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# Localization and lattice relaxations in non-periodic deterministic structures

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**Abstract.** Using a model that includes both electronic and structural degrees of freedom we study one-dimensional structures that are non-periodic but deterministic. The model allows us to follow structural changes induced by changing the number of electrons (i.e., upon doping). Special emphasis is put on localization versus delocalization of the orbitals as a means of estimating the conducting properties. To this end various measures for quantifying the degree of localization are compared and a new one—based on an autocorrelation function of the electron density—is presented. As an example of the application of our model we examine the Fibonacci structure in detail. It is found that the well known self-similarity in the density of states of the undistorted system may be lost upon relaxation and/or doping. As a general result observed both for Fibonacci structures and for other quasiperiodic and incommensurate systems we find that those orbitals that become occupied/emptied upon doping increase their localization indicating less variability of the conductivity.

## 1. Introduction

Electronic and vibrational properties of systems for which the potential is incommensurate with the underlying nuclear backbone continues to be of interest. Such situations occur in, e.g., charge-density-wave (CDW) systems such as the  $\text{MX}_3$  materials ( $M$  = transition metal;  $X$  = chalcogenide) (see e.g., [1]) as well as for crystals in magnetic fields (for a recent reference, see [2]). Some of the first studied materials within this concept include  $\text{MnAu}_3$  [3],  $\text{NaNO}_2$  [4],  $\text{Hg}_{3-x}\text{AsF}_6$  [5], and  $\text{Na}_2\text{CO}_3$  [6]. The subject gained renewed interest as unexpected diffraction patterns for an icosahedral phase of the  $\text{Al}_{0.86}\text{Mn}_{0.14}$  alloy (a so-called quasicrystal) were reported by Shechtman *et al* [7]. These patterns indicated the existence of ordered but aperiodic ('quasiperiodic') structures. It was subsequently demonstrated [8, 9] that one may understand these as the diffraction patterns of a regular higher-dimensional lattice projected onto the three-dimensional space. As a one-dimensional analogue one may construct systems with quasiperiodic potentials by projecting two-dimensional regular lattices onto certain lines (see, e.g., [8, 9]).

In this context the Fibonacci lattice has been considered as the one-dimensional prototype of the quasicrystals [10, 11].

Another reason for the interest in Fibonacci lattices is that they possess a self-similar density of states [12–17] whereas generalized Fibonacci structures of higher order can lose this characteristic [18].

One-dimensional quasiperiodic structures are, moreover, of direct experimental relevance after the reports of successful synthesis of quasiperiodic GaAs–AlAs [19, 20] and Nb–Cu [21] heterostructures. Moreover, it has recently been argued [22] that quasiperiodic magnetic lattices may be used in polarizing neutrons.

In the present work we will distinguish between incommensurable and quasiperiodic structures by defining the latter as systems for which the on-site energies (see below) only take a few discrete values, whereas for the former they span a continuous, finite interval. The Fibonacci chain is an example of a quasiperiodic chain.

One of the central issues in the studies of quasiperiodic and incommensurable one-dimensional structures is to what extent the (electronic, vibrational, photonic, etc) states are localized. It is well known that—within a single-particle picture—all states are delocalized for a purely periodic infinite one-dimensional system, whereas for the equivalent random system they are all localized [23–25]. On the other hand, incommensurable one-dimensional systems have both localized and delocalized states separated by mobility edges [26, 27] whereas all states of the infinite Fibonacci chain are critical [14, 16, 27, 28]. However, synthesized quasiperiodic systems have finite lengths, in which case the separation into localized, delocalized, and critical states is less obvious. Moreover, ‘localization’ is not uniquely defined. Thus, in a number of studies the classification into localized and delocalized states is performed merely by a subjective look at selected states (see, e.g., [29–40]). Only recently have more direct measures of the degree of localization been introduced. These include the resistance as calculated by the Landauer formula [41–45] and the thereto-related inverse localization length [46, 47]. Moreover, the Lyapunov exponent has been used, e.g., by Das Sarma *et al* [48, 49] and by Farchioni *et al* [50]. On the other hand, Hirose *et al* [51] used the inverse participation ratio, whereas Varga *et al* [52] studied both the spatial filling factor and the structural entropy. Finally, Pnevmatikos *et al* [53] used the participation function, which is equivalent to the information entropy of Varga *et al* [52].

One of the objectives of the present work is to compare various of the proposed measures for a simple system for which an intuitive feeling for the localization is easily developed. In addition we shall propose a new measure that seems to be consistent with the immediate expectations. This will form the basis of section 2.

Subsequently, we shall report results of a theoretical study of the electronic properties of one-dimensional quasicrystals. In the case of more or less localized states it may be speculated that the conducting properties of these materials can be varied over many orders of magnitude by controlled doping. However, the system may respond to the doping by modifying the underlying lattice structure thereby ultimately leading to changes in the localization of the orbitals. A further purpose of the present work is therefore to present a model that takes this effect into account. To our knowledge there has only been one related study aimed at this interplay between structure and localization in incommensurable one-dimensional systems [53]. Our model is related to but differs in important aspects from that of Pnevmatikos *et al* [53]. Moreover, Pnevmatikos *et al* focused on an incommensurable structure whereas we shall concentrate on a quasiperiodic system.

We write the total Hamiltonian of our system of interest as a sum of an electronic part and a lattice part. For the electronic part we use a tight-binding Hamiltonian

$$\hat{H}_e = \sum_n \epsilon_n \hat{c}_n^\dagger \hat{c}_n - \sum_n t_{n,n+1} (\hat{c}_{n+1}^\dagger \hat{c}_n + \hat{c}_n^\dagger \hat{c}_{n+1}). \quad (1)$$

Here,  $\hat{c}_n$  and  $\hat{c}_n^\dagger$  are the annihilation and creation operators, respectively, of an electron on site  $n$ ,  $\epsilon_n$  are the on-site energies, and  $t_{n,n+1}$  the nearest-neighbour hopping integrals. We shall here for the sake of simplicity neglect the spin variable and allow thus each orbital to contain up to two electrons. Furthermore, we include only one orbital per site. As a representative example of a quasiperiodic system we study the Fibonacci lattice for

which the on-site energies  $\epsilon_n$  take one of two values according to the Fibonacci sequence. Alternatively, one may allow the hopping integrals to oscillate. This possibility will, however, not be considered here. It should be mentioned at this point that the Fibonacci chain has been the subject of a number of other theoretical studies (see, e.g., [35], [38], [39], [47], [50], [51] and [54]). However, as a (more realistic) generalization we will here allow the hopping integrals  $t_{n,n+1}$  to depend on the bond lengths, such that the system is allowed to react against doping. This will be discussed in detail in section 3. A detailed discussion of the results for the Fibonacci lattice is presented in section 4 and some other quasiperiodic and incommensurable systems for which the on-site energies  $\epsilon_n$  are non-periodic but deterministic will be discussed briefly in section 5. We conclude in section 6. For the sake of completeness we add that a preliminary version of the present work has been published elsewhere [55].

## 2. Degree of localization

We consider a ring molecule or a linear chain consisting of a large number  $N$  of sites. For this we solve the Schrödinger equation

$$\hat{H}_e \sum_{n=1}^N c_{i,n} \varphi_n = \epsilon_i \sum_{n=1}^N c_{i,n} \varphi_n \tag{2}$$

where  $\varphi_n$  is the Wannier orbital of the  $n$ th site. In our own calculations we shall exclusively consider ring molecules. In order to quantify the localization of the  $i$ th eigenfunction we define an autocorrelation function  $G_i(m)$  of the electronic density as

$$G_i(m) = \sum_{n=1}^N |c_{i,n}^2| |c_{i,n+m}^2| \quad m = 0, 1, \dots, N - 1. \tag{3}$$

We use the first 20% of the terms in fitting to a Gaussian by minimizing:

$$\begin{aligned} \Delta_i = & \left[ \frac{1}{N_p} \sum_{m=1}^{N_p} \ln \left( \frac{G_i(m) + G_i(m+1)}{2} - \ln G_i(0) \exp \left[ -\alpha(i) \left( m - \frac{1}{2} \right)^2 \right] \right)^2 \right]^{1/2} \\ & \times \left[ \frac{1}{N_p} \sum_{m=1}^{N_p} \ln \left( \frac{G_i(m) + G_i(m+1)}{2} \right) \right]. \end{aligned} \tag{4}$$

By studying the average of  $G_i(m)$  and  $G_i(m+1)$  we smear out certain oscillatory behaviours that occur in  $G_i(m)$ , e.g., for solitons in *trans*-polyacetylene. Since our typical system size is 200–400 sites we use typically  $N_p \simeq 50$  terms in the fit.  $\alpha(i)$  is subsequently used as our measure of the degree of localization. Since  $\alpha(i)$  is larger (smaller) for more localized (delocalized) states we may relate  $\alpha(i)$  to an inverse localization length.  $\alpha(i)$  is in addition related to the participation function  $P(i) \equiv [G_i(0)]^{-1}$  of Pnevmatikos *et al* [53]. By studying the autocorrelation function we obtain information about the localization of our state of interest independent of where it is actually localized. The parametrization (4) is a way of quantifying the short-range to intermediate-range behaviour of the function  $G_i(m)$  with a single parameter  $\alpha(i)$ . In fitting with a Gaussian we indirectly assume the state to

be localized inside a potential of approximately harmonic shape. We stress that this way of quantifying the localization is independent of the type of system and is computationally efficient.

Alternatively, one may quantify the localization using quantities related to the Lyapunov exponent, which for self-averaging systems is

$$\Gamma(E) = \lim_{N \rightarrow +\infty} \frac{1}{N} \ln \text{Tr} \left( \prod_{i=1}^N M_i(E) \right) = \lim_{N \rightarrow +\infty} \frac{1}{N} \ln \text{Tr} [\mathcal{M}_N(E)]. \quad (5)$$

Here,  $M_i(E)$  is the  $i$ th  $2 \times 2$  transfer matrix. One may show [56] that

$$\Gamma(i) = \lim_{N \rightarrow +\infty} (2N)^{-1} \ln \frac{|c_{N+1,i}|^2 + |c_{N,i}|^2}{|c_{1,i}|^2}. \quad (6)$$

Das Sarma *et al* [48, 49] used instead  $\gamma(i) = (1/N) \ln |c_{N+1,i}/c_{1,i}|$  for finite system sizes  $N$ .  $\gamma(i)$  quantifies the degree of localization far away from the region where the state is actually localized. Thus,  $\gamma(i)$  may be better in describing the localization for large systems, but for our systems of interest (polymers or semiconducting heterostructures as presently synthesized in the laboratory) the system size  $N$  may only be considered intermediate and we therefore consider  $\alpha(i)$  more appropriate.

Varga *et al* [52] studied the spatial filling factor  $q(i)$  defined as

$$q(i) = P(i)/N \equiv [G_i(0)]^{-1} / N. \quad (7)$$

Finally, various measures based on the Landauer formula [41, 57] have been used. This formula gives the resistance  $r_i$  of the  $i$ th orbital of a finite system embedded into a perfect material with no resistance:

$$r_i = (2\pi\hbar/e^-)\rho_i \quad (8)$$

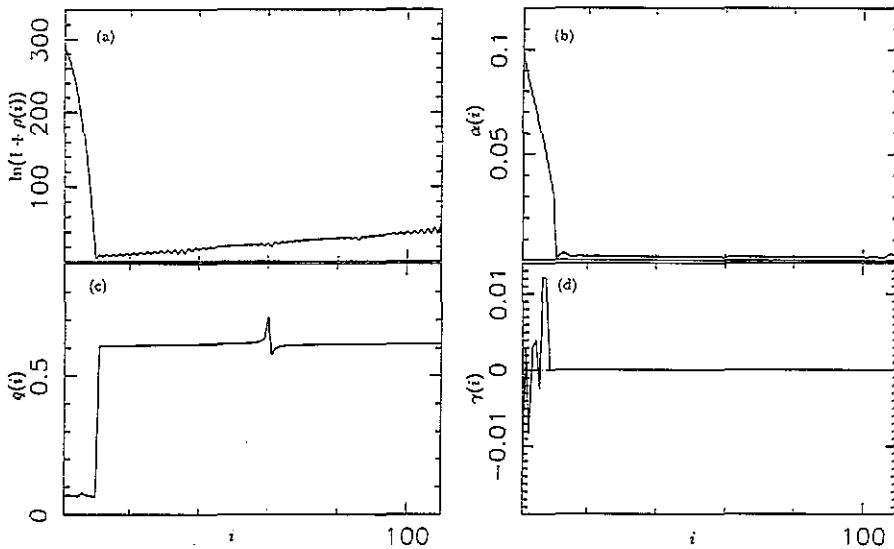
where

$$\rho_i = \{1/[4 - (\varepsilon_i/V_0)]\} \left\{ (\mathcal{M}_N^{11})^2 + (\mathcal{M}_N^{12})^2 + (\mathcal{M}_N^{21})^2 + (\mathcal{M}_N^{22})^2 \right. \\ \left. + (\varepsilon_i/V_0)(\mathcal{M}_N^{11} - \mathcal{M}_N^{22})(\mathcal{M}_N^{12} - \mathcal{M}_N^{21}) - \left[ \varepsilon_i^2/V_0^2 \right] \mathcal{M}_N^{21} \mathcal{M}_N^{12} - 2 \right\} \quad (9)$$

with  $\varepsilon_i$  being the eigenvalue of the  $i$ th orbital,  $V_0$  an external potential (we choose  $V_0 = 50.0$  eV). Instead of studying  $\rho_i$  directly we will consider  $\ln(\rho_i + 1)$ . At this point it is relevant to mention that Das Sarma and Xie [58] have also considered the resistance of a quasiperiodic system. They, however, did not study the resistance as a function of orbital index  $i$  but as a function of the energy of the incoming electron. On the other hand, in applying equation (9) we implicitly assume the  $i$ th orbital to define the Fermi level, which may or may not be true but which allows a detailed look at each orbital separately.

In order to compare  $\alpha(i)$ ,  $P(i)$ ,  $\gamma(i)$ ,  $q(i)$ , and  $\ln(\rho_i + 1)$  we examined a simple system consisting of a potential well formed by ten neighbouring sites inserted into a ring of 100 atoms. We use the Hamiltonian  $\hat{H}_e$  of equation (1) and set the one-site energies  $\varepsilon_n$  of the sites forming the potential well equal to  $-50$  eV below those of the others. All hopping

integrals were set equal to 2.5 eV. In figure 1 we show  $\ln(\rho_i + 1)$ ,  $\alpha(i)$ ,  $q(i)$ , and  $\gamma(i)$  of this simple system (notice that  $P(i)$  and  $q(i)$  are related through equation (7)). In studying  $\gamma(i)$  and  $\rho_i$  we neglect the conceptual problems in using (6) and (9) for a ring molecule. The ten orbitals with the lowest energy are those localized inside the well and the resistance of these orbitals is correspondingly very high. From the first to the tenth orbital the resistance decreases as larger parts of the orbitals protrude from the well.  $\alpha(i)$  shows a thereto related behaviour, whereas the spatial filling factor  $q(i)$  lacks this characteristic differentiation between the energetically lowest orbitals. Moreover, the inverse localization length  $\gamma(i)$  appears not to be correlated with the resistance of the states and thus with the intuitively expected behaviour. It is moreover noticed that  $\ln(\rho_i + 1)$  increases as a function of  $i$  for  $i > 10$  with an approximately constant slope, whereas  $\alpha(i)$  is roughly constant in this interval. This difference can be explained from the dependence of  $\rho_i$  on the external potential  $V_0$  (see equation (9)). On the other hand,  $q(i)$  shows some variation for  $i$  between 58 and 67, which appears to be uncorrelated with the actual localization or shape of the orbitals.



**Figure 1.** (a) The resistance  $\ln(\rho_i + 1)$ , (b) our criterion of the degree of localization  $\alpha(i)$ , (c) the spatial filling factor  $q(i)$ , and (d) the inverse localization length  $\gamma(i)$  of a potential well of ten neighbouring atoms with on-site energies  $\epsilon_n = -50$  eV embedded in a ring of 100 atoms with  $\epsilon_n = 0$ . All quantities are shown as functions of orbital index  $i$ .

In order to obtain an idea of the quality of the fit of equation (4) we add that for the first ten states  $\Delta(i)$  lies in the range between 0.1 and 0.2, and for the extended states ( $i = 11-110$ )  $\Delta(i)$  is less than 0.1. Since the fit of equation (4) involves only one parameter, we find this quality satisfactorily. In total  $\alpha(i)$  is accordingly seen to correlate well with the actual localization, and we shall therefore use this measure throughout the rest of the paper.

### 3. The model

In order to study the structure and the electronic orbitals of arbitrary chains or ring molecules consisting of two types of atom (A and B) and having one orbital per site we use a modified Su-Schrieffer-Heeger (SSH) [59–61] model. Our model Hamiltonian  $\hat{H}$  contains thereby one (tight-binding) part  $\hat{H}_e$  for the electrons (see equation (1)) and a remainder ( $\hat{H}_l$ ) for the lattice energy:

$$\hat{H} = \hat{H}_e + \hat{H}_l. \quad (10)$$

The hopping integrals  $t_{n,n+1}$  are linearized in the bond lengths:

$$t_{n,n+1} = t_0 - a(u_{n+1} - u_n) \quad (11)$$

which is a good approximation for small displacements  $u_n$  of the atoms.  $t_0$  is the hopping integral for the undisturbed system ( $u_n = 0$ ) and  $a$  is an electron-phonon coupling constant. The on-site energies  $\epsilon_n$  take two values  $\epsilon_A$  and  $\epsilon_B$  depending on the type of the corresponding atom.

The lattice energy  $\hat{H}_l$  is written as

$$\hat{H}_l = \frac{1}{2} \sum_n [K_1(u_{n+1} - u_n)^2 + K_2(u_{n+1} - u_n)(1 - \delta_{\epsilon_{n+1}, \epsilon_n})]. \quad (12)$$

The Kronecker symbol ensures that the second term on the right-hand side vanishes for identical neighbours.

We define the neutral system as one with one electron per site and seek then for given  $\epsilon_A$ ,  $\epsilon_B$ ,  $t_0$ , and  $a$  the constants  $K_1$  and  $K_2$  such that the average  $|u_n|$  is as small as possible for the structure with the lowest total energy  $E_{\text{tot}} = E_l + E_e$ . We shall refer to this system as the rigid one.

In addition we study systems where we take over the parameter values of SSH except for the two different types of on-site energy. This system will be called flexible. Compared with the model of Pnevmatikos *et al* [53] we have defined the neutral system as one with one electron per site, whereas they use zero electrons per site. Therefore, Pnevmatikos *et al* have  $K_2 = 0$ .

Since we are interested in lattice relaxations it is crucial to be able to optimize the structure automatically for any given number of electrons. This is achieved by using the forces as follows.

According to the adiabatic (Born-Oppenheimer) approximation the motion of the atoms is described by trajectories following Newton's law [62–64]:

$$m\ddot{u}_n = F_n = -\partial E_{\text{tot}}/\partial u_n. \quad (13)$$

The force  $F_n$  is the sum of a lattice part

$$F_{l,n} = -K_1(2u_n - u_{n+1} - u_{n-1}) - K_2(\delta_{\epsilon_n, \epsilon_{n+1}} - \delta_{\epsilon_n, \epsilon_{n-1}}) \quad (14)$$

and an electronic part

$$F_{e,n} = -2a(P_{n,n-1} - P_{n,n+1}). \quad (15)$$

Here,  $P_{n,m}$  is the bond-order matrix

$$P_{n,m} = \sum_{i=1}^N b_i c_{i,n}^* c_{i,m} \quad (16)$$

where  $b_i$  is the occupation number of the  $i$ th orbital.

The optimal geometry is calculated iteratively using

$$u_n^{(j)} = \xi F_n^{(j-1)} + u_n^{(j-1)} \quad (17)$$

with  $\xi \ll 1$  and  $j$  being an iteration index.  $\xi$  is proportional to the square of a time step. It should be mentioned here that the identification of the global minimum in a high-dimensional space is a general and non-trivial problem [65–67], such that only by repeating calculations for different start geometries may we hope to end up with the global total-energy minimum.

Since an open chain tends to shrink if the four outermost atoms are not fixed, we alternatively use a ring consisting of  $N$  atoms. Such a ring contains two sites between which the quasiperiodicity is interrupted. The consequence of this irregularity is the occurrence of interface states.

We first checked the whole procedure by performing calculations on a finite ( $N = 200$ ) *trans*-polyacetylene chain (actually a ring molecule) using the standard values of Su *et al* [59–61] (i.e.,  $t_0 = 2.5$  eV,  $\alpha = 4.1$  eV  $\text{\AA}^2$ ,  $\epsilon_A = \epsilon_B = 0$ ,  $K_1 = 21.0$  eV  $\text{\AA}^2$  and  $K_2 = 0$ ). The SSH model has been extensively studied and reproduces the experimentally observed bond-length alternation for the neutral system. Thus, the so-called staggered coordinate

$$\chi_n = (-1)^n u_n \quad (18)$$

is a constant different from zero. The model predicts furthermore the occurrence of solitons when the system is dilute doped. A soliton is related to a more or less localized change of sign in the staggered coordinate and induces an orbital with the major components close to the node of  $\chi_n$ . Depending on whether  $\chi_n$  changes from being positive to being negative or vice versa one distinguishes between a soliton and an antisoliton.

As expected, the optimized structure of the neutral system possesses a clear alternation in the bond length. The displacements  $u_n$  of the carbon atoms parallel to the axis of the polymer,  $\chi_n = 0.039 \text{ \AA} \pm 0.0013 \text{ \AA}$ , are in good agreement with the theoretical results of Su *et al* ( $\chi_n = 0.04 \text{ \AA}$ ). Upon doping with two electrons a well separated soliton–antisoliton pair is created. This pair induces two energetically degenerate states in the middle of the energy gap separating valence and conduction bands. It is well known that the major part of such a state in *trans*-polyacetylene is localized over roughly 14 carbon atoms, and  $\alpha(i)$  for these gap states compared with  $\alpha(i)$  for the delocalized Bloch states thus gives an estimate of the changes in  $\alpha(i)$  upon strong localization.

In figure 2 we show therefore  $\alpha(i)$  both for the neutral and for the doped system. As is seen, a well localized state (figure 2(b)) has an  $\alpha$  value of about  $5 \times 10^{-3}$  whereas extended states have  $\alpha(i) \simeq 5 \times 10^{-4}$  (see figure 2(a)). This is in qualitative agreement with our studies on the potential well for which the energetically deepest state is localized to about ten atoms ( $\sim 10\%$  of the total system size) and has an  $\alpha(i)$  value of about 0.1 as compared to a state that is extended over 100 atoms, which has an  $\alpha(i)$  value of about  $6 \times 10^{-4}$ . However, the soliton-induced state is less localized than those of the potential well discussed in the preceding section.



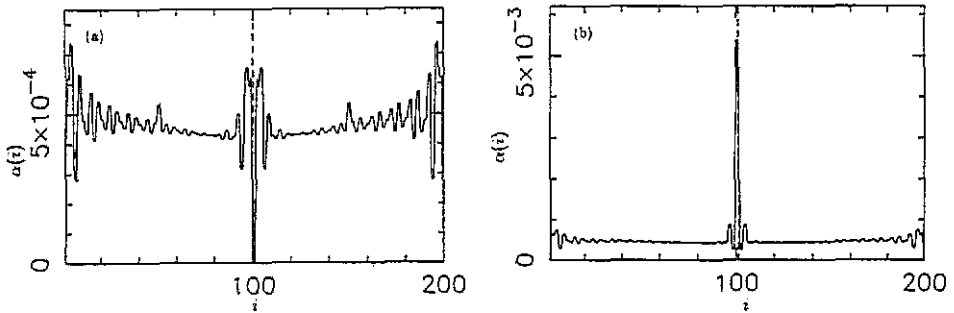


Figure 2. Degree of localization  $\alpha(i)$  of a finite *trans*-polyacetylene ring molecule containing  $N = 200$  sites. (a) corresponds to the neutral regular chain, whereas the chain of (b) has been doped with two electrons. The latter case leads to two degenerate gap states induced by a soliton-antisoliton pair. These states are those around the Fermi level. The vertical broken lines separate occupied and unoccupied states.

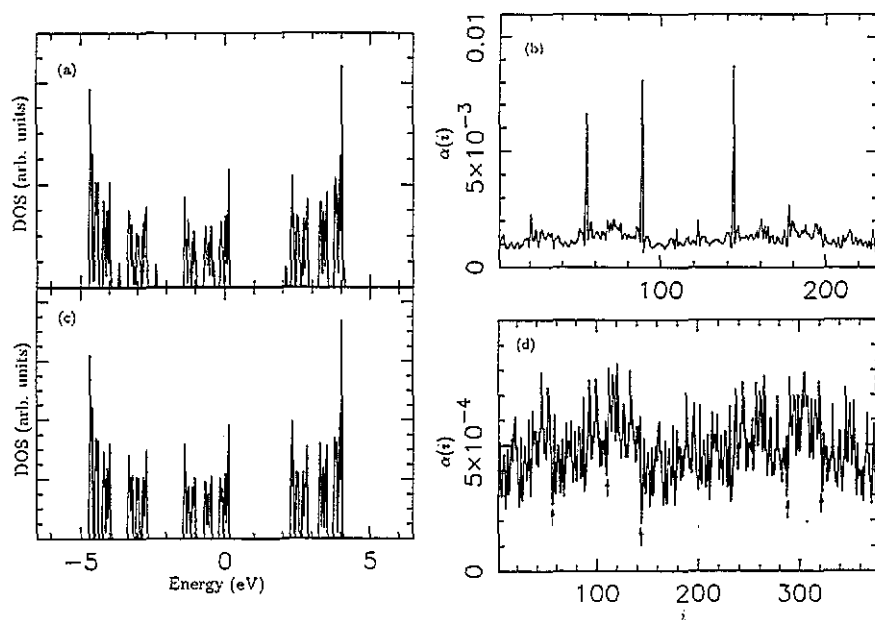
#### 4. The Fibonacci lattice

We now turn to quasiperiodic chains. As an example we study the Fibonacci structure. It consists of two different types of atom, A and B, and is generated recursively by the stacking rules  $S(n+1) = S(n) + S(n-1)$  and  $D(n+1) = D(n)D(n-1)$ . Here,  $S(n)$  is the number of atoms of the  $n$ th generation and  $D(n)$  represents the atomic sequence. The ratio  $\lim_{n \rightarrow \infty} [S(n)/S(n-1)]$  is given by the golden mean  $\tau = \frac{1}{2}(1 + \sqrt{5})$ . The Fibonacci lattice is a special case of the generalized Fibonacci structures, for which the stacking rules are  $S(n+1) = [S(n)]^p + [S(n-1)]^q$  and  $D(n+1) = [D(n)]^p [D(n-1)]^q$  with  $\tau(p, q) \equiv \lim_{n \rightarrow \infty} [S(n)/S(n-1)] = \frac{1}{2}[(p^2 + 4q)^{\frac{1}{2}} + p]$ . In our case we use  $D(1) = A$  and  $D(2) = B$  corresponding to  $S(1) = S(2) = 1$ .  $\tau$  becomes then also the ratio between the numbers of A and B atoms.

As mentioned above, the density of states of the Fibonacci lattice is self-similar whereas for the generalized Fibonacci lattice the existence of this property depends on the values of  $p$  and  $q$  [18]. We first considered a ring containing the first 11 generations (232 atoms) as well as one with only the 14th generation (377 atoms) for which all  $u_n$  were set equal to zero. As mentioned in the previous section interface states tend to show up. Their importance could, however, be reduced by considering only one large generation.

In figure 3 both the total density of states (DOS) and the degree of localization  $\alpha(i)$  for the two systems are shown. In the smaller system (figures 3(a),(b)) interface states are those having the dominating  $\alpha(i)$  whereas these states are essentially absent in the larger system (figures 3(c),(d)). Otherwise, there is no significant difference between the results for the two systems, so we will only in the following consider the larger one. The interface states in the smaller system are also observed in the DOS as extra gap states (at  $\sim -3.6$ ,  $-2.4$ , and  $2.2$  eV).

We notice that the DOS (figure 3(c)) is approximately self-similar. Moreover,  $\alpha(i)$  indicates that in contrast to the results of Mott for a disordered system [68] all states have the same order of magnitude in the degree of localization. As indicated from the results for a soliton in *trans*-polyacetylene, a well localized state (see section 3 and figure 2(b)) has an  $\alpha(i)$  value of the order of  $5 \times 10^{-3}$  whereas all states in the large Fibonacci system have  $\alpha(i)$  values of  $3 - 7 \times 10^{-4}$ . At most we may distinguish between energy intervals with more or less (de)localized states; the borders between them are marked with arrows in

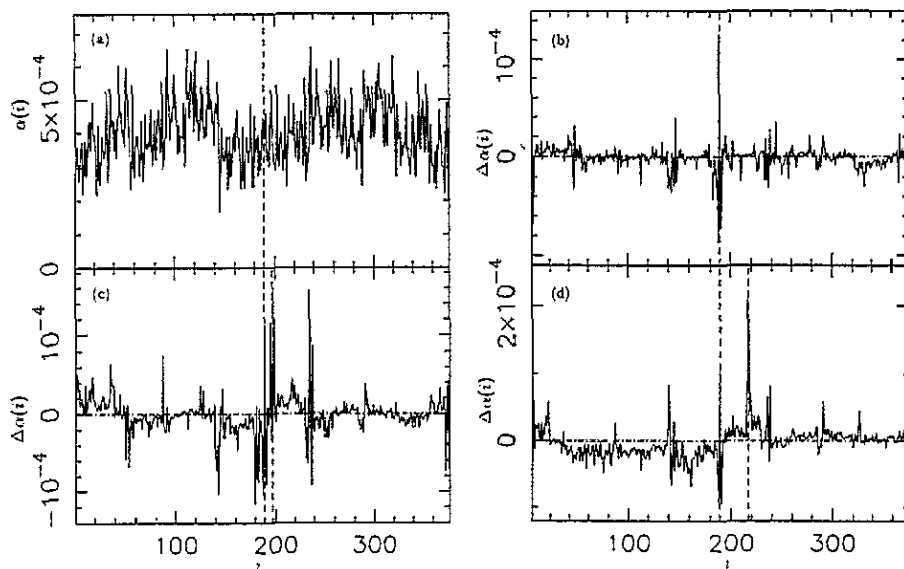


**Figure 3.** The (a, c) total DOS and (b, d) degree of localization  $\alpha(i)$  of the Fibonacci system with (a, b) the first 11 and (c, d) the 14th generation. No geometry relaxation is allowed, i.e. all  $u_n$  are zero. The arrows in (d) separate more and less localized states.

figure 3(d). Alternatively, we may—as often is done—classify all the states as intermediate between localized and delocalized; i.e., as critical.

We now allow the geometry to relax. The relaxation may destroy the pure quasiperiodicity such that in the case of an infinite system the states will no longer necessarily be critical. The flexibility of the system depends on the choice of the constants  $K_1$  and  $K_2$ . For the rigid system we choose these parameters such that all  $u_n$  values are close to zero ( $|u_n| < 1.5 \times 10^{-3} \text{ \AA}$ ) for the neutral (undoped) Fibonacci chain.  $|u_n|$  becomes then  $< 1.5 \times 10^{-2} \text{ \AA}$  in the doped systems. Thereby the quasiperiodicity is only marginally disturbed. For  $\epsilon_A = 1.5 \text{ eV}$ ,  $\epsilon_B = -1.5 \text{ eV}$ ,  $a = 4.1 \text{ eV \AA}$ , and  $t_0 = 2.5 \text{ eV}$  the values  $K_1 = 120.0 \text{ eV \AA}^2$  and  $K_2 = 14.0 \text{ eV \AA}$  satisfy this condition. The values of  $t_0$  and  $a$  are those usually assumed to be realistic for *trans*-polyacetylene.

The DOS and the degree of localization change only little upon geometry relaxation. For the doped system we present therefore only the changes in the degree of localization. In figure 4  $\alpha(i)$  of the neutral system, and the change in the degree of localization upon doping with one (0.27%), 16 (4.2%) and 56 (14.9%) electrons are shown. The difference  $\Delta\alpha(i)$  before and after doping is useful in exploring the change in the localization of the  $i$ th orbital. If  $\Delta\alpha(i) > 0$  the  $i$ th orbital becomes more localized upon doping. There is a general trend for the states above the Fermi level of the neutral system to become more localized upon doping while the change in the DOS is negligible. This tendency is stronger when more electrons are added. It is moreover observed that the states at the Fermi level of both the neutral and the doped systems become more localized upon doping. Two remarks of caution are, however, relevant here. First of all, the lattice relaxations may lead to a situation where some orbitals change energetical order. This may show up as a relatively large and strongly oscillating  $\Delta\alpha(i)$ . Second, due to orthogonality of the orbitals, an increased localization of some orbitals results in changes of the localization of the other orbitals. Despite these



**Figure 4.** (a) The degree of localization  $\alpha(i)$  of the neutral rigid Fibonacci system consisting of the 14th generation. (b–d) The changes of  $\alpha(i)$  upon doping with (b) one electron, (c) 16 electrons, and (d) 56 electrons.  $\Delta\alpha(i) > 0$  implies that the  $i$ th state becomes more localized upon doping. The left-hand broken line in (c) and (d) marks the Fermi level of the neutral system whereas the right-hand one marks the Fermi level of the doped system.

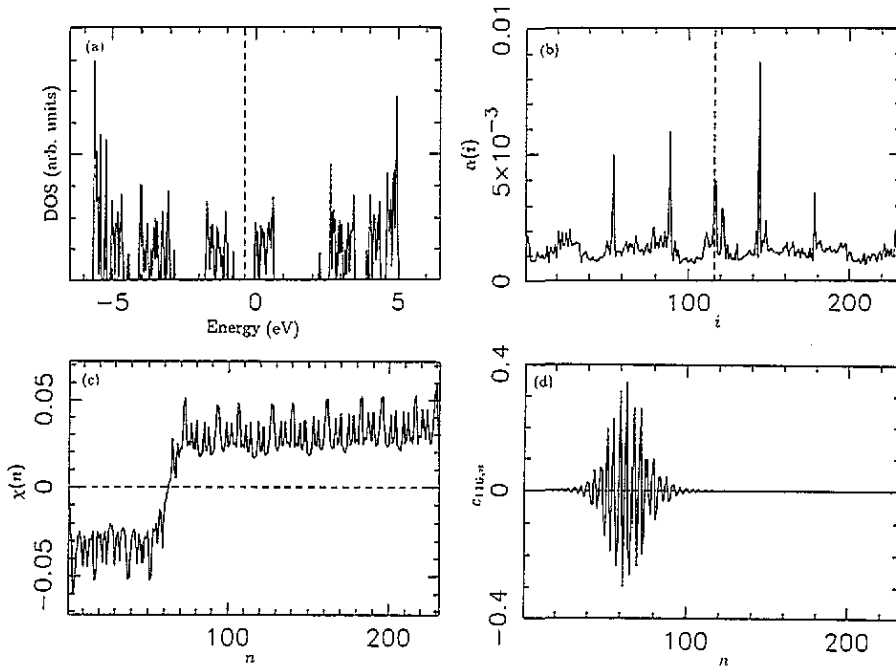
comments one of the important conclusions of this study is that the system tends to react upon doping by increasing the localization of the orbitals in the proximity of the Fermi level, thus reducing the conductivity.

Finally, for the sake of completeness we mention that the system possesses certain symmetries. Interchanging  $\epsilon_A$  and  $\epsilon_B$  and removing  $n_{el}$  instead of adding  $n_{el}$  electrons lead to essentially identical results. This result is not restricted to the Fibonacci system. Furthermore, upon removing electrons instead of adding some exploratory calculations indicate that the main difference is that  $\Delta\alpha(i)$  changes sign. In that case too, we do accordingly observe an increased localization of those orbitals that change occupancy.

Choosing the parameters as  $\epsilon_A = 1.5$  eV,  $\epsilon_B = -1.5$  eV,  $a = 4.1$  eV Å,  $t_0 = 2.5$  eV,  $K_1 = 21.0$  eV Å<sup>2</sup>, and  $K_2 = 0$  we obtain a more flexible system. The lattice relaxation is relatively large ( $|\mu_n| \lesssim 0.06$  Å). For both systems, i.e., the smaller one containing the first 11 generations and the larger one containing only the 14th generation, a gap is created around the Fermi level (figures 5(a), 6(a)). Thereby the self-similarity in the DOS is lost. In figures 5(b) and 6(b) it can be seen that the orbitals closest to the Fermi level belong to the most localized states and that one of them for the larger system is actually an interface state. Furthermore, we found nodes in the staggered coordinate  $\chi_n$  (figures 5(c), 6(c)). For the smaller system (figure 5) these nodes are well separated whereas for the larger one they are close (actually close to the interface). Comparing figures 5(c,d) and 6(c,d) we see that the uppermost occupied orbital is located to the nodes of  $\chi_n$ , and by further comparison with the DOS curves (figures 5(a), 6(a)) it is observed that these states appear at energies where the unrelaxed system has a gap.

The regularity of the staggered parameter  $\chi_n$  is remarkable: for the system containing nearly 400 atoms it takes only a few values.

Upon doping with 56 electrons significant lattice relaxations are observed. This leads



**Figure 5.** (a) DOS, (b)  $\alpha(i)$ , (c) staggered coordinate  $\chi(i)$ , and (d) wavefunction of the highest occupied state of the neutral, flexible Fibonacci system with the first 11 generations.

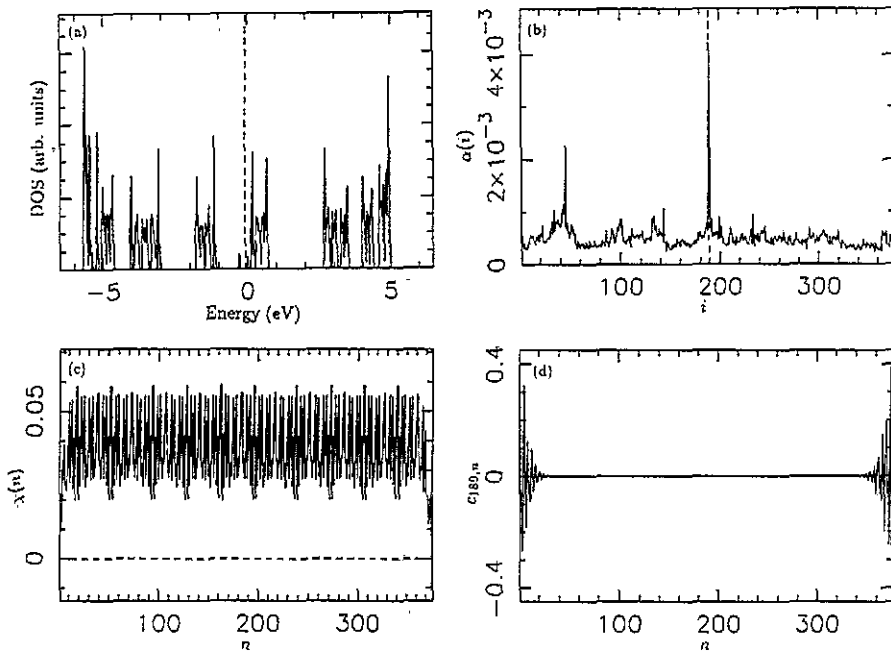
to large changes in the DOS (figures 7(a), 8(a)). The highest occupied state is a gap state for the small system and is located near the interface. For the larger system the Fermi level is found in a 'band'. This results in differences in the degree of localization (figures 7(b), and 8(b)). The geometry, shown here as the staggered coordinate  $\chi_n$ , resembles that of a soliton lattice for the small system (figure 7(c)), i.e.  $\chi_n$  changes sign almost regularly, whereas  $\chi_n$  is less regular for the larger system (figure 8(c)). As for the undoped systems a number of orbitals close to the Fermi level (cf. figures 7(d) and 8(d)) are confined to a relatively small fraction of the total system. For the smaller system the doping-induced increase in the localization of the frontier orbitals of the doped system is readily observed (figure 7(b)), whereas similar changes are largely absent for the larger system (figure 8(b)).

In all the systems studied here a larger part of the orbitals closest to the Fermi level appear to be well localized, partly due to lattice relaxations. This indicates a low conductivity. We should, however, stress that phonons may assist the charge transport, e.g. by the formation of mobile polarons. This effect has not been included here but could be studied with the present model.

## 5. Other quasiperiodic and incommensurable structures

It has been reported [48,49,69] that the properties of an incommensurable structure for which the on-site energies obey

$$\epsilon_n = \lambda \cos(dn^{\nu}) \quad (19)$$

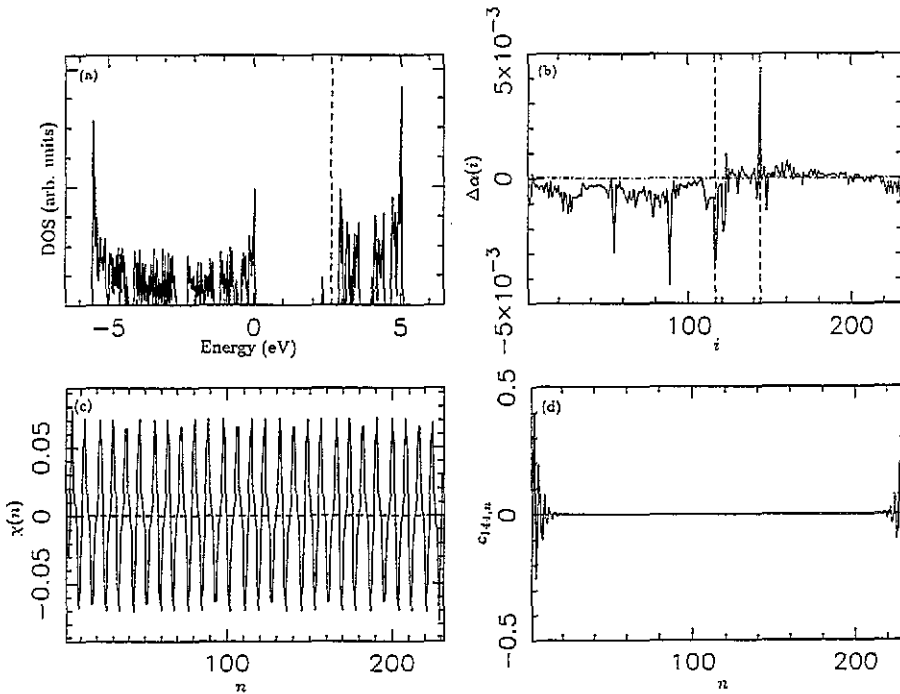


**Figure 6.** (a) DOS, (b)  $\alpha(i)$ , (c) staggered coordinate  $\chi(i)$ , and (d) wavefunction of the highest occupied state of the neutral, flexible Fibonacci system with the 14th generation.

where  $d/\pi$  is an irrational number, depend on the parameters  $\lambda$  and  $\nu$ . For  $\lambda < 2$  and  $0 < \nu < 1$  the properties are those of a purely incommensurable structure.  $\lambda < 2$  and  $\nu > 1$  give, on the other hand, a so-called pseudo-random system for which all states are localized.

Our criterion for the degree of localization confirms this differentiation. In figure 9 we show the DOS and  $\alpha(i)$  of systems for which the atoms A and B are randomly distributed (i.e.,  $\epsilon_n$  assumes the two values  $\pm 1.5$  at random) as well as for systems with on-site energies given by equation (19). All parameters except for the on-site energies are chosen according to the rigid systems and ring molecules of  $N = 300$  sites were studied. The DOS and the localization of the orbitals of the incommensurable system with the on-site energies  $\epsilon_n = 1.5 \cos(3.5n^2)$  have the same characteristics as the system with the randomly distributed atoms. Both have one broad band without any gap, and the energetically lowest and highest orbitals are the most localized orbitals, but the other states are also strongly localized. The incommensurable structure with the on-site energies obeying  $\epsilon_n = 1.5 \cos(3.5n^{0.9})$  has much more regular DOS and  $\alpha$  curves. When we compare with the results for the Fibonacci systems of the preceding section we observe a significantly larger average localization for the systems of figure 9, except for the last one. However,  $\alpha(i)$  of figure 9(b) is roughly a smooth function of  $i$  with a minimum for  $i \simeq 150$ , whereas the 'sharp' changes of  $\alpha(i)$  for  $i \simeq 20$  and  $280$  in figure 9(d) may be an indication of mobility edges. Such edges are absent in figure 9(f) where only the sharp peaks (due to the states that appear in the gaps around  $\pm 3$  eV in figure 9(e)) are remarkable.

We also studied a generalized Fibonacci system [15, 18, 38] for which the lattice was not allowed to relax. For the ninth generation with  $p = 2$  and  $q = 1$  there is no self-similarity in the DOS (figure 10(a)). Instead one notices a wide band around the energy zero. The states



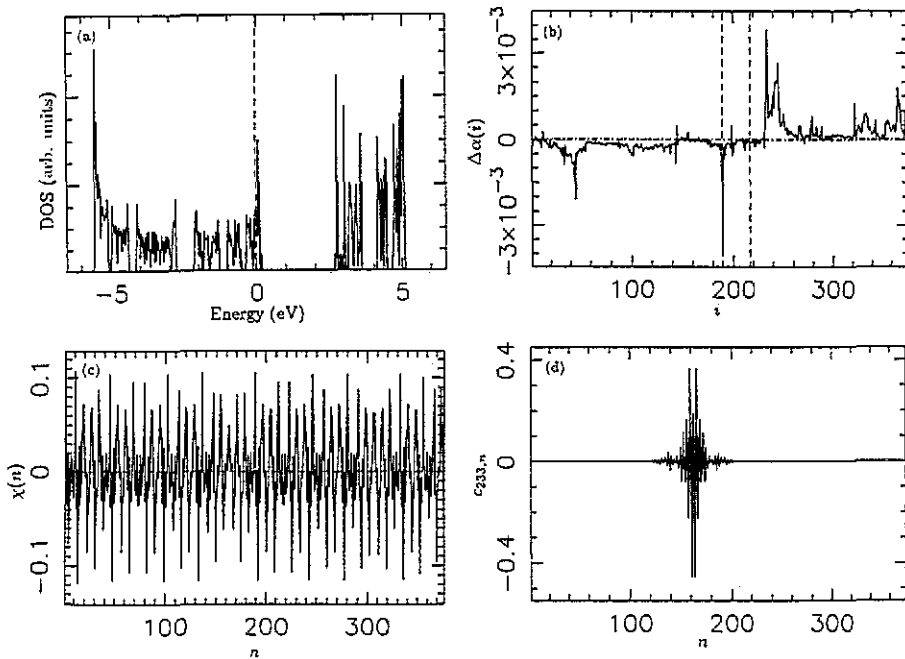
**Figure 7.** (a) DOS, (b)  $\alpha(i)$ , (c) staggered coordinate  $\chi(i)$ , and (d) wavefunction of the highest occupied state of the flexible Fibonacci system with the first 11 generations upon doping with 56 electrons.

of this band are extended ( $\alpha(i) < 5 \times 10^{-4}$ ) whereas the other states are more localized (figure 10(b)). Moreover, there are edges in the degree of localization that one may identify as mobility edges in the sense of Mott. Thus, this system also differs significantly from the 'normal' Fibonacci system.

In the context of the one-dimensional quasiperiodic structures the so-called Thue–Morse potential is often studied [46, 70–78]. The sequence of the on-site energies  $\epsilon_n$  is generated by using the rules  $S(n+1) = 2S(n)$  and  $D(n+1) = \overline{D(n)}D(n)$ , where  $\overline{D(n)}$  is the inverse sequence of  $D(n)$  (i.e.,  $\epsilon_A$  and  $\epsilon_B$  are interchanged). In our case we used  $D(1) = A$ . We calculated the DOS and the degree of localization for a ring with the tenth generation and did not allow for geometry relaxation (figure 10(c,d)). In the DOS there is obviously no self-similarity whereas the  $\alpha$  values show variations of the same order of magnitude as those of the generalized Fibonacci system except for some strongly localized states. No clear mobility edges are observed. Since, however,  $\alpha(i)$  of figure 10(d) is comparable with that of figure 3(b) we believe that many of the results found for the Fibonacci system also are relevant for the Thue–Morse system.

## 6. Conclusions

The present paper has focused on electronic and structural properties of non-periodic, deterministic one-dimensional chains. To this end we have developed a model that includes both electronic and structural degrees of freedom. The model includes a simple tight-binding

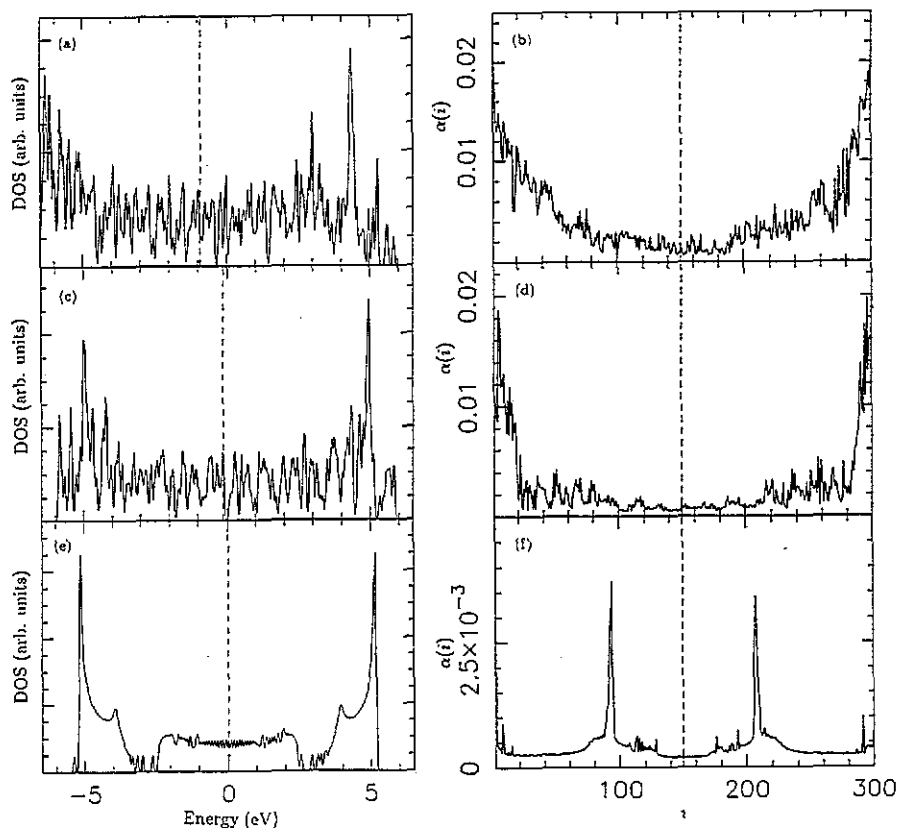


**Figure 8.** (a) DOS, (b)  $\alpha(i)$ , (c) staggered coordinate  $\chi(i)$ , and (d) one of the wavefunctions of the highest occupied states of the flexible Fibonacci system with the 14th generation upon doping with 56 electrons.

description of the electrons with one orbital per site and a harmonic approximation for the lattice part. The nearest-neighbour hopping integrals are allowed to vary as a function of bond length. Two parameter sets were considered: one (corresponding to a rigid system) for which the neutral system (= one electron per site) was essentially undisturbed, and one (a flexible system) for which the neutral system also experienced some lattice relaxations. We stress at this point that except for the relatively short communication by Pnevmatikos *et al* [53] this is the first time that such a model has been proposed for and applied to this class of systems.

One of the main objectives of the present work was the interplay between localization and structure. It was hence crucial to have an accurate measure of the localization. We therefore compared various proposals as well as presenting our own,  $\alpha$ , which was based on an autocorrelation function of the electron density. For a simple model system  $\alpha$  turned out to be well correlated with the actual localization of the orbitals and to be comparable or superior to other proposals. In particular,  $\alpha$  appears to be useful when studying systems of intermediate size as synthesized in the laboratory.

As the main application of the model we studied a Fibonacci chain. It was found that for the rigid system the lattice relaxations were minor (both for the neutral and the doped systems) such that the DOS essentially retained its self-similarity. This was contrasted by the results for the flexible system, for which the system relaxed, which in turn led to significant changes in the density of states. Except for one case we observed an increased localization of the orbitals around the Fermi level upon doping. This important result indicates that the conducting properties of the quasiperiodic materials may not be as controllable as one may think at first sight, but that the system opposes the doping by localizing the electrons.



**Figure 9.** (a, c, e) DOS and (b, d, f) degree of localization  $\alpha(i)$  of a system for which (a, b) the atoms A and B are randomly distributed, (c, d) the on-site energies are given by  $\epsilon_n = 1.5 \cos(3.5n^2)$  and (e, f)  $\epsilon_n = 1.5 \cos(3.5n^{0.9})$ . In all three cases all the other parameters are the same as for the rigid Fibonacci system.

As further examples of application of our model we studied briefly various quasiperiodic and incommensurable structures. For some of these  $\alpha$  could be used in demonstrating the existence of mobility edges.

The large present interest in non-periodic deterministic structures is partly due to diffraction patterns of the icosahedral phase of  $\text{Al}_{0.86}\text{Mn}_{0.14}$ . Since diffraction experiments has continued to be of importance in exploring the properties of those structures, it would be interesting to extend the present study by including the calculation of diffraction patterns both for relaxed and for unrelaxed structures. However, as demonstrated recently by Krajčí and Hafner [79], the lattice relaxations for the Al-Mn quasicrystals have only minor effects on the diffraction patterns.

Another area that is often used in the study of quasiperiodic materials is their vibrational properties as determined, e.g., by Raman scattering. These also could be explored using the present model.

Finally, we have discussed here localization as a means to obtain insight into the conducting properties of the material. However, phonon-assisted conductivity (e.g. through polarons) has been neglected and may—when included—lead to some modifications in our conclusions. These effects may be studied using our model.



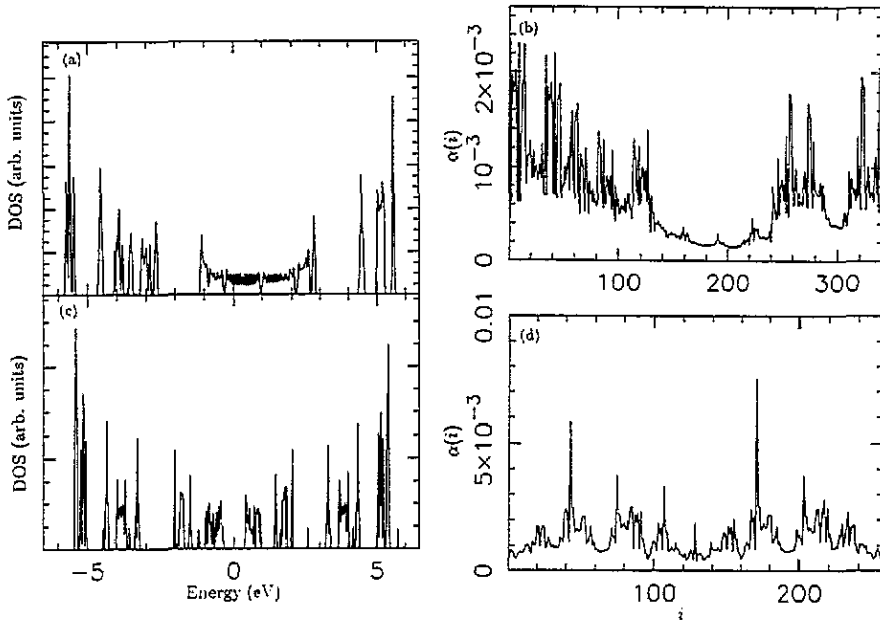


Figure 10. (a, c) DOS and (b, d) the degree of localization  $\alpha(i)$  of (a, b) a generalized Fibonacci system with the ninth generation and (c, d) a Thue-Morse system with the tenth generation. All  $u_n$  are set equal to zero for both systems.

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