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# Electron Energy Bands of One-Dimensional Random Alloys*

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A method for calculating the density of states for an infinite, one-dimensional random alloy is obtained by investigating the asymptotic behavior of the trace of the "transmission" matrix which relates the values taken on by the wave function and its derivative at either end of the crystal. This matrix can be calculated if the potentials of the constituent $A$ and $B$ atoms, $V_A$ and $V_B$, are given. The equations are first derived for a very general case, and then the results of a calculation for an alloy in which the $A$ and $B$ atoms have equal concentrations is shown for the case that $V_A$ and $V_B$ are $\delta$-function potentials. Certain generalizations of the method for treating other nonperiodic problems are discussed briefly.

## I. INTRODUCTION

In order to investigate qualitatively the band structure of random alloys, while minimizing the mathematical difficulties, we consider a one-dimensional model. The method to be developed gives an asymptotic expression for the density of states in the limit as the length of the crystal approaches infinity, and does not rely on perturbation theory.

Other investigations of various one-dimensional models have appeared in the recent literature. Schmidt[1] has derived an equation for the density of states of an infinite random alloy which may be solved by iteration, although no calculations were shown. Landauer and Helland[2] have used a method first suggested by James[3] to calculate the density of states of a random alloy made up of 150 atoms. They used the same method to treat a one-dimensional liquid metal made up of 150 atoms. Frisch and Lloyd,[4] and Ford[5] have investigated the latter problem for the infinite case. Domb, Maradudin, Montroll, and Weiss[6] studied the vibration spectrum of a disordered linear chain. They used the "moment-trace method"; with machine calculations they obtained results closely related to some of ours.

Our method can be applied to a variety of nonperiodic models, but we will emphasize the one described in Sec. II. We will also present a certain amount of background material there. In Sec. III the basic equations are developed; in Sec. IV these are applied to the special case of delta-function potentials. In Sec. V we discuss some generalizations of the method.

## II. GENERAL PROPERTIES OF THE MODEL

We will investigate the eigenvalues of the one-electron Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\Psi=E\Psi, \tag{1}$$

with certain boundary conditions. The $x$ axis is divided into cells of length $d$, the $n$th cell being the interval $nd\leq x<(n+1)d$; a local coordinate system for the $n$th cell is given by

$$x_n=x-nd.$$

The one-electron potential function, $V(x)$, is specified by giving its form in each cell:

$$V(x)=V_n(x_n),\quad nd\leq x<(n+1)d.$$

In our model of a random alloy, the $V_n(x_n)$ may take on two possible forms. If $V_n(x_n)=V_A(x_n)$, the $n$th cell is said to contain an $A$ atom, and if $V_n(x_n)=V_B(x_n)$, the $n$th cell is said to contain a $B$ atom. (The condition that the potential depends only on the type of atom in the cell neglects the variations due to the environment of the atoms.) We specify further that $V_A(x_n)$ and $V_B(x_n)$ are symmetric about the center of the cells, and that $V_A(0)=V_A(d)=V_B(0)=V_B(d)$ so that $V(x)$ is a continuous function of $x$. The arrangement of the $A$ and $B$ atoms in the lattice is random, but the concentration of $A$ atoms, $C_A$, and the concentration of $B$ atoms, $C_B=1-C_A$, are fixed numbers.

Boundary conditions are imposed on Eq. (1) by considering a finite crystal $0\leq x<Nd$, where $N$, the number of atoms in the crystal, is large enough that end effects can be ignored. We will use the periodic boundary conditions

$$\begin{aligned}\Psi(0)&=\Psi(Nd),\\ \Psi'(0)&=\Psi'(Nd).\end{aligned} \tag{2}$$

A simple choice for the form of the functions $V_A(x_n)$ and $V_B(x_n)$, which is used in the Kronig-Penney model of a random alloy, is

$$\begin{aligned}V_A&=(\hbar^2/md)P_A\delta(x_n-\tfrac{1}{2}d),\\ V_B&=(\hbar^2/md)P_B\delta(x_n-\tfrac{1}{2}d),\end{aligned} \tag{3}$$

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[1] H. Schmidt, Phys. Rev. **105**, 425 (1957).

[2] R. Landauer and J. C. Helland, J. Chem. Phys. **22**, 1655 (1954).

[3] H. M. James and A. S. Ginsbarg, J. Phys. Chem. **57**, 840 (1953).

[4] H. L. Frisch and S. P. Lloyd, Phys. Rev. **120**, 1175 (1960).

[5] J. Ford, J. Chem. Phys. **30**, 1546 (1959).

[6] C. Domb, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, J. Phys. Chem. Solids **8**, 419 (1959).

where $P_A$ and $P_B$ are real constants. This model was considered by Saxon and Hutner[7] who were led to conjecture that an energy band which is forbidden for both the pure crystal made up of $A$ atoms and the pure crystal made up of $B$ atoms is also forbidden for a random $AB$ alloy. This was later verified by Luttinger,[8] whose proof remains valid for potentials that do not have the simple form of Eq. (3).

In order to explain the motivation behind the method that we will use, it is necessary to employ certain theorems concerning the eigenvalues of Eq. (1) which are proved in a paper by Kramers.[9] Kramers considered a very general case in which the only restrictions on the potential function, $V(x)$, are that it should be real and continuous. His theorems deal with the energy-dependence of the trace of a certain matrix which, in a manner that will be described, yields the eigenvalues of Eq. (1).

Let $\varphi_1(x)$ and $\varphi_2(x)$ be the two linearly independent solutions of Eq. (1), for a given energy, on the interval $\xi \leq x < \xi + L$. A "transmission" matrix $\mathbf{A}$ with elements $\alpha_{ij}$ is defined by the equation

$$\mathbf{\Phi}(\xi+L)=\mathbf{A}(\xi+L,\,\xi)\,\mathbf{\Phi}(\xi), \tag{4}$$

where

$$\mathbf{\Phi}(x)=\begin{bmatrix}\varphi_1(x) & \varphi_1'(x)\\ \varphi_2(x) & \varphi_2'(x)\end{bmatrix}.$$

A typical element of $\mathbf{A}$ is

$$\alpha_{11}=\frac{1}{\Delta}\begin{vmatrix}\varphi_1(\xi+L) & \varphi_2(\xi)\\ \varphi_1'(\xi+L) & \varphi_2'(\xi)\end{vmatrix},$$

where $\Delta$ ($=\det\mathbf{\Phi}$) is the Wronskian of $\varphi_1$ and $\varphi_2$. Since $\Delta(\xi+L)=\Delta(\xi)$, it follows from Eq. (4) that

$$\det\mathbf{A}=1. \tag{5}$$

Solutions of Eq. (1) of the form

$$\chi(x)=c_1\varphi_1(x)+c_2\varphi_2(x)$$

can be formed which satisfy the generalized boundary conditions

$$\chi(\xi+L)=\lambda\chi(\xi),$$
$$\chi'(\xi+L)=\lambda\chi'(\xi),$$

provided $\lambda$ is a solution of the secular equation

$$|\mathbf{A}-\lambda\mathbf{I}|=0.$$

Here $\mathbf{I}$ is the unit matrix. Using Eq. (5), the solutions of this equation are found to be

$$\lambda_\pm=\tfrac{1}{2}[f\pm(f^2-4)^{\frac{1}{2}}], \tag{6}$$

where

$$f=\mathrm{trace}\mathbf{A}.$$

It can easily be shown that the trace, $f$, is independent of the particular choice of basis functions, $\varphi_1$ and $\varphi_2$, among all the linear combinations $\chi$. Thus, for any given potential function, $f$ depends only on the energy. Since $\varphi_1$ and $\varphi_2$ may be chosen real, $f$ is real.

Kramers proved the following theorems: (a) The trace, $f$, is a continuous function of the energy, $E$. (b) There exists an energy $E_0$ such that, if $E<E_0$, then $f>2$. (c) If $E>E_0$, then $f$ is an oscillating function of the energy with an infinite number of maxima and minima. (d) At the maxima, $f\geq 2$, while at the minima, $f\leq -2$. (e) When $f(E)=2$, the eigenvalue $E$ of (1) is nondegenerate unless $\partial f/\partial E=0$, in which case the eigenvalue is twofold degenerate.

These theorems can be used in two ways: If $L$ is set equal to $d$ (the length of a cell), they may be made the basis for a discussion of the band structure of a periodic lattice. Writing $f_d=\mathrm{trace}\mathbf{A}[(n+1)d,\,nd]$ and

$$\lambda_\pm{}^d=\exp(\pm ikd), \tag{7}$$

we see from Eq. (6) that $k$ is real in those energy regions for which $|f_d|\leq 2$ (the allowed bands), and that $k$ is imaginary for $|f_d|>2$ (the forbidden bands). That any periodic lattice will exhibit a sequence of allowed and forbidden bands as the energy increases from $E_0$ on, follows from the behavior of $f(E)$. This is the use that Kramers made of the theorems.

If $L$ is set equal to $Nd$, then the periodic boundary conditions of Eq. (2) can be satisfied for those values of $E$ for which $\lambda=1$ (or $f=2$).

For the periodic lattice, it can be shown that the trace of $\mathbf{A}(Nd,0)$, $f_{Nd}{}^P$ is given by

$$f_{Nd}{}^P=2\cos(Nkd),$$

where $k$ is defined in Eq. (7). The quantity $kd$ varies monotonically from 0 to $\pi$ (or $\pi$ to 0) as the energy traverses an allowed band. Thus, in an allowed band, $f_{Nd}{}^P$ has the energy-dependence as shown by the upper curve in Fig. 1. Except for the highest and lowest values, the energy eigenvalues in the band are twofold degenerate according to theorem (e). These degeneracies for the periodic crystal with periodic boundary conditions are due to the invariance of the system under translations and reflection[10]; they are likely to be absent in a random alloy. Thus, in accordance with theorems (a)-(e), the trace of $\mathbf{A}(Nd,0)$ for a random alloy, $f_{Nd}{}^R$, will have the energy dependence in an allowed band as shown by the lower curve in Fig. 1.

One can see from the preceding how the eigenvalues of Eq. (1) with boundary conditions (2) can be obtained from the trace of $\mathbf{A}(Nd,0)$ and, in a qualitative way, how this trace varies with the energy. In order to carry the investigation further, it is necessary to construct this matrix for the model described at the beginning of this section. This can be done as follows. A matrix,

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[7] D. S. Saxon and R. A. Hutner, Philips Research Repts 4, 81 (1949).

[8] J. M. Luttinger, Philips Research Repts. 6, 303 (1951).

[9] H. A. Kramers, Physica 2, 483 (1935).

[10] J. C. Slater, Technical Note No. 4, Solid State and Molecular Theory Group, Massachusetts, 1953 (unpublished).

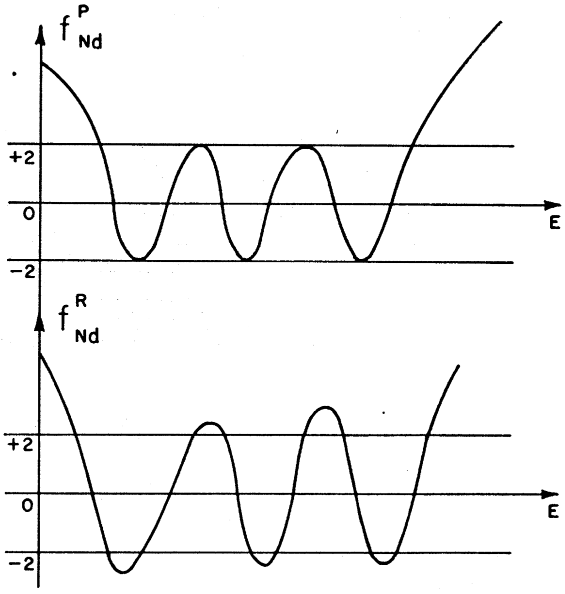

FIG. 1. Qualitative behavior of the trace $f$ as a function of the energy for a periodic and for a random lattice.

$\mathbf{X}_n$, that depends on the shape of the potential in the $n$th cell and on the energy (i.e., is independent of the choice of basis function $\varphi_1$ and $\varphi_2$) can be defined by

$$\mathbf{X}_n = \mathbf{\Phi}^{-1}(nd)\mathbf{A}[(n+1)d, nd]\mathbf{\Phi}(nd). \tag{8}$$

If the $n$th cell contains an $A$ atom, we write $\mathbf{X}_n = \mathfrak{A}$, and if it contains a $B$ atom, $\mathbf{X}_n = \mathfrak{B}$. For a given crystal made up of $N$ atoms, $r$ of them being $B$ atoms, we define

$$\mathbf{P}^i(N,r) = \prod_{n=0}^{N-1} \mathbf{X}_n = \mathfrak{A}\mathfrak{A}\mathfrak{B}\cdots\mathfrak{B}\mathfrak{A}\mathfrak{B}, \tag{9}$$

where the order in which the $\mathfrak{A}$ and $\mathfrak{B}$ matrices appear in this product is the same as the order in which the $A$ and $B$ atoms occur in the crystal. The superscript $i$ indicates which of the $\binom{N}{r}$ distinct crystals that can be formed from $(N-r)$ atoms of type $A$ and $r$ atoms of type $B$ is meant. It is easily seen that the $A$ matrix for that crystal, $\mathbf{A}^i$ is given by

$$\mathbf{A}^i = \mathbf{\Phi}(0)\mathbf{P}^i\mathbf{\Phi}^{-1}(0),$$

and

$$f^i = \text{trace}\mathbf{A}^i = \text{trace}\mathbf{P}^i. \tag{10}$$

The $\mathfrak{A}$ and $\mathfrak{B}$ matrices defined in the previous paragraph are the transpose of similar matrices introduced in a paper by James,[11] and a prescription for calculating them for any potential is given in that paper.

### III. ASYMPTOTIC EVALUATION OF THE ENSEMBLE AVERAGE OF $f^i$

One could, in principle, write down the matrix product $P^i(N,r)$, Eq. (9), and then investigate the eigenvalues of Eq. (1) by taking the trace of this product. This approach would be quite arduous, and it would require that we specify the exact sequence of atoms in the crystal whereas, in practice, only the concentrations $C_A$ and $C_B$ are measurable quantities for a random alloy. The basic assumption in an energy-band investigation of a random alloy is that the distribution of energy eigenvalues approaches a limiting distribution as $N \to \infty$ which is the same for almost all sequences of atoms (i.e., except for a fraction that goes to zero as $N \to \infty$) so long as the concentrations remain fixed. This assumption has been justified in several papers.[1,4,12] Due to the connection between the trace, $f^i(N,r)$, and the energy eigenvalues, we assert that the traces also approach a limit. This limit, if it exists, will be given by the ensemble average, $\langle f \rangle$, (i.e., the average of the traces for all sequences which have the given concentrations) in the limit as $N \to \infty$. The existence of the limit can be inferred from the asymptotic behavior of $\langle f \rangle$ to be discussed for an example in the next section. One would expect a smoothing out of the rapid oscillations of the individual traces (see Fig. 1) if the random phase factors shifted the eigenvalues, for a finite fraction of sequences, by an amount comparable to their separation. From the existence of a limit of $\langle f \rangle$, we can infer that this is not the case.

We will now derive an expression for the average trace, $\langle f \rangle$. The sum of all possible products that can be formed by permutation of $(N-r)$ $\mathfrak{A}$ matrices and $r$ $\mathfrak{B}$ matrices is equal to the coefficient of $z^r$ in the expansion of $(\mathfrak{A}+z\mathfrak{B})^N$. The average of all these products, $\langle \mathbf{P} \rangle$, is thus given by the contour integral

$$\langle \mathbf{P} \rangle = \frac{1}{2\pi i}\binom{N}{r}^{-1} \oint (\mathfrak{A}+z\mathfrak{B})^N z^{-r-1} dz, \tag{11}$$

where the contour of integration goes once around the origin. The trace of the sum of a set of matrices is equal to the sum of the traces; therefore:

$$\langle f \rangle = \text{trace}\langle \mathbf{P} \rangle. \tag{12}$$

The average matrix, $\langle \mathbf{P} \rangle$, can be put in a more useful form by bringing $\mathfrak{A}+z\mathfrak{B}$ in exponential form. We have

$$D^2 = \det(\mathfrak{A}+z\mathfrak{B}) = 1+2\beta z+z^2, \tag{13}$$

where

$$\beta = ab - \tfrac{1}{2}(\mathfrak{A}_{12}\mathfrak{B}_{21}+\mathfrak{A}_{21}\mathfrak{B}_{12}), \tag{13a}$$

with

$$a = \tfrac{1}{2}\,\text{trace}\mathfrak{A}, \quad b = \tfrac{1}{2}\,\text{trace}\mathfrak{B}.$$

The determinant takes this relatively simple form because $\mathfrak{A}$ and $\mathfrak{B}$ are unimodular [see Eqs. (5) and (8)]. We introduce the matrix

$$\mathbf{G}(z) = \frac{\mathfrak{A}+z\mathfrak{B}-D\,\mathbf{I}\cos p}{iD\sin p}, \tag{14}$$

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[11] H. M. James, Phys. Rev. 76, 1602 (1949).

[12] F. J. Dyson, Phys. Rev. 92, 1331 (1953).

where $p(z)$ is defined by

$$\cos p = (a+zb)/D. \tag{15}$$

The functions $p(z)$ and $D(z)$ can be made single-valued by a choice of Riemann sheets. It can easily be shown that

$$\mathrm{trace}\,\mathbf{G}(z)=0, \tag{16}$$

and

$$\mathbf{G}^2(z)=\mathbf{I}. \tag{17}$$

for any value of $z$. From Eqs. (14) and (17) it follows that

$$\mathfrak{A}+z\mathfrak{B}=D\exp(ip\mathbf{G}), \tag{18}$$

and hence

$$(\mathfrak{A}+z\mathfrak{B})^N=D^N[\mathbf{I}\cos Np+i\mathbf{G}\sin Np]. \tag{19}$$

We can now find the average trace, $\langle f\rangle$, by inserting Eq. (19) into Eq. (11) and making use of Eqs. (12), (14), and (16):

$$\langle f\rangle=\frac{1}{i\pi}\binom{N}{r}^{-1}\oint D^N\cos Np\, z^{-r-1}dz. \tag{20}$$

An asymptotic expression for $\langle f\rangle$ can be found by using the saddle point method of integration. We first break up the integral into the sum of two integrals,

$$\langle f\rangle=K^{+}+K^{-},$$

where

$$K^{\pm}=\frac{1}{2\pi i}\binom{N}{r}^{-1}\oint \exp Nh_{\pm}dz,$$

with

$$h_{\pm}=\pm ip+\ln D-C_B\ln z.$$

The quantity $C_B$ in the last equation is equal to $(r+1)/N$ which is, in the limit as $N\rightarrow\infty$, just the concentration of $B$ atoms. The saddle points of $h_+$ and $h_-$ can be found from the equations

$$dh_{\pm}/dz=0.$$

By manipulation of either of these equations one obtains the following sixth degree algebraic equation for the saddle points of $h_+$ and $h_-$:

$$\sum_{n=0}^{6} c_n z^n=0, \tag{21}$$

$$c_0=(1-a^2)x^2,\quad c_6=1-b^2,$$
$$c_1=2[(\beta-ab)x^2+(1-a^2)\beta x(x-1)],$$
$$c_5=2[\beta-ab+(1-b^2)\beta(1-x)],$$
$$c_2=(1-b^2)x^2+4\beta(\beta-ab)x(x-1)+(1-a^2)[\beta^2(x-1)^2-2x]+(a\beta-b)^2(1+x^2),$$
$$c_4=1-a^2+4\beta(\beta-ab)(1-x)+(1-b^2)[\beta^2(x-1)^2-2x]+(b\beta-a)^2(1+x^2),$$
$$c_3=2\{(1-b^2)\beta x(x-1)+(1-a^2)\beta(1-x)+(\beta-ab)[\beta^2(x-1)^2-2x]+(a\beta-b)(a-b\beta)(1+x^2)\}.$$

In this equation $\beta$ is given by Eq. (13a) and $x=C_B/C_A$. Since the coefficients are real, the complex roots of Eq. (21) occur in conjugate pairs.

If the Riemann sheets that make $h_{\pm}(z)$ single-valued are chosen such that

$$h_-(z^*)=h_+{}^*(z), \tag{22}$$

then the conjugate of any saddle point of $h_+$ is a saddle point of $h_-$. If we consider the contribution to the integrals of just one complex saddle point, $z_1$, we have[13]

$$K_1{}^{+}=(K_1{}^{-})^*=\binom{N}{r}^{-1}[2\pi h''(z_1)]^{-\frac{1}{2}}\exp h_+(z_1).$$

Evaluating $\binom{N}{r}$ by the saddle point method gives

$$\binom{N}{r}^{-1}=2\pi C_B{}^{-\frac{1}{2}}C_A{}^{\frac{3}{2}}\exp(-N\mu),$$

where

$$\mu=\ln C_A+C_B\ln(C_A/C_B).$$

Thus, the contribution to $\langle f\rangle$ from one complex conjugate pair of saddle points is

$$\langle f\rangle_1=Q_1\cos(N\theta+\delta)\exp N\gamma_1, \tag{23}$$

where

$$\theta=\mathrm{Im}\,h_+(z_1),$$
$$\delta=-\tfrac{1}{2}\arg h''(z_1),$$
$$Q_1=2C_A{}^{\frac{3}{2}}C_B{}^{-\frac{1}{2}}|h''(z_1)|^{-\frac{1}{2}},$$
$$\gamma_1=\mathrm{Re}\,h_+(z_1)-\mu.$$

It can be shown that a saddle point of $h_+$ or $h_-$ which is real will in general fall on a branch cut if the Riemann sheets are taken so that Eq. (22) is satisfied. For this case it is convenient to choose the Riemann sheets differently in evaluating the integrals. A real saddle point of $h_+$ will of course not also be a saddle point of $h_-$, and hence the integrals $K^+$ and $K^-$ are quite different. The contribution to $\langle f\rangle$ from the real saddle point $z_2$ of $h_+$ is

$$\langle f\rangle_2=Q_2\exp N\gamma_2, \tag{24}$$

where

$$\gamma_2=h_+(z_2)-\mu,$$
$$Q_2=C_A{}^{\frac{3}{2}}C_B{}^{-\frac{1}{2}}(h''(z_2))^{-\frac{1}{2}}.$$

The quantity $\langle f\rangle_2$ is real since $h_+(z_2)$ is either real or contains an imaginary part of the form $m\pi/N$, where $m$ is an integer. The contribution to $\langle f\rangle$ from a real saddle point of $h_-$ is also real.

For a given energy, all of the saddle points of $h_+$ and $h_-$ are roots of Eq. (21) with the coefficients evaluated at that energy. It is necessary to know the form of the function $\mathrm{Re}\,h_{\pm}(z)$ at that energy to see through which saddle points the path of integration

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[13] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

must pass. It can be seen from Eqs. (23) and (24) that, of these, the complex saddle points for which $\operatorname{Re} h_+(z_1)<\mu$ and the real saddle points for which $h_+(z_2)<\mu$ will contribute nothing in the limit as $N$ approaches infinity.

If, in a given energy region, the only contribution to $\langle f\rangle$ is from one conjugate pair of saddle points, and if one has calculated these saddle points and also $h_+(z_1)$ for a sufficient number of values of the energies in that region to plot $\theta$ as a smooth function of the energy, then the number of allowed states between two energies $E_1$ and $E_2$ in that region can be found from

$$n(E_1,E_2)=\frac{N}{\pi}|\theta(E_1)-\theta(E_2)|. \tag{25}$$

The quantity $\gamma_1$ can be interpreted as a measure of the degree to which the degeneracy that occurs for the pure crystal (see Fig. 1) is removed. An energy region for which the only contribution to $\langle f\rangle$ is from a real saddle point is obviously a forbidden zone for the random alloy. An interpretation of the results for energy regions in which various combinations of the different types of saddle points contribute can also be made in a straightforward manner, although for this case $\langle f\rangle$ may not have the form required by Kramers' theorems. It would then be necessary to conclude that the traces $f^i$ do not approach a limit. In the following example no such problem arises.

## IV. APPLICATION TO THE KRONIG-PENNEY MODEL

We have made a calculation of the energy band structure for a Kronig-Penney model of a random alloy [see Eq. (3) for the potentials; we took $P_A$ and $P_B$ negative as did Saxon and Hutner]. This case is particularly simple because $\beta$ [see Eq. (13a)] is equal to unity for all values of the energy. Due to this simplification, the sixth degree algebraic equation for the saddle points of $h_+$ and $h_-$ is replaced by the following cubic equation:

$$\sum_{n=0}^{3} c_n' z^n=0, \tag{26}$$

$$c_0'=(1-a^2)x^2,\quad c_3'=1-b^2,$$
$$c_1'=(1-2ab+a^2)x^2-2(1-a^2)x,$$
$$c_2'=(1-2ab+b^2)x^2-2(1-b^2)x,$$

where $x=C_B/C_A$, as before. A qualitative, graphical study of the functions $\operatorname{Re} h_\pm(z)$ at various energies, aided by a calculation of the roots of Eq. (26), shows that: (1) In the doubly forbidden energy region,[14] $|a|>1$ and $|b|>1$, Eq. (26) has three real roots. Two of these roots correspond to saddle points through which the path of integration must pass, but for one of them $h_+(z_2)<\mu$ so that it contributes nothing in the limit as $N\to\infty$. Thus, the only contribution to $\langle f\rangle$ is from one real saddle point and therefore the doubly forbidden region is a forbidden band for the random alloy. (2) In the singly allowed region, $|a|>1$ and $|b|\leq 1$, there are two different cases that arise. For energies above a certain critical energy, $E_c$, Eq. (26) has three real roots and the situation is the same as it is for the doubly forbidden region. For energies less than $E_c$, Eq. (26) has one real and two complex conjugate roots and the situation is the same as it is for the doubly allowed region that will be discussed next. (3) In the doubly allowed region, $|a|\leq 1$ and $|b|\leq 1$, Eq. (26) has one real and two complex conjugate roots. The real root does not contribute and one of the complex roots is a saddle point of $h_+$ while the other is a saddle point of $h_-$ so that $\langle f\rangle$ is given by Eq. (23). Energies in this region are in an allowed band for the random alloy.

Since the energy regions for which the random alloy has a forbidden band correspond to the regions for which Eq. (26) has three real roots, while regions for which the random alloy has an allowed band correspond to the regions for which Eq. (26) has one real and two complex roots, it follows that the allowed and forbidden bands can be specified by an investigation of the energy dependence of the discriminant of this cubic equation alone. Thus, we have a relatively simple criterion for specifying the forbidden bands of a Kronig-Penney random alloy that is more restrictive than the one

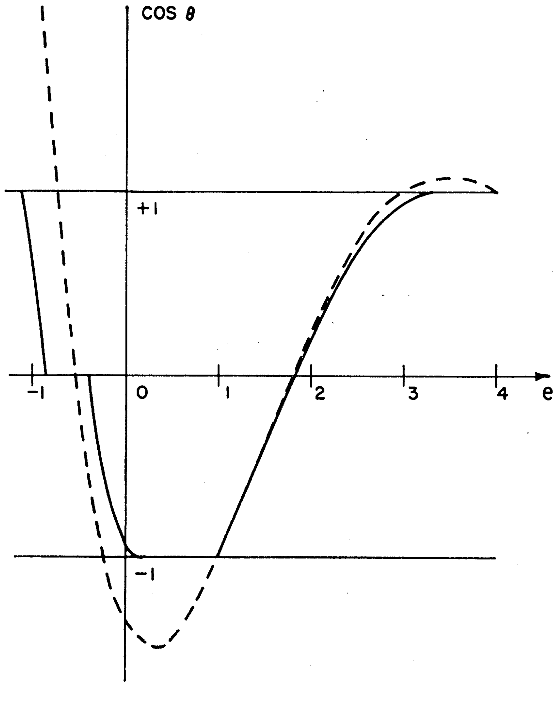

FIG. 2. Cos$\theta$ as a function of the reduced energy $e=(8md^2/h^2)E$ for a Kronig-Penney model with $P_A=\pi$, $P_B=\pi/2$, $C_A=C_B=\frac{1}{2}$. Solid curve represents present theory; dashed curved, virtual-crystal method.

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[14] Since trace $\mathfrak{A}=2a$, an energy region for which $|a|>1$ is a forbidden band for a crystal made up of $A$ atoms, while a region for which $|a|\leq 1$ is an allowed band.

proved by Luttinger, although there is no conflict between the two criteria.

In order to get more detailed information about the number of states in each allowed band and about the distribution of these states within the band, we have determined numerically the energy dependence of $\theta$, and used Eq. (25). It is convenient to plot $\cos\theta$ versus $E$ rather than $\theta$ itself, and this is shown in Fig. 2 for the case $P_A=-\pi$, $P_B=-\pi/2$, and $C_A=C_B=\frac{1}{2}$. For comparison we also plot in that figure a calculation of $\cos\theta$ using the virtual-crystal approximation of Nordheim[15] and Muto.[16] The virtual-crystal approximation, which is based on perturbation theory, reduces for the simple Kronig-Penney case to replacing the random lattice with the potential

$$V_n(x_n)=(\hbar^2/md)(C_AP_A+C_BP_B)\delta(x_n-\tfrac{1}{2}d). \qquad (27)$$

For a periodic lattice we have, from Eq. (7), $\theta=kd$.

In Fig. 3 we show the allowed and forbidden bands of the random alloy compared with those of the pure $A$ crystal, the pure $B$ crystal, and the ordered $AB$ alloy. The number that appears in each allowed band is the number of states in that band.

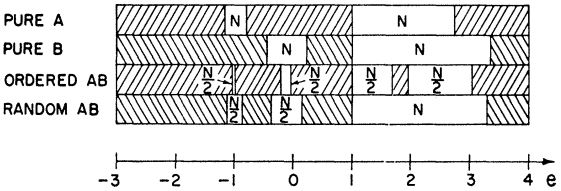

FIG. 3. Allowed and forbidden bands in a one-dimensional crystal. The numbers in blank spaces which represent the allowed bands, give the number of states.

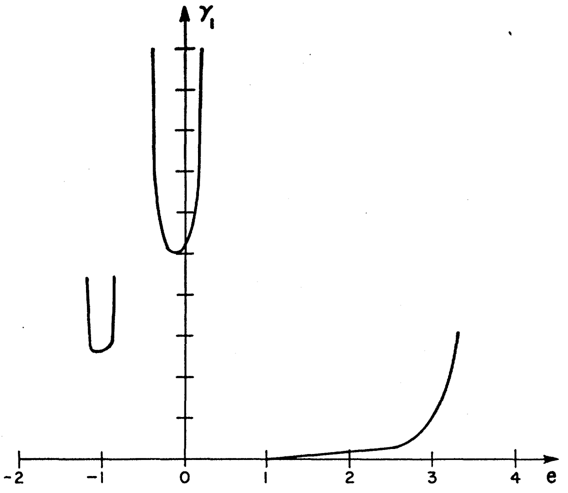

FIG. 4. The parameter $\gamma_1$ as a function of the reduced energy $e$.

The results of this investigation can be summarized as follows: (1) The lowest lying allowed band of the random alloy, which is in a region of negative energy, contains a number of states equal to the number of $A$ atoms in the crystal. (The $A$ atom in our example has the deeper well.) (2) The next allowed band contains a number of states equal to the number of $B$ atoms in the crystal. (Of course, the factors of $\frac{1}{2}$ occur in these zones in Fig. 2 because $C_A=C_B=\frac{1}{2}$.) (3) The allowed bands that lie in higher energy regions each contain $N$ states and $\theta$ behaves qualitatively as in the higher band shown. (4) The distribution of the states within these high energy allowed zones is quite like the distribution that is obtained from the Nordheim-Muto virtual-crystal model except that the density of states tails off more slowly at the high-energy end of the allowed zone. Results 1 and 2 corresponds to the appearance of localized states associated with the bound state of the $A$ or $B$ atoms, while result 4 is in agreement with the suggestions of Parmenter[17] as to the corrections that should be made to the Nordheim-Muto theory.

Additional calculations show that the two low-energy sub-bands each containing $N/2$ states coalesce into one band with $N$ states when the difference in potentials, $P_A-P_B$, is made smaller.

The quantity $\gamma_1$, as can be seen from Fig. 4, is large in the two low-lying allowed zones. In the allowed zone of higher energy, it is zero at the low-energy end, it increases slowly as the doubly allowed zone is traversed, and it increases more rapidly in the singly allowed zone.

Although the machine calculations of Landauer and Helland[2] were for a finite crystal made up of two different types of square wells, certain of their results may be compared with ours. In particular, they also obtained allowed bands in the negative energy regions made up of localized states, whereas at higher energies some of the forbidden bands which occur for the ordered $AB$ alloy are absent in the case of the random $AB$ alloy.

Thus, the band structure that our method predicts for the Kronig-Penney model of a random alloy is in agreement with that which one would expect from the work of Luttinger, Parmenter, and Landauer and Helland.

## V. GENERALIZATIONS

In the above, only the periodic boundary conditions of Eq. (2) were considered. It can be shown from Eq. (4) that the fixed end-point boundary conditions, $\Psi(0)=\Psi(Nd)=0$, are satisfied at those energies for which the element $P_{21}{}^i$ of the matrix $\mathbf{P}^i$ [see Eq. (9)] vanishes. The average of the functions $P_{21}{}^i$ over all possible permutations is given by

$$\langle\mathbf{P}\rangle_{21}=\frac{1}{2\pi i}\binom{N}{r}^{-1}\oint D^{N-1}(\mathfrak{A}_{21}+z\mathfrak{B}_{21})\frac{\sin Np}{\sin p}dz,$$

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[15] L. Nordheim, Ann. Physik **9**, 607 and 641 (1931).

[16] T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **34**, 377 (1938).

[17] R. H. Parmenter, Phys. Rev. **97**, 587 (1955).

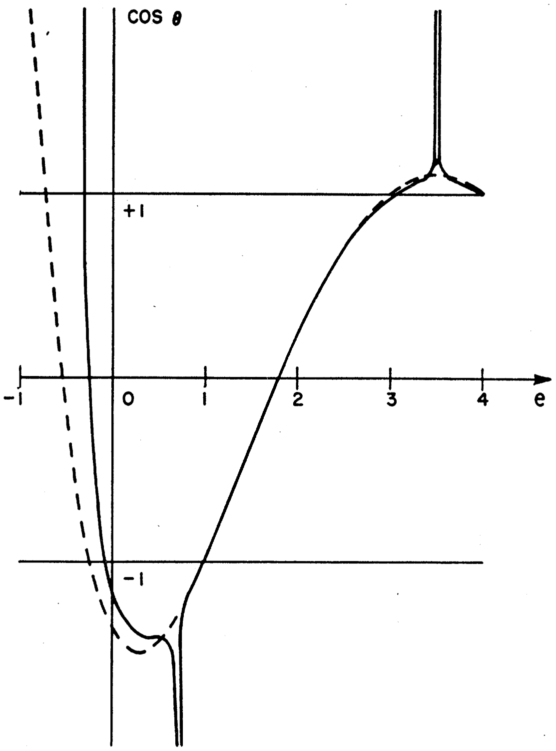

FIG. 5. Cos$\theta$ as a function of $e$ as obtained with the scattering-matrix method (solid curve) (reference 18), and with the virtual-crystal method (dashed curve).

where the quantities appearing in this integral are as defined in the preceding sections of this paper, and the contour of integration encloses the origin. An asymptotic expression for this integral would be expected to reflect the properties of $P_{12}{}^{i}$ for any random sequence, and could thus be made the basis of a band structure investigation for the fixed end-point boundary conditions.

The band structure for a random alloy made up of more than two types of atoms can be described by replacing the contour integral of Eq. (11) with a multiple contour integral. Also, the unit cells of the different types of atoms that occur in the crystal can have different lengths, since the properties of the matrices needed for the derivation of Eq. (11) are not affected by this change.

Another type of random system on which band structure investigations have been made recently is the one-dimensional liquid metal. By this is meant a linear array of atoms which are all of one kind, but whose positions are random. A simple model of such a system to which our method can be applied is obtained by considering a random sequence of atoms and spacers, the spacers being short cells in which the potential is zero.

Although the methods described in this paper can be applied to many one-dimensional problems of interest, a generalization to three-dimensional problems would not be straightforward. It can still be used to check the validity of approximate three-dimensional theories, such as the one developed by one of us,[18] by applying the latter to a one-dimensional case. This was done for a simple Kronig-Penney model. The results are shown in Fig. 5, where we have plotted cos$\theta$ as a function of $E$ as found with the method of reference 18 and as calculated with the virtual-crystal method. Although we do not get the splitting of the lowest band into sub-bands, as predicted by our present work, the correction to the virtual-crystal theory in the higher energy bands is in the right direction.

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[18] J. Korringa, J. Phys. Chem. Solids 7, 252 (1958).