Electronic states of quasicrystals from the multiple scattering theory

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Abstract. We propose a reciprocal-space version of the KKR band theory and use it to study the electronic structure of a quasiperiodic system. Explicit, numerical results are presented for a Fibonacci chain of square well potentials.

1. Introduction

Although mathematical techniques for describing the structure of quasicrystals [1] are now well developed [2], methods for calculating their electronic spectra are still in a primitive state [3, 4, 5]. Evidently, the problem is that while the lack of conventional periodicity precludes the use of the all powerful Bloch theorem, finite cluster real space techniques are also of limited value due to the fact that quasiperiodicity is the property of infinitely long sequences. In this paper we present a method which deals with the electronic structure of quasiperiodic systems in reciprocal space but without relying on the Bloch theorem.

In structure determinations, based on diffraction experiments, the observable is the structure constant $S(k)$. For periodic systems $S(k)$ is characterized by the Bragg peaks. For quasicrystals $S(k)$ consists of a dense set of delta functions with variable weights. The most useful descriptions of such quasiperiodic systems are prescriptions for calculating $S(k)$. Our aim is to develop a method for solving Schrödinger's equation for a quasiperiodic array of potential wells using the structure constant of sites, $S(k)$ directly.

Of course, in lowest order perturbation theory the first corrections to the plane wave spectrum involve $S(k)$ directly [6]. However, the analysis cannot be continued to higher order and the interesting systems like $Al_{80}Mn_{20}$ or $Ti_{0.9}V_{0.1}$ all contain strong scatterers. The way forward is to note that the multiple scattering approach to the electronic structure, as used by Korringa [7] in his derivation of the KKR method of band theory, separates the problem of individual scattering centres and that of their geometrical arrangement [7, 8, 9]. In what follows we shall make use of this unique feature of that approach.

We shall consider non-overlapping spherically symmetric potential wells. The scattering of an electron at each site i is exactly described by the partial wave scattering amplitude

$$f_{i,L}(\varepsilon) = (1/2i)(\exp(i2\delta_l^i(\varepsilon) - 1)) \tag{1}$$

where $\delta_l^i(\varepsilon)$ is the usual scattering phase shift for the angular momentum channel l. The

geometrical arrangement of the scattering centres will enter the theory through the structure factor $g_{L,L'}(R_i - R_j; \varepsilon)$ which describes the propagation of free, spherical waves whose angular momentum about the site R_j is L', where L' denotes both the azimuthal and polar quantum numbers: m' and l' respectively, and about the j'th site is L. We shall cast the multiple scattering equations into such a form that the arrangements of sites enter into the determination of the eigenvalues and eigenfunctions only through the strucure constant $S(k)$.

The most efficient descriptions of the structure constant $S(k)$ for quasiperiodic systems appear to be those which make use of Bragg peaks which project down from a higher dimensional space into the subspace of natural dimension with incommensurate orientation [2, 10]. This suggests that we could also consider the Schrödinger equation in the same, higher dimensional space, where the potential function is periodic, and study ways of projecting the solutions back into the natural space [11]. The main achievement of the present paper is a method which bypasses the need to study the Schrödinger equation in higher dimensions. Accordingly, once the projection to find the structure constant $S(k)$ has been accomplished for a given problem, in our approach, the solution of the Schrödinger equation proceeds in the natural reciprocal space using $S(k)$.

In the next section we derive the fundamental equations of the new approach. In section 3 we illustrate how the method works for a simple one-dimensional model.

2. Multiple scattering theory for a quasiperiodic arrangement of scatterers in reciprocal space

We wish to find the energy eigenstates of a Schrödinger equation corresponding to an arbitrary arrangement of non-overlapping spherically symmetric scattering centres [8, 9]. The multiple scattering approach to this problem is to look for a set of self-consistent incident and scattered waves such that the incident wave to every site is the sum of the scattered waves from all the other sites. For each site labelled by i we take the Lth incident partial wave to be the form of $a_L^i(\varepsilon) j_l(\sqrt{\varepsilon}|r_i|) Y_L(\hat{r}_i)$ where $r_i = r - R_i$, $\hat{r}_i$ is the unit vector in the direction of r_i and Y_L is the usual, complex spherical harmonic. The self-consistency condition mentioned above implies [8, 9] that the amplitudes $a_L^i(\varepsilon)$ satisfy the following set of linear equations:

$$\sum_{j,L} (t_L^{-1}(\varepsilon)\delta_{L,L'}\delta_{i,j} - g_{L,L'}(R_{ij}; \varepsilon))a_L^j(\varepsilon) = 0 \tag{2}$$

where the single-site t-matrix on the energy shell $t_L(\varepsilon)$ is simply related to the scattering amplitude $f_L(\varepsilon)$ by $t_L(\varepsilon) = (1/\sqrt{\varepsilon})f_L(\varepsilon)$, and the real space KKR structure factor matrix, $g_{L,L'}(R_{ij}; \varepsilon)$ is given by

$$g_{L,L'}(R_{ij}; \varepsilon) = 4\pi i \sum_L i^{l-l'-l''} C_{L'L}^{L''} h_{l''}^+(\sqrt{\varepsilon}|R_{ij}|) Y_L(\hat{R}_{ij}). \tag{3}$$

In the last of these relations $h_{l''}^+$ is a spherical Hankel function, and the Gaunt numbers are defined by

$$C_{L'L}^{L''} = \int d\Omega \ Y_L(\Omega) Y_{L'}(\Omega') Y_{L''}(\Omega). \tag{4}$$

Clearly, the energy eigenvalues are determined from the condition that the determinant of the coefficients in equation (2) should vanish:

$$\|t_L^{-1}(\varepsilon)\delta_{L,L'}\delta_{i,j} - g_{L,L'}(\mathbf{R}_{ij};\varepsilon)\| = 0. \tag{5}$$

For a periodic crystal we could use Bloch's theorem and search for the solution of equation (2) in the form

$$a_L^i = a_L(\mathbf{k})\exp(\mathrm{i}\mathbf{k}\mathbf{R}_i). \tag{6}$$

This leads to the familiar KKR result that

$$\|t_L^{-1}(\varepsilon)\delta_{L,L'} - g_{L,L'}(\mathbf{k};\varepsilon)\| = 0 \tag{7}$$

where $g_{L,L'}(\mathbf{k};\varepsilon)$ is the lattice Fourier transform of $g_{L,L'}(\mathbf{R}_{ij};\varepsilon)$. Namely

$$g_{L,L'}(\mathbf{k};\varepsilon) = \sum_i \exp(\mathrm{i}\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j))g_{L,L'}(\mathbf{R}_{ij};\varepsilon). \tag{8}$$

For a quasiperiodic system we may attempt to find the solution of equation (2) by using a full Fourier transform instead of the Bloch condition as in equation (6). Using the usual box quantization to generate a discrete set of wave vectors we write

$$a_L^i = \sum_k a_L(\mathbf{k})\exp(-\mathrm{i}\mathbf{k}\mathbf{R}_i). \tag{9}$$

Substituting equation (9) into equation (2), multiplying by $\exp(\mathrm{i}\mathbf{k}\mathbf{R}_i)$ and summing over i, we find

$$\sum_{k'}\left(\underline{t}^{-1}(\varepsilon)S(k-k') - \sum_{k''}S(k-k'')\underline{g}(k'';\varepsilon)S(k''-k')\right)\underline{a}(k) = 0 \tag{10}$$

where for simplicity we have introduced the matrix notation in the L indices. The $S(\mathbf{k})$ structure constant is given by

$$S(\mathbf{k}) = \sum_i \exp(\mathrm{i}\mathbf{k}\mathbf{R}_i) \tag{11}$$

and $g_{L,L'}(\mathbf{k};\varepsilon)$ is the Fourier-transform

$$g_{L,L'}(\mathbf{k};\varepsilon) = \int \mathrm{d}^3r\, g_{L,L'}(\mathbf{r};\varepsilon)\exp(\mathrm{i}\mathbf{r}\mathbf{k}). \tag{12}$$

Furthermore

$$g_{L,L'}(\mathbf{R}_{ij};\varepsilon) = \sum_k \exp(-\mathrm{i}\mathbf{k}\mathbf{R}_{ij})g_{L,L'}(\mathbf{k};\varepsilon). \tag{13}$$

For a quasiperiodic lattice, $S(\mathbf{k})$ can be obtained by projection from a periodic lattice of higher dimensions [2, 10]. As a consequence, $S(\mathbf{k})$ has the form

$$S(\mathbf{k}) = \sum_G C(\mathbf{G}^\perp(\mathbf{G}^\parallel))\delta(\mathbf{k}-\mathbf{G}^\parallel) \tag{14}$$

where the $\mathbf{G}$s are the reciprocal lattice vectors of the higher dimensional periodic lattice, $\mathbf{G}^\parallel$ is the projection of $\mathbf{G}$ onto the subspace of the quasicrystal while $\mathbf{G}^\perp$ is the projection of $\mathbf{G}$ onto the complementary subspace.

Substituting the expression above into equation (10) we find that

$$\underline{t}^{-1}(\varepsilon)\underline{b}(k - G_1^{\parallel}) - \sum_{G_2^{\parallel}} C(G_1^{\perp} - G_2^{\perp})\underline{g}(k - G_2^{\parallel}; \varepsilon)\underline{b}(k - G_2^{\parallel}) = 0 \qquad (15)$$

where

$$\underline{b}(k) = \sum_{G^{\parallel}} C(k - G^{\perp})\underline{a}(k - G^{\parallel}). \qquad (16)$$

This is then our principal formal result. The particular values of k and ε for which equation (15) has solutions give the dispersion relation ε_k and the corresponding coefficient functions $b_L(k)$ describe the related eigenfunctions. As advertised, being based on equations (14), (15) and (16) our procedure involves the arrangement of sites only through the structure constant $S(k)$. It can be regarded as the reciprocal space KKR equation for quasiperiodic systems.

It is interesting to note that equation (15) shows some resemblance to that derived by Lu and Birman [11] but, as it is clear, we did not have to introduce a higher dimensional pseudo-Schrödinger equation.

Note that the set of $G^{\parallel}$ vectors is infinitely dense. Thus equation (15) is an integral equation rather than a set of linear equations as it would be for a periodic structure.

In this paper we do not propose a general method for solving equation (15). Instead, we investigate a simple and straightforward approximation scheme with relevance to quasiperiodic potentials. The procedure is based on the observation that equation (15) becomes readily tractable if $S(k)$ is periodic in k. Fortunately, within the projection technique for generating $S(k)$ there is a natural sequence of approximations which render $S(k)$ periodic. This geometrical construction of successively better approximations to $S(k)$ is often referred to as the Euclidean algorithm. It consists of taking higher and higher rational approximations for the irrational, or incommensurate orientation [2] of the subspace into which the periodic structure is projected. In the next section we illustrate how this method works by explicit calculations for a Fibonacci chain of square well potentials.

3. Solution in one dimension

One-dimensional models for electrons in quasiperiodic potentials have been studied well before the advent of quasicrystals. This subject is interesting in itself and the problem is fairly well understood. In what follows we consider a one-dimensional model without suggesting that our way is a particularly useful approach to this problem. Our concern is to illustrate how the essentially three-dimensional method of the previous section works in practice. For this reason we deal with chains of square-well potentials in ways which are as closely analogous to three-dimensional procedures as possible.

It has been shown by Butler [12] that with the identifications shown in table 1 one can obtain the one-dimensional KKR equations in the same way and the same form as in three dimensions. In this table, $l = 0, 1$ correspond to the symmetric and antisymmetric solutions of the Schrödinger equation. So equation (15) can be written as

$$\underline{t}^{-1}(\varepsilon)\underline{b}(k - G_1^{\parallel}) - \sum_{G_2^{\parallel}} C(G_1^{\perp} - G_2^{\perp})\underline{g}(k - G_2^{\parallel}; \varepsilon)\underline{b}(k - G_2^{\parallel}) = 0 \qquad (17)$$

where $\underline{t}$ and $\underline{g}$ now represent 2×2 matrices. Using a one-dimensional version of the

Table 1.

3D	1D
$Y_0(\hat{x})$	$1/\sqrt{2}$
$Y_1(\hat{x})$	$\mathrm{sgn}(x)/\sqrt{2}$
$j_l(z)$	$\cos(z - \frac{1}{2}l\pi)$
$n_l(z)$	$\sin(z - \frac{1}{2}l\pi)$
$h_l^+(z)$	$\exp(z - \frac{1}{2}l\pi)$

Euclidean algorithm to approximate $S(k)$, one obtains a series of structure constants, each containing discrete, equally spaced delta function peaks as shown in figure 1. For any of these structure constants the sum over all G can be divided into a finite and infinite sum:

$$\sum_{G_2^{\parallel}} C(G_1^{\perp} - G_2^{\perp})g(k - G_2^{\parallel}; \varepsilon)\underline{b}(k - G_2^{\parallel})$$

$$= \sum_{m=1}^{N} \sum_{n} C[G_1^{\perp} - G_m^{\perp}(G_m^{\parallel} + n\Delta)]\underline{g}[k - (G_m^{\parallel} + n\Delta); \varepsilon]$$

$$\times \underline{b}[k - (G_m^{\parallel} + n\Delta)] \tag{18}$$

where Δ is the period of $S(k)$ (see figure 2):

$$C[G^{\perp}(G^{\parallel} + n\Delta)] = C[G^{\perp}(G^{\parallel})). \tag{19}$$

As a first step towards solving equation (18) for C given by equation (19), we may suppose that $\underline{b}(q)$ is also periodic; e.g.

$$\underline{b}(q + n\Delta) = \underline{b}(q). \tag{20}$$

With the help of this assumption, equation (18) can be rewritten to read

$$\underline{t}^{-1}(\varepsilon)\underline{b}(k - G_n^{\parallel}) - \sum_{m=1}^{N} \bar{C}(G_n^{\parallel} - G_m^{\parallel})\tilde{g}(k - G_m^{\parallel}; \varepsilon)\underline{b}(k - G_m^{\parallel}) = 0 \tag{21}$$

where

$$\tilde{g}(k - G_m^{\parallel}; \varepsilon) = \sum_{n} \underline{g}(k - (G_m^{\parallel} + n\Delta); \varepsilon) \tag{22}$$

$$\bar{C}(G^{\parallel}) = \sum_{G^{\perp}}^{(G^{\parallel})} C(G^{\perp}). \tag{23}$$

In the latter formula the superscript $(G^{\parallel})$ indicates that the summation should be taken over all G vectors with the same (fixed) $G^{\parallel}$ but different $G^{\perp}$ components. The discrete set of the $G^{\parallel}$ vectors may be denoted by $\{K_n\}$ (figure 1). Evidently equation (21) has a solution if

$$\|\underline{t}^{-1}(\varepsilon)\delta_{n,m} - \bar{C}(K_n - K_m)\tilde{g}(k - K_m; \varepsilon)\| = 0 \qquad n, m = 1, 2, \ldots, N. \tag{24}$$

It is easy to show that the structure constant $S(k) = \sum_K \bar{C}(K)\delta(k - K)$ belongs to the real
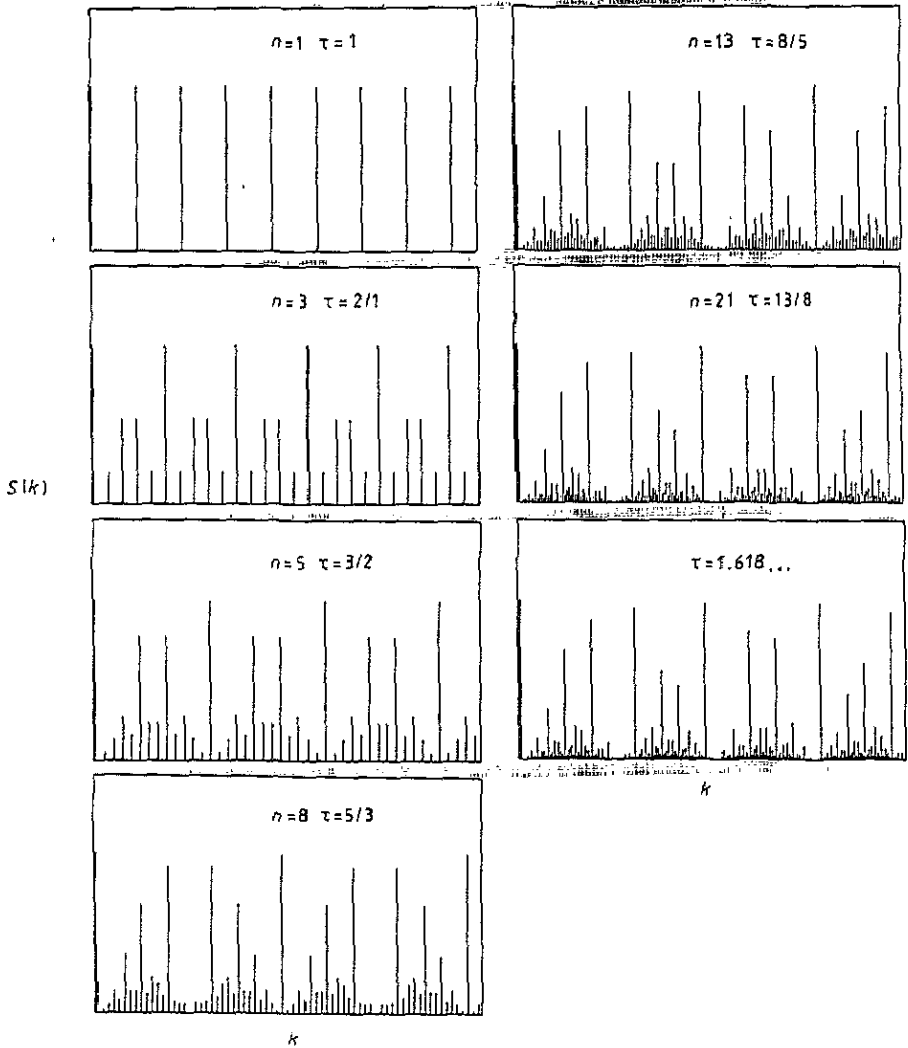
Figure 1. The structure constants of the various approximants. $n = 8$, $\tau = 5/3$ corresponds to the exact Fibonacci chain.

space rational approximants. Thus, it is satisfying to note that the solution of equation (24) is the same as the solution to the familiar $1, 3, 5, 8, 13, \ldots$ atoms per unit cell KKR equation. In what follows we shall investigate the eigenvalue spectra of our model by finding pairs of ε and k for which equation (24) is satisfied, and then by determining the corresponding $\underline{b}(k)$s.

4. The method of 'folding out'

Solving equation (24) one obtains the band structure in the central, small Brillouin zone: $-\delta/2 \leqslant k \leqslant \delta/2$. Unfortunately, for higher and higher order rational approximates this
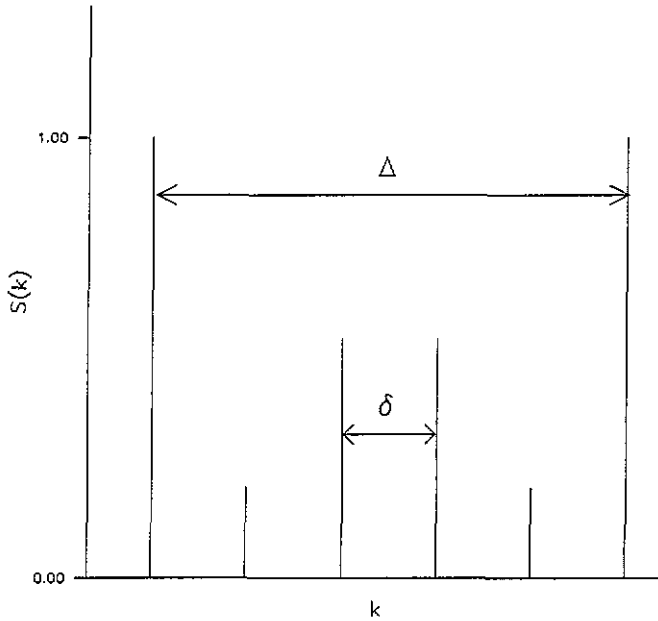
Figure 2. The figure explains the definition of δ and Δ.

Brillouin zone is, progressively, smaller and smaller and the conventional description of the electronic structure becomes less and less useful. In fact, in the quasicrystalline limit, the states will be labelled by the band index ν only as k ceases to be a good quantum number. Evidently, this is due to the loss of translational invariance which leaves us with a densely ordered set of energy levels without any quantum number to label them. Under such circumstances the usual procedure is to study the statistics of the levels [13]. For instance, having reached the above conclusions in connection with the problem at hand, Holzer [13] followed this route. Here we shall propose an alternative.

Our method is based on the fact that while the eigenvalues $\varepsilon_{k,\nu}$ of equation (24) are periodic with the period δ, the components $b_n^{\nu}(k)$ of eigenvectors are different in each small Brillouin zone $K_n - \delta/2 \leqslant k \leqslant K_n + \delta/2$ and repeat only with the repeat 'distance' Δ. This allows us to assign, uniquely, each state labelled by k, ν to a particular small Brillouin zone $K_n - \delta/2 \leqslant k \leqslant K_n + \delta/2$ within the large Brillouin zone $-\Delta/2 \leqslant k \leqslant \Delta/2$ according to the size of $|b_n^{\nu}(k)|$. In short, we associate the state k, ν with the small Brillouin zone $K_n - \delta/2 \leqslant k \leqslant K_n + \delta/2$ where the square of the amplitude $|b_n^{\nu}(k - K_n)|^2$ is the largest. Evidently, this procedure lends meaning to k outside the small Brillouin zone $-\delta/2 \leqslant k \leqslant \delta/2$ all through the large Brillouin zone $-\Delta/2 \leqslant k \leqslant \Delta/2$. Note, that $\Delta \rightarrow \infty$ instead of 0 as the quasicrystalline limit is approached and hence k remains a useful variable, although not a good quantum number, even in that limit.

To see how the 'folding out' procedure works, consider equation (24) for $\bar{C}_{nm} = \bar{C}(K_n - K_m)$ replaced by a diagonal matrix $\bar{C}\delta_{mn}$; $b_n^{\nu}(k)$ only in the small Brillouin zone $K_n - \delta/2 \leqslant k \leqslant K_n + \delta/2$, namely where

$$\|\underline{t}^{-1}(\varepsilon) - \bar{C}\underline{g}(k - K_n; \varepsilon)\|_{.\varepsilon_{k,\nu}^0} = 0 \tag{25}$$

and $b_{n'}^{\nu}(k) = 0$ for all $n' \neq n$. Thus within a wide range band of energies we can drop the
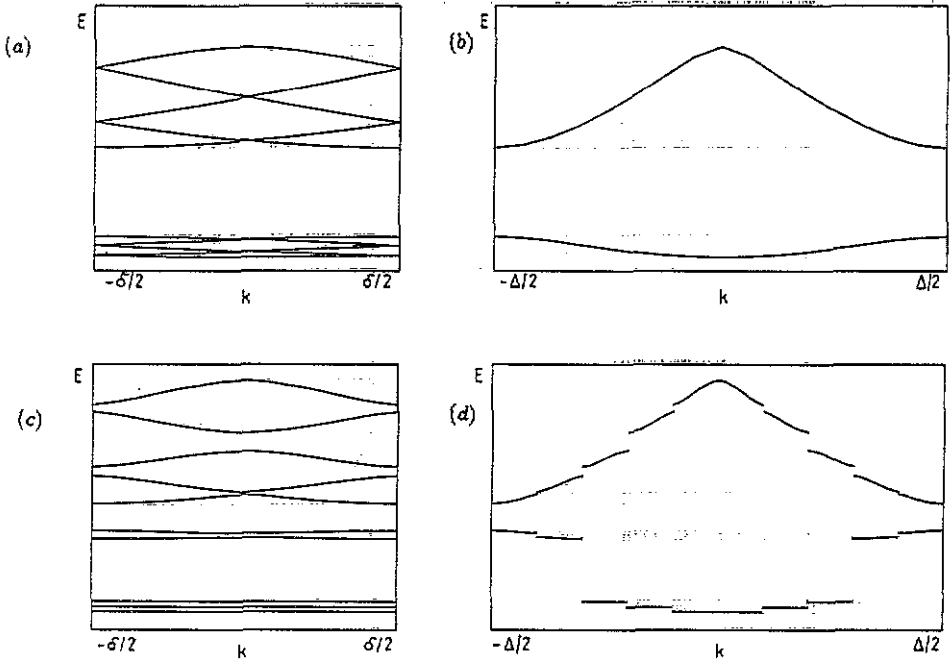
Figure 3. (*a*) The energy spectrum calculated using equation (24) for the diagonal $\bar{C}$. This band structure corresponds to one atom per unit cell lattice with a lattice constant $2\pi/\Delta$. (*b*) The energy bands for the same structure as 3(*a*), but in Brillouin zone $(-\Delta/2, \Delta/2)$, calculated using equation (7). (*c*) The energy spectrum calculated using equation (24) with the off-diagonal $\bar{C}$ components switched on. (*d*) The outfolded bands of figure 3(*c*). For the whole demonstration the $\tau_3 = 2/1$ rational approximant has been used as a model.

band index ν and label the state by $k + K_n$. Moreover, it is easy to show that the dispersion relations ε_k in the various small Brillouin zones match up at the zone boundaries. In fact, equation (25) can be recognized as the KKR equation for a chain with real space unit cell whose size is $2\pi/\Delta$ and, hence, the Brillouin zone is the interval $-\Delta/2 \leqslant k \leqslant \Delta/2$. This is illustrated in figure 3 where we show $\varepsilon^0_{k,\nu}$ calculated by solving equation (25) in both the small and the large Brillouin zones.

Let us refer to the single non-zero $b^\nu_{n,0}(k)$ in the diagonal $\bar{C}_{n,m}$ limit as the *principal amplitude* of the state. When the off-diagonal elements of $\bar{C}_{n,m}$ are restored, e.g. we solve equation (24) instead of equation (25), for each state there will be finite amplitudes $b^\nu_n(k)$ corresponding to all the small Brillouin zones centred on the reciprocal lattice vectors $-\Delta/2 \leqslant k \leqslant \Delta/2$ in addition to the principal amplitude. Nevertheless, we continue to plot $\varepsilon_{k,\nu}$ in the Brillouin zone which is associated with its principal amplitude. This is our 'folding out' scheme. The result of the procedure for the $\bar{C}_{nm} = \bar{C}\delta_{mn}$ cases are compared with the folded out full solutions of equation (24) in figure 3. Clearly, the off-diagonal components of $\bar{C}_{nm}$ gave rise to gaps at the small Brillouin zone boundaries. If we were to estimate the sizes of these gaps using perturbation theory we would find that they are proportional to the structure constant at K_n, e.g. $S(K_n)$, and the corresponding Fourier transform of the potential function [11, 13]. Although the gap sizes oscillate with changes in the strength of the potential functions in the exact numerical solutions to equation (24), the large gaps nevertheless appear at K_ns where $S(K_n)$ is
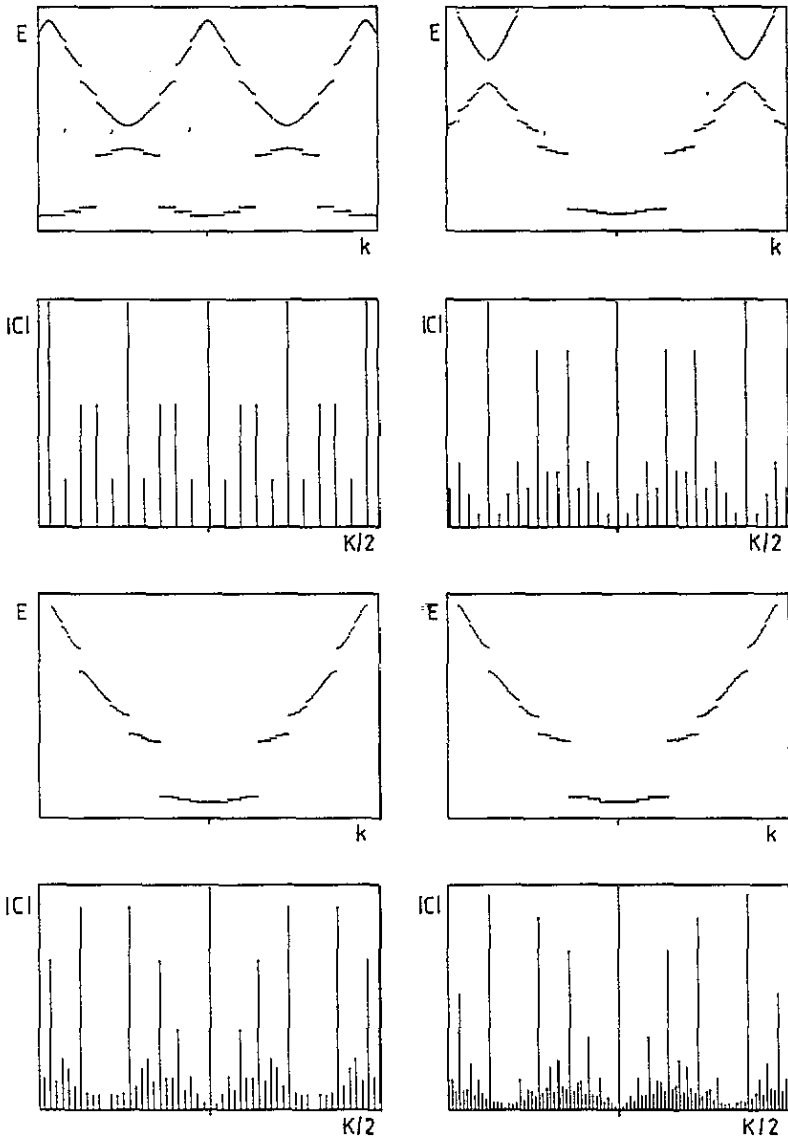
Figure 4. The calculated band structures of various rational approximants corresponding to 3, 5, 8 and 13 atoms per unit cell plotted together with the amplitudes of the structure constant $|S|$. We scaled the latter figures with a factor of two in order to show the coincidence of the peaks and the gaps in the energy spectrum.

large. This is illustrated in figure 4 where we display the results for the rational approximants $\tau_n = 2/1, 3/2, 5/3, 8/5$, which correspond to 3, 5, 8 and 13 sites per real space unit cell.

There are three final comments on the above results. Firstly, we note that at the low energy part of the spectra, where the occupied states will be found, the overall picture converges rather rapidly; namely, the large gaps occur at k vectors where $S(k)$ is large,

and these points no longer shift substantially as the order of the approximation increases. Thus, although k is not a good quantum number, neither is it a useless variable. In fact, our folding out procedure allowed us to make a contact between the electronic structure and principal features of the structure factor $S(k)$ measured in diffraction experiments. As the reader may recall this was the main purpose of setting up our reciprocal space KKR formalism.

The second remark concerns the fine structure of the energy 'bands'. These continue to change as the quasicrystalline limit is approached and the small Brillouin zone of our discussion shrinks to zero. Evidently, our final result is not a dispersion relation, ε_k, which is a continuous function of k. Nevertheless, states in an energy range δE about E are associated with a region of wave vector space δk about k. In short we could expect that the main features of the above 'band' structure will manifest themselves in a momentum spectral function which could not be defined in terms of the limiting process by the Euclidean algorithm. We shall return to this question in a separate publication.

Our third and final remark is a reiteration of the fact that although we have studied here only a one-dimensional model explicitly, the procedure of the reciprocal space KKR formalism and the Euclidean algorithm for implementing it is fully applicable in two and three dimensions. Of course, we hasten to add that the rate of convergence will depend on how well it works in those more demanding circumstances.

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