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Electronic transmission coefficient for the single-impurity problem in the scattering-matrix approach

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The ability of a rupture of translational invariance in a one-dimensional chain to control the through chain electron propagation is studied on the model system $\cdots AAABAAA \cdots$. A discrete formulation of the one-dimensional scattering theory is considered with the help of the transfer-matrix technique. A tight-binding Hamiltonian, with a single orbital per center, is used to represent the chemical nature of the perturbated chain. The electronic transmission coefficient and the change in the chain electronic density of states induced by the defect B are analytically calculated from the scattering matrix S. The complete dependence on the electronic transmission of the energetic position of the impurity orbital and of its couplings with the chain is analyzed in detail. Possible applications of the model to the design of molecular switches are described by means of the effective Azbel's transmission coefficient.

I. INTRODUCTION

In the last few years, polymeric systems have been the subject of a large number of theoretical studies. Several methods using the translational invariance through Bloch's theorem are now available and a quantum-chemical understanding of the structures and properties of these one-dimensional compounds can be carried out at different levels of accuracy.[1–4] However, from an experimental point of view, polymers are often far from the regular one-dimensional (1D) structures generally assumed in these calculations. Impurities, defects, and topological disorder can exist and the samples often appear as amorphous systems. These defects have important consequences on the conductive properties of the polymeric material. Understanding the influences of such deviations from the translational invariance on the transport properties is a problem of current interest.[5–8]

Although the disorder may appear on a very large scale, a first step toward a better chemical understanding of the influence of impurities and defects in polymer chains is to study the effect of a local rupture of the translational invariance. This is the approach which has been chosen here. The polymer considered is a perfect periodic chain, made of A as repeating unit, in which a *finite* chemical system B has been inserted,

$$\cdots AAABAAA \cdots .$$

For this single-impurity problem, density-of-states calculations have been the subject of considerable efforts, from the simple tight-binding model[9] up to the self-consistent-field (SCF) Hartree-Fock level.[10–12] "Exact" perturbative approaches, within the Green's-function formalism, are generally used for these calculations. Because of their topological simplicity, one-dimensional systems can be conveniently studied with recursive methods. These methods originate from the transfer matrix technique introduced by Schmidt[13] and Hori[14,15] and have been recently reviewed by Biczo.[16] They have been mainly used for the study of end effects, on polymers[17,18] or at cristal surfaces. They are usually considered as an alternative efficient mathematical tool for the calculation of density of states or of wave-function coefficients.

However, these calculations do not provide any direct insight into the conductance of the chain plus defect system. Following Stone,[19] the scattering matrix S is a very useful tool, compared with the Green's function, to characterize the elastic scattering process introduced by the defect B. This S matrix is currently calculated with the transfer matrix technique. The scattering channels through the defect are associated with the modulus-one eigenvalues of the spatial propagator of the periodic chain. The through defect electronic transmission coefficient can be calculated from the reduction of the transfer matrix to these specific channels. The energy-average of this coefficient is directly related to the conductance of the chain controlled by the defect, in the linear response approximation.[20–23] Notice that the change in the chain density of states associated with the defect can also be derived from the S matrix.[24]

The system $\cdots AAABAAA \cdots$ studied here is characterized by a monoelectronic "tight-binding" Hamiltonian. Many functions (or orbitals) have to be considered to model A and B, as long as a precise chemical description of the unit cell and the impurity is needed. However, in this initial study, an oversimplified model has been chosen, in which each unit (A or B) is represented by a single function. The main qualitative features of the symmetry rupture induced by B can be extracted from such a simple Hamiltonian.

Within this simple approach, an analytical calculation of the scattering matrix, and thus of the transmission coefficient, is presented. The small number of energetic parameters used here to describe the $\cdots AAABAAA \cdots$ chain, and the possibility of an analytical calculation of the S matrix, lead to a complete analysis of the influence of B on the properties of the entire system.

This study of the transmission properties is of special interest in the field of conductive polymers, which can be poisoned by various defects.[25–30] It can help in understanding the influence of defects on the conductivity of the sample. It can also give useful information for the design of an active chemical unit to be inserted in a one-dimensional chain in order to control the electronic transfer.[31–35] Our system can be used as an oversimplified model for a molecular switch. Either a change of the impurity energy level or a modification of the nature of its coupling with the chain is considered, and the associated control abilities are discussed.

The scattering matrix and the transmission coefficient are presented in Sec. II. In Sec. III the transfer matrix technique is recalled, with emphasis on the physical meaning of the eigenvalues of the periodic part propagator. The impurity control of the chain transmission properties is studied in Sec. IV. The analytical expressions for the transmission coefficient and the differential density of states are derived, as functions of the Hamiltonian control parameters characterizing the chemical nature of the defect. The variations of the transmission coefficient are analyzed when the nature of the defect is modified. The two types of model molecular switches are finally compared.

II. SCATTERING MATRIX AND TRANSMISSION COEFFICIENT

The standard way to characterize the influence of a defect embedded in a periodic chain is to plot, for a given energy E, the eigenvector $|\Psi(E)\rangle$ of the Hamiltonian H of the system developed on a chosen basis set, expecting a localization effect.[7,8] Such a direct study is cumbersome since it may require the plotting of a huge number of curves. One may then try to *extract some reduced information from H,* that would lead to an easier study. The more common way is to analyze the density of states $\rho(E)$,[10–12,17,18] following, for example, the apparition of localized states in the gaps.[9,18] However, $\rho(E)$ characterizes the energy repartition of the H eigenvalues but contains no information on the modulus of the wave function itself. For this purpose, the standard charge-bond-order matrix can be evaluated from the Green's-function method,[12] or from cluster calculations.[6] Although this matrix is a very important tool for the chemical structure, it does not provide any direct information on the alteration by the impurity of the electronic transmission properties of the chain.

An useful tool to extract such information is the scattering matrix $\underline{S}(E)$ that relates the amplitudes of the outgoing waves to those of the incoming waves on the defect (Fig. 1)

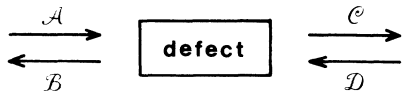


FIG. 1. Schematic representation of the outgoing and incoming waves on the defect.

$$\begin{bmatrix} \mathcal{C} \\ \mathcal{B} \end{bmatrix} = \underline{S}(E) \begin{bmatrix} \mathcal{A} \\ \mathcal{D} \end{bmatrix} . \tag{1}$$

It provides two energy-dependent scalar quantities: the transmission coefficient $t(E)$, which is related to the chain low-voltage conductance,[20–23] and the well-known differential density of states $\Delta\rho(E)$. This latter is only considered in this paper as a tool in order to help in the understanding of the $t(E)$ variations.

This approach was first introduced for the study of localization in disordered solid-state systems.[19] The only condition for the determination of $\underline{S}(E)$ is the current conservation along the chain, a condition which is easily fulfilled for simple tight-binding systems with only elastic scattering processes (see Appendix A). This current conservation is equivalent to the unitarity of the $\underline{S}(E)$ matrix.

The simplest method to calculate $\underline{S}(E)$ is to use the transfer matrix[19,36–39] which relates left to right propagating wave amplitudes,

$$\begin{bmatrix} \mathcal{C} \\ \mathcal{D} \end{bmatrix} = \underline{T}(E) \begin{bmatrix} \mathcal{A} \\ \mathcal{B} \end{bmatrix} . \tag{2}$$

The Green's function can also be used in order to derive $\underline{S}(E)$,[23] but is not as convenient as the transfer matrix for such a one-dimensional single impurity problem.

Since $|\Psi(E)\rangle$ and $|\Psi(E)\rangle^*$ are both solutions of the Schrödinger equation, the transfer matrix has the following structure:

$$\underline{T}(E) = \begin{bmatrix} F(E) & G^*(E) \\ G(E) & F^*(E) \end{bmatrix} . \tag{3}$$

The transfer matrix is easily related to the scattering matrix $\underline{S}(E)$ by

$$\underline{S}(E) = \frac{1}{F^*(E)} \begin{bmatrix} 1 & G^*(E) \\ -G(E) & 1 \end{bmatrix} .$$

The transmission coefficient is then

$$t(E) = \frac{|\mathcal{C}|^2}{|\mathcal{A}|^2} = \frac{1}{|F(E)|^2} . \tag{4}$$

It describes the scattering properties of the defect *at energy E.* The electrons scattered by the impurity are provided and collected by the periodic chains, and in these chains free carriers appear only in a small interval around the Fermi level μ. Therefore $t(E)$ is generally averaged to get an energy-independent transmission coefficient, the effective transmission coefficient, first introduced by Azbel:[21,22]

$$t_{\text{eff}}=\int_{-\infty}^{+\infty} t(E)\left[-\frac{\partial f}{\partial E}\right]dE\ , \tag{5}$$

where $f(E,\mu,\tau)=(e^{(E-\mu)/k_b\tau}+1)^{-1}$ is the Fermi distribution with μ the Fermi level of the periodic chain and τ the temperature of the system.

The density of states (DOS) is also modified by the defect. The variation of the DOS associated with the perturbation of the periodic system can be calculated with the transfer matrix T.[24] In the periodic case the density of states is the derivative of the phase θ of the eigenvector with respect to the energy: $\rho(E)\approx\partial\theta/\partial E$. The argument of $F(E)$ represents the phase shift induced by the defect. Then the change in the density of states is obtained by the energy derivative of this phase shift,[24]

$$\Delta\rho(E)=-\frac{1}{\pi}\frac{d}{dE}\arg(F(E))\ . \tag{6}$$

III. PROPAGATION AND TRANSFER MATRIX

The transfer matrix technique consists in choosing, for a given energy E, the amplitude of the wave function $|\Psi(E)\rangle$ on two consecutive units of the one-dimensional chain. With this initial condition, all the other components of $|\Psi(E)\rangle$ are calculated by backward and forward application of a spatial propagator. This technique is applied in the following to the $\cdots AAABAAA\cdots$ tight-binding chain considered in Sec. I with a Hamiltonian:

$$\begin{aligned}H={}&\omega|s_0\rangle\langle s_0|+\alpha(|s_{-1}\rangle\langle s_0|+|s_0\rangle\langle s_{-1}|)\\&+\beta(|s_0\rangle\langle s_1|+|s_1\rangle\langle s_0|)\\&+\sum_{\substack{n=-\infty\\(n\neq 0)}}^{+\infty} e|s_n\rangle\langle s_n|\\&+\sum_{\substack{n=-\infty\\(0\neq n\neq 1)}}^{+\infty} h(|s_n\rangle\langle s_{n+1}|+|s_{n+1}\rangle\langle s_n|)\ .\end{aligned} \tag{7}$$

This Hamiltonian is controlled by a set of five parameters, e,h,ω,α,β, where ω is the energy of the function $|s_0\rangle$ chosen to model B and α (β) the cell coupling between B and the left (right) part of the A chain (Fig. 2).

The eigenvectors $|\Psi(E)\rangle$ of the Hamiltonian H (7) are developed on the chosen tight-binding basis $|s_p\rangle$,

$$|\Psi(E)\rangle=\sum_p C_p(E)|s_p\rangle\ . \tag{8}$$

In this case the spatial propagator is obtained by the product of elementary propagators constructed from the transformation of the standard second-order difference equation system derived from the Hamiltonian (7),

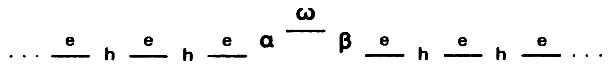


FIG. 2. Graphic representation of the tight-binding Hamiltonian of the chain containing the defect B.

$$hC_{n-1}+(e-E)C_n+hC_{n+1}=0\ ,\quad |n|>1 \tag{9a}$$

$$hC_{-2}+(e-E)C_{-1}+\alpha C_0=0\ , \tag{9b}$$

$$\alpha C_{-1}+(\omega-E)C_0+\beta C_1=0\ , \tag{9c}$$

$$\beta C_0+(e-E)C_1+hC_2=0\ , \tag{9d}$$

in a system of vectorial first-order difference equations.[40] If $\mathbf{R}_n$ is the vector

$$\begin{bmatrix}C_n\\C_{n-1}\end{bmatrix},$$

the elementary propagator $\underline{P}(E)$ on the periodic chain, defined by $\mathbf{R}_{n+1}=\underline{P}(E)\mathbf{R}_n$ for $|n|>1$, and the ones associated with the propagation through the defect, defined by $\mathbf{R}_{i+1}=\underline{P}_i(E)\mathbf{R}_i$ for $i=-1,0,+1$, are given by

$$\underline{P}(E)=\begin{bmatrix}\dfrac{E-e}{h} & -1\\ 1 & 0\end{bmatrix}, \tag{10a}$$

$$\underline{P}_{-1}(E)=\begin{bmatrix}\dfrac{E-e}{\alpha} & -\dfrac{h}{\alpha}\\ 1 & 0\end{bmatrix}, \tag{10b}$$

$$\underline{P}_0(E)=\begin{bmatrix}\dfrac{E-\omega}{\beta} & -\dfrac{\alpha}{\beta}\\ 1 & 0\end{bmatrix}, \tag{10c}$$

$$\underline{P}_1(E)=\begin{bmatrix}\dfrac{E-e}{h} & -\dfrac{\beta}{h}\\ 1 & 0\end{bmatrix}. \tag{10d}$$

In such a propagative procedure, the choice of the initial and boundary conditions is very important. Since the usual cyclic boundary condition[16] (equivalent to introduce a periodic distribution of defects B) is not used here, the only restriction on the $\mathbf{R}_n$ is that $\|\mathbf{R}_n\|$ must be bounded when $|n|$ goes to infinity. At each energy E, the propagation is initialized by the choice of two arbitrary parameters, i.e., one of the $\mathbf{R}_n$ (e.g., $\mathbf{R}_{-1}$). Then the dimension of the subvectorial space associated to an H eigenvalue E depends on the boundary conditions. Its dimension is 2 when E belongs to the continuous part of the $\sigma(H)$ spectrum, but 1 for a $\sigma(H)$ discrete level and 0 when E does not belong to $\sigma(H)$.

When $\mathbf{R}_{-1}$ is supposed to be known, all the $\mathbf{R}_n$ vectors are directly calculated by products of the four elementary propagators defined in (10),

$$\mathbf{R}_n=\begin{cases}\underline{P}^{(n-2)}(\underline{P}_1\underline{P}_0\underline{P}_{-1})\mathbf{R}_{-1}\ \text{ for } n\geq 2\ , & \text{(11a)}\\ \underline{P}^{(n+1)}\mathbf{R}_{-1}\ \text{ for } n\leq -1 & \text{(11b)}\end{cases}$$

To relate $\underline{T}(E)$ defined in (2) with the propagators appearing in (11), one needs the fundamental property that the propagation on a periodic chain produces only, for the allowed energies, a phase shift on the wave function at the tight-binding level. Usually, this property is used directly, leading to the decomposition of the $\mathbf{R}_n$ before and after the defect on the incoming and outgoing plane waves. However, the exact application of this property must be based on a precise spectral analysis of $\underline{P}(E)$.

The relation between the propagation on a periodic chain and the spectral properties of $\underline{P}(E)$ comes from the identity $[\underline{P}(E)]^n=\underline{U}^{-1}[\underline{D}(E)]^n\underline{U}$, with $\underline{D}(E)$ the diagonal form of $\underline{P}(E)$ and $\underline{U}$ the associated similarity transformation. When this transformation is applied to (11),

$$\mathbf{V}_{-1}=\underline{U}^{-1}\boldsymbol{R}_{-1}=\begin{bmatrix} v_{-1} \\ w_{-1} \end{bmatrix}$$

can be chosen instead of $\mathbf{R}_{-1}$ as an initial condition. The

$$\mathbf{V}_n=\underline{U}^{-1}\mathbf{R}_n=\begin{bmatrix} v_n \\ w_n \end{bmatrix}$$

are given by propagation, in a way to distinguish between the two semi-infinite chains and the defect,

$$\mathbf{V}_n=\begin{cases}[\underline{D}(E)]^{(n-2)}\mathbf{V}_2 \quad \text{for } n\geq 2 \ , & (12\text{a}) \\ [\underline{D}(E)]^{(n+1)}\mathbf{V}_{-1} \quad \text{for } n\leq -1 \ , & (12\text{b})\end{cases}$$

$$\mathbf{V}_2=\underline{\tilde{P}}(E)\mathbf{V}_{-1} \ , \tag{12c}$$

where $\underline{\tilde{P}}(E)$ is a new propagator, which characterizes the defect on the $\mathbf{V}_n$ vectors, defined by

$$\underline{\tilde{P}}=\underline{U}^{-1}\underline{P}_1\underline{P}_0\underline{P}_{-1}\underline{U} \ . \tag{13}$$

The principal (not often used) interest of the $\underline{P}(E)$ diagonalization is the distinction between propagative and nonpropagative channels. This distinction comes from the existence of both real and complex valued eigenvalues belonging to the $\underline{P}(E)$ spectrum.

Even for the single-channel system studied here, the two well-known energy regions associated with the notion of conduction band can be distinguished, depending on the sign of the $\underline{P}(E)$ discriminant $\Delta=q^2-4$, with $q=(E-e)/h$ (Fig. 3).

Region I. $\Delta>0$, i.e., $|E-e|>2|h|$, the $\underline{P}(E)$ eigenvalues are real, different from 1 and -1. From the characteristic equation of $\underline{P}(E)$, their product is 1: one of them is then greater than 1 in absolute value. When, for example,

$$\underline{D}(E)=\begin{bmatrix} \lambda & 0 \\ 0 & \lambda^{-1} \end{bmatrix} ,$$

with $|\lambda|>1$, then from (12b) $w_n=\lambda^{-(n+1)}w_{-1}$ for $n\leq -1$, and because $\|\mathbf{R}_n\|$ must be bounded for large negative n, $w_{-1}=0$. In the same way, from (12a) and for large positive n, $v_2=0$.

$\mathbf{V}_2$ and $\mathbf{V}_{-1}$ are linked together through the defect by $\underline{\tilde{P}}$ [Eq. (12c)]. Since $w_{-1}=0$, $v_2=\tilde{P}_{11}v_{-1}$ and a nonzero bounded solution only exists for $\tilde{P}_{11}=0$. $\tilde{P}_{11}$ is a function of the energy E. Its zeros in region I correspond to a set of discrete eigenvalues in the forbidden band of the periodic system. In that case, the dimension of the eigenspace associated with the eigenvalue E is 1 ($w_{-1}=0$). These states are localized on the impurity: their coordinates decrease as $|\lambda|^{-|n|}$ as $|n|\to+\infty$.

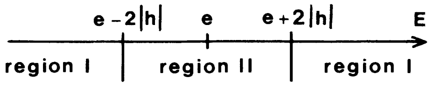


FIG. 3. Distinction of two regions on the energy axis, induced by the nature of $\underline{P}(E)$ eigenvalues.

Region II: $\Delta<0$, i.e., $|E-e|\leq 2|h|$, the eigenvalues are complex of modulus one: $e^{i\theta},e^{-i\theta}$, θ given by the band dispersion relation $E=e+2h\cos\theta$. In that case, v_n and w_n are always bounded. No condition is present. So E is an eigenenergy of H and each pair of initial conditions (v_{-1},w_{-1}) gives an eigenvector: the degeneracy is 2.

The other consequence of the $\underline{P}(E)$ diagonalization is that the transfer matrix $\underline{T}(E)$ can be easily related to the transformed propagator through the defect $\underline{\tilde{P}}(E)$. Since only a propagative characterization of the chain plus defect system is interesting in that context, each $C_n(E)$ in region II is decomposed from (12a) and (12b) on incoming and outgoing plane waves on each side of the defect,

$$C_n=\begin{cases}e^{2i\theta}v_{-1}e^{in\theta}+e^{-2i\theta}w_{-1}e^{-in\theta} & \text{if } n\leq -1 \ , \\ e^{-i\theta}v_2e^{in\theta}+e^{i\theta}w_2e^{-in\theta} & \text{if } n\geq 1 \ ,\end{cases}$$

or equivalently,

$$C_n=\begin{cases}\mathcal{A}e^{in\theta}+\mathcal{B}e^{-in\theta} & \text{if } n\leq -1 \ , \\ \mathcal{C}e^{in\theta}+\mathcal{D}e^{-in\theta} & \text{if } n\geq 1 \ .\end{cases}$$

The amplitudes on the left ($n\leq -1$) and on the right ($n\geq 1$) are related by the transfer matrix $\underline{T}(E)$ (2), which is given from (12c) by

$$\underline{T}(E)=\begin{bmatrix} \tilde{P}_{11}e^{-3i\theta} & \tilde{P}_{12}e^{i\theta} \\ \tilde{P}_{21}e^{-i\theta} & \tilde{P}_{22}e^{3i\theta} \end{bmatrix} . \tag{14}$$

The transfer matrix characterizes how much the delocalized eigenvectors of the periodic chain at energy E are interrupted, reflected, by the obstacle or, in other words, to what extent the two semi-infinite chains are electronically connected through the impurity at an energy E.

IV. IMPURITY CONTROL OF THE TRANSMISSION

A. Control parameters of the transmission

The set of parameters $(e,h,\omega,\alpha,\beta)$ controlling H (7) can be restricted to three independent dimensionless parameters $X=(\omega-e)/h$, $Y=\alpha/h$, and $Z=\beta/\alpha$. These parameters have an easy interpretation: X is the energy difference between A and B in units of h, Y is the interaction on the left in units of h, and Z characterizes the asymmetry of the interaction.

The analytical calculation of $F(E)$, $t(E)$, and $\Delta\rho(E)$, as functions of X,Y,Z, is presented in Appendix B, following the spectral analysis of $\underline{P}(E)$. We report here the principal results. If we set

$$W=Y\frac{(1+Z^2)^{1/2}}{\sqrt{2}} ,$$

the transmission coefficient is given by

$$t(E)=t_1 t_2 \tag{15}$$

with

$$t_1=\frac{4}{\left[Z+\frac{1}{Z}\right]^2}\,,$$

$$t_2=\frac{1}{1+\frac{[X+q(W^2-1)]^2}{W^4(4-q^2)}}\,,$$

and the differential density of states is

$$\Delta\rho(E)=-\frac{1}{\pi|h|}\frac{[qX+4(W^2-1)]}{W^2(4-q^2)^{3/2}}\times\frac{1}{1+\frac{[X+q(W^2-1)]^2}{W^4(4-q^2)}}\,. \tag{16}$$

An important indicator to understand the $t(E)$ variations is the change in the number of states within the band, when the defect is inserted. From (6)

$$\Delta N=\int_{E_{\mathrm{bot}}}^{E_{\mathrm{top}}}\Delta\rho(E)dE=-\frac{1}{\pi}[\arg(F(E))]_{q=-2}^{q=2}\,,$$

then from (23) and (24)

$$\Delta N=\begin{cases}1 & \text{if } |X|<2|W^2-1| \text{ and } |W|<1\,,\\ -1 & \text{if } |X|<2|W^2-1| \text{ and } |W|>1\,,\\ 0 & \text{if } |X|>2|W^2-1|\,.\end{cases}$$

Moreover, from Levinson's theorem,[41] the change in the total number of states (band plus discrete levels) must be constant: $\Delta\tilde{N}=1$. It corresponds to the addition of the state $|s_0\rangle$ modeling B to the pair of semi-infinite chains of A units (see discussion below).

All equations previously described are unchanged when Y is replaced by $-Y$ or when X and q are both replaced by $-X$ and $-q$. The discussion will then be limited to positive values of X and Y. Moreover, $t_2(E)$ and $\Delta\rho(E)$ do not depend independently on Y and Z but only on $W=[Y(1+Z^2)^{1/2}]/\sqrt{2}$.

This means that the general case ($Z\neq 1$) can be derived from the symmetric one ($Z=1$) just by a change in the scale of the Y axis. Only t_1 explicitly depends on Z (Fig. 4). This factor t_1 diminishes the transmission coefficient $t(E)$ as soon as Z is no more equal to 1. We will thus study the case $Z=1$, X and Y positive.

B. The case $X=1$

Let us first take $X=1$ and increase the coupling Y. For $X=1$, the state $|s_0\rangle$ associated with the defect is at the $\frac{3}{4}$ position within the band, located between $q=-2$ and $q=+2$ (Fig. 5).

Figure 6 shows the energetic position of the discrete levels as a function of Y, Figs. 7 and 8 are samples of $t(E)$ and $|h|\Delta\rho(E)$ curves for selected values of Y.

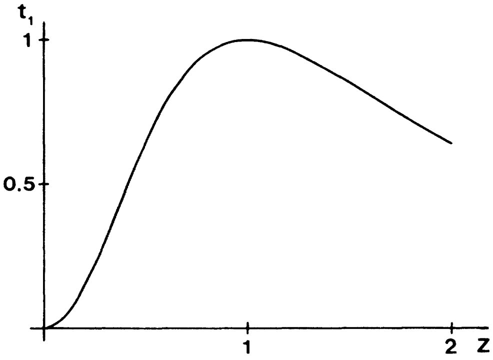


FIG. 4. First factor t_1 of the transmission coefficient $t(E)=t_1 t_2$ as a function of $Z=\beta/\alpha$.

For small values of the coupling Y, no discrete level appears out of the band. The impurity B introduces one state in the continuous spectrum that can be seen as a sharp peak in the density of states. The mixing between B and the chains is weak and the defect state appears as a δ-like function. The chain is "disconnected" by the impurity in a large range of energy: $t(E)$ is very weak except for a small interval, centered on the energy level of the impurity, where a narrow resonance is present. This is a tunneling effect through the defect B.

When Y increases (e.g., 0.4, 0.6), so does the mixing between the impurity B and the semichains. This mixing is mainly antibonding because of the nonsymmetric position of state $|s_0\rangle$ in the band. Consequently, the peak in $\Delta\rho$ is shifted to higher energies, is broadened, and is gradually spread over the whole band in a "U-like" function, characteristic of the DOS of a 1D system. In the same way the resonance in the transmission coefficient becomes larger and is shifted up.

A new phenomena appears suddenly as soon as Y is larger than $\sqrt{2}/2$ ($\sim$0.707). Figure 6 shows that a discrete level has emerged upon the band. State B has been ejected out of the band by antibonding mixing with the chains. The change in the number of states in the band is accordingly zero. The change in the density of states then has a positive and negative part that counterbalance upon integration. The resonance in $t(E)$ is lost: the value 1 is not reached anymore.

As the coupling Y goes beyond $\sqrt{3}/\sqrt{2}$ ($\sim$1.22) a second level appears below the continuous spectrum; a state of the band has been pushed down by bonding com-

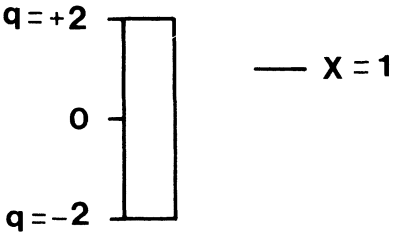


FIG. 5. Position of the impurity level B within the band of the period system $[-2,+2]$ in the case $X=(\omega-e)/h=1$.

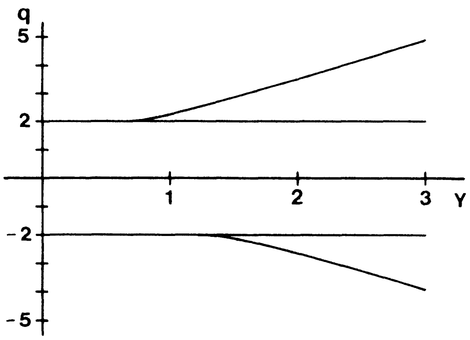


FIG. 6. Energetic position of the discrete levels out of the band, as a function of $Y=\alpha/h$, in the case $X=(\omega-e)/h=1$ and $Z=\beta/\alpha=1$.

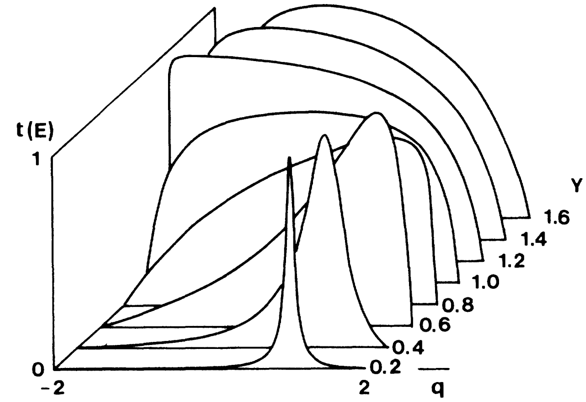


FIG. 7. Transmission coefficient $t(E)$ within the band $q=(E-e)/h=-2,+2$ for different values of the cell coupling $Y=\alpha/h$ $(X=1, Z=1)$.

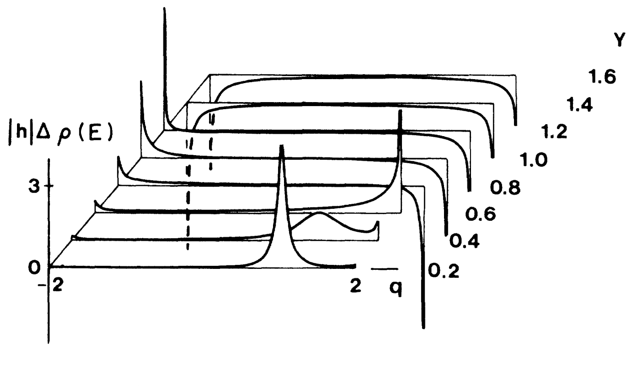


FIG. 8. Change in the chain density of states within the band, $|h|\Delta\rho(E)$, associated with the presence of the defect B, for different values of the cell coupling $Y=\alpha/h$ $(X=1, Z=1)$.

bination with the state introduced by B. Hence, the change in the number of states in the band is -1. The $\Delta\rho$ is a "U-like" negative function and the transmission coefficient is a broad curve that again reaches 1 because tunneling occurs through the removed state.

As an example we plot in Fig. 9 the electronic density $|C_n|^2$ as a function of site position for the two discrete levels in the case $Y=1.35$. The higher level ($q=2.66$) is mainly centered on B, while the A contributions dominate in the lower one ($q=-2.03$), in complete agreement with the previous discussion about the nature of these states.

C. The X,Y plane

What happens when X, the energy level of the defect B, is modified?

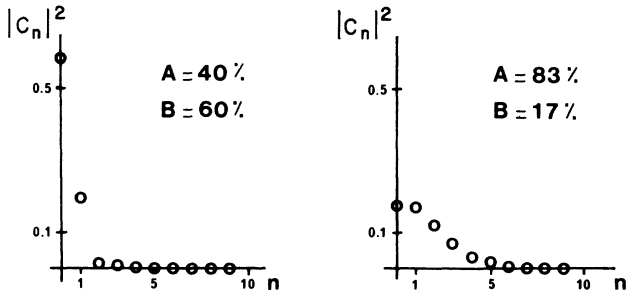
Figure 10 shows the change in the number of states ΔN as a function of X and Y. The previous sample of curves is located there on the dotted line. The zone where the impurity state is added to the band ($\Delta N=1$) is reduced when X increases and disappears when the defect level is located out of the band ($X>2$). The position of the discrete levels as a function of Y, in the case $X=2.5$, is presented in Fig. 11: The level upon the band is always present. In the same way the ejection of a bonding discrete level below the band occurs at higher Y when the level X is increased.

The value of the maximum of the transmission coefficient $t(E)$, all over the band, is given in Fig. 12 as a function of X and Y. Notice that this maximum is 1 as soon as the change in the number of states in the band is different from zero (1 or -1). Its variations are very fast in the region where Y is small, that is, when the interaction between A and B is small compared with the A-A interaction along the chain.

D. The defect B as an active switching element

Two conditions have to be simultaneously fulfilled to give a high value for the effective transmission coefficient t_{eff} (5): a resonance must be present in $t(E)$ and its energetic position must be close to the Fermi level $[-(\partial f/\partial E)$ is a δ-like function of width $\sim k_b T]$.

The Fermi level is introduced by the dimensionless



q = 2.66

q = -2.03

FIG. 9. Electronic density $|C_n|^2$ as a function of the site position and A/B ratio for the two discrete levels in the case $Y=1.35$ $(X=1, Z=1)$. $n=0$ corresponds to the site of the defect B.

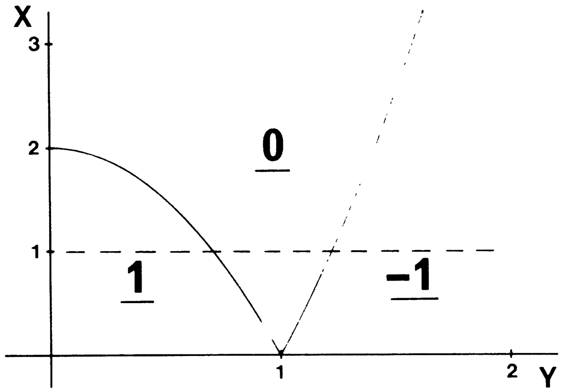


FIG. 10. Change in the number of states within the band ΔN, when the defect is inserted, as a function of $X=(\omega-e)/h$ and $Y=\alpha/h$ $(Z=1)$.

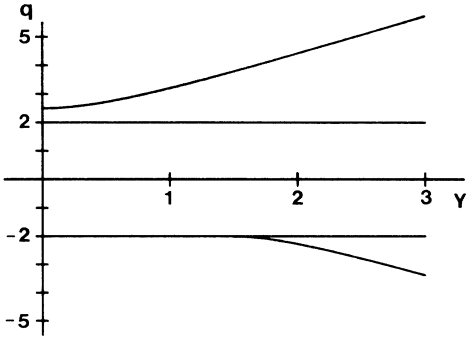


FIG. 11. Energetic position of the discrete levels out of the band, as a function of $Y=\alpha/h$, in the case $X=(\omega-e)/h=2.5$ and $Z=\beta/\alpha=1$.

variable $q_\mu=(\mu-e)/h$. At low temperature $t_{\text{eff}}\simeq t(h)$. Figure 13 shows $t_{\text{eff}}(X,Y)$, in this low temperature case, for $Z=1$ and $q_\mu=1$: t_{eff} reaches the value 1 only on the curve

$$X=q_\mu(1-Y^2)\ . \tag{17}$$

As it was noticed before, the decrease of t_{eff} when one leaves the above curve is fast in the case of small A-B interaction, and in this case t_{eff} is high only in the close neighborhood of the Fermi level. The effect of a nonzero temperature is only sensitive in this region of small Y, that is, in the case where $t(E)$ allows rapid variations, and appears as a smoothing of the t_{eff} surface.

From Fig. 13, t_{eff} can be a fast varying function of the parameters X, Y (and Z) defining the nature of the system. Hence, even a small change in the electronic characteristics of the impurity B (ω, α, and β) can lead to an important variation of the transmission coefficient t_{eff}.

Two types of elementary variations can be produced in order to model an active defect.[31,35] The first one is associated with a change in the energy level of the impurity B. We then need to study t_{eff} as a function of X. The second one is associated with a change in the interaction between B and the neighboring A. This can be represented by a Z variation, going from a symmetric coupling $(Z=1)$ to an asymmetric and $(Z\neq 1)$.

The comparison of the switching ability of this model with the control of the dynamics of the isolated ABA system has been presented elsewhere.[39] In the following we underline the qualitative behavior, with a different set of parameters that facilitates the chemical interpretation.

The control of t_{eff} by X is directly apparent in Fig. 13. Three vertical sections are presented in Fig. 14(a) in the case $q_\mu=1$ and for $\tau=10$ and 300 K $(Z=1)$. The curve is sharp in the case of small Y: A small variation in X may have important consequences in t_{eff}. The maximum is close to $X=1$. In the case of small interaction the narrow resonance in $t(E)$ is near X and then coincides with the Fermi level if $X=q_\mu$.

For larger interactions the curve is broadened: The

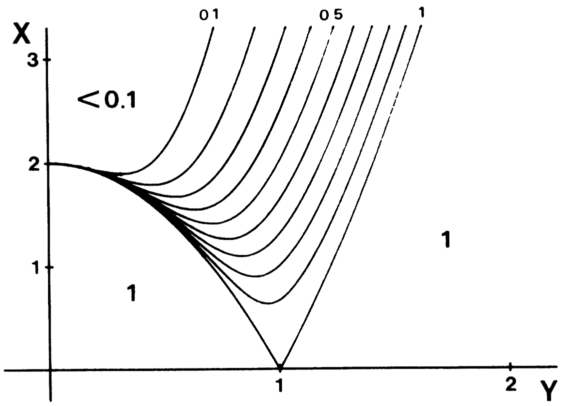


FIG. 12. $t(E)$ maximum over the band, as a function of $X=(\omega-e)/h$ and $Y=\alpha/h$ $(Z=1)$.

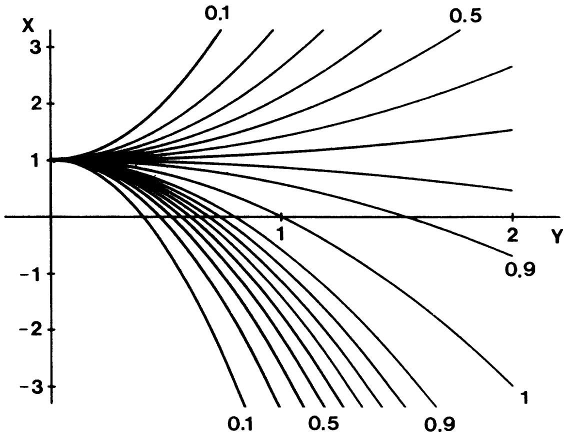


FIG. 13. Effective transmission coefficient t_{eff} (X,Y) in the low-temperature case for $Z=1$ and $q_\mu=1$.

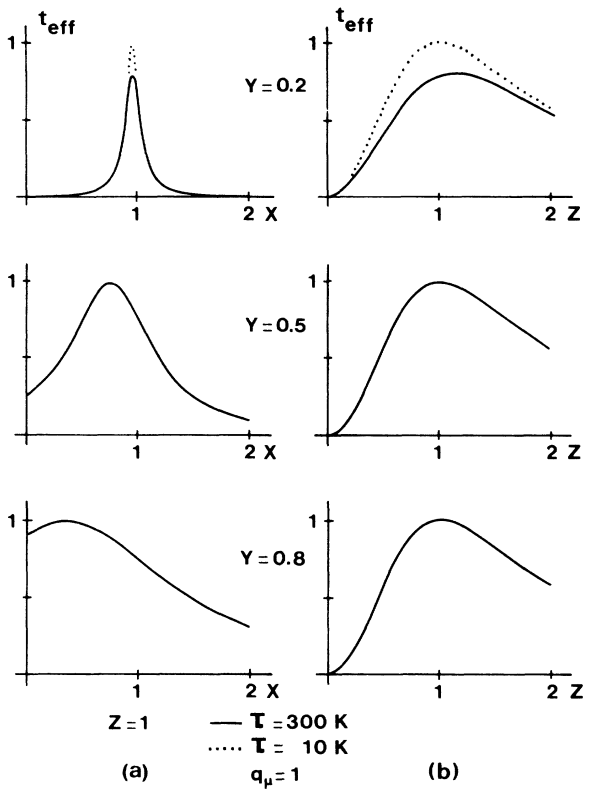


FIG. 14. Switching ability of the effective transmission coefficient t_{eff} for $q_\mu = 1$ and $Y = 0.2$, 0.5, and 0.8. (a) shows the switching ability as a function of X for $Z = 1$. (b) shows the switching ability as a function of Z for optimal X. Two different temperature cases are shown: $\tau = 300$ and 10 K.

switching effect is rapidly less effective. The maximum is displaced to $X \leq 1$. Due to the antibonding nature of the interaction, the energy level of the impurity must be lower than q_μ in order to get a $t(E)$ maximum around q_μ. The case $Y > 1$ gives a very flat maximum for a negative value of X (see Fig. 13).

The influence of a finite temperature (dotted line in Fig. 14) is only sensitive in the case of small Y, as was explained before. It partially destroys the good switching effect in that case.

Notice that, with a given chemical system, a change in the Fermi level of the chain shifts the position of the maximum of t_{eff} as a function of X. The switching effect is improved as $|q_\mu|$ is increased within the band, but the temperature effect becomes more effective.

Things are quite different when we want to control t_{eff} by Z, that is, to study the influence of an asymmetric interaction ($\alpha \neq \beta$). A first control is done by the function t_1 (Fig. 4) that only depends on Z. It implies that the maximum 1 for t_{eff} can only be reached for $Z = 1$. For the second factor t_2 in $t(E)$ [Eq. (15)] a variation of Z is equivalent with a change in the scale of the Y axis. Therefore it can be seen in Fig. 13 as a shift in Y. In order to coincide with t_1 maximum ($Z = 1$), t_{eff} must reach 1 in the X-Y plane, i.e., X, Y, and q_μ must verify (17). This imposes a severe condition on the system that could be carried out by varying the Fermi level q_μ. In that case, t_{eff} only depends on Z and q_μ at low temperature. However, the t_2 contribution is flat and no real improvement of t_1 can be achieved [Fig. 14(b)] except if the Fermi level is close to the band edge. On the other hand, no destruction of the switching effect occurs for high coupling Y. If X, Y, and q_μ depart from relation (17), the decrease of the switching ability is abrupt only in the case of small coupling Y.

V. CONCLUSION

In this paper the consequences of a local rupture of translational invariance on the transmission properties of a one-dimensional chain have been studied. The system $\cdots AAABAAA \cdots$ has been modeled at the tight-binding level. The presence of a single defect on a chain keeps the energy band intact but scatters the Bloch waves that built the solution of the periodic system at each allowed energy E. In the band, the defect B is then characterized by a scattering matrix $\underline{S}(E)$ that describes its effect on the Bloch functions of the periodic chain. The transmission coefficient $t(E)$ of an electron at energy E through the defect, which is directly related to the chain conductance,[20–23] can then be extracted from $\underline{S}(E)$, together with the differential density of states. From a technical point of view we have extracted from the Hamiltonian the elementary propagators of the system. The transfer matrix technique was then used: The scattering channels originate from the modulus-one eigenvalues of the period chain propagator. Analytical expressions were then derived for the transmission coefficient $t(E)$ and the change in the density of states $\Delta\rho(E)$. Following Azbel,[21,22] an energy-averaged transmission coefficient t_{eff} has also been considered.

The variations of these quantities have then been discussed as functions of the parameters characterizing the chemical nature of the defect: The influence of the energetic position of the impurity level and of its coupling with the chain have been analyzed. The transmission coefficient is strongly dependent upon the energetic parameters: a small coupling induces a sharp resonance while broader transmission curves occur for larger coupling. Furthermore, the maximum value 1 for $t(E)$ can only be reached when the number of states added to the band by the defect is 1 or -1: tunneling happens through the defect state or the removed band state.

The Fermi level of the chain is considered through the effective transmission coefficient t_{eff}. A high t_{eff} value can only be reached when a resonance in $t(E)$ is close to the Fermi level, where the free carriers can be found.

Finally we have shown how a control in the effective transmission coefficient t_{eff} can be produced by varying either the energy level of the defect or the symmetry of its coupling with the chain. The first case seems appropriate for systems where the coupling between the chain and the defect is small: abrupt variations are present. The position of the narrow transmission maximum can be tuned by the Fermi level. However, this behavior is temperature dependent. In the second case, condition (17) must be, at least roughly, fulfilled in order to get a good control of the transmission coefficient t_{eff}.

A change in the Fermi level can help in this way. The control is less effective than in the first case and large couplings are better since they allow greater deviations from (17) and avoid a temperature-dependent effect.

This model approach shows that, in order to understand the influence of an impurity on a polymer chain, we need a good knowledge of the involved interactions. The design of a molecular device with an adjustable Fermi level appears to be an important goal. An improved model, more realistic on a chemical viewpoint, is under investigation.

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APPENDIX A

Let us introduce K_n, a function of the C_n,

$$K_n=\frac{1}{i}(C_n^*C_{n+1}-C_nC_{n+1}^*)\ . \tag{A1}$$

K_n is a translational invariant of the system chain plus defect. To demonstrate this result, let us first show that K_n is an invariant of the periodic chain. The C_n are then related by the second-order difference equation (9a),

$$h(C_{n-1}+C_{n+1})=(E-e)C_n\ ,$$

or (with h, e, and E real)

$$h(C_{n+1}^*+C_{n-1}^*)C_n=(E-e)C_n^*C_n=h(C_{n-1}+C_{n+1})C_n^*\ .$$

Therefore

$$h(C_{n+1}^*C_n+C_{n-1}^*C_n)=h(C_{n-1}C_n^*+C_{n+1}C_n^*)$$

and

$$C_{n-1}^*C_n-C_{n-1}C_n^*=C_n^*C_{n+1}-C_nC_{n+1}^*\ ,$$

which means that

$$K_{n-1}=K_n\ . \tag{A2}$$

If K_n is rewritten

$$K_n=\frac{1}{i}[C_n^*(C_{n+1}-C_n)-C_n(C_{n+1}^*-C_n^*)]\ .$$

K_n appears as a discrete equivalent of the probability current

$$\mathbf{J}=\frac{\hbar}{2mi}(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*)\ .$$

Then Eq. (A2) is the discrete equivalent of the conservation law

$$\mathrm{div}\mathbf{J}=0\ .$$

The "current" associated with the solution of the periodic chain $C_n=\mathcal{A}e^{in\theta}+\mathcal{B}e^{-in\theta}$ is $K_n=2\sin\theta(|\mathcal{A}|^2-|\mathcal{B}|^2)$.

For a chain with a defect, the current on each side of it can be related by the transfer matrix [(2) and (3)]

$$|\mathcal{C}|^2-|\mathcal{D}|^2=|F(E)\mathcal{A}+G^*(E)\mathcal{B}|^2-|G(E)\mathcal{A}+F^*(E)\mathcal{B}|^2$$
$$=[|F(E)|^2-|G(E)|^2](|\mathcal{A}|^2-|\mathcal{B}|^2)\ .$$

So

$$K_{\mathrm{right}}=\det[\underline{T}(E)]K_{\mathrm{left}}\ .$$

But from (13) and (10)

$$[\det[\underline{T}(E)]=\det(\underline{\tilde{P}})=\det(\underline{P}_1)\det(\underline{P}_0)\det(\underline{P}_{-1})$$
$$=1\ .$$

Then $K_{\mathrm{right}}=K_{\mathrm{left}}$ and K_n is a translational invariant of the chain with the defect.

APPENDIX B

Let us first calculate $\underline{P}_1\underline{P}_0\underline{P}_{-1}$ from (10) with $X=(\omega-e)/h$, $Y=\alpha/h$, $Z=\beta/\alpha$, and $q=(E-e)/h$:

$$\underline{P}_1\underline{P}_0\underline{P}_{-1}=\begin{bmatrix} q & -YZ \\ 1 & 0 \end{bmatrix}\begin{bmatrix} \dfrac{q-X}{YZ} & -\dfrac{1}{Z} \\ 1 & 0 \end{bmatrix}\begin{bmatrix} \dfrac{q}{Y} & -\dfrac{1}{Y} \\ 1 & 0 \end{bmatrix}$$

$$=\begin{bmatrix} \dfrac{q^2(q-X)}{ZY^2}-q\left[Z+\dfrac{1}{Z}\right] & -\dfrac{q(q-X)}{ZY^2}+Z \\ \dfrac{q(q-X)}{ZY^2}-\dfrac{1}{Z} & -\dfrac{(q-X)}{ZY^2} \end{bmatrix}$$

$$=\begin{bmatrix} a & b \\ c & d \end{bmatrix}\ .$$

Region I. $|q|>2$, determination of the localized states out of the band.

The eigenenergies are solutions of $\tilde{P}_{11}=0$, that is, calculating $\tilde{P}_{11}$ from (13),

$$a\lambda+b-c-\frac{d}{\lambda}=0\ . \tag{B1}$$

λ is the $\underline{P}(E)$ eigenvalue of modulus greater than 1,

$$\lambda=\frac{q+\mathrm{sgn}(q)\left[q^2-4\right]^{1/2}}{2}$$

$$\text{with }\mathrm{sgn}(q)=\begin{cases}+1 & \text{if } q>0\ ,\\ -1 & \text{if } q<0\ .\end{cases}$$

After the substitution of this value of λ in (B1), one obtains the equation

$$q(a-d)+2(b-c)=-\mathrm{sgn}(q)(q^2-4)^{1/2}(a+d)\ , \tag{B2}$$

whose solutions determine the energetic position of the discrete levels out of the band.

In order to solve (B2), one may in a first step take the square of this equation. After some manipulation one gets

$$(q-X)^2-q(q-X)Y^2(1+Z^2)+Y^4(1+Z^2)^2=0\ . \tag{B3}$$

Consequently the number of localized states is less or equal to 2 (second-degree equation for q). Furthermore, one can easily see that the two solutions of (B3)are real and indeed located out of the band. However, condition (B3) is not sufficient: spurious solutions have been introduced when taking the square of (B2). We need to test back Eq. (B2) on each solution of (B3): this determines the number of localized states out of the band $[-2,2]$ (see discussion in Sec. IV).

Region II. $|q|<2$. In order to study the delocalized states in the band we need to calculate again $\tilde{P}_{11}(E)$. $\underline{P}_1\underline{P}_0\underline{P}_{-1}$ was calculated already but, now, λ [eigenvalue of $\underline{P}(E)$] is different,

$$\lambda=\frac{q+i(4-q^2)^{1/2}}{2} \; ;$$

therefore

$$\tilde{P}_{11}=\frac{a+d}{2}+i\left[\frac{(d-a)q+2(c-b)}{2(4-q^2)^{1/2}}\right] ,$$

and if we replace a,b,c,d by their values

$$\mathrm{Re}(\tilde{P}_{11})=\frac{1}{2ZY^2}[(q^2-1)(q-X)-qY^2(1+Z^2)]$$

$$\mathrm{Im}(\tilde{P}_{11})=\frac{1}{2ZY^2(4-q^2)^{1/2}} \times[(-q^3+3q)(q-X)+(q^2-2)Y^2(1+Z^2)] \; .$$

In order to calculate the transmission coefficient and the change in the density of states we need

$$F=e^{-3i\theta}\tilde{P}_{11} \quad \text{with } \cos\theta=\frac{q}{2} \; ,$$

and after some algebra one can write

$$\mathrm{Re}(F)=\frac{1}{2}\left[Z+\frac{1}{Z}\right] , \tag{B4}$$

$$\mathrm{Im}(F)=\frac{1}{ZY^2(4-q^2)^{1/2}}[X+q(W^2-1)] \; . \tag{B5}$$

The transmission coefficient $t(E)$ given by (15) and the differential density of states $\Delta\rho(E)$ given by (16) are then derived from (4), (6), (B4), and (B5).

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[1] J. M. André, Adv. Quantum Chem. **12**, 65 (1980).

[2] M. Kertesz, Adv. Quantum Chem. **15**, 161 (1982).

[3] M. H. Whangbo, in *Extended Linear Chain Compounds,* edited by J. S. Miller (Plenum, New York, 1982), Vol. 2, p. 127.

[4] *Quantum Chemistry of Polymers—Solid State Aspects,* Vol. 123 of *NATO Advanced Study Institute, Series C,* edited by J. Ladik and J. M. André (Reidel, Dordrecht, 1984).

[5] P. R. Surjan and H. Kuzmány, Phys. Rev. B **33**, 2615 (1986).

[6] J. T. L. Navarrete and G. Zerbi, Solid State Commum. **64**, 1183 (1987).

[7] K. Tanaka, S. Yamanaka, M. Oiji and T. Yamabe, Synth. Met. **22**, 247 (1988)

[8] S. Jeyadev and E. M. Conwell, Phys. Rev. B **37**, 8262 (1988).

[9] G. F. Kventsel and Y. A. Kruglyak, Theor. Chim. Acta **12**, 1 (1968).

[10] J. Ladik and M. Seel, Phys. Rev. B **13**, 5338 (1976).

[11] M. Seel, G. Del Re, and J. Ladik, J. Comput. Chem. **3**, 451 (1982).

[12] M. Seel, Int. J. Quantum Chem. **26**, 753 (1984).

[13] H. Schmidt, Phys. Rev. **105**, 425 (1957).

[14] J. Hori and T. Asaki, Prog. Theor. Phys. **17**, 523 (1957).

[15] J. Hori, *Spectral Properties of Disordered Lattices* (Plenum, New York, 1968).

[16] G. Biczo, Can. J. Chem. **63**, 1992 (1985).

[17] M. Gies, M. Seel, and J. Ladik, J. Mol. Struct. **150**, 267 (1987).

[18] M. Seel and J. Ladik, Phys. Rev. B **32**, 5124 (1985).

[19] A. D. Stone, J. D. Joannopoulos, and D. J. Chadi, Phys. Rev. B **24**, 5583 (1981).

[20] R. Landauer, Philos. Mag. **21**, 863 (1970).

[21] M. Ya. Azbel, Phys. Lett. **78A**, 410 (1980).

[22] M. Ya. Azbel, Solid State Commun. **45**, 527 (1983).

[23] D. S. Fisher and P. A. Lee, Phys. Rev. B **23**, 6851 (1981).

[24] Y. Avishai and Y. B. Band, Phys. Rev. B **32**, 2674 (1985).

[25] G. Wolmershauser, R. Jotter and T. Wilhem, J. Phys. (Paris) Colloq. **44**, C3-729 (1983).

[26] J. C. W. Chien, G. N. Babu, and J. A. Hirsch, Nature (London) **314**, 723 (1985).

[27] J. C. W. Chien, G. N. Babu, J. Chem. Phys. **82**, 441 (1985).

[28] H. Kuzmány and J. Kurti, Synth. Met. **21**, 95 (1985).

[29] D. Schafer-Siebert, S. Roth, C. Budrowski, and H. Kuzmány, Synth. Met. **21**, 285 (1987).

[30] F. Zuo, A. J. Epstein, X. Q. Yang, D. B. Tanner, G. Arbuckle, and A. G. MacDiarmid, Synth. Met. **17**, 433 (1987).

[31] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).

[32] H. Sixl and D. Higelin, *Proceedings of the Second International Symposium in Molecular Electronics Devices,* Washington, D.C., 1981, edited by S. L. Carter (Dekker, New York 1984).

[33] F. L. Carter, Physica (Utrecht) D **10**, 175 (1984).

[34] H. Tanaka, S. Yamanaka, T. Koike, and I. Yamabe, Phys. Rev. B **32**, 2731 (1985).

[35] C. Joachim, J. Mol. Electron. **4**, 125 (1988).

[36] E. Abrahams and M. J. Stephen, J. Phys. C **13**, L377 (1980).

[37] M. E. Mora, R. Perez, and Ch. B. Sommers, J. Phys. (Paris) **46**, 1021 (1985).

[38] J. Stein and C. Joachim, J. Phys. A **20**, 2849 (1987).

[39] P. Sautet and C. Joachim, J. Phys. C **21**, 3939 (1988).

[40] S. Goldberg, *Introduction to Difference Equations* (Wiley, New York, 1958).

[41] R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966,) Sec. 11.2.