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Electronic spectra of strongly modulated aperiodic structures

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We consider the tight-binding Hamiltonian on strongly modulated aperiodic chains (e.g., quasiperiodic, self-similar, random). The site energies are distributed according to a given binary sequence ($V_n = \pm V$), the hopping integral t being a constant. We investigate the strong-modulation regime ($V \gg t$) by means of degenerate perturbation theory. We thus derive systematic expansions in powers of t/V for the spectrum, the density of states, and other quantities of interest, like the total electronic binding energy. This investigation goes beyond the molecular approximation; it amounts to exploring recursively the pattern of resonances between molecular states along the structure, which can be either "local" or "itinerant." The approach is worked out in detail on several classical examples of self-similar chains: Fibonacci, Thue-Morse, period doubling. The hierarchy of gaps thus obtained is put in perspective with the rigorous gap-labeling theory; the quantitative predictions for the density of states and the binding energy are extensively compared with numerical data.

I. INTRODUCTION

The investigation of physical properties of deterministic aperiodic structures has been the subject of an intense activity in the past years, revived by the experimental discovery of quasicrystals.[1,2] Aperiodic structures represent an intermediate type of order between the periodic (crystalline) and the random (amorphous, glassy) states of matter.

Physical properties of aperiodic structures are very rich, even if one restricts oneself to linear equations (lattice dynamics, electron propagation), and to the test case of one-dimensional (1D) structures, i.e., sequences or chains. The spectra of these linear problems are generically *singular continuous*. The associated eigenfunctions are neither extended (absolutely continuous spectrum), nor localized (pure point spectrum), but they exhibit an intermediate kind of behavior, referred to as *critical*. These peculiarities can given rise to a novel kind of quantum transport, somewhat intermediate between ballistic and diffusive.[3] There is some numerical evidence for the presence of critical states in 2D and 3D quasicrystal models.[4,5] Furthermore, the existence of critical states may provide an explanation of the unusual properties of the electrical conductivity of quasicrystals: It decreases if temperature is lowered, and if the structural quality of the sample is improved by annealing. These features can be understood by assuming that the propagation of electrons is diffusive on length scales larger than the mean free path, but is unconventional (nonballistic) on smaller scales.[6]

Most results obtained so far concern 1D aperiodic chains. The prototype model is the discrete Schrödinger equation, describing electrons in the tight-binding approximation

$$(\mathcal{H}\psi)_n = t\psi_{n-1} + t\psi_{n+1} + V_n\psi_n = E\psi_n \ . \tag{1.1}$$

The site energies V_n form an arbitrary deterministic aperiodic sequence, with sufficient homogeneity properties, whereas the hopping integral t is assumed to be constant. A case of special interest is that of self-similar chains, modeled by a sequence V_n of site energies generated by a substitution.[7] A substitution is a set of rules for constructing iteratively self-similar structures (sequences, chains, tilings, etc.), made of a finite number p of symbols or letters (bonds, tiles, etc.) A few classical examples will be recalled and investigated below. It is worth noticing that all the quasicrystalline symmetries observed so far, with axes of order 5, 8, 10, and 12, correspond to those of tilings generated by binary substitutions ($p = 2$).[8,9] Furthermore any aperiodic sequence may now have a physical realization, in the form of an epitaxially grown semiconductor superlattice.

A considerable amount of work has been devoted to theoretical investigations of spectral properties of self-similar chains, using various analytical or numerical approaches. We shall only quote the review papers,[10–13] which provide overviews of these topics. From the standpoint of mathematical physics, the essential results are as follows. Linear operators, such as the Hamiltonian (1.1), built from deterministic aperiodic structures, have generically a singular continuous spectrum, supported by a Cantor set with zero Lebesgue measure, i.e., zero bandwidth. This has been proven rigorously for several self-similar sequences: Fibonacci,[14–16] Thue-Morse,[17] period doubling.[18] A general analysis has been presented more recently,[19] which applies to most sequences of interest, including all those we have just quoted, but not, e.g., to the Rudin-Shapiro sequence.

Another important feature of these problems is the

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gap-labeling property. The spectral gaps can be labeled by integers, for a large class of structures, in any dimension, including quasiperiodic and self-similar ones.[10,20,21] This means that in every gap the (constant) integrated density of states (IDOS) is an integer linear combination of a known, finite or infinite, set of basic numbers. For 1D sequences taking finitely many values, those numbers are the frequencies $f(w)$ of all the possible words, i.e., finite patterns w in the sequence.

A detailed analysis of spectral properties is possible in several limiting cases. The regime of a weak modulation ($V_n \ll t$) can be investigated by perturbative methods. For quasiperiodic chains, quantitative results can be derived, concerning the spectrum, the density of states (DOS), and the electronic binding energy, as exemplified by the analysis of the canonical 1D quasicrystal model, generalizing the Fibonacci chain.[22] For arbitrary self-similar chains, a perturbative analysis of the IDOS (Refs. 23 and 24) shows that the spectral gaps can still be related to singularities of the Fourier transform of the sequence. This yields predictions for the scaling behavior of the width Δ of a given gap as a function of the modulation strength V. One has the power law $\Delta \sim V^{2/(2-\alpha)}$, where α is the local Hölder exponent of the Fourier intensity, at the wave vector q_0 where the gap opens in the $V \to 0$ limit, i.e., $\int_{q_0-\varepsilon}^{q_0+\varepsilon} S(q)dq \sim \varepsilon^{\alpha}$. If q_0 is a Bragg diffraction ($\alpha=0$), the gap opens linearly; if q_0 is a peak of singular scattering ($\alpha>0$),[25,9] the gap width is smaller than linear in the weak-modulation regime.

The converse situation of a *strong modulation* ($V_n \gg t$) has also been investigated. Several authors (Refs. 26–29, 23) have underlined the key importance of *atomic* and *molecular* states in that regime. The molecular approximation, to be recalled below, has been shown[23] to yield a good quantitative understanding of the spectrum and the IDOS in a large variety of examples. By means of perturbative, and/or real-space renormalization-group arguments,[26,28,29] the hierarchical band-splitting pattern of the spectra of specific quasiperiodic and hierarchical models has been explained. Some scaling features of the wave functions of these models at special energies have also been interpreted in this framework.

The main goal of this paper is to develop a systematic and quantitative perturbation theory in the strong-modulation regime, going beyond the molecular approximation. Unlike renormalization-group approaches, the present work does not rely on self-similarity, and is therefore of quite general applicability; its efficiency will be demonstrated through a detailed comparison with numerical data. We will consider, for the sake of simplicity, binary chains, made of two types of atoms, called A and B. Without loss of generality, we can assume that the site energies take two opposite values, namely $V_n = V\varepsilon_n$, where $\varepsilon_n = \pm 1$ is dictated by the type of the nth atom along the chain, according to the rule

$$\begin{aligned} &A \text{ atom:} \quad V_n = V \quad (\varepsilon_n = 1)\ , \\ &B \text{ atom:} \quad V_n = -V \quad (\varepsilon_n = -1)\ . \end{aligned} \tag{1.2}$$

The setup of this paper is as follows. In Sec. II we present our general approach to the problem, using degenerate perturbation theory in quantum mechanics. The next sections are devoted to an application of this formalism to several classical examples of self-similar aperiodic chains, already considered, e.g., in Refs. 19, 20, 21, and 23: Fibonacci (Sec. III), Thue-Morse (Sec. IV), period doubling (Sec. V). Section VI contains a short discussion.

II. GENERAL RESULTS

A. Degenerate perturbation theory

The purpose of this section is to derive a systematic perturbative expansion for the spectrum and the IDOS of the tight-binding Hamiltonian (1.1), with a binary sequence of site energies, in the regime of a strong modulation ($t \ll V$).

We recall that the IDOS, denoted hereafter by $H(E)$, is the fraction of eigenstates with energies less than E. This reads formally

$$H(E) = \mathrm{Tr}\,\theta(E-\mathcal{H}) = \lim_{N\to\infty} \frac{1}{N} \sum_{1 \le a \le N} \theta(E - E_a)\ , \tag{2.1}$$

with $\theta(x)$ being Heaviside function, and where Tr(.) denotes the density of trace of an operator, i.e., its trace per site in the thermodynamic limit of an infinitely long chain. The explicit form in Eq. (2.1) involves the N energy levels $\{E_a\}$ associated with a finite patch of the structure containing N atoms; the limit is independent of boundary conditions. The DOS $\rho(E)$ is the formal derivative of $H(E)$, i.e.,

$$\begin{aligned} \rho(E) = dH/dE &= \mathrm{Tr}\,\delta(\mathcal{H} - E) \\ &= \lim_{N\to\infty} \frac{1}{N} \sum_{1 \le a \le N} \delta(E_a - E)\ . \end{aligned} \tag{2.2}$$

In most of the situations considered hereafter, the DOS is a singular continuous measure, so that $\rho(E)$ has to be thought of as a generalized function, or a distribution. The reader is referred to Ref. 30 for a mathematical exposition of these topics.

The starting point of our perturbative analysis is as follows. The Hamiltonian (1.1) can be recast as

$$\mathcal{H} = V(\mathcal{H}^{(0)} + \lambda W)\ . \tag{2.3}$$

In this expression, the unperturbed Hamiltonian $\mathcal{H}^{(0)}$ is diagonal, and its matrix elements read

$$\mathcal{H}^{(0)}_{n,n} = \varepsilon_n = \pm 1\ , \tag{2.4}$$

with the notation (1.2), whereas the perturbation consists in the nondiagonal part of $\mathcal{H}$, i.e., the hopping integrals. The small expansion parameter is the dimensionless ratio

$$\lambda = t/V\ , \tag{2.5}$$

and W is the tridiagonal hopping matrix

$$W_{m,n} = \delta_{m,n+1} + \delta_{m,n-1}\ , \tag{2.6}$$

with Kronecker symbols.

We look for a formal power-series expansion of the solutions of the eigenvalue equation (1.1), of the form

$$\begin{aligned}&E=V(E^{(0)}+\lambda E^{(1)}+\lambda^2E^{(2)}+\lambda^3E^{(3)}+\cdots)\ ,\\&\psi=\psi^{(0)}+\lambda\psi^{(1)}+\lambda^2\psi^{(2)}+\lambda^3\psi^{(3)}+\cdots\ .\end{aligned}\tag{2.7}$$

By expanding Eq. (1.1), we obtain the recursive system of equations

$$(\mathcal{H}^{(0)}-E^{(0)})\psi^{(0)}=0\ ,\tag{2.8a}$$

$$(\mathcal{H}^{(0)}-E^{(0)})\psi^{(1)}=(E^{(1)}-W)\psi^{(0)}\ ,\tag{2.8b}$$

$$(\mathcal{H}^{(0)}-E^{(0)})\psi^{(2)}=(E^{(1)}-W)\psi^{(1)}+E^{(2)}\psi^{(0)}\ ,\tag{2.8c}$$

$$(\mathcal{H}^{(0)}-E^{(0)})\psi^{(3)}=(E^{(1)}-W)\psi^{(2)}+E^{(2)}\psi^{(1)}+E^{(3)}\psi^{(0)}\ .\tag{2.8d}$$

Solving the system (2.8) amounts to the standard problem of degenerate perturbation theory in quantum mechanics. In this paper we shall need explicit results up to the third order included, in an arbitrary degenerate situation. The derivations exposed below follow the spirit of the book by Piron.[31]

1. *Zeroth order: the atomic approximation*

Equation (2.8a) expresses that $\psi^{(0)}$ is an eigenstate of the diagonal Hamiltonian $\mathcal{H}^{(0)}$, and that the associated eigenvalue is one of the reduced site energies, namely $E^{(0)}=\pm1$. The hopping between different atoms is entirely neglected, whence the name of atomic approximation.

We define for further reference the eigenspace $\mathcal{S}(E^{(0)})$ of $\mathcal{H}^{(0)}$ associated with the eigenvalue $E^{(0)}$, with $E^{(0)}=\pm1$. Consider a finite patch of the sequence, consisting of N_A A atoms and N_B B atoms, i.e., $N=N_A+N_B$ atoms in total. It is obvious that the eigenvalue $E^{(0)}=1$ of $\mathcal{H}^{(0)}$ is N_A times degenerate, whereas $E^{(0)}=-1$ is N_B times degenerate. In other words, the dimension of $\mathcal{S}(1)$ is N_A, and the dimension of $\mathcal{S}(-1)$ is N_B. Both eigenspaces, as well as all subspaces to be considered hereafter, are thus extensively degenerate.

The evaluation of the DOS within this approximation goes as follows. Let $f(A)=\lim_{N\to\infty}(N_A/N)$ and $f(B)=\lim_{N\to\infty}(N_B/N)$ denote the frequencies of both types of letters in the infinite sequence. We thus obtain

$$\rho^{(0)}(E)=f(A)\delta(V-E)+f(B)\delta(-V-E)\ .\tag{2.9}$$

2. *First order: the molecular approximation*

Equation (2.8b), and the next ones, can be solved in the following elegant way, along the lines of Ref. 31. We choose once for all the value of $E^{(0)}$, with $E^{(0)}=\pm1$. Let $P^{(0)}$ be the orthogonal projector onto $\mathcal{S}^{(0)}=\mathcal{S}(E^{(0)})$, and $Q^{(0)}=1-P^{(0)}$.

By applying $P^{(0)}$ to Eq. (2.8b), we obtain an eigenvalue equation for $\psi^{(0)}$, of the form

$$(\mathcal{H}^{(1)}-E^{(1)})\psi^{(0)}=0\ ,\tag{2.10}$$

where the first-order effective Hamiltonian $\mathcal{H}^{(1)}$, defined as an operator on $\mathcal{S}^{(0)}$, reads

$$\mathcal{H}^{(1)}=P^{(0)}WP^{(0)}\ .\tag{2.11}$$

Furthermore, by applying the supplementary projector $Q^{(0)}$ to Eq. (2.8b), we get

$$Q^{(0)}\psi^{(1)}=-G^{(0)}W\psi^{(0)}\ ,\tag{2.12}$$

where the Green's function

$$G^{(0)}=Q^{(0)}(\mathcal{H}^{(0)}-E^{(0)})^{-1}Q^{(0)}\tag{2.13}$$

is the pseudoinverse of $(\mathcal{H}^{(0)}-E^{(0)})$. The other component $P^{(0)}\psi^{(1)}$ remains undetermined so far.

In the present situation, the effective Hamiltonian $\mathcal{H}^{(1)}$ can be diagonalized explicitly. Choose $E^{(0)}=1$ for definiteness. The operator $\mathcal{H}^{(1)}$ only couples neighboring A atoms. It suffices therefore to consider the molecules, i.e., the connected clusters made of A atoms. On such a molecule, consisting of exactly N atoms, the eigenvalue equation of $\mathcal{H}^{(1)}$ reads, after a suitable renumbering of the atoms

$$(\mathcal{H}^{(1)}\psi)_n=\psi_{n+1}+\psi_{n-1}=E^{(1)}\psi_n\quad(1\le n\le N)\ ,\tag{2.14}$$

with Dirichlet boundary conditions ($\psi_0=\psi_{N+1}=0$).

Equation (2.14) admits N molecular states, labeled by an integer $1\le a\le N$, with energies

$$E_a^{(1)}=2\cos\frac{a\pi}{N+1}\ ,\quad\text{i.e.,}\ E_a=V+2t\cos\frac{a\pi}{N+1}\ .\tag{2.15}$$

The associated normalized wave functions read

$$\psi_{a,n}=\left[\frac{2}{N+1}\right]^{1/2}\sin\frac{an\pi}{N+1}\ .\tag{2.16}$$

As a consequence, the DOS of tight-binding electrons on an arbitrary chain can be written in the molecular approximation, in analogy with Eq. (2.9). We have

$$\begin{aligned}\rho^{(1)}(E)=\sum_{n\ge1}\Bigg[&f(nA)\sum_{1\le a\le n}\delta\left[V+2t\cos\frac{a\pi}{n+1}-E\right]\\&+f(nB)\sum_{1\le a\le n}\delta\left[-V+2t\cos\frac{a\pi}{n+1}-E\right]\Bigg]\end{aligned}\tag{2.17}$$

where $f(nA)$ [respectively, $f(nB)$] denote the frequencies of the molecules made of n A atoms (respectively, of n B atoms). The results (2.9) and (2.17) are compatible because of the sum rules $\sum_{n\ge1}nf(nA)=f(A)$, $\sum_{n\ge1}nf(nB)=f(B)$.

3. *Second order*

Equation (2.8c) can be solved in analogy with Eq. (2.8b). We assume that $\psi^{(0)}$ belongs to $\mathcal{S}^{(1)}$, the linear space of common solutions to both Eqs. (2.8a) and (2.10). Let $P^{(1)}$ be the orthogonal projector onto $\mathcal{S}^{(1)}$, and $Q^{(1)}=1-P^{(1)}$, and $\overline{Q}^{(1)}=Q^{(1)}-Q^{(0)}=P^{(0)}-P^{(1)}$.

By applying $P^{(0)}$ to Eq. (2.8c), we get

$$(\mathcal{H}^{(1)}-E^{(1)})P^{(0)}\psi^{(1)}=E^{(2)}\psi^{(0)}-P^{(0)}WQ^{(0)}\psi^{(1)}\ .\tag{2.18}$$

By acting with $P^{(1)}$ on Eq. (2.18), and using the result (2.12), we obtain again an eigenvalue equation for $\psi^{(0)}$, of the form

$$(\mathcal{H}^{(2)}-E^{(2)})\psi^{(0)}=0\ , \tag{2.19}$$

where the second-order effective Hamiltonian, defined as an operator on $\mathcal{S}^{(1)}$, reads

$$\mathcal{H}^{(2)}=-P^{(1)}WG^{(0)}WP^{(1)}\ . \tag{2.20}$$

Furthermore, by applying $Q^{(1)}$ to Eq. (2.18), and using again Eq. (2.12), we also get

$$\overline{Q^{(1)}}\psi^{(1)}=G^{(1)}WG^{(0)}W\psi^{(0)}\ , \tag{2.21}$$

where the Green's function

$$G^{(1)}=Q^{(1)}(\mathcal{H}^{(1)}-E^{(1)})^{-1}Q^{(1)} \tag{2.22}$$

is the pseudoinverse of $(\mathcal{H}^{(1)}-E^{(1)})$ in $\mathcal{S}^{(0)}$. The other component $P^{(1)}\psi^{(1)}$ remains undetermined so far.

4. *Third order*

Finally, Eq. (2.8d) can be solved in analogy with Eqs. (2.8b) and (2.8c). We assume that $\psi^{(0)}$ belongs to $\mathcal{S}^{(2)}$, the linear space of common solutions to Eqs. (2.8a), (2.10), and (2.19). Let $P^{(2)}$ be the orthogonal projector onto $\mathcal{S}^{(2)}$, and $Q^{(2)}=1-P^{(2)}$.

By applying successively the projectors $P^{(0)}$, $P^{(1)}$, and $P^{(2)}$ to Eq. (2.8d), and after some manipulations using the results (2.12) and (2.21), we are again left with an eigenvalue equation for $\psi^{(0)}$, of the form

$$(\mathcal{H}^{(3)}-E^{(3)})\psi^{(0)}=0\ , \tag{2.23}$$

where the third-order effective Hamiltonian, defined as an operator on $\mathcal{S}^{(2)}$, reads

$$\mathcal{H}^{(3)}=P^{(2)}WG^{(0)}(W-WG^{(1)}W-E^{(1)})G^{(0)}WP^{(2)}\ . \tag{2.24}$$

5. *Comments*

Degenerate perturbation theory in quantum mechanics, and more generally for operators in Hilbert space, may seem to be a standard and well-studied subject. To our surprise the results derived above are not easy to find in the literature.

First, in the absence of any degeneracy, i.e., if the spectrum of $\mathcal{H}^{(0)}$ consists of discrete nondegenerate energies $E_n^{(0)}$, the Rayleight-Schrödinger formulas are recovered. Indeed, Eqs. (2.11), (2.20), and (2.24), respectively, yield

$$E_n^{(1)}=W_{n,n}\ , \tag{2.25a}$$

$$E_n^{(2)}=\sum_{m\neq n}\frac{W_{n,m}W_{m,n}}{E_n^{(0)}-E_m^{(0)}}\ , \tag{2.25b}$$

$$E_n^{(3)}=-W_{n,n}\sum_{m\neq n}\frac{W_{n,m}W_{m,n}}{(E_n^{(0)}-E_m^{(0)})^2}+\sum_{l\neq n,m\neq n}\frac{W_{n,l}W_{l,m}W_{m,n}}{(E_n^{(0)}-E_l^{(0)})(E_n^{(0)}-E_m^{(0)})}\ . \tag{2.25c}$$

Equations (2.25a) and (2.25b) can be found in most textbooks on quantum mechanics, whereas the result (2.25c) is much more seldomly given (see, e.g., Ref. 32).

In an arbitrary degenerate situation, one is led to diagonalize the successive effective Hamiltonians $\mathcal{H}^{(1)}$ of Eq. (2.11), $\mathcal{H}^{(2)}$ of Eq. (2.20), $\mathcal{H}^{(3)}$ of Eq. (2.24), and so on. Most textbooks only mention $\mathcal{H}^{(1)}$, whereas Piron[31] also derives $\mathcal{H}^{(2)}$, and $\mathcal{H}^{(3)}$ is novel as far as we know.

Coming back to tight-binding electrons, the molecular approximation yields the result (2.17) for an arbitrary chain (periodic, aperiodic, random). The DOS $\rho^{(1)}(E)$ of Eq. (2.17) consists of δ functions, which correspond to discontinuities in the IDOS $H^{(1)}(E)$. The amplitudes, or weights, ΔH_α of these discontinuities are equal to the frequencies of the relevant molecules. In spite of its simplicity, this approximation is not very well-known. In the context of deterministic aperiodic structures, it seems to have been derived first for the Thue-Morse sequence,[33] before it was generalized and applied to many other examples in Ref. 23. A similar approach had actually been applied before to the Anderson Hamiltonian on a disordered binary chain, where each atom is at random either of type A, or of type B, with respective probabilities p and $r=1-p$. In this situation, the sums in Eq. (2.17) run over all the possible values $n\geq 1$ of the molecular size, and the corresponding frequencies are the statistical weights $f(nA)=r^2p^n$, $f(nB)=p^2r^n$. The corresponding prediction of the form (2.17) has been investigated at length, especially in connection with Lifshitz tails.[34,24] A closely related problem, namely the study of harmonic excitations (phonons) of a binary alloy, with atomic masses $m_n=m$ or $m_n=\infty$, has been solved even longer ago.[35]

The situation becomes more involved with the next orders of the perturbation theory exposed above, which amounts to a systematic investigation of all possible resonances between molecular states, starting with the second order, which brings corrections of order t^2/V to the extensively degenerate energy levels of the molecular states. The resonance pattern depends on the underlying structure in an intricate way, so that no general formula can be written down explicitly. The outcome of the second- or third-order perturbations will be evaluated on several examples in the next sections of this paper.

Two alternatives can occur, at any order p of the strong-modulation perturbation theory. (i) The effective Hamiltonian $\mathcal{H}^{(p)}$ only couples finitely many molecular states. We thus obtain local resonances, strictly supported by finite patches of the chain. The relevant subspaces remain extensively degenerate. The corresponding contribution to the DOS consists of δ functions. (ii) The effective Hamiltonian $\mathcal{H}^{(p)}$ couples infinitely many molecular states. We thus obtain itinerant resonances, propagating along the whole chain. The diagonalization of $\mathcal{H}^{(p)}$ in the relevant subspace is usually as complicated a task as the diagonalization of the original Hamiltonian $\mathcal{H}$. The corresponding contribution to the DOS in a (continuous) band.

In both cases, the weights ΔH_α of the δ and of the bands are equal to the frequencies $f(w)$ of given words w in the sequence. As a consequence, the IDOS in every gap which appears at any order in perturbation theory is an integer linear combination of such frequencies. This is in accord with the gap-labeling theory.[20,21] On the other hand, since the matrix elements of both $\mathcal{H}^{(0)}$ and W are all equal to ±1, the construction of the successive Hamiltonians $\mathcal{H}^{(p)}$ is essentially a matter of combinatorics. These points will become clearer in the next sections, where several examples will be investigated in detail.

B. Sum rules for the DOS

The DOS of the tight-binding Hamiltonian (1.1) obeys exact nonperturbative integral identities, known as sum rules, which will be used extensively hereafter as cross-checks for our perturbative results. A simple derivation of the sum rules goes as follows.[24] Consider the moments μ_k of the DOS of any order $k \geq 0$. These quantities are defined as

$$\mu_k = \text{Tr}\mathcal{H}^k = \int_{-\infty}^{+\infty} E^k \rho(E) dE \ , \tag{2.26}$$

with the normalization $\mu_0 = 1$. These moments can be alternatively evaluated in the basis of atomic orbitals, namely

$$\mu_k = \langle (\mathcal{H}^k)_{n,n} \rangle = \lim_{N\to\infty} \frac{1}{N} \sum_{1 \leq n \leq N} (\mathcal{H}^k)_{n,n} \ , \tag{2.27}$$

where we have introduced the Cesàro average $\langle \cdots \rangle$ of a local quantity along the chain. Equation (2.27) yields closed-form expressions for the moments μ_k, which hold for any physically reasonable sequence, with sufficient homogeneity properties. The first ones read

$$\mu_1 = \langle V_n \rangle \ , \tag{2.28a}$$

$$\mu_2 = \langle V_n^2 \rangle + 2t^2 \ , \tag{2.28b}$$

$$\mu_3 = \langle V_n^3 \rangle + 6t^2 \langle V_n \rangle \ , \tag{2.28c}$$

$$\mu_4 = \langle V_n^4 \rangle + 4t^2(2\langle V_n^2 \rangle + \langle V_n V_{n+1} \rangle) + 6t^4 \ . \tag{2.28d}$$

III. THE FIBONACCI CHAIN

A. Definition

The Fibonacci sequence is the simplest of all deterministic aperiodic sequences. It is built recursively by the following rules, acting on two letters:

$$\sigma_F: \left| \begin{array}{l} A \to AB \\ B \to A \ . \end{array} \right. \tag{3.1}$$

Such a transformation is called a substitution. It acts on symbols called letters. Reference 7 provides a complete mathematical review on these topics, whereas Refs. 36 and 9 give comprehensive introductions to more physical aspects.

To the Fibonacci substitution is attached the substitution matrix, or counting matrix

$$\mathbf{M}_F = \begin{bmatrix} \text{No. of } A\text{'s in } \sigma_F(A) & \text{No. of } A\text{'s in } \sigma_F(B) \\ \text{No. of } B\text{'s in } \sigma_F(A) & \text{No. of } B\text{'s in } \sigma_F(B) \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} . \tag{3.2}$$

The eigenvalues λ_i of a substitution matrix give access to a great deal of geometrical and structural information (see, e.g., Refs. 36 and 9). In the present case, they read $\lambda_1 = \tau$ and $\lambda_2 = -\tau^{-1}$, where

$$\tau = (1+\sqrt{5})/2 \tag{3.3}$$

is the golden mean, which obeys the quadratic equation $\tau^2 = \tau + 1$.

Consider the words $A_k = \sigma_F^k(A)$ and $B_k = \sigma_F^k(B)$, obtained by acting repeatedly with σ_F on the initial letters. Both series of words converge to the infinite Fibonacci sequence $F = ABAABABAABAAB\ldots$, which is self-similar, since it obeys $F = \sigma_F(F)$, and the substitution σ_F acts on large distances as a similarity, i.e., a dilatation by the scaling factor $\lambda_1 = \tau$. The word $A_k = B_{k+1}$ consists of F_{k+2} atoms, among which F_{k+1} are A's, and F_k are B's, where F_k are the Fibonacci numbers, defined by the recursion

$$F_k = F_{k-1} + F_{k-2} \quad (k \geq 2) \ , \tag{3.4}$$

with $F_0 = 0, F_1 = 1$. The identity $F_k = [\tau^k - (-\tau^{-1})^k]/\sqrt{5}$ makes the connection with the eigenvalues of the substitution matrix of Eq. (3.2).

The Fibonacci sequence is also the simplest of all quasicrystals. It is quasiperiodic, as it can, e.g., be generated by the cut-and-project algorithm from the square lattice. Furthermore, as we have just argued, it is self-similar with a scaling factor τ. These properties are shared by the 3D models of prefect icosahedral phases, and by the celebrated 2D Penrose tiling.

B. The strong-modulation regime

Let us now turn to the analysis of the tight-binding Hamiltonian (1.1), with a Fibonacci sequence of site energies, according to the rule (1.2), as a first application of the general approach exposed in Sec. II.

1. First order

The Fibonacci chain is made of three types of molecules: A, AA, and B. Their frequencies $f(1A)$, $f(2A)$, and $f(B)$ can be determined by means of the substitution rules (3.1), and more precisely by expressing that the substitution acts as a dilatation by τ. We thus obtain the equations $f(A)+f(B)=1=\tau f(A)$, $f(A)=\tau f(B)$, $f(B) = \tau^2 f(1A)$, and $f(1A)+2f(2A)=f(A)$, which yield

$$\begin{gathered} f(1A) = \tau^{-4} = 5 - 3\tau \ , \quad f(2A) = \tau^{-3} = 2\tau - 3 \ , \\ f(A) = \tau^{-1} = \tau - 1 \ , \quad f(B) = \tau^{-2} = 2 - \tau \ . \end{gathered} \tag{3.5}$$

The DOS of the Fibonacci Hamiltonian within the molecular approximation is obtained by inserting the results (3.5) into the expression (2.17)

$$\begin{aligned} \rho^{(1)}(E) = {} & \tau^{-2}\delta(-V-E) + \tau^{-3}\delta(V-t-E) \\ & + \tau^{-4}\delta(V-E) + \tau^{-3}\delta(V+t-E) \ . \end{aligned} \tag{3.6}$$

2. Second order

We now turn to the investigation of the splitting of each of the extensively degenerate molecular levels of Eq. (3.6), due to the second-order Hamiltonian $\mathcal{H}^{(2)}$ of Eq. (2.20).

a. A molecules. In the Fibonacci chain, the A molecules are separated from each other by a distance of at least five lattice spacings. As a consequence, they are not coupled by $\mathcal{H}^{(2)}$, which decomposes into a product of independent 1×1 matrices supported by individual A molecules, which read $\mathcal{H}^{(2)}_{1A}=1$. The levels at $E=V$ are thus not split at this order, but only shifted by the amount t^2/V.

b. B molecules. The action of the second-order Hamiltonian $\mathcal{H}^{(2)}$ distinguishes between the isolated B molecules and those which come in pairs. (i) *Isolated B molecules:* The isolated B molecules have the environment $AA\underline{B}AA$; they have a frequency τ^{-5}. Their situation is similar to that of the A molecules. We readily get $\mathcal{H}^{(2)}_{1B}=-1$. (ii) *Pairs of B molecules:* The pairs of B molecules have the environment $AA\underline{B}A\underline{B}AA$; they have a frequency τ^{-4}. $\mathcal{H}^{(2)}$ acts on them as a product of independent 2×2 matrices

$$\mathcal{H}^{(2)}_{2\times 1B}=-\frac{1}{2}\begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix}, \tag{3.7}$$

with eigenvalues $E^{(2)}=-\frac{1}{2}$ and $-\frac{3}{2}$.

c. AA molecules. The situation of the AA molecules with respect to the second-order Hamiltonian $\mathcal{H}^{(2)}$ is similar to that of the B molecules. (i) *Isolated A A molecules:* The isolated AA molecules have the environment $BAB\underline{AA}BAB$; they have a frequency τ^{-6}. Each of them supports two molecular states of the form [(2.15), (16)]. We obtain $\mathcal{H}^{(2)}_{1\times 2A}=\frac{1}{2}$, independently of the molecular state under consideration. (ii) *Pairs of A A molecules:* The pairs of AA molecules have the environment $BAB\underline{AA}B\underline{AA}BAB$; they have a frequency τ^{-5}. For each of the two molecular states mentioned just above, labeled by the value of $E^{(1)}=\pm 1$, $\mathcal{H}^{(2)}$ acts as a product of independent 2×2 matrices, of the form

$$\mathcal{H}^{(2)}_{2\times 2A}=\frac{1}{4}\begin{bmatrix} 2 & E^{(1)} \\ E^{(1)} & 2 \end{bmatrix}, \tag{3.8}$$

with eigenvalues $E^{(2)}=\frac{1}{4}$ and $\frac{3}{4}$.

The DOS of the Fibonacci Hamiltonian to second order in the strong-modulation regime can be evaluated by gathering the results of this subsection. We thus obtain ten groups of extensively degenerate energy levels, namely

$$\rho^{(2)}(E)=\sum_{1\le\alpha\le 10}\Delta H_\alpha(E_\alpha-E)\ . \tag{3.9}$$

The energies E_α and the associated weights ΔH_α are listed in Table I.

As an analytical check of the prediction (3.9), we have used the sum rules of Sec. II B. For the Fibonacci chain, we have $\langle V\rangle=[1-2f(B)]V=(2\tau-3)V$ and

$$\langle V_nV_{n+1}\rangle=[1-4f(B)]V^2=(4\tau-7)V^2\ ,$$

so that Eq. (2.28) yields

$$\mu_1=(2\tau-3)V,\quad \mu_2=V^2+2t^2,\quad \mu_3=(2\tau-3)V(V^2+6t^2)\ , \tag{3.10}$$
$$\mu_4=V^4+4(4\tau-5)V^2t^2+6t^4\ .$$

It is readily checked that the moments evaluated from the prediction (3.9) coincide with the expressions (3.10), up to terms of order t^2 included.

C. Applications

1. Preliminaries: the trace map

Let us now compare the analytical results of the perturbative approach to numerical data concerning various physical quantities. The latter have been obtained by means of the transfer-matrix formalism and of the trace-map technique, which we now summarize briefly.

The eigenvalue equation (1.1) can be recast as

$$\begin{bmatrix}\psi_{n+1}\\ \psi_n\end{bmatrix}=\mathbf{T}_n\begin{bmatrix}\psi_n\\ \psi_{n-1}\end{bmatrix}, \tag{3.11}$$

where the 2×2 matrix with unit determinant

$$\mathbf{T}_n=\begin{bmatrix}(E-V_n)/t & -1\\ 1 & 0\end{bmatrix} \tag{3.12}$$

is the transfer matrix associated with the nth atom of the chain. We have either $\mathbf{T}_n=\mathbf{T}_A$ or $\mathbf{T}_n=\mathbf{T}_B$. The propagation along any patch of the chain is thus described by a product of matrices $\mathbf{T}_n$.

We define the $\mathbf{A}_k$ as the products of transfer matrices associated with the words $A_k=\sigma_F^k(A)$. The traces of those matrices

$$X_k=\mathrm{tr}\,\mathbf{A}_k \tag{3.13}$$

obey a remarkable polynomial recursion formula, known as the *trace map*,[37,38] namely

$$X_k=X_{k-1}X_{k-2}-X_{k-3}\quad(k\ge 2)\ , \tag{3.14}$$

with the initial conditions $X_{-1}=(E+V)/t$, $X_0=(E-V)/t$, $X_1=(E^2-V^2)/t^2-2$.

Consider the periodic approximant of the Fibonacci chain obtained by repeating the word A_k in a periodic way. The spectrum of the Hamiltonian (1.1) on that approximant consists of F_{k+2} bands, one per atom in the unit cell. The band edges are the solutions of the equations $X_k(E)=\pm 2$. The trace X_k is indeed a polynomial in E of degree F_{k+2}.

The trace-map approach, developed initially for the Fibonacci sequence, has since then been shown to hold for any substitutional sequence.[39,40] It provides chiefly a very accurate numerical tool; it has also been the starting point of several rigorous investigations, such as Refs. 15, 19, and 41.

2. DOS

The analytical prediction (3.9) concerning the DOS of the Fibonacci Hamiltonian in the strong-modulation regime is compared in Fig. 1 with numerical data obtained by means of the trace-map approach, for $t/V=0.5$, and $k=12$, i.e., $F_{14}=377$ atoms per cell (the difference in IDOS between the Fibonacci chain and that approximant is below the resolution of the plot). The agreement is fully satisfactory. In particular the ten discontinuities listed in Table I are the most clearly visible structures of the

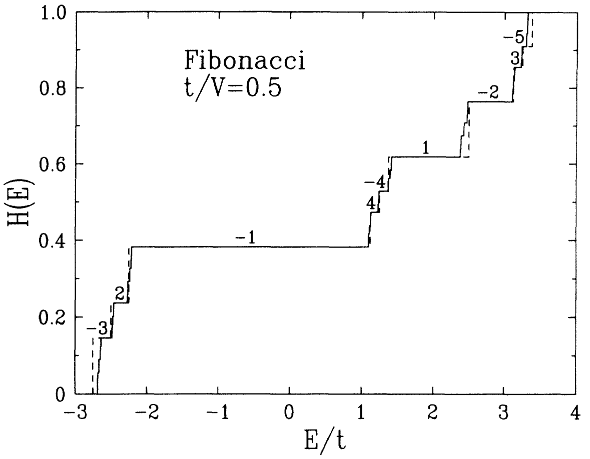

FIG. 1. IDOS $H(E)$ of tight-binding electrons on the Fibonacci chain, plotted against reduced energy E/t: comparison between numerical data (full line), and analytical prediction of perturbation theory (3.9) (dashed line). The gaps are labeled according to Eq. (3.15).

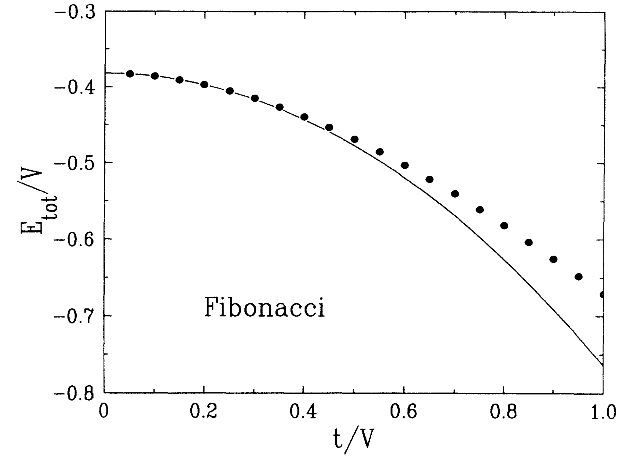

FIG. 2. Reduced total electronic binding energy $E_{\rm tot}/V$ of the Fibonacci chain, plotted against t/V: comparison between numerical data (dots), and analytical prediction of perturbation theory (3.17) (line).

plot. The nine corresponding gaps have been labeled by integers m, according to the gap-labeling formula[10,20,21]

$$H(\text{gap}) = \text{Frac}(m\tau) \ , \tag{3.15}$$

where $\text{Frac}(x) = x - \text{Int}(x)$ denotes the fractional part of the real number x.

3. *Binding energy*

We have also tested the efficiency of the strong-modulation perturbation theory on the total electronic binding energy, a quantity that is sensitive to more global aspects of the spectrum.

The total binding energy at zero temperature reads

$$E_{\rm tot} = \int_{-\infty}^{E_F} E\rho(E)dE \ . \tag{3.16}$$

We assume, for the sake of simplicity, that the Fermi energy lies at $E_F=0$, in the main gap of the spectrum. The result (3.9), together with the observation that the binding energy is an even function of t, i.e., a function of t^2, yields the estimate

$$E_{\rm tot} = -\tau^{-1}(V + t^2/V) + \mathcal{O}(t^4/V^3) \ . \tag{3.17}$$

TABLE I. DOS of tight-binding electrons on the Fibonacci chain in the strong-modulation regime: energies E_α and weights ΔH_α entering the outcome (3.9) of second-order perturbation theory.

E_α	ΔH_α
$-V-3t^2/2V$	τ^{-4}
$-V-t^2/V$	τ^{-5}
$-V-t^2/2V$	τ^{-4}
$V-t+t^2/4V$	τ^{-5}
$V-t+t^2/2V$	τ^{-6}
$V-t+3t^2/4V$	τ^{-5}
$V+t^2/V$	τ^{-4}
$V+t+t^2/4V$	τ^{-5}
$V+t+t^2/2V$	τ^{-6}
$V+t+3t^2/4V$	τ^{-5}

Figure 2 presents a comparison between this prediction and numerical values obtained by means of the trace-map approach. A very good agreement can be observed for $t/V \ll 1$.

IV. THE THUE-MORSE CHAIN

A. Definition

The Thue-Morse sequence is defined by the binary substitution

$$\sigma_{\rm TM}: \left| \begin{array}{l} A \to AB \\ B \to BA \ . \end{array} \right. \tag{4.1}$$

The analysis of this example will follow closely the setup and the notation introduced in Sec. III. The associated substitution matrix, defined in analogy with Eq. (3.2), namely

$$\mathbf{M}_{\rm TM} = \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} , \tag{4.2}$$

has for eigenvalues $\lambda_1=2$ and $\lambda_2=0$. The integer value of λ_1 is related to the fact that both $\sigma_{\rm TM}(A)$ and $\sigma_{\rm TM}(B)$ consist of two letters. Such substitutions of constant length have been investigated extensively, in connection with the theory of finite *automata*.[7]

The words $A_k = \sigma_{\rm TM}^k(A)$ and $B_k = \sigma_{\rm TM}^k(B)$ both consist of 2^k letters. Furthermore, these words are the mirror image of each other, so that A atoms and B atoms play equivalent roles in the infinite Thue-Morse chain $ABBABAABBAABABBA\ldots$. This peculiar symmetry of the Thue-Morse sequence also explains the singular continuous nature of its Fourier transform, whereas general arguments, based on the analysis of the substitution matrix (4.2) (see, e.g., Refs. 36 and 9), would predict a limit-periodic sequence. Physical models based on the Thue-Morse chain have been studied, e.g., in Refs. 42, 43, 33, 23, 41, and 17.

B. The strong-modulation regime

As a consequence of the equivalence between both types of letters in the Thue-Morse sequence, the spectrum of the Hamiltonian (1.1) with Thue-Morse potential is symmetric with respect to the origin of energies $E=0$. We have in particular $\rho(E)=\rho(-E)$, so that one can restrict the analysis to $E>0$, i.e., to A atoms in the strong-modulation regime.

1. *First order*

The Thue-Morse chain is made of two types of A molecules: A and AA. Their frequencies can again be determined by means of the substitution rules (4.1). We thus obtain $f(1A)+2f(2A)=f(A)=f(B)$ and $4f(2A)=f(B)+f(2A)$, whence

$$\begin{aligned} &f(1A)=f(2A)=f(1B)=f(2B)=1/6\ , \\ &f(A)=f(B)=1/2\ . \end{aligned} \tag{4.3}$$

The DOS of the Thue-Morse Hamiltonian within the molecular approximation thus reads

$$\begin{aligned} \rho^{(1)}(E)=\tfrac{1}{6}[\delta(V-t-E)+\delta(V-E)+\delta(V+t-E)] \\ +(E\rightarrow -E)\ . \end{aligned} \tag{4.4}$$

2. *Second order*

The action of the second-order Hamiltonian $\mathcal{H}^{(2)}$ on the Thue-Morse chain does not couple any two different A or AA molecules. As a result, we obtain the expressions $\mathcal{H}^{(2)}_{1A}=1$ and $\mathcal{H}^{(2)}_{2A}=\frac{1}{2}$, the latter being independent of the molecular state under consideration.

3. *Third order*

In order to investigate the first splittings which take place beyond the molecular approximation, we have to go to third-order perturbation theory. The Thue-Morse chain is the only example where such an analysis will be performed in detail.

a. A molecules. (i) *isolated A molecules:* The isolated A molecules occur in the following two mirror-symmetric environments: $AAB\underline{A}BBAA$ and $AABB\underline{A}BAA$; they have altogether a frequency $f=f(A)/8=\frac{1}{24}$. The corresponding third-order Hamiltonian vanishes: $\mathcal{H}^{(3)}_{1A}=0$. (ii) *triplets of A molecules:* The triplets of A-molecules occur in the following two mirror-symmetric environments: $\underline{A}BB\underline{A}BAAB\underline{A}$ and $\underline{A}BAAB\underline{A}BB\underline{A}$; they also have altogether a frequency $f=f(A)/8=\frac{1}{24}$. On each triplet, the third-order Hamiltonian defines a 3×3 matrix

$$\mathcal{H}^{(3)}_{3\times 1A}=\frac{1}{4}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}\ , \tag{4.5}$$

with eigenvalues $E^{(3)}=0$ and $\pm\sqrt{2}/4$.

b. AA molecules. We define as $\mathcal{S}^{(1)}=\mathcal{S}^{(2)}$ the subspace associated with the energy $E^{(1)}=\pm 1$. The AA molecules may have three different environments, to be considered separately. (i) *$BABB\underline{AA}BBAB$ environment:* These AA molecules have a frequency $f=\frac{1}{24}$. For every value of $E^{(1)}$, the third-order Hamiltonian is the constant $\mathcal{H}^{(3)}_{2A}=-E^{(1)}/4$. (ii) *$BBAB\underline{AA}BABB$ environment:* These AA molecules also have a frequency $f=\frac{1}{24}$. For both values of $E^{(1)}$, the third-order Hamiltonian vanishes: $\mathcal{H}^{(3)}_{2A}=0$. (iii) *$AB\underline{AA}BB\underline{AA}BA$ environment:* These AA molecules coupled in pairs have altogether a frequency $f=\frac{1}{12}$. In the subspace corresponding to every value of $E^{(1)}$, the third-order Hamiltonian is the 2×2 matrix

$$\mathcal{H}^{(3)}_{2\times 2A}=\frac{E^{(1)}}{8}\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}\ , \tag{4.6}$$

with eigenvalues $E^{(3)}=-E^{(1)}/4$ and 0.

TABLE II. Same as Table I, for the Thue-Morse chain [see Eq. (4.7)].

$E_\alpha>0$	ΔH_α
$V-t+t^2/2V$	1/12
$V-t+t^2/2V+t^3/4V^2$	1/12
$V+t^2/V-\sqrt{2}t^3/4V^2$	1/24
$V+t^2/V$	1/12
$V+t^2/V+\sqrt{2}t^3/4V^2$	1/24
$V+t+t^2/2V-t^3/4V^2$	1/12
$V+t+t^2/2V$	1/12

The DOS of the Thue-Morse Hamiltonian to third order in the strong-modulation regime can be evaluated by gathering the results of this subsection. We thus obtain fourteen groups of energy levels that are extensively degenerate, namely

$$\rho^{(3)}(E)=\sum_{1\le\alpha\le 7}\Delta H_\alpha[\delta(E_\alpha-E)+\delta(-E_\alpha-E)]\ . \tag{4.7}$$

The energies $E_\alpha>0$ and the associated weights ΔH_α are listed in Table II.

As an analytical check of the prediction (4.7), we have used the sum rules of Sec. II B. For the Thue-Morse chain, we have $\langle V\rangle=\langle V^3\rangle=0$, and

$$\langle V_n V_{n+1}\rangle=[4f(2A)-1]V^2=-V^2/3\ ,$$

so that Eq. (2.28) yields

$$\mu_1=0,\quad \mu_2=V^2+2t^2,\quad \mu_3=0,\quad \mu_4=V^4+20V^2t^2/3+6t^4\ . \tag{4.8}$$

It is readily checked that the moments evaluated from the prediction (4.7) coincide with the expressions (4.8), up to terms of order t^2 included.

C. Applications

1. *Trace map*

We consider again, in analogy with the Fibonacci chain, the traces X_k of the transfer matrices $\mathbf{A}_k$ associated with the words $A_k=\sigma^k_{\mathrm{TM}}(A)$. Those quantities obey the polynomial trace map[42,17]

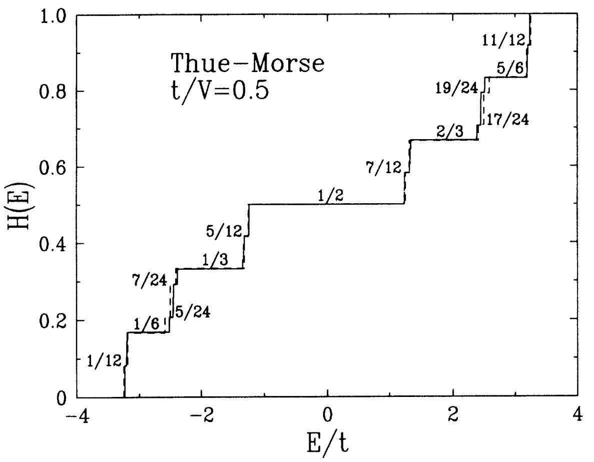

FIG. 3. Same as Fig. 1, for the Thue-Morse chain [see Eqs. (4.7) and (4.10)].

$$X_k=(X_{k-1}-2)X_{k-2}^2+2 \quad (k\geq 3)\ , \tag{4.9}$$

with the initial conditions $X_1=(E^2-V^2)/t^2-2$ and

$$X_2=(E^4+V^4)/t^4-2(V^2/t^2+2)E^2/t^2+2\ .$$

2. *DOS*

The analytical prediction (4.7) concerning the DOS of the Thue-Morse Hamiltonian in the strong-modulation regime is compared in Fig. 3 with numerical data obtained by means of the trace-map approach, for $t/V=0.5$, and $k=9$, i.e., $2^9=512$ atoms per cell. The agreement is again fully satisfactory.

The gaps predicted by Eq. (4.7) have been indexed according to the rigorous gap-labeling formula[17,43,20,21]

$$H(\text{gap})=\frac{1}{3}\frac{m}{2^n}\ , \tag{4.10}$$

with m (odd) and $n\geq 1$ being natural integers.

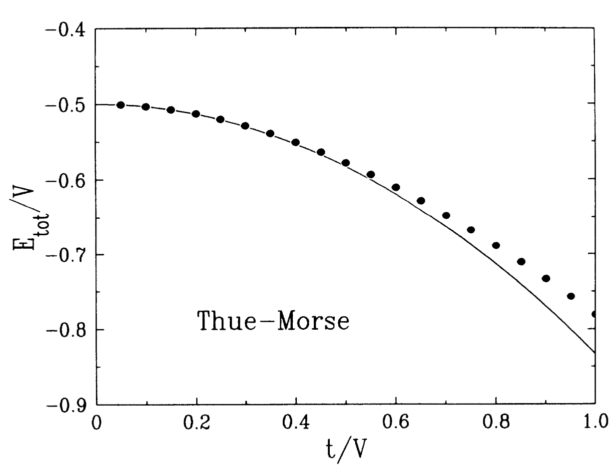

FIG. 4. Same as Fig. 2, for the Thue-Morse chain [see Eq. (4.11)].

3. *Binding energy*

With the conventions of Sec. III C 3, we obtain the following estimate for the total binding energy:

$$E_{\text{tot}}=-V/2-t^2/(3V)+\mathcal{O}(t^4/V^3)\ . \tag{4.11}$$

Figure 4 presents a comparison between this prediction and numerical values obtained by means of the trace-map approach. A very good agreement can again be observed.

V. THE PERIOD-DOUBLING CHAIN

A. Definition

The period-doubling sequence is defined by the binary substitution

$$\sigma_{\text{PD}}:\left|\begin{array}{l}A\rightarrow AB\\ B\rightarrow AA\end{array}\right.\ . \tag{5.1}$$

The analysis of this example will again follow closely the setup and the notation introduced in Sec. III. The associated substitution matrix reads

$$\mathbf{M}_{\text{PD}}=\begin{bmatrix}1 & 2\\ 1 & 0\end{bmatrix}\ , \tag{5.2}$$

and its eigenvalues are $\lambda_1=2$ and $\lambda_2=-1$. Here again, the words $A_k=\sigma_{\text{PD}}^k(A)$ and $B_k=\sigma_{\text{PD}}^k(B)$ both consist of 2^k letters. The period-doubling sequence is known to be limit periodic. Physical models based on the period-doubling chain have been studied in Refs. 23 and 18.

B. The strong-modulation regime

1. *First order*

The period-doubling chain consists of isolated B atoms, and of two types of A molecules: A and AAA. Their frequencies can again be determined by means of the substitution rules (5.1), which yield

$$f(1A)=f(3A)=1/6\ ,\quad f(A)=2/3\ ,\quad f(B)=1/3\ . \tag{5.3}$$

The DOS of the period-doubling Hamiltonian within the molecular approximation thus reads

$$\rho^{(1)}(E)=\tfrac{1}{3}\delta(-V-E)+\tfrac{1}{6}\delta(V-t\sqrt{2}-E)+\tfrac{1}{3}\delta(V-E)+\tfrac{1}{6}\delta(V+t\sqrt{2}-E)\ . \tag{5.4}$$

2. *Second order*

a. B molecules. (i) *isolated B molecules:* The isolated B molecules have the environment $AAA\underline{B}AAA$; they have a frequency $f=\frac{1}{12}$. The second-order Hamiltonian is a constant on each of them: $\mathcal{H}_B^{(2)}=-1$. (ii) *triplets of B molecules:* The triplets of B molecules have the environment $AAA\underline{B}A\underline{B}A\underline{B}AAA$. They also have a frequency $f=\frac{1}{12}$. On each of them, the second-order Hamiltonian is the 3×3 matrix

$$\mathcal{H}^{(2)}_{3\times B}=-\frac{1}{2}\begin{bmatrix}2&1&0\\1&2&1\\0&1&2\end{bmatrix}, \tag{5.5}$$

with eigenvalues $E^{(2)}=-1$ and $-1\pm\sqrt{2}/2$.

b. A and AAA molecules. In the molecular approximation, every AAA molecule supports three eigenstates, given by Eqs. (2.15) and (2.16). Their energies and wave functions read

$$\begin{aligned}a&=1:\ E^{(1)}=\sqrt{2}\ ,\quad \psi=(1/2,\sqrt{2}/2,1/2)\ ;\\ a&=2:\ E^{(1)}=0\ ,\quad \psi=(\sqrt{2}/2,0,-\sqrt{2}/2)\ ;\\ a&=3:\ E^{(1)}=-\sqrt{2}\ ,\quad \psi=(1/2,-\sqrt{2}/2,1/2)\ .\end{aligned} \tag{5.6}$$

(i) *AAA molecules—local resonances:* As far as the states with $a=1$ and $a=3$ are concerned, the situation of the AAA molecules is similar to that of the B atoms. *Isolated AAA molecules:* The isolated AAA molecules have the environment $BAB\underline{AAA}BAB$; they have a frequency $f=\frac{1}{24}$. The second-order Hamiltonian is a constant on each of them, namely $\mathcal{H}^{(2)}_{1\times 3A}=\frac{1}{4}$. *Triplets of AAA molecules:* The triplets of AAA molecules have the environment $B\underline{AAA}B\underline{AAA}B\underline{AAA}B$; they also have a frequency $f=\frac{1}{24}$. On each of them, and for each state ($a=1$ or $a=3$), the second-order Hamiltonian is the 3×3 matrix

$$\mathcal{H}^{(2)}_{3\times 3A}=\frac{1}{8}\begin{bmatrix}2&1&0\\1&2&1\\0&1&2\end{bmatrix}, \tag{5.7}$$

with eigenvalues $E^{(2)}=1/4$ and $(2\pm\sqrt{2})/8$. (ii) *A and AAA molecules—itinerant resonances:* The atomic states of the A molecules are degenerate with the eigenstates of the AAA molecules corresponding to $a=2$ in Eq. (5.6). In the subspace spanned by all these states, the second-order Hamiltonian $\mathcal{H}^{(2)}$ is an infinite Jacobi (tridiagonal) matrix. This phenomenon of itinerant resonance, alluded to in Sec. II A 5, will be studied in detail in the present example.

Let us denote A molecules by a letter X, and AAA molecules by a letter Y. We thus obtain a binary sequence $XYXXXYYYXXXYYY\ldots$, which inherits most of the characteristics of the period-doubling sequence from which it is derived. Both sequences are self-similar and limit periodic; it can be shown by inspection that the X-Y sequence is generated by the binary substitution

$$\sigma_{XY}:\left|\begin{array}{l}X\to XXY\\ Y\to XXYYY\ .\end{array}\right. \tag{5.8}$$

The eigenvalue equation for $\mathcal{H}^{(2)}$ reads

$$(\mathcal{H}^{(2)}\Psi)_k=T_{k-1,k}\Psi_{k-1}+T_{k,k+1}\Psi_{k+1}+U_k\Psi_k=E^{(2)}\Psi_k\ , \tag{5.9}$$

where the integer k labels the successive X letters (A molecules) and Y letters (AAA molecules) along the chain. The diagonal and nondiagonal matrix elements read

$$U_X=1,\quad U_Y=1/2,\quad T_{X,X}=1/2,\quad T_{X,Y}=T_{Y,X}=\sqrt{2}/4\ ,\quad T_{Y,Y}=1/4\ . \tag{5.10}$$

The effective Hamiltonian $\mathcal{H}^{(2)}$ of Eq. (5.9) is as complicated as the tight-binding Hamiltonian (1.1). Hence we shall not be able to evaluate its DOS $\rho_{\text{band}}(E^{(2)})$ exactly. Nevertheless, the parameters of $\mathcal{H}^{(2)}$ have the remarkable properties $U_X-2T_{X,X}=U_Y-2T_{Y,Y}=0$ and $T_{X,Y}/T_{X,X}=T_{Y,Y}/T_{Y,X}$, which ensure that the bottom of the spectrum lies at $E^{(2)}=0$, i.e., $E=V$ for the original tight-binding problem. More interestingly, the eigenstates become asymptotically extended as $E^{(2)}\to 0$. The technicalities are exposed in the Appendix.

The existence of extended states at $E=V$ holds beyond perturbation theory. Indeed at this special energy any two successive A atoms are transparent, in the sense that the corresponding transfer matrix reads $\mathbf{T}_A^2=-\mathbf{1}$. As a consequence, the eigenstates at $E=V$ coincide on the period-doubling chain and on the periodic chain with unit cell AB. Furthermore $E=V$ can be checked to be an internal band edge of the latter periodic structure. We shall come back to this phenomenon in Sec. VI.

The DOS of the period-doubling Hamiltonian to second order can be evaluated by gathering the results of this subsection. We thus obtain ten groups of energy levels, namely

$$\rho^{(2)}(E)=\sum_{1\le\alpha\le 10,\alpha\ne 7}\Delta H_\alpha\delta(E_\alpha-E)+\frac{V\Delta H_7}{t^2}\rho_{\text{band}}\left[E^{(2)}=\frac{V(E-V)}{t^2}\right]. \tag{5.11}$$

The energies E_α and the associated weights ΔH_α are listed in Table III. The case $\alpha=7$ corresponds to the band of resonant states studied just above. The corresponding DOS is obtained by transforming $\rho_{\text{band}}(E^{(2)})$ according to $E=V+(t^2/V)E^{(2)}$.

As an analytical check of the prediction (5.11), we have again used the sum rules of Sec. II B. For the period-doubling chain, we have $\langle V\rangle=V/3$, $\langle V^3\rangle=V^3/3$, and

$$\langle V_nV_{n+1}\rangle=[4f(3A)-1]V^2=-V^2/3\ ,$$

so that Eq. (2.28) yields

TABLE III. Same as Table I, for the period-doubling chain [see Eq. (5.11)].

E_α	ΔH_α
$-V-(2+\sqrt{2})t^2/2V$	1/12
$-V-t^2/V$	1/6
$-V-(2-\sqrt{2})t^2/2V$	1/12
$V-\sqrt{2}t+(2-\sqrt{2})t^2/8V$	1/24
$V-\sqrt{2}t+t^2/4V$	1/12
$V-\sqrt{2}t+(2+\sqrt{2})t^2/8V$	1/24
$V+E^{(2)}(\text{band})t^2/V$	1/3
$V+\sqrt{2}t+(2-\sqrt{2})t^2/8V$	1/24
$V+\sqrt{2}t+t^2/4V$	1/12
$V+\sqrt{2}t+(2+\sqrt{2})t^2/8V$	1/24

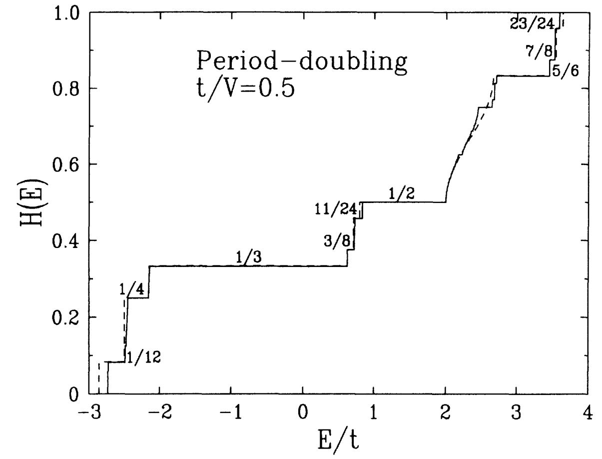

FIG. 5. Same as Fig. 1, for the period-doubling chain [see Eqs. (5.11) and (5.15)]. The DOS ρ_{band} of the band of itinerant resonances has been approximated by that of a homogeneous harmonic chain [see Eq. (A5)], with $M=3$, and $E=V+t^2\mathcal{E}/V$.

$$\mu_1=V/3,\quad \mu_2=V^2+2t^2,\quad \mu_3=V^3/3\ ,$$
$$\mu_4=V^4+20V^2t^2/3+6t^4\ . \tag{5.12}$$

In order to check that the moments evaluated from the prediction (5.11) coincide with the expressions (5.12), up to terms of order t^2 included, we have used the sum rule for the first moment of the Hamiltonian $\mathcal{H}^{(2)}$ of Eq. (5.9), which reads

$$\int E^{(2)}\rho_{\text{band}}(E^{(2)})dE^{(2)}=\langle U_k\rangle=(U_X+U_Y)/2=3/4\ . \tag{5.13}$$

C. Applications

1. *Trace map*

We consider again the traces X_k of the transfer matrices $\mathbf{A}_k$ associated with the words $A_k=\sigma_{\text{PD}}^k(A)$. Those quantities obey the polynomial trace map[23,18]

$$X_k=(X_{k-2}^2-2)X_{k-1}-2\quad (k\geq 2)\ , \tag{5.14}$$

with the initial conditions $X_0=(E-V)/t$, $X_1=(E^2-V^2)/t^2-2$.

2. *DOS*

The analytical prediction (5.11) concerning the DOS of the period-doubling Hamiltonian in the strong-modulation regime is compared in Fig. 5 with numerical data obtained by means of the trace-map approach, for $t/V=0.5$, and $k=9$, i.e., $2^9=512$ atoms per cell. The agreement is again very satisfactory, in spite of the approximation made for the band of itinerant resonances (see figure caption).

The gaps predicted by Eq. (5.11) have been indexed according to the rigorous gap-labeling formula[18,21]

$$H(\text{gap})=\frac{1}{3}\frac{m}{2^n}\ , \tag{5.15}$$

with m (odd) and $n\geq 1$ being natural integers.

3. *Binding energy*

With the conventions of Sec. III C 3, we obtain the following estimate for the total binding energy:

$$E_{\text{tot}}=-\tfrac{1}{3}(V+t^2/V)+\mathcal{O}(t^4/V^3)\ . \tag{5.16}$$

Figure 6 presents a comparison between this prediction and numerical values obtained by means of the trace-map approach. A very convincing agreement can again be observed.

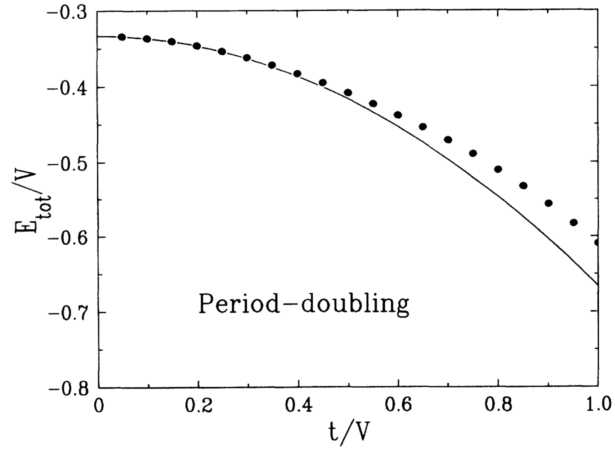

FIG. 6. Same as Fig. 2, for the period-doubling chain [see Eq. (5.16)].

VI. DISCUSSION

In this work we have studied the tight-binding Hamiltonian on aperiodic chains, in the strong-modulation regime ($t\ll V$). Taking the hopping matrix as a perturbation, we have introduced a systematic approach which yields predictions for the spectrum, the DOS, and related quantities, in the form of power series in the dimensionless ratio t/V. Along the scheme of degenerate perturbation theory in quantum mechanics, we are led to diagonalize successive effective Hamiltonians $\mathcal{H}^{(p)}$ ($p=1,2,3$, etc.).

Second-order effective Hamiltonians equivalent to $\mathcal{H}^{(2)}$ have been derived by means of real-space renormalization-group arguments, in the case of self-similar chains,[29] and more recently for 2D quasiperiodic tilings,[44] by means of the Schur formula. Furthermore, the idea of taking kinetic energy as a perturbation has also been put forward and explored in a more general context.[45]

The first-order step, namely diagonalizing $\mathcal{H}^{(1)}$, is equivalent to the molecular approximation, for which general formulas can be written down explicitly. The situation gets more involved at the next orders, starting with the second-order Hamiltonian $\mathcal{H}^{(2)}$. Indeed, a complex pattern of resonances show up, which strongly depends on the structure under study. In the case of local resonances (only finitely many molecular states are coupled), the DOS remains discrete at this order of approximation, whereas for itinerant resonances (infinitely many molecular states are coupled), a (usually continuous) band appears in the spectrum, again to this order in t/V.

The predictions of the strong-modulation perturbative analysis correctly reproduce the main gap structure of the spectra, as dictated by the rigorous gap-labeling theorems. As far as quantitative aspects are concerned, this approach also provides accurate estimates for the DOS, and for various quantities of physical interest, such as the total binding energy, or the electronic specific heat. This efficiency has been demonstrated by extensive comparisons with numerical data. Three examples of self-similar chains have been investigated in detail. Apart from being among the very most classical examples, these cases illustrate the variety of possible kinds of behavior. The Fibonacci sequence is the prototype of the generic case, whereas the other two examples exhibit their own peculiarities. There is no splitting at second-order for the Thue-Morse sequence. The period-doubling chain has a very prominent band of itinerant resonances ($\frac{1}{3}$ of the total IDOS), ending up at the special energy $E=V$, where the chain has extended eigenstates.

The resonances which occur at any order in this perturbative approach have been termed with the unusual words "local" and "itinerant," in order to emphasize that the pattern of resonances which show up in the strong-modulation analysis is not simply related a priori to the nature (extended, localized, or critical) of the eigenstates on the chain. For self-similar chains generated by substitutions, the eigenstates are believed to be generically chaotic and critical, for any $t/V \neq 0$. There can, however, exist extended states at special values of the energy E. This question has been the purpose of several recent works (see Ref. 46, and the references therein). The underlying mechanism seems to have been first described on the example of the random dimer model.[47] Consider a chain made of two types of words, X and Y, e.g., $X=AA$ and $Y=AB$. Let $\mathbf{T}_X$ and $\mathbf{T}_Y$ be the corresponding transfer matrices. If $\mathbf{T}_X = \pm 1$ and $|\mathrm{tr}\mathbf{T}_Y| \leq 2$, or vice-versa, then one type of segments is transparent to the propagation, whereas E is in a band of the periodic structure made of the other type of segments. The eigenstates are truly extended in this situation, which can only occur for a discrete set of special values of the energy, dependent on t and V. If this phenomenon persists up to arbitrarily high values of the modulation strength V, then it has to show up in our approach, at some order in perturbation theory. This has been demonstrated in detail for the special energy $E=V$ of the period-doubling chain. To close up, we mention a recent work[48] on the scaling behavior of the localization length of the random dimer problem, with results similar to those of our Appendix.

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APPENDIX

In this appendix we investigate a special class of tridiagonal Hamiltonians defined on binary chains made of X and Y atoms, namely

$$(\mathcal{H}\Psi)_k = T_{k-1,k}\Psi_{k-1} + T_{k,k+1}\Psi_{k+1} + U_k\Psi_k = \mathcal{E}\Psi_k \ . \tag{A1}$$

The five parameters are assumed to be all positive, and to obey the identities

$$U_X - 2T_{X,X} = U_Y - 2T_{Y,Y} = 0 \ , \quad \frac{T_{X,Y}}{T_{X,X}} = \frac{T_{Y,Y}}{T_{Y,X}} = Z \ . \tag{A2}$$

These properties hold for the second-order Hamiltonian $\mathcal{H}^{(2)}$ of Eq. (5.9).

Let us set $\Psi_k = (-1)^k \Phi_k$ [respectively, $\Psi_k = (-1)^k Z \Phi_k$] if the kth letter is a Y (respectively, an X). In terms of the transformed wave function Φ_k, the eigenvalue equation (A1) assumes the form

$$2\Phi_k - \Phi_{k-1} - \Phi_{k+1} = \mathcal{E} M_k \Phi_k \ , \tag{A3}$$

where we recognize the dynamical equation for harmonic vibrations (phonons) on an aperiodic chain. $\mathcal{E}$ stands for the reduced squared frequency, and the M_k for the atomic masses. The latter are distributed according to $M_k = 1/T_{X,X}$ (respectively, $M_k = 1/T_{Y,Y}$) if the kth letter is an X (respectively, a Y).

On a uniform chain, where all the masses M_k are equal to a constant M, the phonons are extended Bloch waves. Their wave vector q is related to the frequency by the dispersion relation

$$\mathcal{E} M = 2(1-\cos q) \ , \tag{A4}$$

so that the DOS reads

$$\rho(\mathcal{E}) = \frac{1}{\pi}\frac{dq}{d\mathcal{E}} = \frac{1}{\pi}\left[\frac{M}{\mathcal{E}(4-\mathcal{E}M)}\right]^{1/2} . \tag{A5}$$

The case of random chains has been studied at length.[49] Of special interest is the low-frequency limit ($\mathcal{E} \to 0$). In this regime, irrespective of the nature of the sequence, the excitations approximately follow the dispersion relation (A4) of a uniform chain with the mean atomic mass $\langle M \rangle$, namely

$$q \approx (\mathcal{E}\langle M \rangle)^{1/2} \quad (\mathcal{E} \to 0) \ . \tag{A6}$$

As a consequence, the DOS exhibits the universal power-law van Hove singularity

$$\rho(\mathcal{E}) \approx \frac{1}{2\pi}(\langle M \rangle / \mathcal{E})^{1/2} \quad (\mathcal{E} \to 0) \ . \tag{A7}$$

Moreover, the vibrational eigenmodes become asymptotically extended near the band edge, again irrespective of the nature of the sequence. It is indeed clear that Eq. (A3) admits the two extended solutions $\Phi_k = 1$ and $\Phi_k = k$ at $\mathcal{E} = 0$ exactly. In the case of a random sequence of masses, the law of divergence of the localization length ξ reads[49]

$$\xi \approx \frac{8}{\mathcal{E}} \frac{\langle M \rangle}{\langle M^2 \rangle - \langle M \rangle^2} \quad (\mathcal{E} \to 0) \ . \tag{A8}$$

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