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Numerical study of localized electronic states in disordered and doped conjugated polymers

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bstract The nature of electronic states in disordered and doped π-conjugated polymers is investigated. By means of a direct diagonalization cedure (Lanczos algorithm) and use of Continued Fractions Representation (CFR) we study, within the Su-Schrieffer-Heeger (SSH) model, numerically effects of site and bond-type model impurities and solitons (geometrical defects in polyacetylene) on the electronic structure of *trans*-polyacetylene nd polythiophene. We find that for energy eigenvalues equal to the impurity levels, electronic states are localized. Also for each soliton, there exists localized electronic state which is situated at the midgap. Our results show (due to Peierls-distortion) that even in critical concentration (~ 10%) of ndom distribution of solitons, the bandgap will not be closed

ywords Disordered polymers, numerical study, localized electronic states

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. Introduction

uring the past two decades, much effort has been devoted to understanding of π-conjugated polymers [1-7]. From hysical point of view, most interest has been on the structural, lectronic and conduction properties. Among various types of olymers, poly-acetylene (PA), especially *trans*-polyacetylene, nd polythiophene (PT) have drawn much attention of the esearchers. This has been due to the fact that while being the implest π-conjugated polymers, they also have considerable otential applications as alternative conductors. For example he possibility of the metal-insulator transition and the capability f becoming a very conductive material like copper [7] has been he reason for the experimental and theoretical investigations n the physical properties of PA in comparison to the other ype of polymers. There are many articles concerning the study f ground and excited states of these quasi-one dimensional ystems [7-13]. At present, however, some of the most interesting nd active research areas are the study of the effects of disorder nd impurities upon π-electrons' behaviour, lattice-relaxation nd on the increasing of conductivity. The factor that directly affects the conductivity of this system has been found to be the appearance of the localized electronic states due to the presence of impurities and defects. In this paper we present a detailed numerical study of this aspect of the problem by means of direct diagonalization [14] and use of Continued-Fractions Representation (CFR), and thus we investigate the effects of model impurities (site and bond-type) and solitons (geometrical defects in PA structure) on π-electrons wave functions. The paper is organized as follows :

In Section 2, we introduce the model Hamiltonian and then describe the method for calculation of the density of states (DOS) of π-electrons. In Section 3, the effects of the impurities and defects on the electronic structure are presented. In general, we find that (i) Site and bond-type model impurities produce localized electronic states in bandgap (intragap states) and beyond the energy bands (ultraband states). In addition, there may be other localized electronic states which are situated at the center of the gap and are produced by the presence of one or several solitons. (ii) For low concentration of impurities the polymeric chain preserves its main periodic characteristics and one is able to use the CFR scheme just as one does for a regular chain. In Section 4, the magnitude of the wave functions, $|\psi|^2$, for some typical samples is calculated. We find that the wave

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functions are well localized around site and bond-type impurities for the states at the upper edge of each band but they have semilocalized behaviour for energy values at the lower edge of the same band. Finally, Section 5 gives a summary and the conclusions.

2. The model Hamiltonian and description of the method

There are many conjugated polymers with similarities and differences in their structural, electronic and conduction properties. Compared to the others, however, *trans*PA (and also PT) has a very simple geometrical structure and may become highly conductive. Thus, the investigations of its physical properties has been the center of attention for the last decade.

To present a correct theoretical model it becomes necessary to understand the structural and electronic characteristics of π-conjugated polymers. As pointed above, PA has a very simple structure so that each monomer only contains carbon and hydrogen atoms. All of the polymer atoms lie in one plane and the carbon atoms are SP^2 hybridized. The SP^2 hybridized carbon atom has two types of bond, the three σ-bonds in the plane of the polymer and the π-bond perpendicular to this plane. In molecules with SP^2 hybridized carbon atoms, it is often sufficient to take only the π-electrons into account to calculate the electronic properties. This is due to the fact that the σ-bonds forms completly filled bands in considerably lower energies, whereas energies at and around the Fermi level coincide with the π-electrons and so the π-bonds lead to the partially filled energy band that is responsible for the significant electronic properties of PA. The two-fold degeneracy in ground state of *trans*-PA is another important characteristic of this quasi-one dimensional system. Addition of charged dopants, creates geometrical defects in the polymer. In PA these defects, as the most important excitations, are 'solitons' [1]. The soliton defect changes the geometry from one ground-state into the other and the lattice potential energy decreases due to the presence of the defect, so the soliton formation energy is quite small. PT, on the other hand, is a specific example of a π-conjugated polymer in which the ground-state degeneracy is weakly lifted and the important excitations are polarons and bipolarons [7].

2.1. The model Hamiltonian :

The following generalized Hamiltonian is used for description of doped PA

$$H = H_{SSH} + H_s + H_b, \tag{1}$$

where H_{SSH}, H_s and H_b are the well-known *SSH* Hamiltonian [1, 15], the site-type model impurities Hamiltonian and the bond-type model impurities Hamiltonian, respectively. For the *SSH* Hamiltonian we have

$$H_{SSH} = -\sum_n [t_0 + \alpha(u_n - u_{n+1})]\left(|n><n+1| + |n+1><n|\right)$$

$$+\frac{1}{2}K\sum(u_n - u_{n+1})^2 + \sum\frac{P_n^2}{2M} \tag{2}$$

in which the first term is the π-bond electronic energy t_0 the nearest-neighbour transfer integral of an undimerized chain α the electron-phonon coupling constant and $|n>$ is the stat vector of π-bond on the n-th carbon atom. The reference energ is chosen such that the carbon onsite energy is zero. The secon term in eq. (2) approximates the effect of σ-electrons using stiffness constant K which is determined both by the direct ion ion interactions and by the σ-electron interactions M is th mass of a (CH) unit, u_n the displacement of the n-th carbon ato from its equilibrium position and P_n is the momentum conjuga to u_n. The spin and e–e interaction are ignored and the periodi boundary conditions is applied. Throughout this paper for bandgap $2\Delta_0 = 1.4\ eV$, we shall use the parameters of Ref

So, $\alpha = 4.1eV/\mathring{A},\ K = 21eV/\mathring{A}^2,\ t_0 = 2.5eV$ These correspond to a equilibrium dimerization amplitude $u_0 \approx 0.0$

The H_s Hamiltonian is given by

$$H_s = \sum |m> V_m^s <$$

in which the local potential $\pm V_m^s$, corresponds to the accepto type (for sign +) or the donor-type (for sign –) impurity at m site. The bond-type impurity Hamiltonian is given by

$$H_b = \sum V_m^b\left(|m> < m+1| + |m+1> < m|\right)$$

where V_m^b is the bond-type impurity strength acts on the b between sites m and $m+1$. $V_m^b < 0$ ($V_m^b > 0$) leads to intrag states (ultraband states).

The above discussion may be extended to build the mod Hamiltonian for PT. For this purpose and also to model th explicity lifting of the ground state degeneracy, one can add th following term to SSH Hamiltonian [16]

$$\Delta H = \Delta_e \sum (-1)^n\left(|n>< n+1| + |n+1>< n|\right), \qquad ($$

in which $\Delta_e << \Delta_0$ modulates the one-electron potential thereb giving rise to a one-electron energy gap in the absence o lattice distortion [7].

2.2 Description of the method :

To study the impurity states, solitons and their effects on π electrons wave functions, we present our method for th calculation of these effects on the electronic structure. Takin the lattice to be homogeneously dimerized, *i.e.*, neglect of a lattice relaxation due to the electron-phonon interactio (following Ref. [17]), the advanced and retarded temperatu double-time Green functions are written

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

$$G^{\pm}_{nm}(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dEe^{-iEt}G^{\pm}_{nm}(E\mp i\eta)\,;\;\eta\to+0. \qquad (7)$$

In eq. (6), $\theta(t)$ is Heaviside step function, $a_n(a_n^{\dagger})$ nihilation (creation) operator of an electron at n-th site and gular braket denote the thermodynamic average. The set of uations of motion for Green function matrix element $_{nm}(E\mp i\eta)=G^{\pm}_{nm}(\omega_{\mp})$ with $\omega_{\mp}=E\mp i\eta$ can be written as 8]

$$(\omega_{\mp}-\varepsilon_n)\,G^{\pm}_{nm}=\delta_{nm}+t_{n-1,m}G^{\pm}_{n-1,m}+t_{m,n+1}G^{\pm}_{m,n+1}. \qquad (8)$$

Throughout this study, ε_n and t_n are onsite energy (is ken to be zero) and nearest-neighbour transfer integral, spectively. Our task is to evaluate the diagonal Green function $_{nn}$, the imaginary part of which gives the local density of ates $\rho_n(\omega_{\mp})$. Considering only the retarded Green function $_{nn}(\omega_+)=G_{nn}$ with $\omega_+=\omega$, then $\rho_n(\omega)$ is given as

$$\rho_n(\omega)=-\frac{1}{\pi}\lim_{\pi\to 0}\mathrm{Im}\left\{G_{nn}(\omega)\right\};\;\omega=E+i\eta. \qquad (9)$$

ollowing Ref. [18], the diagonal matrix element $G_{nn}(\omega)$ an be represented as

$$G_{nn}(\omega)=\frac{}{\omega-\varepsilon_n-\Gamma_n^- -\Gamma_n^+}, \qquad (10)$$

where the self-energies $\Gamma_n^{\pm}$ are given by Continued-Fractions

$$\Gamma_n^- = \cfrac{t^2_{n-1,n}}{\omega-\varepsilon_{n-1}-\cfrac{t_{n-1,n-2}}{\omega-\varepsilon}}$$

$$\Gamma_n^+ = \cfrac{t_{n,n+1}}{\omega-\varepsilon_{n+1}-\cfrac{t^-_{n+1,n+2}}{\omega-\varepsilon_{\dots}}} \qquad (11)$$

The CFR of the one-particle Green functions has already been widely used for tight-binding electrons [18, 19] and different methods have been applied to obtain a suitable convergence. It should be noted that, however, most studies have been aimed at getting the electronic band structure of non-translationally invariant systems. Here, one usually starts from the local environment the atom and using approximate methods to obtain the convergence by termination of the Continued-Fractions [18]. The advantages of the CFR become clear when treating the π-conjugated polymeric chain, as the periodic nonuniform systems (alternating bond). In the case of perfectly dimerized, these chains have bonds as ... $t_+t_-t_+t_-$ ... leading to exact values for the Continued-Fractions (11). If $t_+=t_-$ with period 1 is defined as a basis for comparison (uniform chain) then for $t_+\neq t_-$ the Continued-Fractions (11) will have a period 2 and can be written

$$\Gamma_n^-=\frac{t_-}{\omega-\Gamma_n^+}\qquad \Gamma_n^+=\frac{}{\omega-\Gamma_n} \qquad (12)$$

For perfectly dimerized PA with $u_n=(-1)^n u_0$ and $2\Delta=8\alpha u_0$, one obtains $t_{\pm}=\left[t_0\pm\frac{1}{2}(-1)^n\Delta_0\right]$ in which (with $\varepsilon_n=0$) $\Delta_0=1.4\,eV$ is magnitude of the bandgap. Solving eqs. (12) for $\Gamma_n^{\pm}$, the following form will be resulted for $G_{nn}(\omega)$:

$$G_{nn}(\omega)=\pm \qquad (13)$$

in which $\beta(\omega)=\left[(\omega^2-t_+^2-t_-^2)^2-4t_+^2t_-^2\right]$. With $\eta\to 0$, *i.e.*, for $\omega=E$ the dominator in eq. (13) is real and nonzero within the regions $(t_+^2+t^2)<E^2<t_+^2-t_-^2$, but it is imaginary for $t_+^2-t_-^2<E^2<(t_+^2+t_-^2)$. It follows that the density of states $\rho_n(E)$, is finite in latter region and is given as

$$\rho_n(E)=\frac{E}{\pi\sqrt{\beta(E)}}. \qquad (14)$$

It is clear that $\rho_n(E)$ vanishes in the former region. Calculating $\rho_n(E)$, one can find the expected electronic structure of PA (or PT) in which valance and conduction bands separated by a gap of width $2\Delta_0$ (for further details Ref. [18] is recommended). It is straightforward to extend this analysis to higher periods of 2 and there are no principal difficulties in proceeding the analytic calculations of $\rho_n(E)$ for larger periods, except that they become more cumbersome [20].

The energy eigenvalues spectrum $\{E\}$, and the corresponding electronic wave functions $\{\psi\}$, are calculated using a direct diagonalization procedure based on the Lanczos algorithm [14]. This diagonalization method is known to be very efficient for large matrices. We applied this method to the Hamiltonian (2) with the periodic boundary conditions and the resulting energy spectrum was used to calculate the electronic DOS. The results of the numerical calculations for the DOS of a perfectly dimerized PA (PT) chain is presented in Figure 1.

3. The effects of the impurities and solitons on the electronic structure

Although in general, the CFR is not applied to disordered systems containing a random distribution of impurities, our results show so far as the concentration of dopants is taken to be small ($\leq$ 10% in a long chain), the system under consideration preserves the homogeneously geometrical periodicity and one can extend the use of CFR together with the recursion method (its main advantage is its high numerical stability) in case of such irregular systems. A complete formalism and discussion of the method may be found in Ref. [21]. We used this method for calculation of the DOS, and we found that for *trans*-PA chains containing dopants in which the Hamiltonian (with nearest-neighbour interactions) has a tridiagonal representation, the Continued-Fractions for self-energies $\Gamma_n^{\pm}$ became quickly convergent and in comparison to the results of Section (2), these new results indicate, no principal changes. Similar applications of this procedure may be found in the literature, for example we refer to the well-known papers of Turchi *et al* [20], Haydock *et al* [22], and Wiessmann and Cohan [23].

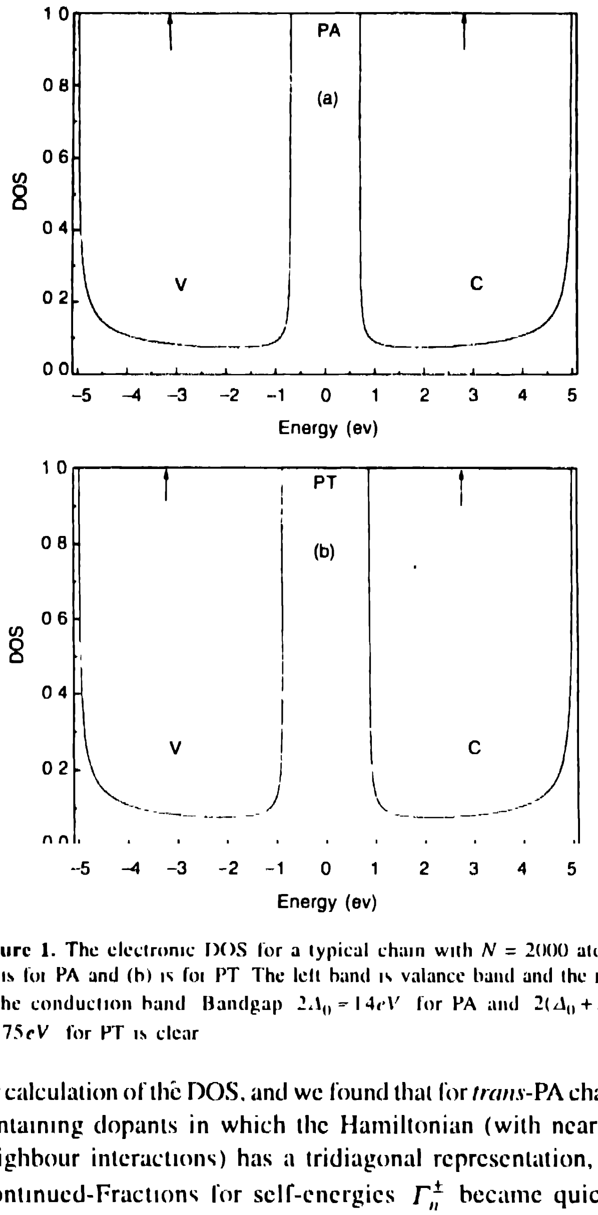

Figure 1. The electronic DOS for a typical chain with $N = 2000$ atoms (a) is for PA and (b) is for PT The left band is valance band and the right is the conduction band Bandgap $2\Delta_0 = 1.4eV$ for PA and $2(\Delta_0 + \Delta_e) = 1.75eV$ for PT is clear

3.1 Site, Interstitial and bond-type impurities :

It is well-known that the ground-state of the Hamiltonian (2) with one-electron per site (*i.e.*, in the half-filled band problem), is dimerized and a bandgap $2\Delta_0$ is opened at the Fermi level separating the states of the filled valance band from those of the empty conduction band. Adding one or several impurities of either type (interstitial-type or site and bond-type impurity) and the creation of solitons markedly affect the electronic structure. Our calculations confirm the above statements which are discussed in detail below.

The experimental measurements [24-26] indicate that the enhancement of impurity concentration of either type in the 'pristine' samples of PA, cause to increase the conductivity Thus, for high doping concentrations (~ 10%), contrary to the conventional semiconductors the metal-insulator transition occur in these materials and even the 'best' samples become metalic with a nonzero conductivity at zero temperature [27]. Throughout this study, the maximum percentage of the impurities and solitons is taken to be 8% and 10%, respectively.

Another important point is that in the presence of impurities the localized electronic states occur in the forbidden energy regions, *i.e.*, in the bandgap (intragap states) as well as beyond the electronic structure, *i.e.*, below the bottom of the valance band and above the top of the conduction band (ultraband states). The single-impurity problem has already been studied widely by different methods [7,28,29]. Thus in this section, we present our results on the effects of random distribution of impurities of either type on the electronic structure and in the next section we will discuss the localization of electronic state and show that the localized electronic states occur at the energy eigenvalues equal to the impurity levels

Our studies started with considering a perfectly dimerized lattice, where we investigated the effects of distortions due to introducing of impurities, on the electronic structure of system. In order to discuss the effects of a random distribution of site type impurities, we added the Hamiltonian (3), *i.e.* $H_s = \sum_m m > V_m^s < m$ to SSH Hamiltonian in which the V_m^s are independent variables that, with a finite concentration (0.08 in our samples), randomly occupy the lattice sites $V_m^s < 0$ $(V_m^s > 0)$ corresponds to impurity of donor (acceptor) type. In general, the enhancement of the $|V_m^s|$ causes the increase of the magnitude of the wave function at impurity sites The details of our investigations of the effect of various kinds of impurities are discussed below :

(i) $V_m^s < 0$ (donor-type impurity) produces localize electronic states at the bottom of the conduction band (intragap states) as well as the bottom of the valance band (ultraband states). For deeper impurity potential, *i.e.*, larger $|V_m^s|$, the intragap energy states are extended towards the midgap ($E = ($ while those at the bottom of valance band approach to ve large negative energy values (Figure 2(a)).

(ii) For $V_m^s > 0$ (acceptor-type impurity) the similar behavio is observed, *i.e.*, we obtain the strongly localized states at t top of conduction band and weaker localized states at the top valance band (Figure 2(b)).

(iii) We also investigate another impurity distribution in whi the impurities settle in the interstitial regions. Such impuriti modify the electronic onsite energy on both ends of the bo by the same amount, so we simulate this type of model impuri as a distribution of paired-sites randomly placed on the chain. In comparison to the site-type model impurity, we find that the electronic structure undergoes only a few modifications. Figure 2(c) shows this situation. Introducing these type of impurities into the sample of Figure 1, the results for $C = 0.08$ and $|V_m'|= 0.4\,t_0$ are ploted in Figure 2. The study of these figures show that, as expected, the site-type impurities destroy the intrinsic electron-hole symmetry of the SSH Hamiltonian [1]. Therefore with this type of impurities the electronic structure (the bandgap and the edges of band) to be changed nonsymmetrically. On the other hand, however, a random distribution of bond-type impurities does not affect the symmetry.

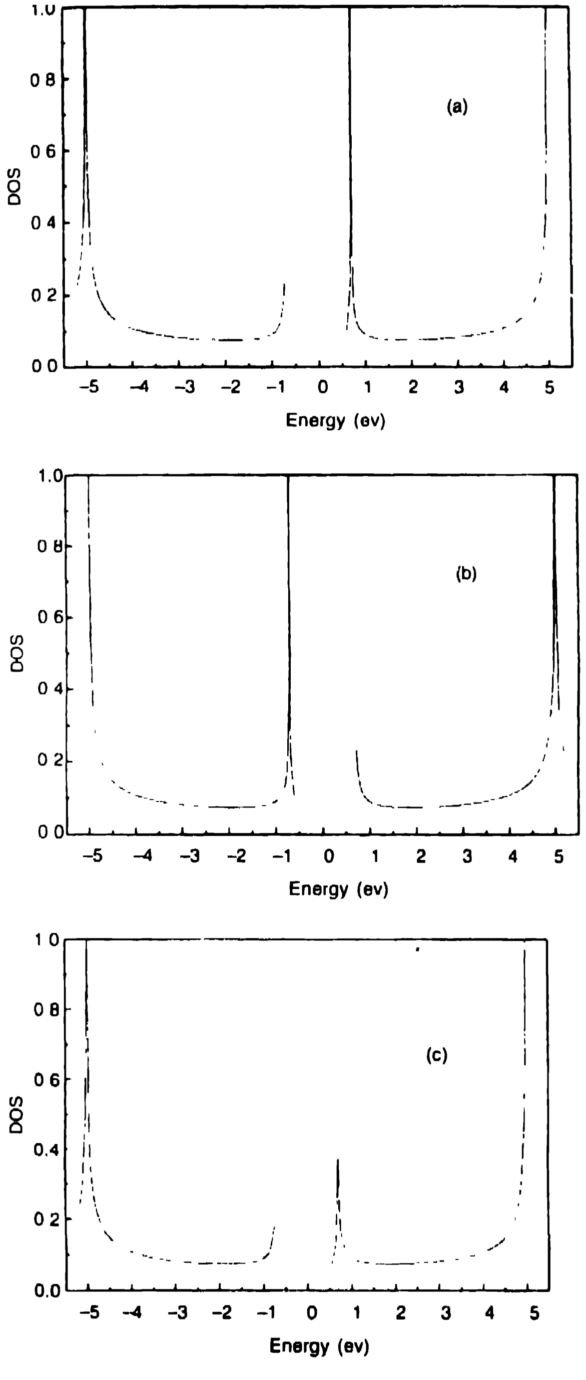

Figure 2. The DOS of *trans*-PA chain with site-type impurities The concentration of impurity is $C = 0.08$ (a) is for $V_m' = -0.4t_0$ (donor). (b) is for $V_m' = +0.4t_0$ (acceptor) and (c) is for impurities of interstitial-type with the same parameters in (a).

The addition of the Hamiltonian (4), *i.e.*, $H_b = \sum_m V_m^b(|m> <m+1|+|m+1> <m|)$ to SSH Hamiltonian induces states due to bond-type impurities. These localized states always occur in pairs, symmetrically located with respect to midgap ($E = 0$). For $V_m^b > 0$ always produces a pair of ultraband states If the sign of V_m^b is chosen such that strengthens a weak bond or weakens a strong bond, then a pair of intragap states is produced. Figure 3 shows this situation for $C = 0.08$ of bond-type impurities with $|V_m^b|= 0.2\,t_0$.

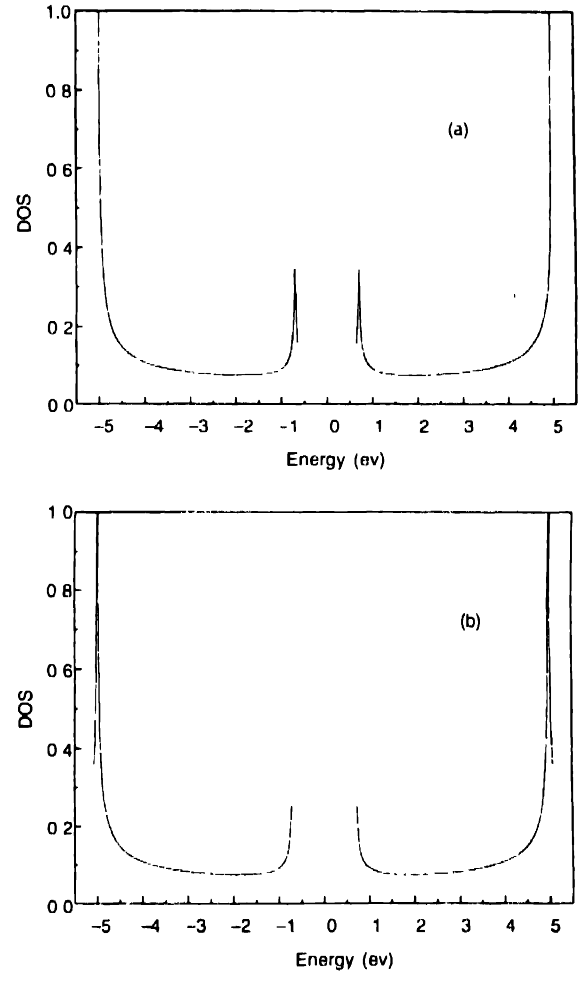

Figure 3. The DOS of *trans*-PA chain with bond-type impurities The concentration of impurity is $C = 0.08$ with $|V_m^b|= 0.2t_0$ (a) is shown intragap and (b) ultraband states

3.2 Solitons :

The solitons in PA that can propagate freely, are domain walls between the two degenerate phases of dimerization, a phase with ($+ u_0$) and the other with ($-u_0$). We are interested in those general properties of the solitons that depend on symmetries of the Hamiltonian (2). For a long chain, a soliton corresponds to a phonon field configuration that approaches the phase (+ u_0) for $N \rightarrow -\infty$ and the phase ($-u_0$) for $N \rightarrow +\infty$, and also minimizes the total energy [1]. In the presence of a soliton the total number of electrons or states in the filled valance band in the vicinity of the soliton decreases by one-half [7], so that if one calculates the energy to create a soliton in a large but finite chain, a difficulty arises. To overcome this problem and to make sure that the total number of states in the valance band is an integer, it is suggested that following the creation of a soliton, an antisoliton to be created, too [1]. Accordingly, there is a valance band depletion of one state. Our results show this electronic state is produced at top of valance band at $E \approx -0.33\, eV$. As discussed before, from the electron-hole symmetry of the SSH Hamiltonian it follows that one state is also missing from the conduction band. This electronic state is produced at the bottom of conduction band at $E \approx +0.33\, eV$. The peaks numbered 1 and 2 in Figure 4(a) show this situation. Any increase in the number of solitons is directly proportional to the number of these symmetrically paired-states. Thus, the solitons in undoped polyacetylene structure are directly responsible for narrowing of the bandgap. We find that for one soliton, the bandgap is lowered about 0.1 eV. Our investigations suggest that even if the increase of concentration of solitons, with a random distribution, approaches the critical amount (~ 10%) the bandgap will not close. In general, due to Peierls – distortion, the system remains insulating for all doping levels. In order to observe how the bangap is suppressed, one needs to consider three-dimensional (3D) effects. Adding interchain interactions in 3D-polymeric systems leads to the gapless state [13]. As the interchain interaction is turned on the bandgap is reduced and closed at a certain critical concentration of solitons.

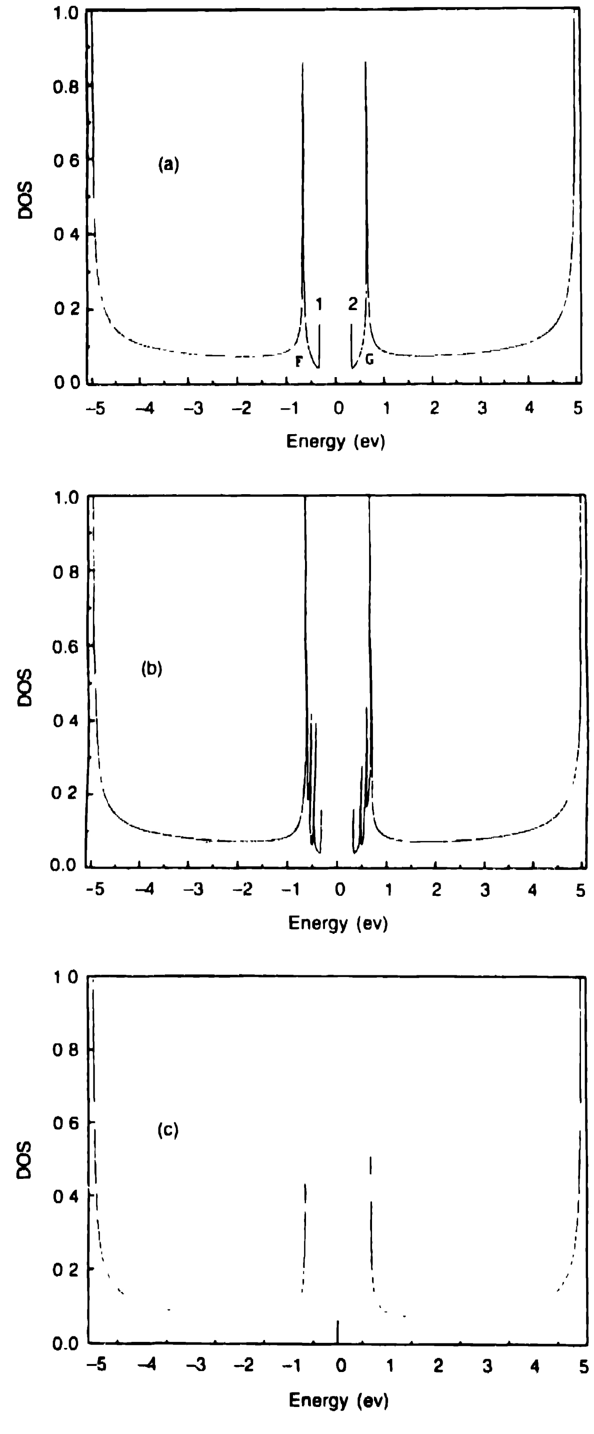

Figure 4. The electronic structure of *trans*-PA in the presence of solitons (a) is for one soliton. The peaks 1 and 2 are discussed in the text (b) is for three solitons (c) shows the localized electronic state at midgap.

In the perfectly dimerized *trans*-PA, the displacements of the carbon atoms are described by $u_n = (-1)^n u_0$. In the presence of solitons these displacements are determined such that to minimize the total energy and to give the optimum shape for the soliton. Accordingly, the displacements of the carbon atoms are modeled as [30, 31]

$$u_n = (-1)^n u_0 \prod_m \tanh\left[\frac{(n-m)a}{\xi}\right] \tag{15}$$

where $2\xi \approx 14a$, with $a = 1.22$ Å (lattice constant), is the width of a soliton. (ma) is the location of the center of m the soliton on the chain. In our model, the m variables are generated such that the domain walls do not overlap. For values of the parameters α, K, u_0 and ξ, the soliton formation energy at rest is $E \approx 0.6\Delta_0$ eV [1]. Since the chemical potential is midgap for the undoped sample, this shows a soliton is less costly to create than an electron (hole). It is for this reason that solitons are spontaneously generated when charged dopants are injected into the sample [7]. Figure 4(a) shows one soliton at the center of the chain and Figure 4(b) shows three solitons with centers symmetrically placed with respect to the center of a chain with $N = 2001$ atoms, respectively. When a soliton is created a localized electronic state is produced at the midgap. In fact it is a combination of the symmetry states 1 and 2. Figure 4(c) shows this state (for more clarity the intragap states F and G are not shown). The presence of the intragap states F and G is obvious. Because when a soliton is created (in our model at site $m = 1001$) on a dimerization phase (+ u_0 or $-u_0$), the single-bonds (weak) and the double-bonds (strong) are interchanged with each other (Figure 5). Now, compared with the results of Subsection 3.1,

Figure 5. The scheme of a soliton in PA. the soliton changes the dimerization from one ground-state to the other, *i e*, the single and double-bonds are interchanged. The length of the soliton has been reduced for clarity

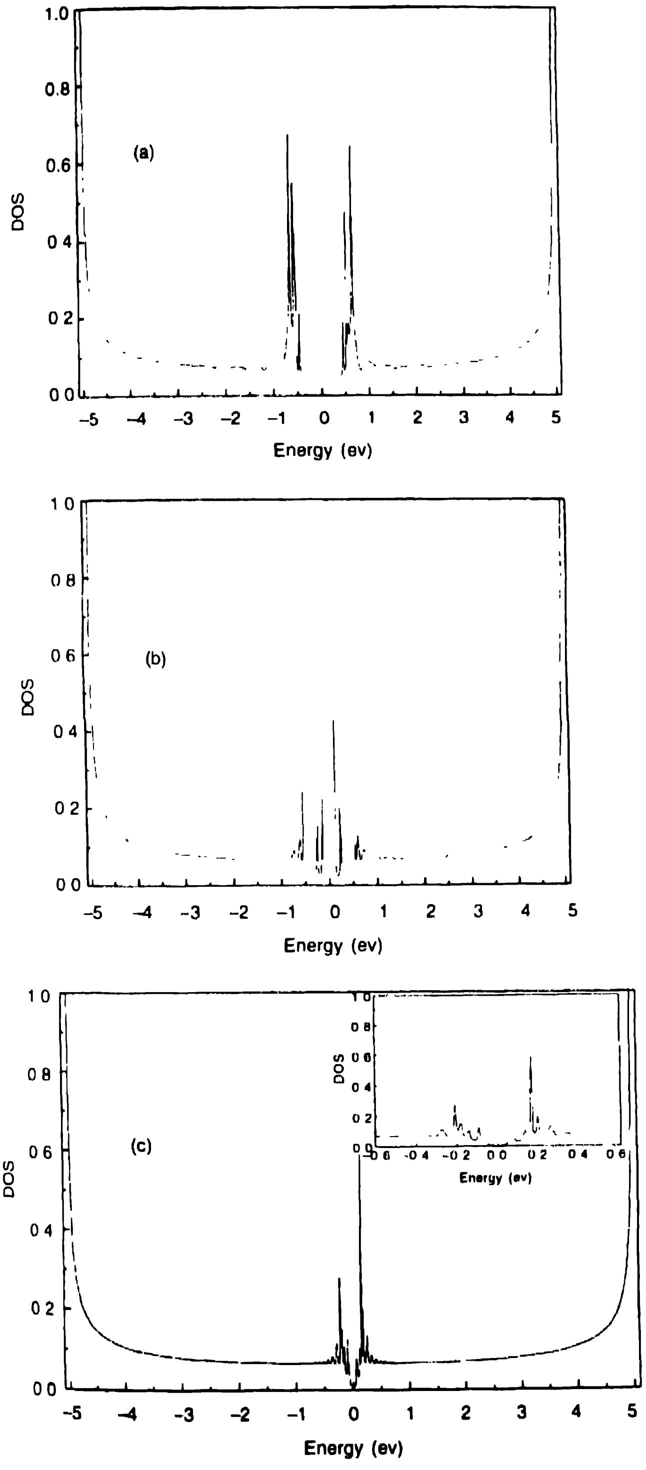

Figure 6. The electronic structure of a *trans*-PA chain in the presence of randomly distributed solitons. In (a) the concentration is $C = 0.02$, (b) $C = 0.05$ and (c) $C = 0.1$ The inset shows near the midgap.

this situation corresponds to the case of bond-type impurity which leads to intragap states. In our model, the centers of the solitons are placed at fixed distances from each other and from the chain ends. The distribution of solitons remain symmetric, with respect to the center of chain, up to certain concentration and beyond that we have a random distribution for the solitons. To ensure that the first and the last bond of the carbon chain remains a double bond, we have placed an even (odd) number of solitons on chains with an even (odd) number of carbon atoms.

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 [31]. 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 PA. Figure 6 shows the effect of different concentrations of the solitons on the electronic structure of a chain with $N = 2000$ atoms. Figure 6(c) suggested that even in critical concentration (~ 10%) with random distribution of solitons, the bandgap is not closed.

In Figure 7, we have shown the magnitude of the wave function $|\psi_0|^2$, associated with the localized electronic state at the midgap for a typical sample with $N = 201$ atoms. The localized state is exponentially confined around the soliton to the region with the approximate width ξ. Since in our model, the center of the soliton is placed on site $m = 101$ (odd), then by symmetry, $|\psi_0|^2$ is only non-zero on odd sites.

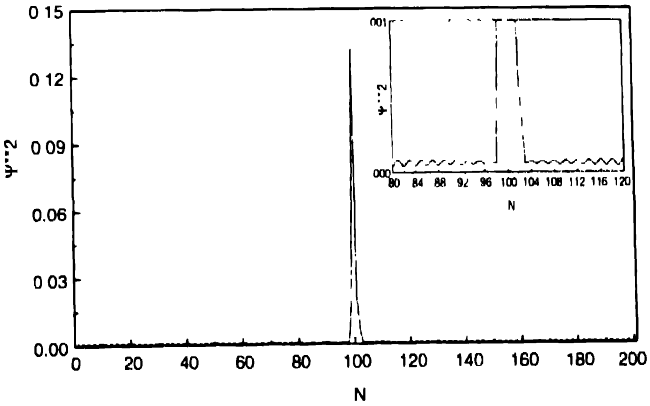

Figure 7. The magnitude of the wave function, $|\psi_0|^2$, for the localized electronic state at the midgap The inset shows the region with the approximate width ξ

4. The localized impurity states

To study the π -electrons behaviour, we calculated numerically the magnitude of the wave function, $|\psi_0|^2$, for those energy eigenvalues where the impurity levels occur. We apply the direct diagonalization to the electronic part of the Hamiltonian (2) with the periodic boundary conditions. The π -electrons are scattered when encountered by the impurities that act as forward (site-type impurity) or backward (bond-type impurity) scattering centers. Therefore one expects that the amplitude of the wave function to increase around the impurity. In other words, there occurs 'localization', which means that the amplitude of the wave function becomes very large around the impurity in a limited region and decays rapidly outside this region The localization mostly occurs exponentially (in the regime of strong localization), *i.e.*, the asymptotic behaviour of the magnitude of the wave function is given as $|\psi(r)|^2 \sim e^{\frac{|r|}{\lambda}}$ [32], where λ is the localization length and $|r|$ is the distance from the center of the localized wave Our results show that the wave functions of the π-electrons are localized at the location of the impurity levels (according to the sign of impurity potential) and this localization is strong for the energy eigenvalues above the conduction band (ultraband states) and weaker for the intragap states. Figure 8 shows the magnitude of the wave functions, $|\psi_E|^2$, (correspond to Figure 2(b)) for energy eigenvalues at the upper edge of a certain site-type impurity band. The concentration of impurities is chosen to be $C = 0.08$, and the strength of impurity potential is chosen to be $V_m^s = +0.4\, t_0$ (acceptor-type). It is clear that for the eigenvalue number $E = 199$ (above the conduction band) the magnitude of $|\psi_E|^2$ is larger than that for $E = 99$ (above the valance band). In other words, the former is localized and the latter has only semi-localized behaviour.

According to the above discussion, it is expected that for $V_m^s < 0$ (donor-type) the states at the bottom of the conduction band have semi-localized behaviour and at the bottom of the valance band extended. Figure 9 shows the wave function behaviour for eigenvalues number $E = 103$, 104 (the bottom of the conduction band) for $C = 0.08$ and $V_m^s = -0.4\, t_0$

Figure 10 shows the results of bond-type impurities with concentration $C = 0.08$ and the strengths of the potential $V_m^b = -0.2\, t_0$ (the intragap states) and $V_m^b = +0.2\, t_0$ (the ultraband states). In general, we find that the states at the upper edge of a certain band are localized around the impurities while the states at the bottom of the same band have only semi-localized behaviour.

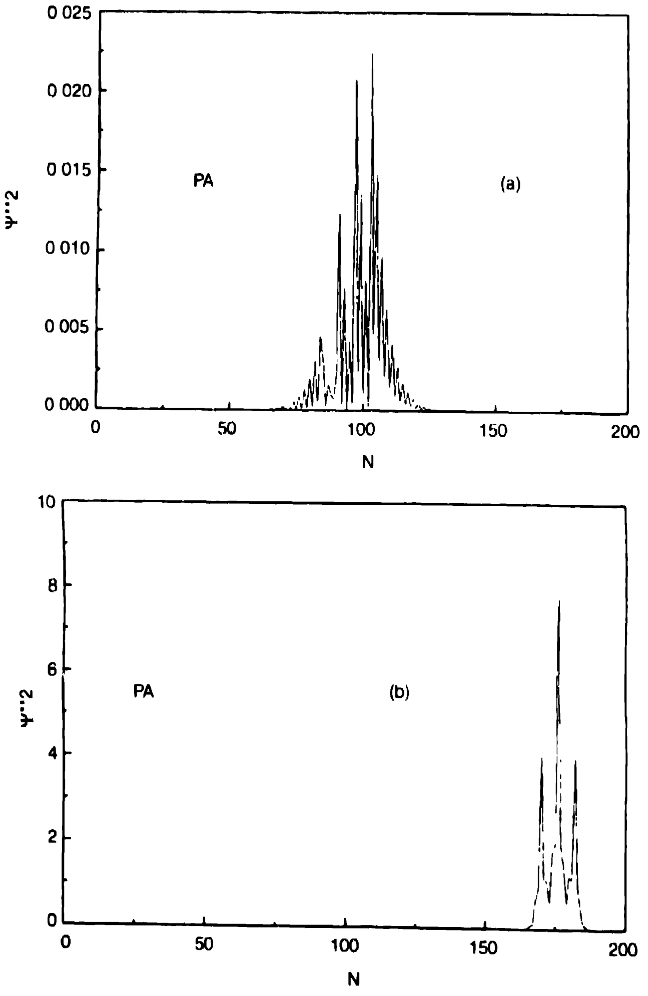

Figure 8. Magnitude of the wave function, $|\psi_E|^2$, for a typical sample contains acceptor-type impurities with $N = 200$ atoms $C = 0.08$ and $V_m^s = +0.4\, t_0$ are chosen (a) is for $E = 99$ (the top of the valance band) and (b) is for $E = 199$ (the top of the conduction band)

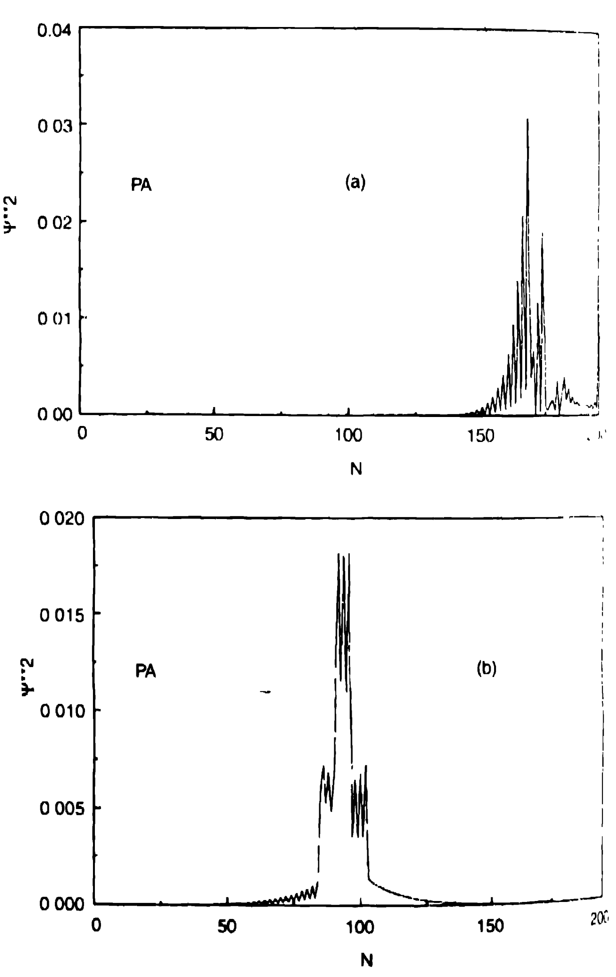

Figure 9. Magnitude of the wave function, $|\psi_E|^2$, for a typical sample contains donor-type impurities with $N = 200$ atoms. $C = 0.08$ and $V_m^s = -0.4\, t_0$ are chosen. (a) is for $E = 103$ and (b) is for $E = 104$ (the bottom of the conduction band).

Summary and conclusions

In this paper, we have investigated in detailed the effects of several kinds of impurities and also solitons on the electronic structure of π-conjugated polymers. By means of a direct diagonalization procedure we found numerically the energy eigenvalue of the Hamiltonian (2) and corresponding eigenfunctions. Using the Continued-Fraction Representation (CFR) we have calculated the density of states (DOS) for some π-conjugated chains (PA and PT) in the presence of impurities and solitons. We conclude that using the CFR for above samples leads to acceptable results. Furthermore, we have numerically studied the nature of the π-electron states in *trans*-polyacetylene with site and bond-type model impurities. We find that the strongly localized states occur at the upper edge of a certain band.

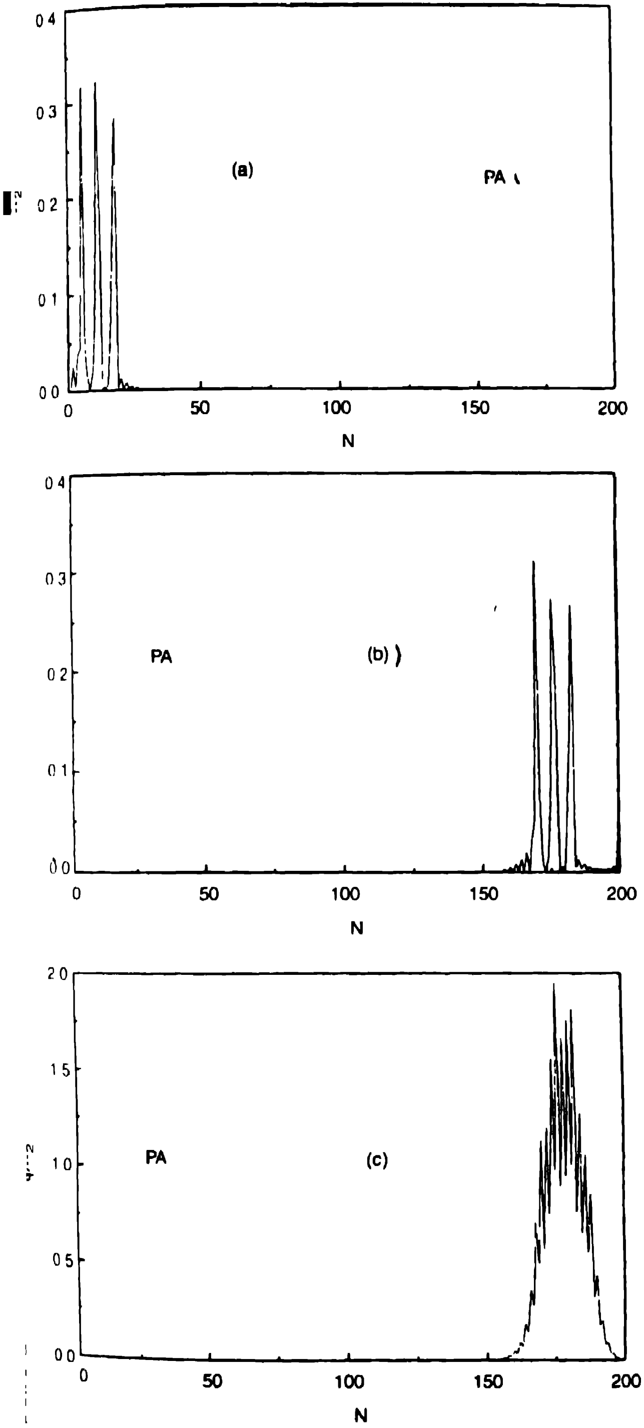

Figure 10. Magnitude of the wave function, $|\psi_E|^2$, for a typical sample contains bond-type impurities with $N = 200$ atoms In (a) and (b) $C = 0.08$ $= -0.2\, t_0$ are chosen. (a) is for $E = 99$ (the top of the valance band) d (b) is for $E = 102$ (the bottom of the conduction band) (c) is for $E =$ 99 (the top of the conduction band) and $V_m^b = +0.2\, t_0$ (correspond to the ultraband states)

The effect of the presence of solitons on the electronic structure was also studied by this procedure. We see that as a result of the electron-hole symmetry of the SSH Hamiltonian, the paired-states is produced per soliton and a localized electronic state occurs at the midgap. To extend this study to the case of Anderson localization and also the investigation of conductivity, it is important to consider three-dimensional situations with interchain interactions. Calculations in this direction are in progress and the results will be presented in near future.

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