

Variable-range hopping conductivity in quasicrystals

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Abstract

The electronic density of states (DOS) of 1D quasicrystals looks like that of a highly doped, p-type semiconductor: the Fermi level lies in the “impurity band”, which consists of localized states. At low temperatures, the conductivity of an electronic structure of this type is by variable-range hopping, as observed recently in i-Al–Pd–Re. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, Delahaye et al. [1] have observed a variable-range hopping conductivity

$$\sigma = C \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right] \quad (1)$$

in i-Al–Pd–Re at low temperatures T . This behaviour of the conductivity indicates [2] that the electronic density of states (DOS) of the quasicrystal is finite at, and close to, the Fermi energy and that it consists of a distribution, dense in energy, of localized electronic states. In i-Al–Pd–Re, the finite DOS is small (pseudogap), the localization length very large and the conducting states not too far from the Fermi level (within 1 K, as Mott’s law was observed in the temperature range 20–600 mK).

There have been many calculations of the DOS of a Fibonacci chain, or of its approximants [3–8,15], most of which fail to produce convincingly the pseudogap found experimentally [9,16]. The most direct method is to renormalize the energy of an electron injected into the system (dynamic renormalization [10]), by inflation of the sequence of transfer matrices [3,6]. The transfer matrix is a useful expression of the Schrödinger equation in the tight-binding approximation.

The pseudogap occurs above the main band of states [9,16], which is full [3,7]. In fact, the DOS looks like that of a heavily p-doped semiconductor [3]. The “valence” band is the ordinary band of conducting states, whereas

the “impurity” band is constituted by resonant states, fixed points of the (Kohmoto) trace map. These states, absent in simple periodic crystals, are localized, well separated in energy from the conducting states. Quasicrystals are conducting because they have a finite DOS at the Fermi level. Conduction is through variable-range hopping, because these states are localized.

We first recall the arguments of Rivier and Boosé [3], notably the necessity of considering a group of electron states per tile instead of a single tight-binding level, which yield, upon inflation, a dirty p-type semiconductor DOS, with the “impurity band” constituting the pseudogap observed in spectroscopy [9,16] and in electrical and optical properties at high temperatures [11]. We show how this argumentation is extended directly to 2D or 3D, with similar features of the DOS, and why the fixed point states, at and near the Fermi level, are localized. Quasicrystals have therefore the electronic profile for variable-range hopping. The conductivity (1) and the relation between measured and theoretical parameters (T_0 vs. localization length and DOS at the Fermi level), can be read from the relevant two pages of [2]. The argumentation is rigorous. It relies on inflation of a sequence of *mesoscopic* elements, the tiles, each represented by a partially filled group of electronic states. This is how Thouless [12] showed, over 20 years ago, that a wire made of metallic elements has a non-ohmic resistance beyond a certain length.

2. Pseudogap in 1D [3]

Take a tight-binding Hamiltonian \mathbf{H} on a 1D structure. For simplicity, consider a Fibonacci sequence and discriminate

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between two “sites” S and L. Each “site” represents a group of energy levels centered at energy ϵ_S or ϵ_L . The matrix element t of \mathbf{H} between nearest neighbour sites is the same everywhere.

There is a technique called dynamical or energy renormalization, whereby the energy of an electron in a (1D) crystal is renormalized by decimation of the lattice (elimination of every other atom) [10]. In a crystal, this renormalization takes the form of a one-variable, non-linear map of the energy. If the electron energy lies initially within the band, it remains inside the band, where the dynamical map is elliptic. If it lies outside the band (where the map is hyperbolic), it is sent to infinity by renormalization [3,6], and the electronic DOS is zero. In a quasicrystal, deflation symmetry $LS \rightarrow L, L \rightarrow S$, is a natural decimation. Renormalization of the electron energy is a dynamic map (2) involving three variables [4].

2.1. Periodic chain

The 1D electronic DOS of a periodic chain, $\epsilon_S = \epsilon_L = 0$, is obtained simply by decimating the chain repeatedly. At each step, remove every other site and rescale the Schrödinger equation $t(c_{i+1} + c_{i-1}) = \epsilon c_i$, or $\mathbf{X}_{i+1} = \mathbf{M} \cdot \mathbf{X}_i$. Here, \mathbf{X}_{i+1} is the transposed matrix (c_{i+1}, c_i) , with c_i , the probability amplitude that the electron is at site i . The transfer matrix \mathbf{M} is a 2×2 real, unimodular matrix with determinant 1 and trace $s = \text{tr} \mathbf{M} = \epsilon/t$ (here in the representation $M_{11} = s, M_{21} = 1 = -M_{12}, M_{22} = 0$).

The recursion relation, the logistic map $s' = s^2 - 2$ [10], is a non-linear trace map, obtained by taking the trace of the Cayley-Hamilton formula for all four matrix elements of $\mathbf{M}, \mathbf{M}^2 - s\mathbf{M} + \mathbf{I} = 0$ (\mathbf{I} is the 2×2 unit matrix, and $s' = \text{tr} \mathbf{M}^2$). Thus, s , i.e. ϵ parametrizes the eigenvalues of \mathbf{M} ; eigenvectors of \mathbf{M} and \mathbf{H} are in one-to-one relation. States with $|s| < 2$ form a band (elliptic region) and remain, shuffled within the band upon renormalization. States with energies outside the band $|s| > 2$ are mapped to infinity and their density tends to zero (hyperbolic region). We obtain $g(s) = 1/[\pi(4 - s^2)^{1/2}]$, $|s| < 2$, the familiar tight-binding DOS, which is an invariant of the logistic map.

2.2. Quasicrystalline chain

For a quasicrystalline chain, deflation operation is a natural means of decimation. The tight-binding transfer matrices have still determinant 1, but site-dependent trace $\text{tr} \mathbf{M}_S = s_S = (\epsilon - \epsilon_S)/t$ and $\text{tr} \mathbf{M}_L = s_L = (\epsilon - \epsilon_L)/t$. Moreover, s_S and s_L are no longer single energy levels but groups of levels [12], spanning a range of energies $0 \leq |s_S - s_L| \leq w$: in a quasicrystal, each tile (the unit on which inflation acts) contains several atoms, and many electronic states.

Inflation operation is concatenation $w_{i+1} = w_i \cdot w_{i-1}$ of sequences (words) w_i , through substitution $S \rightarrow L \rightarrow LS$. On the transfer matrix, the inflation operation is $\mathbf{M}_{i+1} = \mathbf{M}_{i-1} \cdot \mathbf{M}_i$, with \mathbf{M} real unimodular. The inflation relation is in-

verted $\mathbf{M}_{i-2} = \mathbf{M}_i \cdot \mathbf{M}_{i-1}^{-1}$, and yields, by taking the trace of $\mathbf{M}_{i+1} + \mathbf{M}_{i-2}$, the three variables (s_{i-2}, s_{i-1}, s_i) Kohmoto map:

$$s_{i+1} = s_i s_{i-1} - s_{i-2} \tag{2}$$

with initial conditions $s_{-1} = s_S, s_0 = s_L, s_1 = \text{tr} \mathbf{M}_S \cdot \mathbf{M}_L = s_S s_L - 2, s_i = \text{tr} \mathbf{M}_i$.

The states (s_{i-2}, s_{i-1}, s_i) remain on the surface $s_{i-2}^2 + s_{i-1}^2 + s_i^2 - (s_{i-2} s_{i-1} s_i) = \kappa$, an invariant of the map. There is one surface with parameter $\kappa = (s_S - s_L)^2 + 4$ for each pair of levels (s_S, s_L) . To groups of levels corresponds a stack of invariant surfaces, with $4 \leq \kappa = (s_S - s_L)^2 + 4 \leq w^2 + 4$. The stack of surfaces foliates the space of all possible states. State (x, y, z) has energy $\epsilon/t = f(x^2 + y^2 + z^2)$, where f is a monotonically increasing function of its argument. The full stack of invariant surfaces contributes to the DOS, whereas a Fibonacci chain with one level per site has all its electronic states on a single surface.

In addition, map (2) has fixed points, some isolated (e.g. $(2, 2, 2)$ is a fixed point of order 1 for $\kappa = 4$), others belonging to 1D families, such as

$$(-1, x, -1), \text{ order } 4 \tag{3}$$

$$(1, x, 1), \text{ order } 12 \text{ (stack } \kappa = x^2 - x + 2),$$

$$(-1, -x, -1), \text{ order } 4$$

$$(1, x, -1), \text{ order } 12 \text{ (stack } \kappa = x^2 + x + 2),$$

$$\left(\pm x, \frac{\pm x}{(x-1)}, \pm x \right), \text{ order } 2 \text{ (++) or } 6 \text{ (+--)}$$

$$\left(\text{stack } \kappa = x^2 \left[1 - \frac{1}{(x-1)} + \frac{1}{(x-1)^2} \right] \right),$$

$$(x, 0, 0), \text{ order } 6 \text{ (stack } \kappa = x^2),$$

for all x . If there are any other fixed points, they have dimension ≤ 1 .

Each invariant surface has elliptic and hyperbolic regions, with positive and negative Gaussian curvatures, respectively. As with the logistic map, a point (x, y, z) remains in the elliptic region of the surface when iterated by map (2). The energy density of these states is finite. Conversely, if the point is in the hyperbolic region, it will be mapped to infinity, and the density of such states is zero, except if (x, y, z) is a fixed point. States in the hyperbolic region are usually at higher energies than those in the elliptic region.¹

Consider all states of energy less than ϵ/t . Since the states in the hyperbolic region have zero density, a state contributes to the DOS, if

¹ The manifold separating the regions of positive and negative curvature of the stack of invariant surfaces resembles a deformed cube. It is given, in polar coordinates $3(\epsilon/t)^2 = r^2$, by the equation (misprinted in [3]), $0 = 16 - 4r^2 [1 - \sin^2 \theta (\cos^2 \theta + \sin^2 \phi \cos^2 \phi \sin^2 \theta)] + 3r^4 \sin^2 \phi \cos^2 \phi \sin^4 \theta \cos^2 \theta$.

1. it is in the elliptic region of its invariant surface, or
2. it is a fixed point (3) within the hyperbolic region.

Families of fixed points (3) give a small contribution to the DOS, above the main band 1. Thus, the integrated DOS is $\int_{<} g_c(\varepsilon') d\varepsilon'$ + contribution of fixed point families (3), where the symbol $<$ restricts the integral to energies less than ε/t and within the elliptic region of the stack of invariant surfaces.

The electronic DOS looks like that of a heavily p-doped semiconductor: for each value of κ , each pair of levels (s_S, s_L), there is a 1D tight-binding “valence” band 1, plus the isolated energies of the fixed points (3). For groups of energy levels, a stack of κ 's, the individual valence bands are superposed and the families of fixed points (3) constitute an “impurity” band, a dense (in ε , or in $0 \leq \kappa - 4 \leq w^2$) set of states. The DOS rises through an inflexion point to a maximum, then falls to the much smaller contribution of the fixed point families (3). This sharp fall is the experimentally observed wall (or pseudogap) [9,16]. The Fermi level is in the “impurity” band, just above the top of the “valence” band [3,7].

3. In 2D and 3D

In 2D and 3D, even though the quasicrystalline structure is a *direct product* of inflatable sequences [13], the combinatorics at each vertex or each tile, and thus the precise tight-binding Hamiltonian, are complex. However, inflation is a symmetry operating at a mesoscopic scale, on tiles containing many atoms, averaging over the microscopic fluctuations due to the atomic structure of the material. This is why, in 1D, inflation operates (2) on groups of energy levels instead of single atomic orbitals. For the same reason, it operates on the groups of energy levels, *independently* and *uniformly* in the two (in 2D) or the three directions (in 3D). The electronic DOS is obtained by simple (in 2D) and double (in 3D) convolution of the 1D DOS. The valence band 1 has well-defined energy bounds, even though the wall is not as steep as in 1D. Above the upper bound, all the states contributing to the DOS are fixed points 2. Conversely, the features of the DOS, invariant under inflation operations, are preserved under cut, at the surface of the material.

4. Fixed point states are localized

The electronic DOS at the Fermi level is finite. These states (3) are fixed points, closed orbits of the Kohmoto map (2). They are all localized. Fixed points are eigenstates of the transfer matrix, thus of the Schrödinger equation, with a fixed energy, $\Delta\varepsilon=0$, under a finite number of steps of inflation. The electron remains therefore forever ($\Delta t=h/\Delta\varepsilon$) in the tiles touched by the inflated transfer matrix.

Suppose, ad absurdum, that an electron could escape in a finite time Δt from the fixed point state, with Hamiltonian matrix element V , as it happens for the Friedel–Anderson

virtual bound state of a transition metal impurity in a metal. By the uncertainty principle, the state broadens into a resonance, of finite width $\Delta\varepsilon=\pi g_c V^2$, where g_c is the density of the conducting states into which the electron escapes. But these conducting states are in the hyperbolic region of the map, and their energy is sent to infinity by inflation. Their density g_c is zero. The finite, total DOS g_0 at and around the Fermi level is constituted exclusively of localized states. Thus, the fixed point states are localized, albeit with a large localization length [1].

5. Conductivity

With a finite density of localized electronic states at the Fermi level, electric conductivity at low temperatures is by variable-range hopping (1). The electron hops through (localized) states, at an average distance which is a compromise between two factors: a Boltzmann factor penalizes nearby states because they are less likely to be at the same energy, and a factor proportional to the square of the overlap of the wave functions penalizes long hops [2]. Delahaye et al. [1] measure $T_0=24/(\pi k) [1/(g_0 \xi^3)] \approx 1$ mK. This low temperature implies a large localization length $\xi \approx 300$ nm, as well as a substantial density g_0 of localized, fixed point states (3) at the Fermi level in quasicrystals. The remarkable observation of a variable-range hopping conductivity in i-Al–Pd–Re at low temperatures [1] thus establishes the electronic structure of quasicrystals: finite density of localized states at the Fermi level.

6. Conclusions

Renormalization, or inflation operation, was first used to show that a thin wire (a sequence of similar, but not identical metallic tiles shouldered end-to-end) has, if it is long enough, non-ohmic resistance: it grows exponentially with its length [12]. The electronic structure of each element is a group of energy levels. If an electron diffuses from one (renormalized) tile to the next by using several energy levels of the group, the electrical conductivity remains ohmic. But if the electron hops from one energy level in one tile, to one level in the next, the resistance of the wire increases exponentially with the number of its tiles. The wire is metallic up to a resistance of about $10 \text{ k}\Omega \approx h/(\pi e^2)$ [12].

Inflation symmetry has generic physical consequences: the electronic DOS is that of a heavily doped p-type semiconductor with, at the Fermi level, a small but finite density (pseudogap) of localized states. Inflation symmetry is preserved at the surface of the material. The material (non-stick, non-wet, but also low oxidation, low corrosion, hardness) and physical properties claimed by patents [14] and experiments [1,11] are comprehensive: they apply to all metals with inflation symmetry (quasicrystals, but also their rational approximants), in the bulk and on the surface.

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