Electronic structure of a quasiperiodic system

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The general solution of a Schrödinger equation with a quasiperiodic potential in n dimensions is obtained. A boost technique is presented, which will transform the problem to the solution of a periodic pseudo-Schrödinger equation in $n+m$ dimensions, to which Floquet-Bloch theory is applicable. We show that the eigenfunctions of the original problem and the boosted problem are related to each other by a simple radon transform, and the eigenvalues are exactly equal. We identify the hierarchical gap structure in the energy spectrum observed in numerical simulations and we show that the location of gaps can be indexed by the reciprocal wave vector given by the diffraction pattern of the quasicrystal. The position and the magnitude of the gaps so predicted are in qualitative agreement with numerical simulations.

Since the discovery in 1984 of an Al-Mn alloy with icosahedral symmetry in its diffraction pattern, much theoretical and experimental work has been carried out on these and related systems.[1] Substantial progress has been made toward understanding the structure of these materials in terms of a quasiperiodic lattice and its decoration. However, the physical properties of these exotic materials are less well known. The main difficulty is the need for a systematic analytic approach toward quasiperiodic systems analogous to the Bloch-theorem approach used in the periodic case.

In this Rapid Communication, we provide such a theorem for quasicrystals. It will enable one to draw qualitative conclusions about the wave function and energy spectrum of a quasiperiodic system in n dimensions. We have developed a boost technique by which we obtain a periodic "pseudo-Schrödinger" equation in $n+m$ dimensions which, upon projection down to n dimensions, produces the solutions for the quasiperiodic system.

There have been many numerical simulations of the energy spectrum of a quasicrystal in one, two, and three dimensions.[2] The results indicate that there is a rich structure consisting of many gaps and singularities in the energy spectrum, and new types of wave function, exhibiting extended, critical, and localized behavior. The results of our present analysis are in agreement with those simulations and provide a basis for understanding those results and for further studies.

In this paper, we use the following notation: x, an n-dimensional vector designating the coordinate of the electron; $\{X_i\}$, the lattice point of the quasiperiodic lattice in n dimensions; z, an $(n+m)$-dimensional vector, $z = x \oplus y$, where y is an m-dimensional vector perpendicular to x; $\{Z_j\}$, the lattice point of a periodic lattice in $n+m$ dimensions, $Z = X \oplus Y$ ($\{X\}$ or $\{Y\}$ by themselves do not form a periodic lattice); the reciprocal of (x,y,z,X,Y,Z) is denoted as (q,p,k,Q,P,K).

Consider the Schrödinger equation for an electron in an n-dimensional quasicrystal described by a quasiperiodic potential $V(x)$:

$$\left[-\frac{\partial^2}{\partial x^2} + V(x) \right] \phi(x) = \mu \phi(x) \; ; \tag{1}$$

here $V(x)$ is a quasiperiodic function of x. Without loss of generality one can write

$$V(x) = \sum_i v(x - X_i) \; , \tag{2}$$

with $v(x)$ the electronic potential due to a single ion. The summation is over all the quasilattice points $\{x_i\}$ at which the ions are located. Hence both $V(x)$ and the equation is nonperiodic and the Bloch theorem is not applicable. The idea of our approach is to boost Eq. (1) from n dimensions to higher $n+m$ dimensions, such that one obtains a periodic pseudo-Schrödinger equation in $n+m$ dimensions.

To construct the pseudo-Schrödinger equation let us consider the potential part first. The Fourier transform of $V(x)$ is

$$\bar{V}(q) = \int V(x) e^{iqx} dx = \bar{v}(q) \sum_i e^{iqX_i} = \bar{v}(q) F(q) \; , \tag{3}$$

where $\bar{v}(q)$ is the Fourier transform of a simple ionic potential and $F(q)$ is the structure factor of the quasicrystal.

There are many models for the structure of a quasicrystal. However, the fundamental skeleton of the lattice in all of these structures is similar.[3] For simplicity, we will assume that the structure of a quasicrystal is simply that quasilattice in n dimensions that can be obtained by a projection from an $(n+m)$-dimensional periodic lattice. The structure factor of the quasilattice, namely the diffraction pattern, has been extensively studied,[3] and we follow the general approach of Bak.[4] It is based on the fact that the diffraction pattern of a quasicrystal can be integer indexed. Therefore, we define a quasilattice as a structure in n dimensions whose diffraction pattern can be integer indexed by $n+m$ linear vectors independent over the integer domain. The symmetry of the diffraction pattern will strongly limit the possible m, for example in the case $n=3$ with icosahedral symmetry the minimum m is 3. Mathematically, this means that $F(q)$ can be written as

$$F(q) = \sum_{K_i} f(K_i^{\parallel}) \delta(q - K_i^{\parallel}) \; , \tag{4}$$

where the summation is over a periodic lattice $\{K\}$ in $n+m$ dimensions and $K_i^{\parallel}$ is the component of K on the n-

dimensional subspace spanned by q. The diffraction amplitude generally is a function $K^{\perp}$ which is determined by $K^{\parallel}$.

Define a pseudopotential $U(z)$ in $n+m$ dimensions such that its Fourier transform is

$$\bar{U}(k) = \bar{v}(q)\sum_{K_i} f(K_i^{\parallel})\delta(q-K_i^{\parallel})\delta(p-K_i^{\perp})$$

$$= \sum_{K_i}\bar{U}(K_i)\delta(k-K_i) \; , \qquad (5)$$

where $\{K=K^{\parallel}\oplus K^{\perp}\}$ and $\bar{U}(K)=\bar{v}(K^{\parallel})f(K^{\parallel})$. Therefore,

$$U(z) = \int \bar{U}(k)e^{izk}dk = \sum_{K_i}\bar{U}(K_i)e^{izK_i} = U(z+Z) \qquad (6)$$

is a periodic function of z with fundamental period $\{Z\}$ which is defined as the reciprocal lattice of $\{K\}$ ($Z\cdot K = 2\pi n$, n an integer). From the definition of $U(z)$ one can verify that

$$V(x) = \int U(z)\delta(y)dy \; . \qquad (7)$$

This is the simplest example of a radon transform.[5]

Next we consider how to boost the kinetic operator. An obvious choice is to leave the kinetic operator unchanged but reexpressed in the z coordinates. This turns out to be the critical step whose advantage will be seen shortly. Thus we obtain a boosted pseudo-Schrödinger equation in $n+m$ dimensions:

$$\left[-\frac{\partial^2}{\partial x^2} + U(z)\right]\Psi(z) = E\Psi(z) \; . \qquad (8)$$

In terms of $z = \{z_i\}$ generally

$$\partial^2/\partial x^2 = c_{ij}(\partial^2/\partial z_i\partial z_j) \; ,$$

with the c_{ij} fixed definite coefficients. Then one has

$$\left[-c_{ij}\frac{\partial^2}{\partial z_i\partial z_j} + U(z)\right]\Psi(z) = E\Psi(z) \qquad (9)$$

or, symbolically, $L(z)\Psi(z)=E\Psi(z)$. The operator $L(z)$ is clearly translationally invariant under lattice translation $\{Z\}$. Therefore, the solutions of Eq. (9), according to Floquet theory will have Bloch form which can be indexed by wave vector k,

$$\Psi_k(z) = e^{ikz}\Phi_k(z), \quad E = E(k) \; , \qquad (10)$$

with $\Phi(z+Z)=\Phi(z)$. It is clear from Eq. (9) that $E(k)=E(k^{\parallel})$ is a function of $k^{\parallel}$ only since $\Psi_{(q,p)}(z)$ satisfies the same equation as $\Psi_{(q,p+p')}(z)$, where $k = (k^{\parallel},k^{\perp}) = (q,p)$ and p' is an arbitrary m-dimensional vector. This is important, as we will see that the eigenvalues of Eq. (1) are exactly same as those of Eq. (9) and from physical intuition certainly should not depend on p.

The important result is that the solutions of Eq. (9) are directly related to that of Eq. (1). This can be seen by applying the operator $\int \delta(y)dy$ to both sides of Eq. (9). One gets

$$\left[-\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,y)|_{y=0} = E\Psi(x,y)|_{y=0} \; , \qquad (11)$$

since $V(x)=U(x,y)|_{y=0}$. Comparing with Eq. (1), one immediately gets

$$\mu = \mu(k) = E(k) \; ,$$

$$\phi_k(x) = \Psi_k(z)|_{y=0} = e^{ik^{\parallel}x}\Phi_k(x,y)|_{y=0} \; . \qquad (12)$$

Therefore, the nature of the electronic states in quasicrystals can be understood in terms of a higher-dimensional pseudo-Schrödinger equation. This offers one great advantage, since now one can apply all the techniques which have been developed and extensively studied in the case of crystals to study the analytic properties of Eq. (9) and therefore Eq. (1).

The general approach just described can be used to analyze the analytical properties of the electronic spectrum in quasicrystal. As an example, we will show that in the weak-potential limit the spectrum has a hierarchical structure of gaps. The number of gaps is infinite for the infinite system and the hierarchical structure can be indexed by reciprocal-lattice vectors which are determined from the diffraction pattern of the quasilattice.

To solve Eq. (9) one goes to Fourier space as shown in standard solid-state textbooks.[6] Since $\Phi(z)$ and $U(z)$ are periodic functions, one can make the expansions

$$\Phi(z) = \sum_{k_l} c(K)e^{-iK_l z}, \quad U(z) = \sum_{k_l}\bar{U}(K)e^{-iK_l z} \; . \qquad (13)$$

Substituting Eq. (13) and Eq. (8) into Eq. (9), one gets the basic equation

$$[\varepsilon(k-K)-E(k)]c(K) + \sum_{K'}\bar{U}(K')c(K-K') = 0 \; , \qquad (14)$$

where $\varepsilon(k) = \hbar(k^{\parallel})^2/2M$ is the free-electron energy and the summation is over all lattice points in $n+m$ dimensions. In going to perturbation methods, one faces the problem of small denominators, namely, the near degeneracy problem. This is because ε is a function of $k^{\parallel}$ only, and there are many different K which have their parallel components very close to each other, hence the near degeneracy of ε. However, as we will show, this actually does not cause serious difficulty since the structure factor in the numerator goes to zero faster than the denominator.

Assume $\bar{v}(q)$ is a small smooth quantity (weak coupling, nearly-free-electron approximation). To second-order perturbation the energy eigenvalue is

$$E_K = \varepsilon_K + \sum_{K'(\neq K)} \frac{\langle K|U|K'\rangle\langle K'|U|K\rangle}{\varepsilon_K - \varepsilon_{K'}} \; . \qquad (15)$$

Here we use the notation $E_K = E_K(k)$, $\varepsilon_K = \varepsilon(k-K)$. $|K\rangle$ is a free-electron wave function with wave vector K. If the denominator in the summation is not small, the correction to the energy is second order; therefore, one only needs to restrict the summation to those K' which have eigenvalues close to that of state K. Denoting the set

by K_j, one has

$$E_K = \varepsilon_K + \sum_{K_j(\neq K)} \frac{|\bar{U}(K - K_j)|^2}{\varepsilon_K - \varepsilon_{K_j}}$$

$$\approx \varepsilon_K + \sum_{K_j(\neq K)} \frac{|v(0)|^2 |f(K_j - K)|^2}{2K^{\parallel}(K^{\parallel} - K_j^{\parallel})} \quad , \tag{16}$$

where we have approximated $v(K_j^{\parallel} - K^{\parallel})$ as constant since the argument is a small quantity and only the leading term is kept in the denominator. For fixed $K^{\parallel}$, the set of K_j which has approximately the same parallel component as that of K in general can be written as

$$K_j = K + (\Delta K^{\parallel}, \Delta K^{\perp}) = K + (r_{n+1} - r_n \tau, r_{n+1} \tau + r_n), \tag{17}$$

where r_n are integers, and r_{n+1}/r_n is the successive approximation of the irrational number τ. For the case $\tau = (\sqrt{5} + 1)/2$ is the golden mean and r_n are Fibonacci numbers. From number theory one knows that the best approximation one can make is $r_{n+1} - r_n \tau \propto 1/r_n$. On the other hand, the diffraction amplitude is inversely proportional to $K^{\perp}$ which is the order of r_n. Therefore, the term in the summation is the order of $|v(0)|^2/r^n \approx |v(0)|^2/\tau^n$, which after summation over n is of the order $|v(0)|^2$, and hence it is a second-order correction. So the correction caused by the near degeneracy of different $K^{\perp}$, namely, the "small denominator problem," is of second order and can be therefore neglected.

However, the degeneracy at the Bragg planes still exists. As in the case of a periodic crystal, this degeneracy will open up a gap at the Bragg plane with gap width proportional to the Fourier component of potential at the Bragg point. Thus near the vicinity of K, the eigenvalue can be written as

$$E_K(k) = \varepsilon(k^{\parallel}) \pm |\bar{v}(K^{\parallel})| |f(K)| \quad . \tag{18}$$

One sees that there is an energy-level splitting at every Bragg plane, and the amount of splitting is directly proportional to the structure factor or the diffraction amplitude at the Bragg point. From Eq. (18) the splitting is meaningful only when the structure factor is not too small. In other words, the effect is most important when k is on Bragg planes associated with dominant diffraction spots. Qualitatively when

$$|f(K)| \leq |v(0)| \tag{19}$$

the gap width is of second order, namely, it is the same order as the correction to the spectrum due to near degeneracy of $K^{\perp}$, therefore insignificant. This condition defines an effective reciprocal lattice which is not dense in the reciprocal space. For all practical calculations one need only restrict oneself to this set of K vectors.

As the magnitude of the potential increases the simple perturbation theory just presented will no longer be quantitatively valid. However, one can expect the same qualitative effects will occur. The number of significant energy gaps will increase commensurately. In the strong-coupling tight-binding limit one expects that an infinite number of gaps will show up with the width of each ener-

gy gap having a similar hierarchical structure to that of the diffraction pattern.

The electronic spectrum of quasiperiodic systems in the tight-binding approximation and in the Kronig-Penney potential, and the phonon spectrum have been extensively studied numerically by us and other groups.[2] The common basic conclusions are the following. (1) The spectrum is Cantor-like. There is a hierarchical structure of gaps which is dense in the limit of an infinite system. (2) The gap widths are different at different positions; if one only keeps those gaps which are larger than a certain amount then the spectrum can be divided into bands. (3) The wave functions are mostly critical and extended. There has been some indication of localized states. These
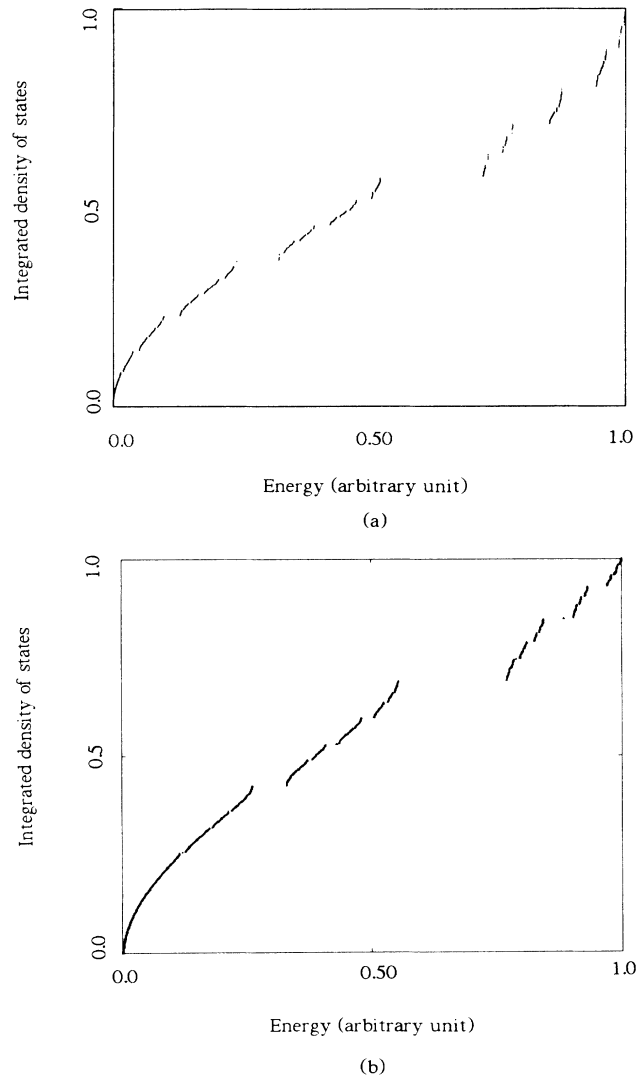

FIG. 1. Vibrational integrated density of states for a one-dimensional quasiperiodic system. (a) Qualitative result predicted by our theory using the simple model described in the text. Details on the construction of the cure are given in the text. (b) Result of a numerical simulation on a lattice with 2000 sites (see Lu, Odagaki, and Birman in Ref. 2).

results now can be easily understood in terms of our present result. Especially the structure of the spectrum follows directly from our analysis. One finds that the hierarchical gap structure is intimately related to the diffraction pattern of the quasicrystal. All gaps can be indexed by wave vectors. And the gap width should be directly proportional to the diffraction amplitude at that wave vector.

In order to illustrate these results, we calculated the vibrational integrated density of states schematically for a one-dimensional quasilattice based on our qualitative predictions. In Fig. 1, we compare the qualitative predictions of the spectrum with previous numerical simulations. We started with the integrated density of states for the vibrational spectrum (the same equation holds for a tight-binding model) in a periodic system. Using the dispersion relation $E = \omega^2 = 4\sin^2(q/2)$ (in dimensionless form) one obtains the integrated density of states $D(E) = (2/\pi)$ $\times \sin^{-1}(\sqrt{E}/2)$. Since the structure factor of a one-dimensional quasilattice (Fibonacci lattice) is analytically known (see Lu and Birman in Ref. 3), assuming a constant $\bar{v}(q)$ we calculated $\bar{U}(K)$ in Eq. (19) for different K. A gap is opened at the energy corresponding to a K value using the dispersion relation above. Near every gap edge the square-root singularity was fitted. The resulting density of states including the first 50 significant gaps are shown in Fig. 1(a). Comparing with Fig. 1(b), which is the result of numerical simulation of 2000 lattice sites, one sees that all the structural features of the spectrum are correctly reproduced. Considering the very crude schematic model we have used, the fitting is remarkable.

The approach we just outlined above is related to other work in the literature. In the course of a study of incommensurate systems, a similar approach has been pursued by Romerio, Janssen, and others.[7] However, it was less systematic and was not pursued in depth. This was based on the judgement that thought the results (such as energy spectrum) are rich in structure, they may not be experimently observable, since the incommensurate term in the conventional incommensurate systems is weak and treated as perturbation. However, in the case of quasicrystals the incommensurability is intrinsic and built into the structure, so the incommensurate potential is not a weak perturbation at all. In fact, the leading incommensurate terms are of the same order $(1, \tau^{-1}, \tau^{-2}, \ldots)$ and there are an infinite number of terms. The effects of this intrinsic incommensurability on the electronic and other physical properties may not be small. We believe systematic analysis could lead to some experimentally observable effect such as the negative differential conductivity in a strong electric field and the oscillating of electric current due to the Stark ladder and the interband or Zener tunneling.[7] The theory can be tested as better and larger quasicrystals are made available for experiments.

In conclusion, we have developed an analytical technique to study physical properties of a quasiperiodic system. After suitably boosting the Schrödinger equation to a higher dimension, we obtained a pseudo-Schrödinger equation which is periodic. Using the general Bloch-Floquet theory, the qualitative properties of eigenvalues and eigenfunctions can be analyzed. Then projecting down the solutions to physical space we find the solution for a quasiperiodic system. The hierarchical gap structure in a quasiperiodic system found in numerical simulations is a natural result of our analysis. We predict that the gap positions can be determined by reciprocal wave vectors tors and the gap width should be proportional to the scattering amplitude at that wave vector. The results are in full agreement with previous numerical simulations. This technique enables one to use the existing methods developed in the studies of crystal systems to study physical properties of quasiperiodic systems.

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