Theoret. Chim. Acta (Berl.) 63, 1–8 (1983)

THEORETICA CHIMICA ACTA

Localized States in Polymeric Molecules III The Electronic Structure of Polyacetylene*

Celso P. de Melo, Humberto S. Brandi** and Alfredo A. S. da Gama

Departamento de Física, Universidade Federal de Pernambuco, 50.000 Recife-PE-Brasil

The Transfer Matrix approach is used to treat the relaxed defect problem in trans-polyacetylene. We use a particular choice of parametrization for the hopping integrals, which is related to the existence of solitons in this material, to discuss its electronic structure. We obtain closed expressions for the density of states and for the wavefunctions associated to the localized state at any site of the chain.

Key words: Polymer – Localized states – Electronic structure.

1. Introduction

Polymers have been subject of intensive studies during the past decade due to the important role they play in different areas of biological, chemical and physical sciences. There is an increasing evidence that several fundamental processes are intrinsically related to the specific details of the electronic structure of these molecules. In this context localized states induced by conformational changes, or associated to the presence of impurity or defect, are of great significance. For instance the induced-fit changes caused by substrate molecules modify the spacial configuration of enzymes which are essential to catalytic reaction [1]. Small concentrations of transition element ions in the metallo-proteins have an effect of catalysing electron transfer processes. On the other hand, the existence of defect can greatly modify the electrical conductivity of these molecules. In fact, one of the most studied polymers is trans-polyacetylene, trans-$(CH)_x$, whose conductivity experiments an enhancement over 10 to 12 orders of magnitude by effect of doping [2].

---

* Work partially supported by the Brazilian Agencies Finep and CNPq.

** On leave of absence from Departmento de Física, Pontifícia Universidade Católica, Cx.P. 38071, Rio de Janeiro, Brasil.

The purpose of papers I and II of this series [3, 4] was to apply the Transfer-Matrix (TM) approach to study the electronic structure of polymeric molecules where the breaking of the periodic regular structure may occur. In this work we will be interested in the study of localized states in trans-$(CH)_x$ which are produced by the breaking of its regular bond alternation. This type of defect has been connected, by Su, Schrieffer and Heeger (SSH), to the existence of soliton in this material [5]. Very recently the TM approach has been applied to study a single site defect (see Fig. 1b) in trans-$(CH)_x$ [6] (the same model has been studied by other authors using different techniques) [7, 8]. Although the simplified model for the defect reproduces qualitatively the main features of the electronic structure of the system it is well known [5, 9] that the defect region has an extension of several CH sites. In the present work we use TM approach to handle the relaxed defect problem, allowing that modification of the regular polymeric structure occur for an arbitrary number of sites.

In the next sections we present a model hamiltonian, discuss the electronic properties of the system and briefly comment our results on the light of the experimental data of Weinberg et al. [9] for the EPR linewidth of polyacetylene.

2. Model Hamiltonian

We consider a model Hamiltonian based on the tight-binding approximation for the π-orbitals written as.

$$H = \sum_i \varepsilon_i C_i^+ C_i + \sum_{ij} (V_{ij} C_i^+ C_j + \text{c.c.}) \tag{1}$$

the operator C_i^+ (C_i) creates (destroys) a π-orbital at site i. We choose the eigenenergies ε_i to be zero since all radicals that constitute the polyacetylene are of the same type (CH). The hopping integrals V_{ij} are assumed to be different

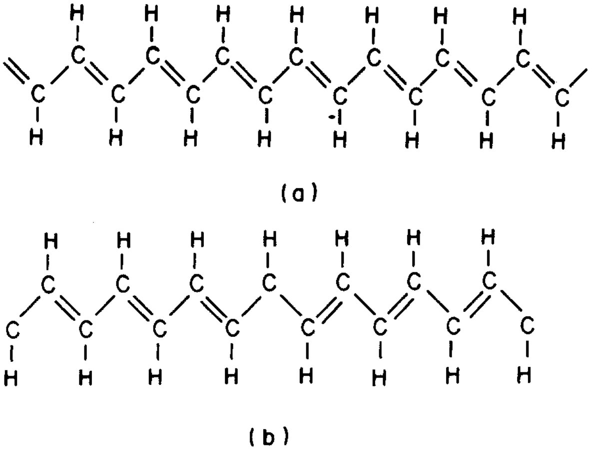

Fig. 1. a. Regular polyacetylene. **b.** Breaking of regular bond alternation is assumed to be confined to a single site

than zero only for nearest-neighbours (i.e. $j = i \pm 1$). The pure dymerized polyacetylene structure (Fig. 1a) can be modeled by considering that the hopping integrals take alternate values V_1 and V_2, which represent a single or double bond. This problem can be easily solved by the TM method. All matrix elements of the Green's function in the site representation can be obtained from Dyson's equation

$$EG = 1 + HG \tag{2}$$

and the spectrum associated with the model Hamiltonian is constituted by two bands corresponding to the regions $[-(1+\beta), -(\beta-1)]$ and $[(\beta-1), (\beta+1)]$, where we have defined $\beta \equiv V_2/V_1$ and all energies are expressed in units of V_1. In the case of polyacetylene $\beta = 1.32$ (to fit data), and throughout this paper we restrict our discussions to the situation $\beta > 1$. The gap of width $2(\beta-1)$ is associated to a Peierls' instability characteristic to this type of 1-D systems.

The local density of states is the same as the one obtained by SSH, and in the band region is given by

$$\rho_0 = \frac{1}{\pi} \operatorname{Im} \frac{|\varepsilon|}{\sqrt{[\varepsilon^2 - (1+\beta)^2][(\beta-1)^2 - \varepsilon^2]}} \tag{3}$$

being zero otherwise.

The lattice defect in Fig. 2 is introduced in our model by arbitrarily defining the reference site 0 as the one associated to the middle of the defect. For simplicity we assume the extension of the defect to be $2\nu + 1$, and take ν as an odd number. Using Dyson's equation in the one orbital per site basis we obtain the following set of coupled linear equations for the matrix elements of the Green's functions associated to the defect region.

$$\begin{aligned} EG_{00} &= 1 + 2\alpha_1 G_{10} \\ EG_{10} &= \alpha_1 G_{00} + \alpha_2 G_{20} \\ EG_{20} &= \alpha_2 G_{10} + \alpha_3 G_{30} \\ &\vdots \qquad \vdots \qquad \vdots \\ EG_{\nu 0} &= \alpha_\nu G_{\nu-1,0} + V_2 G_{\nu+1,0} \end{aligned} \tag{4}$$

where $\alpha_s (1 \le s \le \nu)$ are the hopping integrals, in the defect region. The specific choice of the parameters α will be discussed below. Outside the defect region

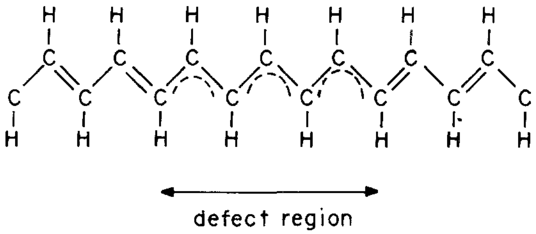

Fig. 2. Defect of size $2\nu + 1 = 7$ in a trans-polyacetylene chain

we have the regular alternating chain and therefore use of Dyson's equation produces the two general expressions:

$$\begin{aligned} EG_{2n,0} &= V_2 G_{2n-1,0} + V_1 G_{2n+1,0} \\ EG_{2n+1,0} &= V_1 G_{2n,0} + V_2 G_{2n+2,0} \end{aligned} \tag{5}$$

where $2n-1 \geq \nu$.

For this region we can define the transfer functions $T_1 = G_{2n,0}/G_{2n+1,0}$ and $T_2 = G_{2n,0}/G_{2n-1,0}$. We can use Eq. (4) to obtain

$$T_1 = \frac{\varepsilon^2 - (\beta^2 - 1) \pm \sqrt{[\varepsilon^2 - (\beta+1)^2)(\varepsilon^2 - (\beta-1)^2]}}{2\varepsilon} \tag{6}$$

and

$$T_2 = \frac{\beta}{\varepsilon - T_1}$$

The choice of signs of the transfer functions (5) is made as usual [10], leading to minus sign above (below) the conduction (valence) band, and plus sign in the gap region. Within the bands the sign is chosen as to lead to a positively defined density of states.

Using the definition of T_1 and T_2, one can solve the equations above for G_{00} to obtain

$$G_{00} = \frac{1}{\Delta_0(\varepsilon)}$$

where

$$\Delta_0(\varepsilon) = \varepsilon - \cfrac{2(\alpha_1)^2}{\varepsilon - \cfrac{\alpha_2^2}{\varepsilon - \cfrac{\alpha_3^2}{\ddots \, \varepsilon - \cfrac{\alpha_\nu^2}{\varepsilon - \beta T_2}}}} \tag{7}$$

As expected the continuous part of the spectrum is in the same energy region as that of the defect-free chain since it is connected to imaginary part of T_2. Therefore it remains to study the existence of localized states outside that region. It is very simple to verify that near the middle of the gap ($\varepsilon = 0$),

$$\Delta_0(\varepsilon = 0) \sim \varepsilon \left(1 + \cfrac{2(\alpha_1)^2}{1 + \cfrac{\alpha_2^2}{1 + \cfrac{\alpha_3^2}{\ddots \, 1 + \cfrac{\alpha_\nu^2}{\beta^2 - 1}}}} \right) \tag{8}$$

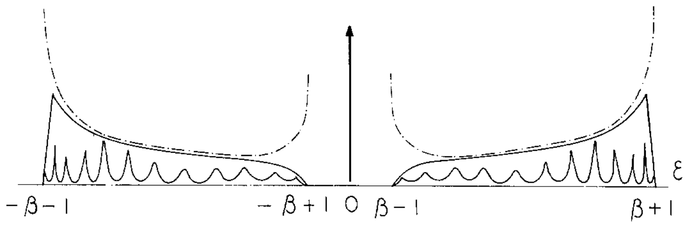

Fig. 3. Density of states for the defect-free chain (dashed line) and for the cases $\nu=1$ and $2\nu+1=25$ (continuous lines). The number of structures observed on the latter two cases are associated to the number of sites affected by the defect

which shows the existence of a pole associated to a symmetric mode at this value of energy. This state splits off symmetrically from the top of the valence band and from the bottom of the conduction band (Fig. 3). It is also easily shown that no other poles occur. We must mention that the pole at the middle of the gap must be relevant for any description of optical, electronic or transport properties of this material, and that the energy of this electronic state is the same as the energy of the localized state associated by SSH to solitons. Furthermore the density of states presents structures which are associated to the number of defects in the chain.

3. Wavefunctions

A map of the wavefunction associated to the localized mode can be obtained by calculating the residues R_{ij} of the pole at $\varepsilon \to 0$, associated to the matrix elements G_{ij} of the Green's function. The signs and the relative amplitudes of the wavefunctions at two sites i and j are given by [11]

$$\frac{\psi_i}{\psi_j}=\frac{R_{ii}}{R_{ij}} \tag{9}$$

and $|\psi_i|^2=R_{ii}$.

Inside the defect region the residues can be easily obtained by solving Eqs. (4) for the off-diagonal elements $G_{s,0}$, where $s \le \nu$; in fact,

$$G_{s,0}=\left(\prod_{p=1}^{s}\frac{\alpha_p}{\Delta_p(\varepsilon)}\right)G_{00} \tag{10}$$

where

$$\Delta_{p-1}(\varepsilon)=\varepsilon-\frac{\alpha_p^2}{\Delta_p(\varepsilon)} \qquad (1 \le p \le \nu)$$

and

$$\Delta_\nu(\varepsilon)=\varepsilon-\beta T_2$$

A straightforward calculation gives $T_1(\varepsilon \to 0)=-\varepsilon(\beta^2-1)^{-1} \to 0$, $T_2(\varepsilon \to 0)=(\beta^2-1)\beta^{-1}\varepsilon^{-1}$ and of course $T_1T_2=-\beta^{-1}$. Using these results in expression

(10) the residues in the defect region ($s \leq \nu$) can be readily obtained as

$$\begin{aligned} R_{s,0} &= (-)^{s/2}\Bigg(\prod_{\substack{p=2\\(\text{even})}}^{s} \frac{\alpha_{p-1}}{\alpha_p}\Bigg) R_{00} \quad && \text{even } s \\ R_{s,0} &= 0 && \text{odd } s \end{aligned} \tag{11}$$

Outside the defect region the wavefunction associated to the localized mode can be also easily calculated by noting that

$$\begin{aligned} G_{\nu+1,0} &= T_2 G_{\nu,0} \\ G_{\nu+2,0} &= T_1 T_2 G_{\nu,0} \\ G_{\nu+3,0} &= (T_1 T_2) T_2 G_{\nu,0} \\ \vdots \quad & \quad \vdots \quad \vdots \; \vdots \end{aligned} \tag{12}$$

From Eqs. (10) and (12) one can see that

$$R_{\nu+1,0} = -\frac{\alpha_\nu}{\beta} R_{\nu-1,0} \tag{13}$$

and therefore using Eqs. (9) and (13)

$$\psi_{\nu+1} = -\frac{\alpha_\nu}{\beta} \psi_{\nu-1} \tag{14}$$

At sites $n \geq \nu$, the transfer matrices can be used to connect different sites, resulting

$$\begin{aligned} \psi_{\nu+2p} &= (T_1 T_2)^{p-1} T_1 \psi_{\nu+1} \\ \psi_{\nu+2p+1} &= (T_1 T_2)^p \psi_{\nu+1} \qquad p \geq 1 \end{aligned} \tag{12}$$

This clearly shows that the wave function still vanishes at the odd sites and for the even sites decays as β^{-p} outside the defect region.

4. Parametrization of the Hopping Integrals

Since one of the main interests in the study of the electronic structure of trans-$(CH)_x$ is related with the soliton properties, we follow SSH assuming that the presence of a soliton of width l in the defect region leads to a specific choice of hopping integrals, given by

$$\alpha_{n+1} \equiv t_{n,n+1} = t_0 - k(u_{n+1} - u_n) \tag{13}$$

To fit the experimental data [5] we take $k = 4.1$ eV/Å, ~2.5 eV and $u_0 = 0.073/\sqrt{3}$ Å. In the SSH calculation the size of the defect $(2\nu + 1)$ and the soliton width (l) are determined by minimizing the energy of the system through the use of a specific trial function; this leads to typical values of $\nu \sim 25$ and $l \sim 7$. It is important to mention that any physical choice for the parametrization must lead to a smooth connection between the hopping integrals inside and outside the defect region.

5. Results and Discussion

SSH based on a WKB-type of approximation, suggested the form

$$\psi_{\nu+1} = -\frac{\alpha_\nu}{\beta}\psi_{\nu-1} \tag{14}$$

to the wavefunction of the localized state associated to the defect. In Fig. 4 we compare this wavefunction with the one we have obtained for the optimum values $\nu = 25$ and $l = 7$. One can see that Eq. (14) is a good approximation for the large n region while overestimating the density of probability for the region close to the center of the defect.

Since the hyperfine splitting at site n is given by

$$a_{\text{eff}} \sim |\psi(n)|^2 \tag{15}$$

one can expect that our results should lead to a better agreement with the experimental data for the spin resonance linewidth of trans-$(CH)_x$ [9].

To illustrate the effect of the relaxation of the defect, we also plot in Fig. 4 the $\nu = 1$ case [6].

As a final comment we must mention that this type of solution for the relaxed defect problem is different than that previously obtained by SSH and to our

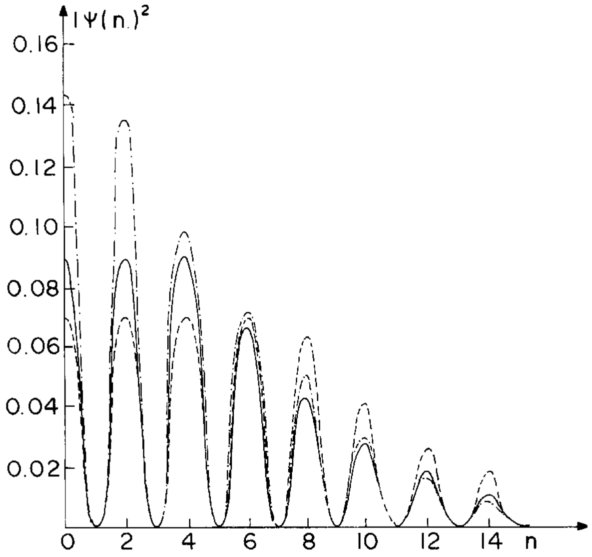

Fig. 4. Probability density associated to the localized state: (——) $\nu = 25$, $l = 7$; (– – –) $\nu = 30$, $l = 10$; (– · – · –) SSH wavefunction (Ref. [5])

knowledge this problem has not been treated by different techniques. The TM method proves to be very adequate to treat this type of problem, since it gives closed analytic solution for the electronic structure of the polymer, and it can be extended to treat more complicated problems such as impurity and doping in this material.

References

1. Gomes, M. A. F., Ferreira, R. C.: Phys. Letters **84A**, 36 (1981)
2. Heeger, A. J.: Comm. Solid State Phys. **10**, 53 (1981)
3. Koiller, B., Brandi, H. S.: Theoret. Chim. Acta (Berl.) **60**, 11 (1981)
4. Brandi, H. S., Koiller, B., Ferreira, R. C.: Theoret. Chim. Acta (Berl.) **60**, 89 (1981)
5. Su, H. P., Schrieffer, J. R., Heeger, A. J.: Phys. Rev. Lett. **42**, 1698 (1979) and Phys. Rev. B **22**, 2099 (1980)
6. Brandi, H. S., de Melo, C. P.: Solid State Commun. **44**, 37 (1982)
7. Pople, J. A., Walmsley, S. H.: Trans. Faraday Soc. **58**, 441 (1962)
8. Bishop, A. R.: Solid State Commun. **33**, 955 (1980)
9. Weinberger, B. R., Ehrenfreund, E., Heeger, A. J., MacDiarmid, A. G.: J. Chem. Phys. **72**, 4749 (1980)
10. de Queiroz, S. L. A., Koiller, B., Maffeo, B., Brandi, H. S.: Phys. Status Solidi (b) **87**, 351 (1978)
11. Papatriantafillou, C. T.: Phys. Rev. B **7**, 5386 (1973)

Received October 18, 1982