Localized states in polymeric molecules. IV. Polyacetylene beyond simple Hückel Model*

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

Departamento de Física, Universidade Federal de Pernambuco, 50000 Recife-PE-Brasil

We have used the transfer matrix technique to study the electronic structure of trans-polyacetylene, within a model Hamiltonian which includes second-neighbors interactions. The results show that the valence and conduction band widths and the energy of the localized state are dependent on the strength of the second neighbors couplings. However, for the physically reasonable range of parameters, the electronic structure of the material is only slightly modified, indicating that a simple Hückel treatment is quite accurate for this system.

Key words: Polyacetylene—localized states—band widths

1. Introduction

In the first paper of this series [1], hereafter referred to as I, the Transfer Matrix (TM) formalism has been extended to deal with long range interactions in polymeric molecules. In that work, the method was restricted to a one-dimensional homogeneous system. However, it is well known that most of the 1-D polymers have structures which cannot be described by the model Hamiltonian used in I. This is, for instance, the case of polyacetylene (PA), one of the most studied polymers in the past few years for reasons which range from its simplicity for testing different band structure calculation schemes [2], to the existence of solitons in the *trans* form of this material [3].

The convenience of using the TM approach to study 1-D systems has been extensively discussed in several previous works [4–6], and lies basically in its simplicity and in the possibility of obtaining analytical results for several quantities associated to the electronic structure of these systems.

It is of interest to study the electronic structure of *trans*-polyacetylene using a model Hamiltonian which goes beyond first-neighbor interactions. Inclusion of second-neighbor interactions would provide an indication of the accuracy of a simple Hückel (first neighbors only) model. In the present work the TM approach of I is extended to treat that system within a model Hamiltonian which includes first and second neighbors interactions. As shown below , this leads to simple analytical results for several physical quantities of interest.

In Sect. 2 we apply the method to pure *trans*-PA. The inclusion of a single-site defect is treated in Sect. 3. We discuss the results and present our conclusions in Sect. 4.

2. Pure trans-polyacetylene

In this section we extend the method discussed in I to the specific case of a pure *trans*-PA chain (Fkg. 1), limiting, for simplicity, the range of interaction to first and second neighbors. The Hamiltonian in the site representation is written as

$$H = \sum_l \varepsilon_l a_l^+ a_l + \sum_{l,l'} (v_{l,l'} a_l^+ a_{l'} + \text{c.c.}) \tag{1}$$

where l specifies the lattice site and $a_l^+(a_l)$ is the creation (destruction) operator for the electronic orbital at site l. Eq. (1) is valid within the π-electron approximation.

Defining an arbitrary reference site $l = 0$, the parameters appearing in (1) are chosen to be

$$\varepsilon_l = 0, \qquad l = 0, \pm 1, \pm 2, \ldots \tag{2}$$

$$v_{l,l'} = \begin{cases} -v_1, & l' = l + (-1)^l \\ -v_2, & l' = l - (-1)^l \\ -v, & l' = l \pm 2 \\ 0, & \text{otherwise,} \end{cases} \tag{3}$$
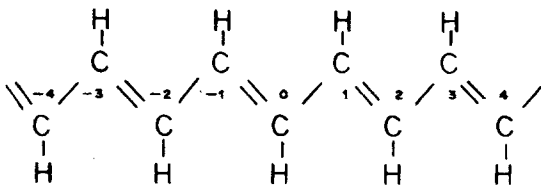

Fig. 1. Regular *trans*-poly-acetylene chain

where $-v_1$ and $-v_2$ represent the first neighbors couplings associated to single and double bonds, respectively. Due to the symmetry of the problem there is only one second neighbor coupling parameter, $-v$.

From the Green's function associated to Eq. (1)

$$G(E) = (E-H)^{-1} = \frac{1}{E}(1+HG) \tag{4}$$

it is possible to obtain several properties of the system such as density of states, wavefunctions, etc.

We may use Dyson's equation

$$EG_{i,j}(E) = \delta_{i,j} + \sum_k H_{i,k}G_{k,j}(E) \tag{5}$$

to obtain

$$EG_{0,0} = 1 - v_2 G_{-1,0} - v_1 G_{1,0} - v(G_{-2,0} + G_{2,0}) \tag{6a}$$

$$EG_{1,0} = -v_1 G_{0,0} - v_2 G_{2,0} - v(G_{-1,0} + G_{3,0}) \tag{6b}$$

$$EG_{2n,0} = -v_{2n-1,0} - v_1 G_{2n+1,0} - v(G_{2n-2,0} + G_{2n+2,0}) \qquad n \geq 1 \tag{6c}$$

$$EG_{2n+1,0} = -v_1 G_{2n,0} - v_2 G_{2n+2,0} - v(G_{2n-1,0} + G_{2n+3,0}) \qquad n \geq 1. \tag{6d}$$

Due to the structure of Eqs. (6c) and (6d), and exact solution may be obtained for this infinite set of equations by introducing the following transfer functions

$$T_1 = \frac{G_{2n+1,0}}{G_{2n,0}} \, n \geq 1 \tag{7a}$$

$$T_2 = \frac{G_{2n,0}}{G_{2n-1,0}} \, n \geq 1. \tag{7b}$$

Through the use of Eqs. (7a) and (7b) in (6c) and (6d), it is easily shown that T_1 and T_2 satisfy the following algebraic equations

$$E + v\left(\frac{1}{T_1 T_2} + T_1 T_2\right) + v_1 T_1 + v_2/T_2 = 0 \tag{8a}$$

$$E + v\left(\frac{1}{T_1 T_2} + T_1 T_2\right) + v_1/T_1 + v_2 T_2 = 0. \tag{8b}$$

After solving this set of equations one gets

$$T_1 = -\frac{1+\beta t}{\varepsilon + x} \tag{9a}$$

$$T_2 = -\frac{t+\beta}{\varepsilon + x} \tag{9b}$$

where all parameters have been expressed in units of v_1, with $\beta \equiv v_2/v_1$, $\lambda \equiv v/v_1$, $\varepsilon = E/v_1$ and

$$x = \left(\frac{\beta}{2\lambda} - \varepsilon\right) \pm \sqrt{\left(\frac{\beta}{2\lambda}\right)^2 - 2\varepsilon\left(\frac{\beta}{2\lambda}\right) + (1+\beta^2)} \tag{10a}$$

$$t \equiv T_1 T_2 = \left(\frac{x}{2\lambda}\right) \pm \sqrt{\left(\frac{x}{2\lambda}\right)^2 - 1}. \tag{10b}$$

Among the four independent solutions of Eqs. (9) only two are associated to the retarded Green's function – those for which $|t(\varepsilon + i\delta)| < 1$, where δ is a small positive number.

We can then solve Eqs. (6) for $G_{0,0}$ and obtain

$$G_{0,0} = \frac{\Delta_{0,0}}{\Delta} \tag{11}$$

where

$$\Delta_{0,0} = \begin{vmatrix} \varepsilon + T_1 + \lambda T_1 T_2 & 0 & \lambda \\ \beta + \lambda T_1 & 1 & 1 + \lambda T_2 \\ \lambda & 0 & \varepsilon + \beta T_2 + \lambda T_1 T_2 \end{vmatrix} \tag{12a}$$
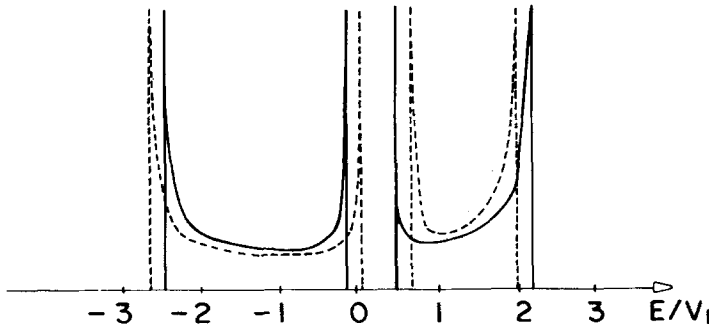
and

$$\Delta = \begin{vmatrix} \varepsilon + T_1 + \lambda T_1 T_2 & \beta & \lambda \\ \beta + \lambda T_1 & \varepsilon & 1 + \lambda T_2 \\ \lambda & 1 & \varepsilon + \beta T_2 + \lambda T_1 T_2 \end{vmatrix}. \tag{12b}$$

The knowledge of G_{00} allows the calculation of the local density of states

$$D(E) = -\frac{1}{\pi} \operatorname{Im} G_{0,0}. \tag{13}$$

As discussed in I the structure of the local density of states is dependent on the second neighbor coupling strength. For the case of interest $\beta > 1$ and

Fig. 2. Local density of states for regular *trans*-polyacetylene. We have used $\beta = 1.32$, and $\lambda = 0.07$ and 0.17 (continuous and dashed curves respectively)

$\lambda < 0.25$ – this leads to two bands in the energy regions defined by $\varepsilon = [-2\lambda - (1+\beta), 2\lambda - (\beta-1)]$ and $\varepsilon = [2\lambda + (\beta-1), -2\lambda + (1+\beta)]$.

One should note that the simple Hückel results are obtained letting λ go to zero, and therefore, the inclusion of second neighbor interactions does not modify neither the band width nor the gap width given by that simpler model. However the relative widths of the lower and upper bands are λ dependent.

This can be seen in Fig. 2 where the local density of states is depicted for $\beta = 1.32$ and reasonable values of λ.

3. Single-site defect

Recently it has been suggested [3] that the great increase in the conductivity of *trans*-PA, resulting from doping, may be explained by a mechanism of solitons associated to the presence of mobile defects in the undoped material. Such defects are a consequence of the breaking of the regular bond alternation during the polymerization process. Due to the very small barrier – estimated to be $\sim$0.02 eV – for the displacement of the center of the defect to the neighboring sites, the defect is expected to be extremely mobile along the chain. By the effect of doping, charge can be transferred to or from the localized (in energy) middle gap state associated to the presence of the defect, thus providing an explanation to the observed [7] huge increase in conductivity.

Although geometrically these defects may extend over several sites [3, 6], a single site defect model (Fig. 3) may lead to very good results concerning the electronic properties of the system [5]. In this Section we use the formalism developed in the previous one, to treat such defect. For convenience we assume that the breaking in the bond alternation occurs at site 0; therefore, only one new parameter is introduced in the calculation, namely, the coupling $v_{-1,1} = -v'$. This leads to the following set of equations for the matrix elements of the Green's function associated to the defect site

$$EG_{0,0} = 1 - 2v_1 G_{1,0} - 2v G_{2,0} \tag{14a}$$

$$EG_{1,0} = -v' G_{-1,0} - v_1 G_{0,0} - v_2 G_{2,0} - v G_{3,0}. \tag{14b}$$

For the other sites the elements are given by Eqs. (6c) and (6d), and therefore the transfer functions are the same as given by Eqs. (9a) and (9b). As a consequence, the band regions are the same as in the pure case, and the new local density of states is obtained after solving Eq. (14a) and (14b) for $G_{0,0}$,
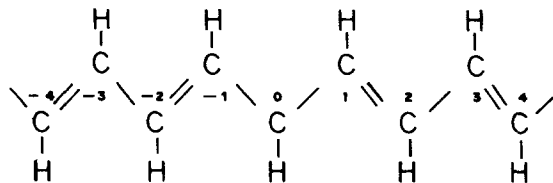
Fig. 3. *Trans*-polyacetylene chain with a single-site defect

resulting in

$$G_{0,0} = \frac{\Delta'_{00}}{\Delta'},$$

(15)

where

$$\Delta'_{0,0} = \begin{vmatrix} \varepsilon + \lambda t + \beta T_2 & 0 & \lambda' \\ 1 + \lambda T_2 & 1 & 1 + \lambda T_2 \\ \lambda' & 0 & \varepsilon + \lambda t + \beta T_2 \end{vmatrix}$$

(16a)

and

$$\Delta' = \begin{vmatrix} \varepsilon + \lambda t + \beta T_2 & 1 & \lambda' \\ 1 + \lambda T_2 & \varepsilon & 1 + \lambda T_2 \\ \lambda' & 1 & \varepsilon + \lambda t + \beta T_2 \end{vmatrix}$$

(16b)

with $\lambda' = v'/v_2$.

The poles of G_{00} correspond to the energy of the symmetric localized state associated to the defect and are easily obtained finding the zeros of $\Delta'_{0,0}$. For the case where only first neighbors interactions are considered, there is only one pole at the middle gap, regardless of the extension of the defect. The weight of this pole may be obtained from the residue of $G_{0,0}$ at the pole's position, having equal contribution from the valence and conduction density of states.

If one considers second neighbors interactions this symmetry can be broken and the pole's position is not necessarily exactly in the middle of the gap (see Table 1). In order to have equal contributions from the valence and conduction bands to the weight of the localized state, we have found that, for the values of parameters appropriate for *trans*-PA, is necessary for λ' to be greater than λ (See Table 2). Physically, this implies that the second neighbor interaction at the defect region must be stronger than in the regular chain – as would result from the existence of a kink at the defect site.
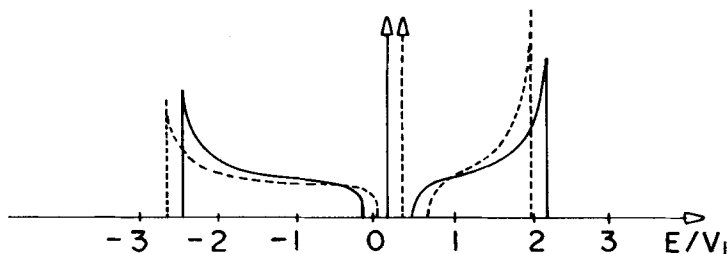
In Fig. 4 we present the local density of states for the site where the defect is centered, for different sets of values of the parameters which lead to equal integrals of the density of valence and conduction states.

Table 1. Energy separation (η) of the localized state position (ε_0) from the middle of the gap (2λ), in units of v_1. We define $\eta = 2\lambda - \varepsilon_0$ and take $\lambda' = \lambda$

β \ λ	0.08	0.10	0.12	0.14
1.2	0.003	0.003	0.004	0.005
1.3	0.006	0.007	0.008	0.010
1.4	0.009	0.011	0.014	0.016
1.5	0.013	0.016	0.019	0.023

Table 2. Values of λ' which lead to equal integrals I_{00} of the local density of states of the valence and conduction bands, for different values of λ, and $\beta = 1.32$. Also shown is the energy separation of the pole to the middle of the gap, $\eta = (2\lambda - \varepsilon_0)$

λ	λ'/λ	I_{00}	η
0.08	2.32	0.36	0.006
0.10	2.32	0.36	0.008
0.12	2.16	0.36	0.010
0.14	2.05	0.35	0.012

Fig. 4. Local density of states for $\lambda = 0.08$; $\lambda' = 0.14$ (continuous) and $\lambda = 0.14$; $\lambda' = 0.29$ (dashed curve). For both cases, $\beta = 1.32$

The wave function for the localized state may be obtained as in Ref. [5–6], evaluating the off-diagonal elements of the Green's function, which are easily obtained from the values of T_1 and T_2 at the pole's position. The results are very similar to those of Ref. [5], except for the fact that the wavefunction does not vanish at the odd sites, although at these sites its value is very close to zero.

4. Discussions and conclusions

The results obtained in the present work concerning the density of states and the pole's position, as well as the wavefunction associated to the localized energy state, indicate that the simple Hückel model quite accurately describes the electronic structure of *trans*-polyacetylene, which is only slightly modified by the inclusion of second-neighbors interactions. Of course this conclusion is dependent on the strengths considered for the relevant parameters. They could be obtained from the experiments with the knowledge of the total band width, the band gap and the valence (or conduction) band width.

Unfortunately, in the literature there are no conclusive experimental data concerning the total π-band width, and the analysis of the results for the lower band density of states is complicated due to the overlap of σ and π bands [8]. Even for the band gap there is difficulty for a precise assignment [9]. We have used the most accepted value of β and chosen a reasonable range of variation for the parameter λ.

As shown in the present work the TM approach is still convenient to treat systems like PA with interactions other than first neighbors. Analytical solutions were obtained when the coupling range was limited to second-neighbors. This is not, however, a restriction of the method, which can be trivially extended to include higher order couplings.

This series of works shows that there exists a large variety of 1-D systems which can be conveniently treated within the framework of the Transfer Matrix method.

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