suggested that the transition to metallic regime would arise from the movement of the Fermi level towards extended states inside the valance band [25]. In addition to this, many other studies have been carried out about the stability of the metallic phase in conducting polymers such as doped-polyacetylene and substituted polyanilines [26-28]. For example, in a series of papers, Harigaya, has studied and supported the possibility of surviving of the metallic regime in polyacetylene [29-31]. However, there are still important factors whose influence on the transition to metallic regime in trans-PA has not yet been fully studied. There has been an increase in the theoretical modeling for studying how the details of trans-PA electronic structures, π -electrons' behavior, and especially correlated disorder in soliton sublattice affect the transition to metallic regime in trans-PA. Here we focus on the correlation between solitons (clusters), as a significant factor, and the presence of disorder in the distributions of single solitons for inducing the transition to metallic regime.

One of the well-known frameworks for studying of conduction and structural properties of trans-PA, that has been widely accepted, is the Su-Schrieffer-Heeger (SSH) model [32]. In a previous paper [33], we have used the SSH model for studying the effects of solitons (without correlation) in producing the localized electronic states in the structure of trans-PA. In this paper a detailed numerical study of the role of correlated solitons for inducing the extended electronic states around the Fermi level of trans-PA is presented. We show that if one considers the necessary conditions for semiconductor-to-metal transition, then SSH model can be a sure base to study the transition to metallic regime in polyacetylene. However, it is worthwhile to apply this model by various techniques for understanding the nature of the metallic phase in trans-PA. So, by means of Lanczos algorithm procedure and the use of Continued-Fraction Representation (CFR) relying on the SSH framework, we investigate the effects of the correlation between solitons and some disordered soliton distributions on the semiconductor-to-metal transition in trans-PA. In section (2), we introduce the Hamiltonian model and then describe the method for the calculation of the density of electronic states (DOS) of trans-PA chains. The results and discussion are presented in section (3) followed by a summary and conclusions in section (4).

2. The Hamiltonian model and description of the method

To present a correct theoretical model it becomes necessary to understand the structural and electronic

characteristics of π -conjugated polymers. In polyacetylene with sp^2 hybridized carbon atoms, it has already been shown that the main contribution to the electronic properties comes from the π -electrons [33-35], such that one may only consider the electronic part of well-known SSH Hamiltonian.

2.1. The Hamiltonian model

According to the above discussion, the electronic part of SSH Hamiltonian is given by,

$$H_{SSH} = - \sum_n t_{n+1,n} (c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}), \quad (1)$$

in which $t_{n+1,n}$ is the nearest-neighbor transfer integral and is given as,

$$t_{n+1,n} = t_0 + \alpha(u_n - u_{n+1}), \quad (2)$$

where t_0 is the hopping integral of an undimerized chain, α the electron-phonon coupling constant and u_n the displacement of the n th carbon atom from its equilibrium position. For perfectly dimerized trans-PA u_n and bandgap are given as $u_n = (-1)^n u_0$, $2\Delta_0 = 8\alpha u_0$, respectively. Throughout this study for $2\Delta_0 = 1.4 \text{ eV}$, we shall use the parameters of Ref.[32].

So, $\alpha = 4.1 \text{ eV}/\text{\AA}$ and $t_0 = 2.5 \text{ eV}$. These correspond to an equilibrium dimerization amplitude $u_0 \approx 0.04 \text{\AA}$.

2.2. Description of the method

Here we present our method summarily based on a generalized Green function formalism for calculation of electronic DOS, and then we study the effects of the selected distributions of soliton on the electronic structure of trans-PA chains. Taking the lattice to be homogeneously dimerized, the advanced and retarded temperature double-time Green functions are written [36],

$$G_{nm}^\pm(t) = \pm i \Theta(\mp t) \left\langle \{a_n(t), a_m^\dagger(0)\} \right\rangle \quad (3)$$

$$G_{nm}^\pm(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dE e^{-iEt} G_{nm}^\pm(E \mp i\eta); \quad \eta \rightarrow 0 \quad (4)$$

where a_n ($a_n^\dagger$) is the annihilation (creation) operator of an electron at n th site, $\Theta(t)$ is Heaviside step function and angular bracket denote the thermodynamic average. A complete formalism and description of the method may be found in our previous paper [33]. Our task is to evaluate the diagonal Green function $G_{nn}^\pm$, the imaginary part of which gives the local DOS, $\rho_n(\omega_\mp)$. Taking into consideration the retarded Green function

$G_{nn}^-(\omega_+) = G_{nn}$ with $\omega_+ = \omega$, then $\rho_n(\omega)$ is given as,

$$\rho_n(\omega) = -\frac{1}{\pi} \lim_{\eta \rightarrow 0} \text{Im}\{G_{nn}(\omega)\}; \quad (5)$$

$$\omega = E + i\eta$$

According to Ref.[33] the following form will be resulted for $G_{nn}(\omega)$,

$$G_{nn}(\omega) = \pm \frac{\omega}{\sqrt{\beta(\omega)}}, \quad (6)$$

in which $\beta(\omega) = [(\omega^2 - t_+^2 - t_-^2)2 - 4t_+^2 t_-^2]$. With $\eta \rightarrow 0$, i.e., for $\omega = E$ the denominator in Eq.(6) is imaginary for $|t_+^2 - t_-^2| < E^2 < (t_+^2 + t_-^2)$. It follows that the DOS, $\rho_n(E)$, is finite in this region and is given as,

$$\rho_n(E) = \frac{E}{\pi \sqrt{\beta(E)}}. \quad (7)$$

It is clear that $\rho_n(E)$ vanishes in the former region. Calculating $\rho_n(E)$ one can find the expected electronic structure of trans-PA in which valance and conduction bands are separated by a gap of width $2\Delta_0$. We calculate the energy eigenvalues spectrum, $\{E\}$, and the corresponding electronic wave functions, $\{\psi\}$, using a direct diagonalization procedure based on the Lanczos algorithm [37]. This diagonalization method is known to be very efficient for large matrices.

2.3. The selected distributions of solitons

It is well-known that the ground-state of the Hamiltonian (1) with one orbital per site is dimerized and a bandgap $2\Delta_0$ is opened at the Fermi level. The existence of the defects such as solitons markedly affects the electronic structure. In the presence of solitons the ground-state of trans-PA is a “soliton lattice” with the centers of solitons approximately equally spaced along the chain. When the electronic states associated with the solitons overlap, a “soliton band” is formed in the bandgap of the undoped polymer. The soliton band is filled or emptied depending on the type of doping (donor or acceptor). Increasing the number of solitons by doping will widen the soliton band and thus reduces the bandgap of polyacetylene. Our investigations suggest that the increase of concentration of solitons will close the bandgap. However, the suppressing of the bandgap is not sufficient for transition to metallic regime. The existence of the extended electronic states near the Fermi level is the most significant feature that has to be taken into consideration. This depends on the kind of soliton distributions. Our results suggest that the distributions of soliton clusters in the presence of randomly distributed single solitons may produce the conditions for transition

to metallic phase. Our calculations are performed for the selected soliton distributions as follows: 1) Homogenous distributions, that give rise to a soliton band in the bandgap of trans-PA. 2) Cluster distributions in such a way that each cluster contains some solitons with equally spaced centers (order), gathered in a small region along the chain. 3) Disordered distributions, in which the centers of solitons inside each cluster and outside the clusters are placed randomly.

For a large chain, a soliton corresponds to a phonon field configuration that minimizes the total energy. In the presence of solitons the displacements of carbon atoms in trans-PA are determined in such a way to minimize the total energy and to give the optimum shape for the soliton. Accordingly the displacements of the carbon atoms are modeled as [38,39],

$$u_n = (-1)^n u_0 \prod_m \tanh\left[\frac{(n-m)a}{\xi}\right], \quad (8)$$

where $2\xi \approx 14a$, with $a = 1.22\text{\AA}$ (lattice constant), is the width of a soliton. (ma) is the location of the m th soliton center on the chain.

3. Results and discussion

In comparison with the experimental results, we choose the concentration of solitons to be 6% which is the threshold to observe the transition to metallic regime in trans-PA. Figure 1 illustrates the order parameter $\phi_n = -(-1)^n u_0$ for the different chains with the selected soliton distributions mentioned above. For a fully dimerized chain $u_n = (-1)^n u_0$, with $u_0 \approx 0.04\text{\AA}$ and for doped samples, in presence of solitons, u_n is given via eq.(8). The order parameter is an easy way to observe the different soliton distributions along the PA chains, since $\phi_n = 0$ means a soliton has been located at the n th site. Figure 1(a) illustrates u_n for a fully dimerized chain and it is shown here for the purpose of comparison. To find the centers of solitons in a more clear way, the results for ϕ_n are presented for short chains containing 200 carbon atoms. Figure 1(b) shows order parameter ϕ_n for a trans-PA chain in which solitons with homogeneous distribution have occupied 6% of total sites of the chain. The homogeneous distributed solitons give rise to the formation of a soliton band in the bandgap of trans-PA. Figures 1(c) and 1(d) illustrate a cluster with 12 solitons, and a cluster with 8 solitons in the presence of some single solitons with random distributions, respectively.

To observe how the electronic structure is changed in the presence of the selected soliton distributions, we have calculated the corresponding results for the π -electrons density of states (DOS). To be more accurate in calculating the DOS, we choose the long chains containing 2000 atoms. Figure 2 shows the order

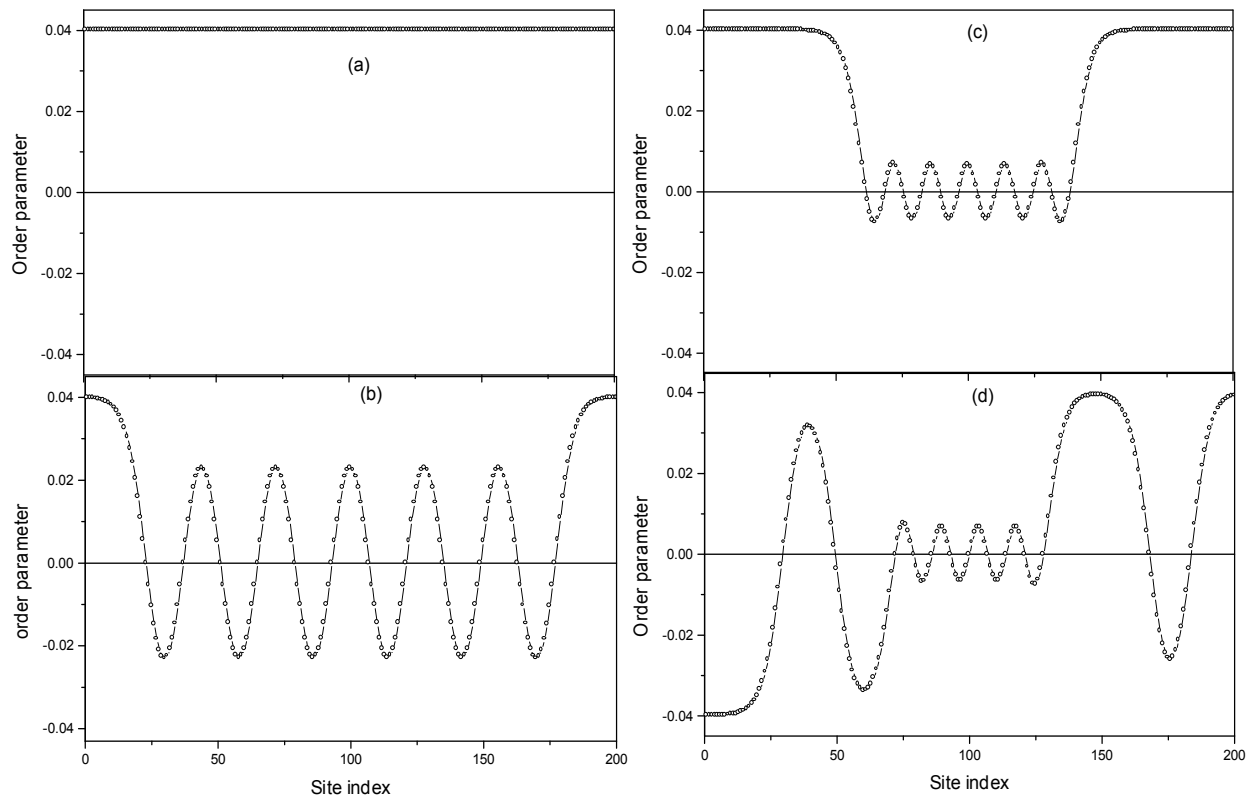


Figure 1. The order parameter φ_n for a chain with $N=200$ atoms; (a) a fully dimerized chain; (b) an homogeneous soliton distribution; (c) a cluster with 12 solitons in the middle of chain; (d) a cluster with 8 solitons plus some randomly soliton distributed.

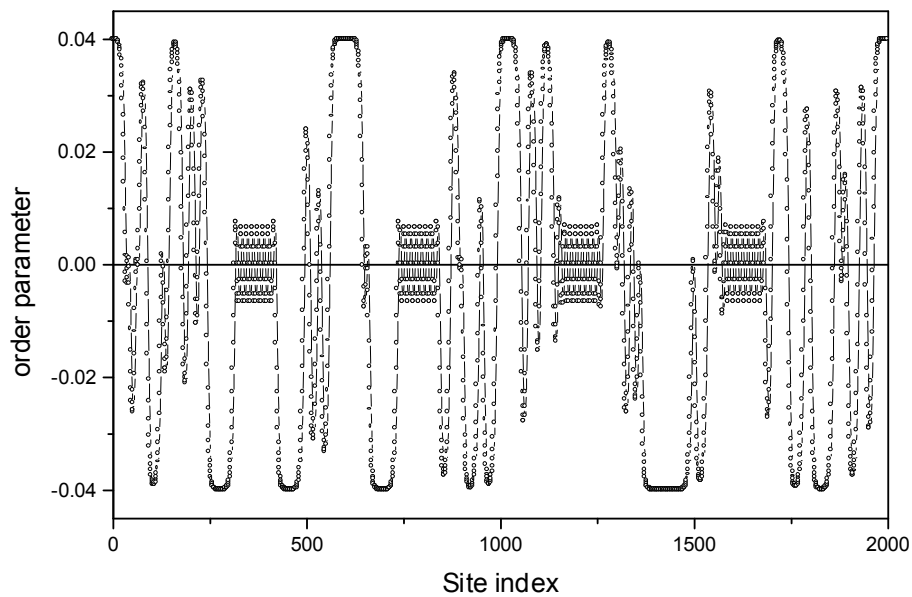


Figure 2. The order parameter φ_n for a chain with $N=2000$ atoms. This chain contains 120 solitons such that 3% of them have been located in 4 clusters and others have been distributed randomly on the chain.

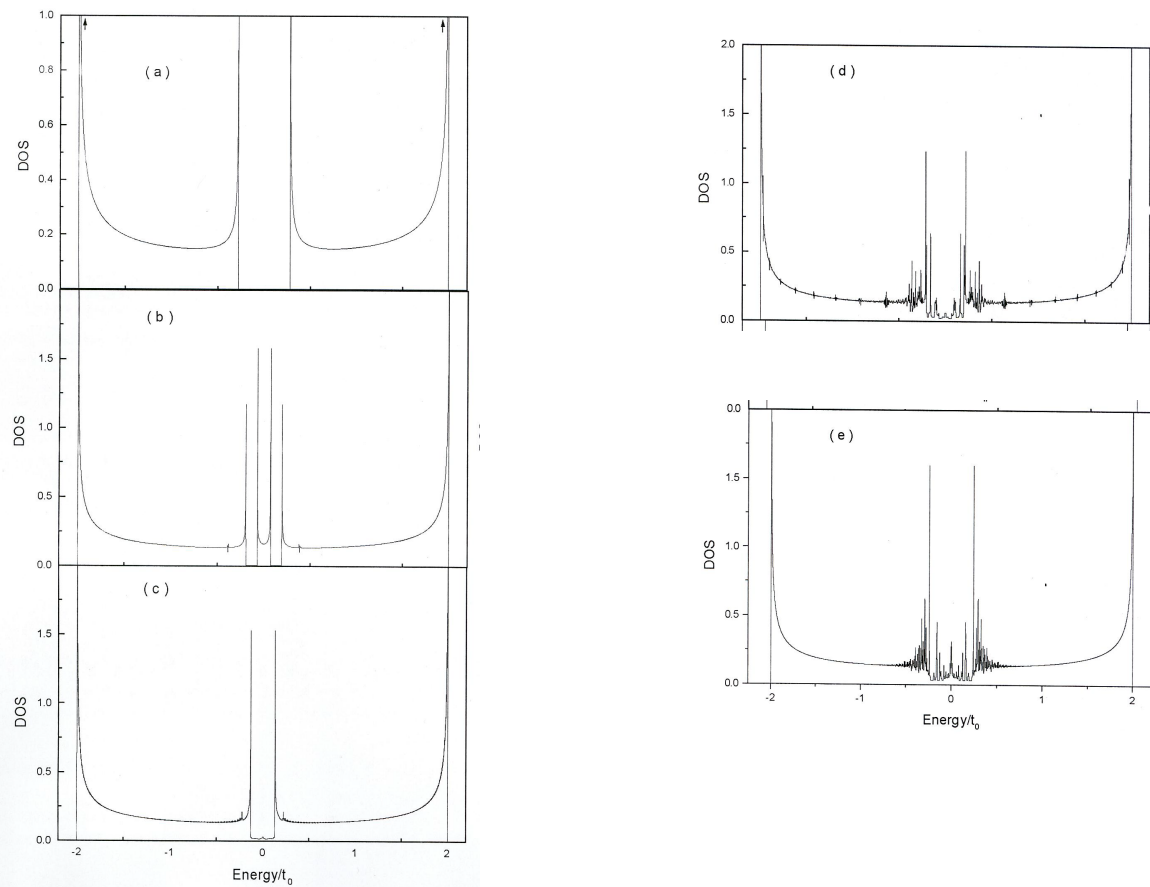


Figure 3. The electronic density of states (DOS) for a typical *trans*-PA chain with $N=2000$ carbon atoms; (a) the electronic structure of a fully dimerized chain; (b) the effects of the homogeneous distributed solitons which give rise to a soliton band into the bandgap of *trans*-PA; (c-e) show the effects of soliton clusters plus disordered soliton distributions (according to the text).

parameter φ_n for one of this chains which is used in our calculations. This chain contains 120 solitons such that 3% of them have been located in 4 clusters and others have been distributed randomly on the chain. Figure 3(a) shows an electronic structure for a fully dimerized chain of *trans*-PA. The energygap 1.4 eV is quite clear and also the spectrum contains valance (left) and conduction (right) bands. In the next figures for the different types of soliton distributions, the concentration of solitons 6% is taken into account. Figure 3(b), corresponding to figure 1(b), shows a soliton band into the bandgap of *trans*-PA. In this figure, the solitons have been distributed homogeneously which is corresponding (from structural point of view) to forming a soliton sublattice in polymer chain. In the presence of the soliton band, the energygap is reduced in *trans*-PA structure. Our results show that by changing the concentration of solitons one can change and control the width of the soliton band and consequently the size of gap in *trans*-PA. Figures 3(c-e) illustrate the effects of the presence of a cluster with 120 solitons (in the middle of chain), a cluster containing 4% of solitons plus 2% single solitons with the random

distributions and finally a cluster containing 3% of solitons plus 3% of single solitons with random distribution, respectively. We can see that if a cluster of solitons with a percentage of disordered distributions of single solitons exist, then the energygap of *trans*-PA is closed. However, 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 electronic states may be localized. In order to obtain a fully characterized metallic regime, we also need the extended electronic states around the Fermi level. Therefore it is necessary to calculate the magnitude of the electronic wave functions at the position of carbon atoms in the PA chain. Considering the corresponding chains of figure 1, we have calculated the magnitude of the wave function $|\Psi_E|^2$ for energy eigenvalues E which are located around the Fermi level. Figure 4(a) shows $|\Psi_E|^2$ for a fully dimerized chain with 200 atoms. In figure 4(b) the behavior of the wave function is shown for a homogeneous distribution of solitons. The

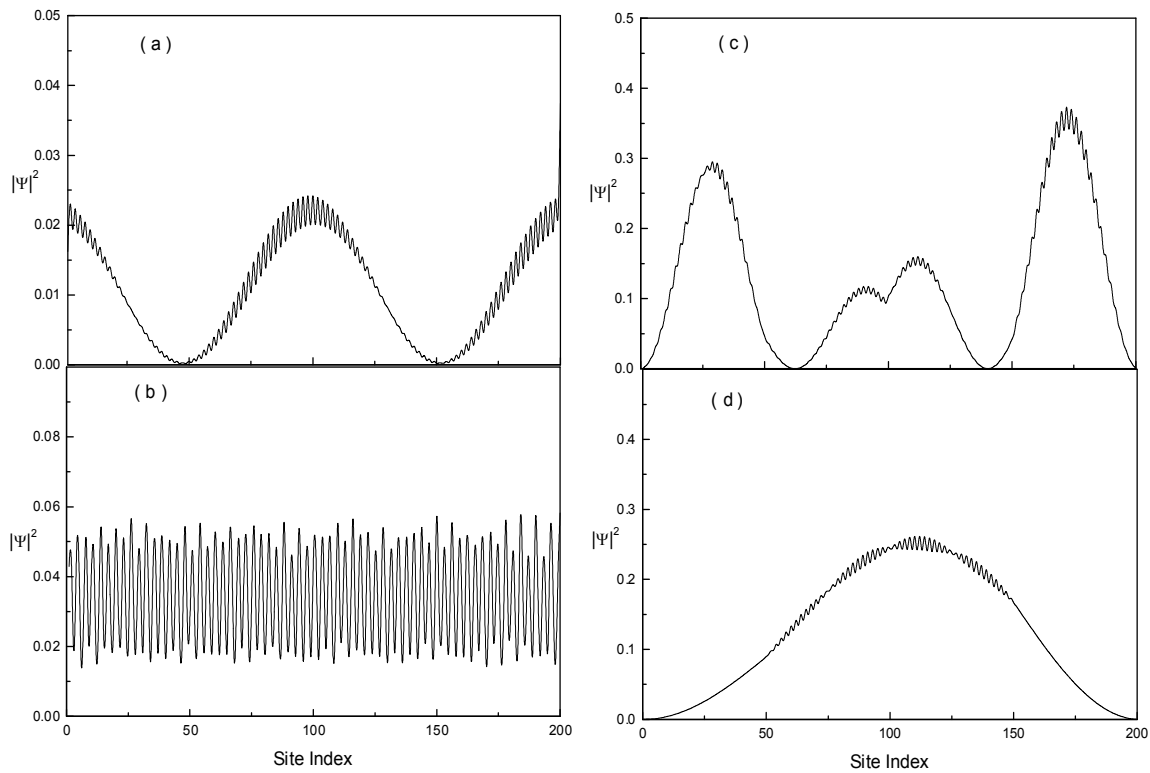


Figure 4. Magnitude of the wave function $|\Psi_E|^2$ for a typical *trans*-PA chain with $N=200$ atoms. In each case the eigenvalue of number 101 (near to Fermi level) has been considered; for a fully dimerized chain; (b) $|\Psi_E|^2$ in presence of homogeneously soliton distributions with 6% concentration; (c) and (d) show $|\Psi_E|^2$ for 4 clusters (each cluster with 3 solitons), a cluster (with 8 solitons) plus some single solitons with randomly distributed, respectively.

concentration of solitons has been taken to be 6%. In this figure the eigenvalue number 101 (close to Fermi level) has been considered. Figure 4(c) shows $|\Psi_E|^2$ for the same eigenvalue in the presence of 4 clusters such that each cluster contains 3 solitons. Figure 4(d) shows a similar situation for the cluster plus a disordered distribution of single solitons on the chain. We can see from this figure that, at the considered soliton concentrations here, the calculated wave functions (for distributions of clusters and randomly distributed single solitons) are delocalized, i.e., a metallic regime can be attained for disordered distributions of solitons. In this special situation the DOS has finite value at the Fermi level and the corresponding eigenfunctions are

delocalized around the Fermi level, thus characterizing a true metal.

4. Summary and conclusions

We have applied some known numerical procedures and models such as Lanczos algorithm, a generalized Green function method in the Continued-Fraction Representation (CFR) as well as SSH model for studying the semiconductor-to-metal transition in *trans*-PA chains. We have shown that it is possible to obtain extended electronic states in the presence of correlated (cluster) and disordered soliton distributions in *trans*-PA chains, which is the most significant condition to true metallic behavior.

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