Abstract submitted

for the San Diego Meeting of the

American Physical Society

19-22 March 1973

Physical Review
Analytical Subject Index
Number 44.1

Bulletin Subject Heading
in which Paper should be placed:
Electronic Structure

Electronic Structure of Disordered Solids and Almost Periodic Functions. P. M. GRANT, IBM Research Laboratory, San Jose, Calif.--A review has been made of the theory of almost periodic functions, a relatively little-used branch of mathematical analysis, for the purpose of uncovering relevant application to the physical question of the electronic structure of disordered solids. The eigenproblem involving an almost periodic potential is treated both abstractly and with numerical experiment on a simple one-dimensional model. Results indicate that the almost periodic potential representation leads to qualitative agreement with existing theoretical and experimental findings regarding penetration of states into the forbidden gap and predominance of indirect optical transitions. Almost periodic functions may well provide a unifying concept encompassing a variety of approaches to the study of disordered systems.

Submitted by
Paul M. Grant
Paul M. Grant
IBM Research Laboratory
San Jose, California

P. M. GRANT

bulletin

OF THE AMERICAN PHYSICAL SOCIETY

Series II, Vol. 18, No. 3

MARCH 1973

INCLUDING THE PROGRAM OF THE
1973 MARCH MEETING IN SAN DIEGO
19–22 MARCH 1973

PUBLISHED FOR THE AMERICAN PHYSICAL SOCIETY
BY THE AMERICAN INSTITUTE OF PHYSICS

energies' at which $D(\epsilon)$ vanishes identically. In the vicinity of these special energies the density of states is shown to exhibit the type of essential singularity suggested by Lifshitz.[2] Furthermore, it was found that the envelope of the density of states associated with the special energies also displayed the Lifshitz type of singularity.

[1]H. Schmidt, Phys. Rev. 105, 425 (1957).
[2]I.M. Lifshitz, Adv. Phys. 13, 483 (1964).

BK 4 The Brillouin Wigner Series, Feenberg Perturbation Theory and the Disorder Problem†. SAMUEL P. BOWEN, University of Wisconsin.--An argument is outlined which suggests that the Anderson analysis of localized electronic states in disordered materials does not necessarily predict the existence of localized states. Conditions for the convergence of the Brillouin Wigner perturbation series are discussed within the context of the substitutionally disordered alloy. A generalization of Feenberg's Perturbation Theory is discussed as a method of calculation of properties of disordered alloys.

†Supported by Wisconsin Alumni Research Foundation.

BK 5 Virtual-Crystal Calculation of the Electronic Structure of $Pb_{1-x}Sn_xTe$.* ROBERT H. LASSETER and SOHRAB RABII, Moore School of Electrical Engineering, University of Pennsylvania--The electronic structure of $Pb_{1-x}Sn_xTe$ pseudo-binary alloys has been calculated using a virtual-crystal limit of the coherent potential approximation[1] (CPA) in conjunction with relativistic augmented plane wave (RAPW) formalism.

The results are in agreement with the "band inversion" model of Dimmock et al.[2] and the composition at which the principle gap goes to zero is in agreement with experiment.

*Supported in part by Naval Ordnance Laboratory Contract No. N60921-70-C-0251, ARPA Order #1597.

[1]Soven, Paul, Phys. Rev. B2, 4715 (1970).
[2]Dimmock, J. O., Melngailis, I., and Strauss, A. J., Phys. Rev. Lett. 16, 1192 (1966).

BK 6 Improved Version of Cellular Method. B. I. BENNETT, J. R. LEITE, and F. HERMAN, IBM Research, San Jose.--We are developing a computationally simple method for studying the electronic structure of complex crystalline solids and molecular clusters. In our approach, the various atoms are contained in (overlapping) equivalent volume spheres, with boundary conditions imposed along the circles defining the intersections of these spheres, and elsewhere as required. We are attempting to determine the minimum boundary condition requirements consistent with physically and mathematically acceptable solutions, as well as the role played by various potential approximations. This information will guide our progress from simple test cases such as diamond to more complex systems. Preliminary results for the diamond crystal will be reported and compared with earlier cellular-type calculations.[1]

BK 7 KKR Band Structure Calculations for Complex Crystals.* J. S. Faulkner, Oak Ridge National Laboratory--A formula for KKR structure constants for crystals having more than one atom per unit cell which has the advantage that the major computational effort is spent only on calculating the relatively small number of structure constants for the associated Bravais lattice was derived by the author from simple manipulations of the basic KKR equations.[1] A new derivation of this formula on the basis of multiple scattering theory has been carried out which makes the meaning of the terms more transparent. This new derivation will be discussed along with a comparison with recent similar work and comments on the application of the formula in practical calculations.

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.
[1]J. S. Faulkner, Physics Letters 31A, 227 (1970).

BK 8 Density of States of Disordered Binary Alloys.* A.ZIN and E.A.STERN, U. of Wash.--The density of states for a disordered binary alloy is calculated using the Tight Binding Approximation for a one band model in a cubic lattice. A new coherent potential scheme has been developed to calculate the change in the self energy operator as a function of concentration. This change arises from the change in the scattering t-matrix when one replaces one type of atom at a single site with another and is calculated by averaging over possible clusters where the probability of a given clusters' composition is a function of concentration. The cluster size used in this calculation is an atom and its nearest neighbors. The perturbing potentials introduced by replacing at a single site one type of atom with another are calculated self-consistently, and are made to satisfy the perfect shielding requirement. It is found that the result differs quantitatively from the single site CPA calculation. The correlation between surrounding atoms gives a significant correction but the major quantitative correction comes from the inclusion of the correctly shielded potentials.

*Supported in part by Air Force Office for Scientific Research

BK 9 Electronic Structure of Disordered Solids and Almost Periodic Functions. P. M. GRANT, IBM Research Laboratory, San Jose, Calif.--A review has been made of the theory of almost periodic functions, a relatively little-used branch of mathematical analysis, for the purpose of uncovering relevant application to the physical question of the electronic structure of disordered solids. The eigenproblem involving an almost periodic potential is treated both abstractly and with numerical experiment on a simple one-dimensional model. Results indicate that the almost periodic potential representation leads to qualitative agreement with existing theoretical and experimental findings regarding penetration of states into the forbidden gap and predominance of indirect optical transitions. Almost periodic functions may well provide a unifying concept encompassing a variety of approaches to the study of disordered systems.

BK 10 Gaussian Vibrational Lineshapes in Semiconducting Chalcogenide Glasses. P.C. TAYLOR, S.G. BISHOP, D.L. MITCHELL, Naval Research Lab, Washington, D.C. and D. TREACY, U.S. Naval Academy, Annapolis, Md.--The sharp vibrational modes observed in chalcogenide glasses based on layer and chain structure compounds are shown to possess Gaussian lineshapes as proposed by Taylor, Bishop and Mitchell[1] and not broad Lorentzians as has also been suggested[2]. Transmission measurements on thin samples (30 to 400μ) of glassy As_2S_3 and As_2Se_3 which were hot pressed or polished from the bulk are consistent with earlier

INTRODUCTION

This talk has as its purpose the bringing to your attention of a rather obscure branch of mathematical analysis which may provide a unifying concept to our way of thinking about disordered solids and in particular their band structures and optical properties. My interest in the subject goes back to the middle 1960's when I was involved in experimental studies on the optical and structural properties of germanium thin films. At that time I happened to stumble across a Dover publication on almost periodic functions and became intrigued with the possibility that here was some mathematics looking for some physics to explain.

I am going to assume most of you have never heard of almost periodic functions and so will spend a little time on their elementary properties. They were discovered by Harald Bohr, brother to the more famous Niels, around 1924, and can be thought of as sort of a 'half-way house' on the path from Fourier series to the Fourier integral. Although studied intensively in the early 1930's by Wiener and Weyl, there seems to have been little attempt to apply the formalism to practical problems, although natural areas would seem to be modulation theory and imperfect diffraction phenomena as well as disordered structures.

FIRST SLIDE

As indicated on the first slide, almost periodic functions can be formally defined as the set af all summable trigonometric series.

- It is most important that the set $\{\lambda_n\}$ be denumerable, This explicitly excludes the set of reals, or the continuum; otherwise we would be merely re-defining the Fourier integral.
- Note the three distinct cases:
  - Purely periodic, where $\{\lambda_n\}$ is just a multiple of the integer set,
  - Limit periodic, where the set $\{\lambda_n\}$ is a subset of the set of rationals,
  - General almost periodic case where one or more of the λ_n are irrational.
- A second and equivalent definition uses the notion of 'translation numbers'. That is, we demand that for some number ϵ, there exist a set $\{\tau_\epsilon\}$ of infinite cardinality such that the given inequality is satisfied over all values of x. Let me mention that for the sake of simplicity, we will speak only of one-dimensional problems in this talk. Now, if f(x) is purely periodic, then the special set of translation numbers for $\epsilon = 0$ of course define the period. It can be shown that under all circumstances the set $\{\tau_\epsilon\}$ must be relativity dense in the sense of an arithmentic progression. That is, there must be no arbitrarily large or small gaps between each of the τ_ϵ . From this property we can prove that simple functions

like $\cos x + \cos\sqrt{2}x$ are almost periodic while those like $\sin x/x$, $\sin x^2$, and $\sin 1/x$ are not.

- Note that forms of Parseval's Theorem and the Mean Value Theorem exist for almost periodic functions.

Now, are almost periodic functions really relevant to the potential arising in disordered solids? This question can be partially answered by noting the following obvious facts about such systems:

- Nearest neighbors never cluster arbitrarily close together, This fundamental degree of openess in the resulting potential is required by the definition of almost periodicity.
- Nearest neighbors are never arbitrarily far apart. Thus the potential must repeat itself within intervals of reasonable length hence affirming another condition on almost periodic functions.

However, from a strictly mathematical point of view the appropriate question to ask is: Is the spectrum of the Fourier transform of the disordered solid potential (or, more properly, the transform of its autocorrelation function) always discrete? The answer is probably not. On the other hand, many, if not all, calculational models of such disordered potentials will have discrete spectra and hence be amenable to description by almost periodic functions.

An illustration is given by the next slide.

SECOND SLIDE

Here the first equation defines the rigid ion approximation, cornerstone of tight binding, as the convolution of an atomic potential with a structure factor defined by the second equation. The structure factor contains all information about order or disorder. For a purely periodic chain s(x) is just a δ-function comb of evenly spaced teeth. If we simulate local fluctuations in atomic sites by adding a cosine term as in equation (3) we obtain the form in equation (4) satisfying that required by the definition of almost periodicity, namely, a trigonometric sum.

We need not have restricted ourselves to such a simple perturbation -- any sum or product of trigonometric terms plugged into equation (3) is reducible to a form recognizable as an almost periodic function.

THIRD SLIDE

Let us now take up the eigenproblem of an almost periodic Hamiltonian. As in the case of pure periodicity, we can learn a lot by studying the almost periodic potential as a perturbation on free electrons. Next slide, please:

— Here the plane wave representation is given by the first equation and the almost periodic potential by the second. The third equation gives the result of applying non-degenerate perturbation theory and using the Mean Value Theorem for almost periodic functions referred to earlier. We easily see that splittings of approximately twice the term coefficients in the potential will occur at wave vectors equal to half of the potential exponent values.

— Although our result, on the surface, might appear trivial and merely identical to the purely periodic treatment found in the texts, we must remember that here the capital K's do not form a sum group or reciprocal lattice. Nonetheless, as long as the potential can be thought of as almost periodic, the eignespectrum can still be represented as a continuous function of plane wave quantum numbers in a sort of extended zone scheme with finite gaps at half of each capital K. With respect to arguments about the validity of E vs. k concepts in

disordered structures, this is a quite profound conclusion.

FOURTH SLIDE

Romerio, in a paper published in J. Math. Phys., discusses in depth the representation theory for an almost periodic Hamiltonian, and I won't go into much detail on that matter here. However, I do want to say something on the possible existence of analogs to Bloch functions for the almost periodic problem. Next slide, please.

The first equation expresses a limit periodic potential with a finite number of terms in its series expansion. Since the exponents are all constant multiples of a set of rational numbers, they can be written in terms of a quotient of integers with respect to a least common denominator $\mathcal{L}$ as shown in equation (2). The reciprocal of the least common denominator defines a reciprocal lattice whose spacings will generally be very small. This is reminiscent of the effect Born Von-Karman boundary conditions have on the periodic case. Thus the eigenfunctions of this special potential can still be written in Bloch function form as shown in equation (3). Note that we have re-written the constant q in (1) as $2\pi/a$ in (3).

Now, for more general almost periodic potentials, either limit periodic with an infinite number of terms or with one or more irrational exponents, the LCD $\mathcal{L}$ tends to infinity with the

result that equation (3) becomes in the limit the Riemann definition of the integral shown in equation (4). Thus the eigenfunctions of almost periodic Hamiltonians will generally not have analogs to the simple Bloch functions of the purely periodic case.

However, from a practical point of view, it will be potentials like (1) with eigenfunctions like (3) that we always have to work with in performing the type of model calculations we will now talk about. The potential model we have chosen to make explicit the major features of the almost periodic eigenproblem is one of a simple cosine - modulated cosine. The results are shown in the next slide.

FIFTH SLIDE

The equations give the potential expression. Note that it is readily expressible in limit periodic form with center and sideband terms as shown. We can think of it as representing a periodic potential of reciprocal lattice vector K=1 perturbed by a long range fluctuation of wave vector $\Delta K = 0.2$. The amplitudes $U_1 = 0.1$ and $U_2 = 0.04$ give the relative strengths of the potential and the fluctuation, respectively. These numbers effectively simulate the removal of long range order and the near preservation of short range order.

The rest of the slide gives the E vs. k dependence resulting from the given potential. If the modulation were not present, the only gap would be, of course, at little k = 0.5. However, with the application of the fluctuation several subsidiary bandlets and gaps appear. The gaps at little k = 0.4 and 0.6 were predicted by our earlier nearly free electron treatment. In addition, smaller gaps occur at intervals separated by the reciprocal of the LCD of the potential arguments.

The larger the wavelength of the modulation, the shorter the extent of the bandlets in k-space, and the larger the modulation amplitude, the flatter the bandlets become which essentially implies onset of localized states.

Also, the main gap at little k = 0.5 is somewhat less than the 0.2 energy units expected without modulation. However, adding in the width of the immediatly adjacent sub-bands just about makes up the difference. Thus, this particular model, and, I believe, the almost periodic potential hypothesis in general, strongly suggests penetration of the nominal energy gap by satellite bands arising from the destruction of long range order.

SIXTH SLIDE

Finally, let's consider what sort of dipole transitions can occur in this kind of band structure. Next slide, please:

Using the Bloch-like eigenfunctions for a limit periodic potential with a finite number of terms, we obtain the indicated selection rule. This says that dipole transitions can only connect states differing by a member of the set of LCD reciprocal lattice vectors, here denoted by capital G.

The rest of the slide depicts the various types of allowed transitions. We have omitted for clarity all bandlets except those adjacent to the nominal. Note how certain 'indirect' transitions can occur amongst these sub-states. We conclude that the almost periodic potential hypothesis then contains the seeds of the so-called non-k conserving transitions invoked to explain the optical properties observed in disordered solids.

CONCLUSION

In summary, we can say that to the extent almost periodic potentials approximate real potentials in disordered materials, verification of several important experimental observations has been achieved. The next step is to investigate which types of site distribution functions lead to almost periodic functions and which do not.

Definition I : Set of all summable trigonometric series:

$$f(x) = \sum_n A_n \, e^{i\lambda_n x}$$

where $\{\lambda_n\}$ are denumerable.

Type (1) Purely Periodic: $\lambda_n = cn$, $n = 0, \pm 1, \pm 2, \ldots$

Type (2) Limit Periodic: $\lambda_n = cr_n$, $r_n \in \{\text{rationals}\}$.

Type (3) General Case: One or more λ_n irrational.

Definition II : Existence of an infinite set of 'translation numbers', $\{\tau_\epsilon\}$, such that:

$$|f(x+\tau_\epsilon) - f(x)| \leqslant \epsilon \; ; \; -\infty < x < \infty$$

where $\epsilon \geqslant 0$.

Parseval's Theorem:

$$\sum_n |A_n|^2 = \lim_{L\to\infty} \frac{1}{2L} \int_{-L}^{L} |f(x)|^2 \, dx$$

Mean Value Theorem:

$$\int_{-\infty}^{\infty} f(x) \, e^{i\lambda x} \, dx = A_n \, \delta(\lambda - \lambda_n)$$

Rigid Ion Approximation

$$V(x) \equiv V_a(x) \circledast s(x) \tag{1}$$

$$s(x) = \sum_{n=-\infty}^{\infty} \delta(x - x_n) \tag{2}$$

$$x_n = na + b \cos \frac{2\pi n a}{L} \tag{3}$$

$$s(x) = \sum_{\ell=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} (-i)^{\ell} J_{\ell}\left[2\pi b \left(\frac{m}{a} + \frac{\ell}{L} \right)\right] e^{i2\pi\left(\frac{m}{a} + \frac{\ell}{L}\right)x} \tag{4}$$

Let: $|k> = e^{ikx}$,

And: $V(x) = \sum_K U(K)\, e^{iKx}$,

Then:

$$E(k) = \frac{\hbar^2 k^2}{2m} + U(0) + \sum_{K \neq 0} \frac{|U(K)|^2}{\frac{\hbar^2}{2m}[k^2 - (k-K)^2]} + \cdots$$

Degeneracies occur at $k = K/2$ which result in first-order splittings of magnitude $2|U(K)|$ on application of degenerate perturbation theory.

Limit Periodic — Finite Number of Terms

$$V(x) = \sum_{n=-N}^{N} U(n)\, e^{iqr_n x},\ r_n \text{ rational} \tag{1}$$

$$\{r_n\} = \{\mu_n/\nu\},\ \{\mu_n\} \in I,\ \nu = \text{LCD} \tag{2}$$

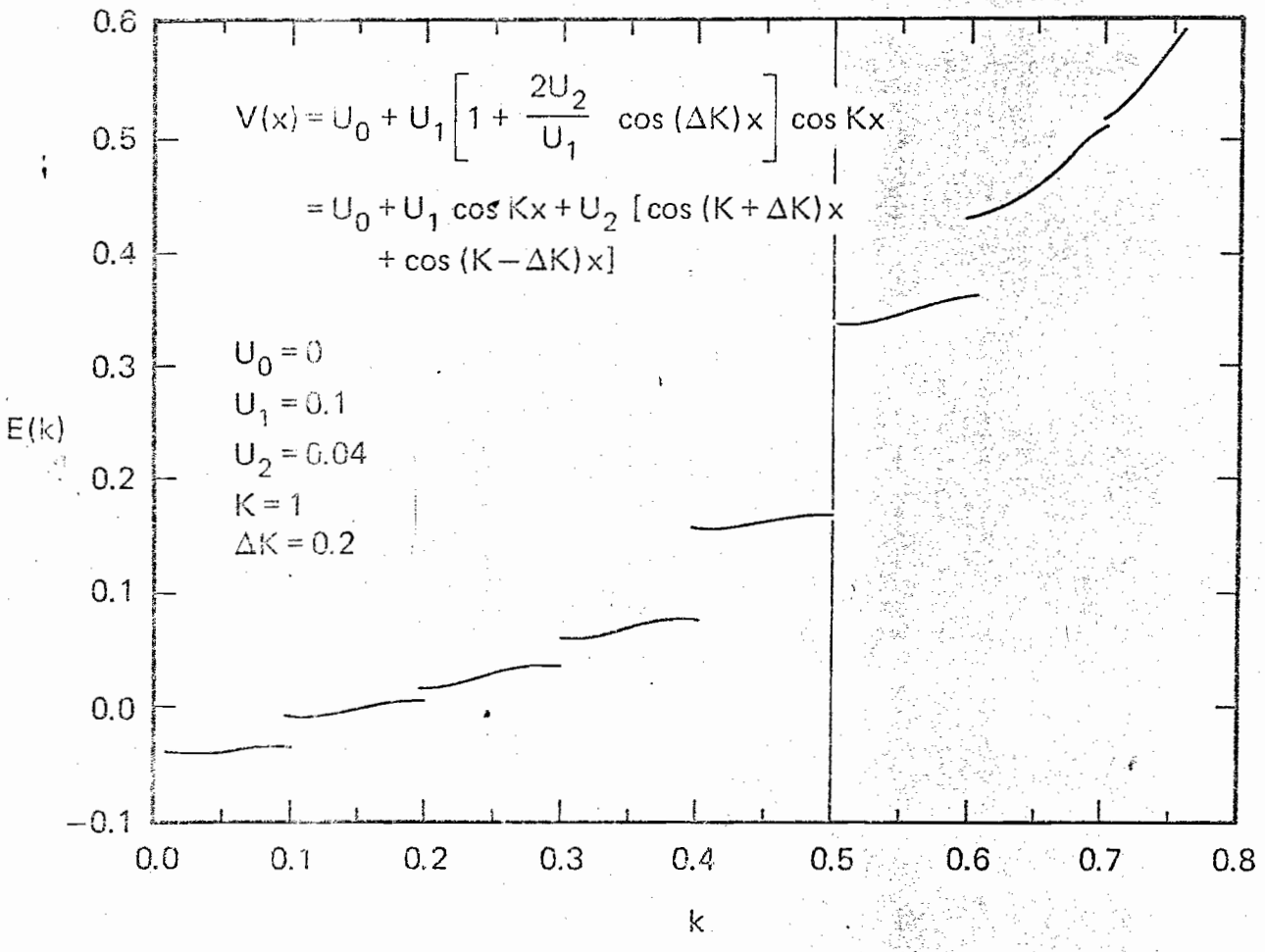
$$\psi_k(x) = \frac{2\pi}{\nu a} \sum_{n=-\infty}^{\infty} \chi(n)\, e^{i\frac{2\pi n x}{\nu a}}\, e^{ikx},\ \{n\} \in I \tag{3}$$

Limit Periodic — Infinite Number of Terms

Almost Periodic

$$\lim_{\nu\to\infty} \frac{2\pi}{\nu a} \sum_{n=-\infty}^{\infty} \chi(n)\, e^{i\frac{2\pi n x}{\nu a}}\, e^{ikx}$$

$$\Rightarrow \int_{-\infty}^{\infty} \chi(k'-k)\, e^{ik'x}\, dk' \tag{4}$$

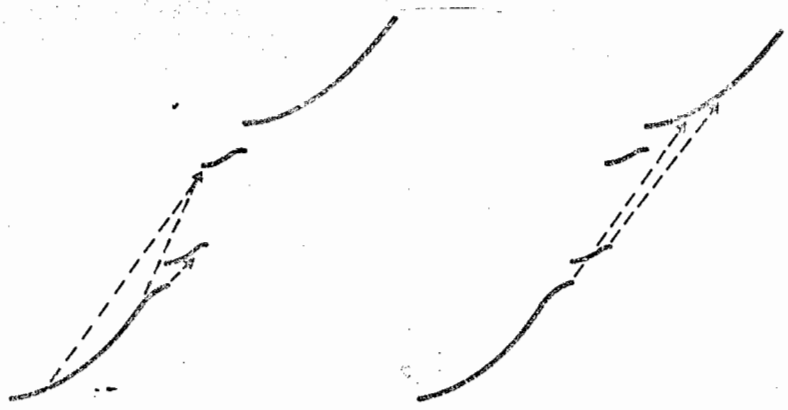

$V(x) = U_0 + U_1\left[1 + \frac{2U_2}{U_1}\cos(\Delta K)x\right]\cos Kx$
$= U_0 + U_1 \cos Kx + U_2\,[\cos(K+\Delta K)x$
$+ \cos(K-\Delta K)x]$
$U_0 = 0$
$U_1 = 0.1$
$U_2 = 0.04$
$K = 1$
$\Delta K = 0.2$
E(k)
k
0.6
0.5
0.4
0.3
0.2
0.1
0.0
−0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

$$\langle k' | p | k \rangle = \sum_{G',G} \chi^*(G')\,\chi(G)(G+k)\;\delta(G+k-G'-k')$$

$$\Rightarrow k - k' = G - G'$$

Direct Transitions, $\Delta G = 0$

Indirect Transitions, Type I, $\Delta G \neq 0$



Indirect Transitions, Type II, $\Delta G \neq 0$