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Localized States in Polymeric Molecules. I. The Transfer Matrix for Long Range Interactions*

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We have extended the transfer matrix technique to determine the Green's function for 1-dimensional systems with long range interactions. The formalism is applied to study the density of states and impurity modes of linear chains; calculations are presented for nearest and next nearest neighbors interactions.

Key words: Polymer – Localized states – Band states.

1. Introduction

In the last few years some authors have discussed the role of impurities in several biophysical processes such as electron transfer reactions in photosynthesis, oxidative phosphorylation [1–3] and in the context of enzymatic activity [4].

There has also been a series of recent works concerning the study of localized states in a polymer chain due to internal rotation, bond alternations or the close approach of a molecule modifying a site of the chain, which simulates a chemical reaction [5–7]. The formation of band gaps and the existence of mechanisms to create localized states may play an important role in the context of chemical reactivity, and in catalytic processes.

Morton-Blake [7] has recently treated this problem, and obtained the electronic structure of a perturbed chain, diagonalizing the complete Hamiltonian using single band extended Bloch orbitals as a basis set. The number of orbitals is truncated by a numerical convergence criterion.

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Although adequate for $3d$ systems, this is not the most convenient approach to treat linear chains, for which exact solutions can be found.

We consider in this work, as in Ref. [7], a one orbital per site model Hamiltonian to describe the electronic states of a polymer ($1d$ crystal, d = 'dimensional') with long range coupling (but finite) between the orbitals. To our knowledge there exists no exact solution to this problem in the literature [7]. We obtain analytic expressions for the Green's function for both "pure" and "perturbed" polymers. The local density of states, the existence and symmetry of the localized modes are discussed. In Sect. 2 we introduce the concept of transfer matrix for long range coupling in the case of the pure chain model. Sect. 3 is devoted to the "perturbed" polymer (single impurity chain); in this case the transfer matrix approach proves to be very convenient since it does not require explicit knowledge of the pure system Green's function, and allows for a complete real space treatment of the problem.

As an example we apply the formalism to the problem of first and second neighbors coupling for an interaction which decays as $1/r^3$ (dipolar interaction). Our calculations indicate that in this case, inclusion of second neighbors coupling does not affect significantly the results, and therefore can be neglected in future work for simplicity.

For the sake of definiteness we note that the formalism presented in Ref. [7] can be unified by regarding segment perturbation as a modification on the self-energy at the "impurity" site and bond compression as a change in the corresponding resonance integrals.

2. Pure Chain

Let us consider the model Hamiltonian written in the site representation as

$$H=\sum_{l}\varepsilon_l a_l^+ a_l+\sum_{ll'} v_{ll'} a_l^+ a_{l'} \tag{1}$$

where l specifies the lattice site and a_l^+, a_l are creation and destruction operators for the electronic orbital at site l. Eq. (1) is restricted to the one-band or one orbital per site approximation.

For the pure chain with coupling range r, the parameters appearing in (1) are:

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

$$v_{ll'}=\begin{cases}-v_{|l-l'|}, & |l-l'|\le r\\ 0, & |l-l'|>r.\end{cases} \tag{3}$$

Relevant features of the systems, such as density of states, transport properties, dynamic response, etc., are directly obtained from the Green's function [8] associated to Eq. (1):

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

The Green's function matrix elements on the localized orbitals basis set satisfy Dyson's equation

$$EG_{ij}(E)=\delta_{ij}+\sum_k H_{ik}G_{kj} \tag{5}$$

which in the case of an arbitrary reference site $j=0$ yields:

$$EG_{0,0}=1-2\sum_{i=1}^{r} v_i G_{i,0} \tag{6.a}$$

$$EG_{p,0}=-\sum_{i=1}^{r} v_i(G_{p+i,0}+G_{|p-i|,0}) \qquad p<r \tag{6.b}$$

$$EG_{p,0}=-\sum_{i=1}^{r} v_i(G_{p+i,0}+G_{p-i,0}) \qquad p\geq r. \tag{6.c}$$

This infinite set of coupled linear equations can be solved exactly; its structure suggests a solution of the form:

$$G_{n,0}=\sum_{i=1}^{r} x_i(T_i)^n. \tag{7}$$

It is easily shown from Eq. (6.c) and (7) that the transfer functions T_i are solutions of the following algebraic equation:

$$E+\sum_{\lambda=1}^{r} v_\lambda\left[(T)^\lambda+\frac{1}{(T)^\lambda}\right]=0 \tag{8}$$

Among the $2r$ solutions for T, there are r associated to the advanced and r to the retarded Green's function. We are concerned with the retarded Green's function, and therefore the criterion for choosing the appropriate solutions is $|T(E+i\varepsilon)|<1$, where ε is a small positive number.

The coefficients x_i in Eq. (7) can be easily determined from (6.a), (6.b), and (7), once the proper solutions of (8) are obtained.

As an example, we briefly discuss the density of states

$$D(E)=-\frac{1}{\pi}\operatorname{Im} G_{0,0} \tag{9}$$

for a pure chain with 1st and 2nd neighbors coupling. In this case Eq. (8) can be solved analytically, since it becomes a reciprocal algebraic equation and the results are of course equivalent to what is obtained from the dispersion relation. The density of states corresponds to a single band, and two different situations occur, according to the value of $v_2/v_1=\lambda$ (we assume positive v_1 and v_2). For $\lambda>\frac{1}{4}$, the band region is $E\in[2v_1(-1-\lambda), 2v_1(\lambda+1/8\lambda)]$; the density of states diverges at the band edges and also at $E=2v_1(1-\lambda)$. For $\lambda<\frac{1}{4}$ the band width is $4v_1$, independent of λ, and the lower edge is at $E=-2v_1(1+\lambda)$; the density of states is singular at the band edges only. In Fig. 1 we present the density of states for $\lambda=1$ and $\frac{1}{8}$ (dipolar interaction).

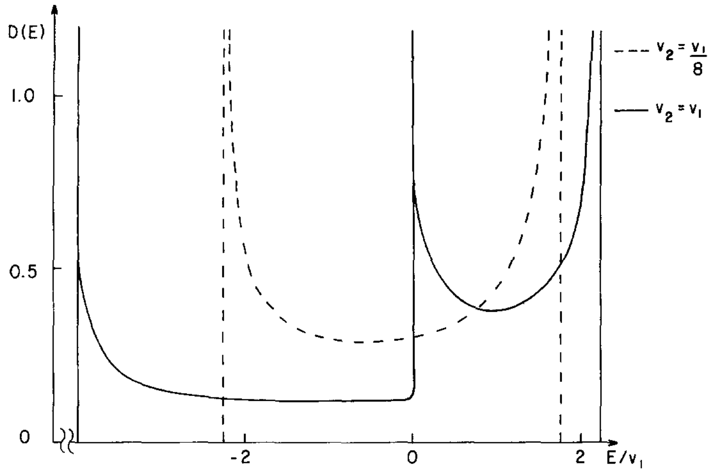

Fig. 1. Normalized density of states for a pure chain with first (v_1) and second (v_2) neighbors coupling. Notice that, contrary to the $v_2 = 0$ case, the density of states is not symmetric with respect to the center of the band. All singularities are square root type, characteristic of 1d systems

3. Single Impurity Chain

We consider a one dimensional chain with a single impurity at site $l = 0$. The Hamiltonian (1) matrix elements for $l, l' \neq 0$ are the same as those of Eqs. (2) and (3); the parameters associated to the impurity are defined as:

$$\varepsilon_{l=0} = \delta \tag{10.a}$$

$$v_{0l'} = \begin{cases} -\bar{v}_{l'}; & |l'| \leq r \\ 0; & |l'| > r. \end{cases} \tag{10.b}$$

The Green's function matrix elements are obtained from Eq. (8), which yields in this case the following set of coupled linear equations

$$(E - \delta) G_{0,0} = 1 - 2 \sum_{i=1}^{r} \bar{v}_i G_{i,0} \tag{11.a}$$

$$E G_{p,0} = -\bar{v}_p G_{0,0} - \sum_{\substack{i=1 \\ i \neq p}}^{r} v_i (G_{p+i,0} + G_{|p-i|,0}) \qquad p \leq r \tag{11.b}$$

$$E G_{p,0} = -\sum_{i=1}^{r} v_i (G_{p+i,0} + G_{p-i,0}) \qquad p > r \tag{11.c}$$

It is possible that the impurity also affects the self energy of its neighbors. The inclusion of $\varepsilon_l \neq 0$ for $l = \pm 1, \pm 2, \ldots, \pm r$ changes the l.h.s. of (11.b) into $(E - \varepsilon_p) G_{p,0}$, but since (11.c) remains unchanged, the solution is obtained by the same procedure described below.

Notice that Eq. (11.c) is the same as (6.c), and therefore the solutions for $G_{n,0}$ ($n \geq 1$) are given by an expression similar to (7):

$$G_{n,0} = \sum_{i=1}^{r} y_i (T_i)^{(n-1)} \qquad n \geq 1 \tag{12}$$

with T_i representing the same r "retarded" solutions of (8). The coefficients y_i ($i = 1, \ldots, r$) together with $G_{0,0}$ are obtained from the set of $r+1$ Eqs. (11.a) and (11.b).

As in the previous section, we particularize the discussion to the 1st and 2nd neighbors coupling; we call

$$\begin{aligned} \lambda &= v_2/v_1 \\ \alpha &= \bar{v}_1/v_1 \\ \beta &= \bar{v}_2/v_1. \end{aligned} \tag{13}$$

The diagonal element of the Green's function relative to the impurity site is:

$$G_{0,0} = \frac{g_1 h_2 - h_1 g_2}{(E-\delta)(g_1 h_2 - h_1 g_2) - \alpha(f_1 h_2 - f_2 h_1) - \beta(f_2 g_1 - f_1 g_2)} \tag{14}$$

where

$$\left.\begin{aligned} f_i &= 2(\alpha + \beta T_i) \\ g_i &= E + (\lambda + T_i + \lambda T_i^2) \\ h_i &= T_i g_i + (1 - \lambda T_i) \end{aligned}\right\} \quad i = 1, 2. \tag{15}$$

The poles of G_{00} correspond to the energies of the symmetric localized impurity states that split off the band for particular values of α, β, and δ. In the case when the impurity introduces only diagonal disorder, i.e. $\bar{v}_1 = v_1$ and $\bar{v}_2 = v_2$, *one* impurity mode is present above (below) the continuum for $\delta > 0$ ($\delta < 0$), which is characteristic for 1d systems, in which local modes are easily "removed" from the band due to the singularities of the density of states at the band edges. In the case of nondiagonal disorder, increasing $\bar{v}_1$ and $\bar{v}_2$ with respect to the host values v_1 and v_2 tends to favour the appearance of local modes, even for $\delta = 0$, while for smaller $\bar{v}_1$ and $\bar{v}_2$, local modes are present only for large enough values of $|\delta|$. This is illustrated in Fig. 2, where we present the energies of the symmetric local modes as a function of δ in the case of diagonal disorder and also for $\alpha = 0.5$ and $\alpha = 2$, keeping $\bar{v}_2 = v_2 = v_1/8$.

Antisymmetric or p-like modes appear as poles of $G_{1,1}$: they exist only when the impurity affects its neighbors' self energy ($\varepsilon_{\pm 1} \neq 0$), which is physically expected for an excitation with zero amplitude at the defect site. Although the inclusion of this effect is trivial in the proposed formalism, we do not present specific calculations for it.

The wave functions of the modes are obtained from the residues of the poles of the matrix elements of G. With respect to the general behavior of the wave

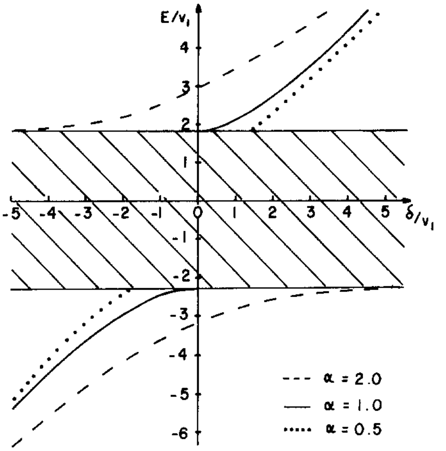

Fig. 2. Energies, in units of v_1, of the local modes as a function of the impurity site perturbation δ for different values of $\alpha = \bar{v}_1/v_1$ and $\bar{v}_2 = v_2 = v_1/8$. The full curve corresponds to $\alpha = 1$ (diagonal disorder only). The dotted curve corresponds to $\alpha = 0.5$ and the dashed curve to $\alpha = 2.0$. The shaded region indicates the continuum spectrum

functions of the local modes, the following remarks apply to *any range r* of the interaction:

(1) There are at most two symmetric modes splitting off the continuum: one above and another below the band.

(2) The relative phase at different sites of the wave function of a symmetric local mode is the same as that of the collective mode associated with the band edge nearest in energy to the local mode outside the cluster of $(2r+1)$ sites interacting with the impurity. In this cluster, the relative phase may change according to the values of $\{\bar{v}_l\}_{l=1,r}$.

(3) The wave functions of local modes decay exponentially into the bulk, being more extended for modes near the band edges.

(4) The same conclusions are valid for p-like modes (when they exist) except, of course, for the antisymmetric character of the wave functions with respect to the impurity site.

In order to test the adequacy of a model which includes only nearest neighbors hoping to describe a system where the interactions involve other neighbors coupling, we study the energies of the local modes for a linear chain with one

Table 1. Energy of the local mode as a function of the impurity site perturbation δ for $v_2 = v_1/8$ (E_0) compared to the results in the nearest neighbors approximation (E'_0). Energies are given in units of v_1. The deviation $\Delta = |(E_0 - E'_0)/E_0|$

δ/v_1	±1	±2	±3	±4	±5
E_0/v_1	2.07	2.74	3.56	4.44	5.36
	−2.46	−2.95	−3.68	−4.51	−5.41
E'_0/v_1	±2.23	±2.83	±3.60	±4.47	±5.38
Δ(%)	7.7	3.3	1.1	0.7	0.4
	9.3	4.1	2.2	0.9	0.6

impurity, which is characterized by diagonal disorder only, in two different situations. In Table 1 we compare the case of first and second neighbors coupling ($v_2 = v_1/8$) with the results for the same system assuming $v_2 = 0$. The continuum limits in these cases are $[-2.25, 1.75]$ and $[-2, 2]$ (in units of v_1), respectively. Notice that the deviation from the nearest neighbors case decreases rapidly as the local mode energy moves away from the band. This is physically expected since the wave functions of the modes far from the continuum in energy are concentrated around the impurity site, being less sensitive to long range effects.

4. Conclusions

The introduction of the transfer matrix leads to a closed solution for the problem of a "perturbed" linear chain with long range interaction. The results indicate that the nearest neighbors model is suitable for the study of local modes even in the case where the coupling with other neighbors v_l $(l > 1)$ is not negligible as compared to v_1, as long as the impurity mode is far enough from the continuum.

The simplicity of this model suggests its application to study a chemical reaction occurring during the collision between a polymer and a reacting molecule. The interaction can be simulated by varying the self-energy and resonance integrals of a given perturbed site of the polymer. Some of these results are presented in the following work.

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