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Electronic States of a Kronig-Penney Crystal with Random Atomic Positions

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The density of states for a one-dimensional system of r identical δ-function atoms randomly distributed on N lattice sites (lattice spacing d) is derived in the limit as r and N approach infinity by a nonperturbational method. The case for which only one atom is allowed on a lattice site (F-D) and the case for which this restriction is dropped (B-E) are both treated. In the limit as r/N and d approach zero, keeping the average number of atoms per unit length fixed, a common limit for the density-of-states function is approached in the F-D and B-E cases. This limiting function is identical with the one found by Klauder using a Brueckner-like approximation.

I. INTRODUCTION

STUDIES of the behavior of an electron in a field of randomly distributed scattering centers are relevant to the understanding of solids with defects, disordered alloys, liquid metals, and the like. Since the application of finite-order perturbation theory to this problem leads to misleading results, it has been necessary to devise other techniques and to concentrate on rather simple models.

A one-dimensional model that has been the focus of considerable interest assumes that identical scattering centers are positioned along the x axis according to a Poisson distribution and that the potential function describing the interaction between the electron and each scatterer is a δ function. Lax and Phillips[1] adapted the node-counting method of James and Ginzbarg[2] to find the integrated density of states for this problem numerically. Frisch and Lloyd[3] treated it analytically using methods from probability theory. Klauder[4] used the Green's function method of many-body theory to investigate several models. He calculated the density of states for the one-dimensional δ-function model in detail using five different types of restricted diagram summations. Methods similar to Klauder's have been applied to the problem of electrical conductivity and to density-of-states calculations.[5]

Throughout this paper we will use a saddle-point method originally put forward by Korringa and the present author[6] to treat one-dimensional models of random binary alloys. The starting point for this method is the matrix formulation introduced by Kramers[7] and developed to a high degree of generality by James[8] which has been used for several treatments[9,10] of the electronic and vibrational states of one-dimensional lattices. We consider arrays of r identical δ-function atoms randomly distributed on N lattice sites as r and N approach infinity. The case where only one atom is allowed on a lattice site (F-D) and where this restriction is dropped (B-E) is treated.

In Sec. II we briefly discuss the assumptions behind the saddle-point method and review the equations for the integrated density of states obtained from it with particular reference to the problems under consideration here. An extension of the method whereby the density of states can be worked out directly from a knowledge of the saddle points is shown. The results of some calculations are given in Sec. III, and certain disagreements with the exact results of Refs. 1 and 3 are pointed out. In Sec. IV we prove analytically that our results, for both cases, become identical with Klauder's Brueckner approximation in the limit as r/n and the lattice spacing approach zero in such a way as to keep the number of atoms per unit length fixed, and we discuss possible interpretations of our results.

II. THE SADDLE-POINT APPROACH

We will consider a one-dimensional lattice made up of N cells each having the same length d. We wish to find eigenvalues of the system,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi=E\psi\,,\qquad \psi(0)=\psi(Nd)\,,\quad \psi'(0)=\psi'(Nd)\,,\tag{1}$$

where the potential, $V(x)$, is defined by specifying its form in each cell. This problem can be treated[6-8] by investigating the trace of the product matrix $\mathbf{P}=\mathbf{X}_0\mathbf{X}_1\mathbf{X}_2\cdots\mathbf{X}_{N-1}$, where $\mathbf{X}_n$ is a 2×2 matrix that depends on the potential in the nth cell and on the energy,

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E. The eigenvalues of the system defined in Eq. (1) are those energies for which $f(E)=\text{trace }\mathbf{P}=2$.

For the models that we are interested in, the potential is defined by giving the number of identical δ-function atoms in each cell. If the nth cell contains q atoms, then in the interval $nd\leqq x\leqq (n+1)d$,

$$V(x)=-q(\hbar^2P/md)\delta(x-(n+\tfrac{1}{2})d)\,,$$

where P is a positive quantity. The exact form of the matrix $\mathbf{X}_n$ will depend on the method used to construct it. Using the method of James,[8] we obtain for a cell containing q atoms

$$\mathbf{A}_q=\mathbf{A}_0+q\mathbf{D}\,, \tag{2}$$

where

$$\mathbf{A}_0=\begin{pmatrix} \cos\alpha d, & -\alpha\sin\alpha d \\ (1/\alpha)\sin\alpha d, & \cos\alpha d \end{pmatrix},$$

and

$$\mathbf{D}=(P/\alpha d)\begin{pmatrix} -\sin\alpha d, & -\alpha(\cos\alpha d+1) \\ (\cos\alpha d-1)/\alpha, & -\sin\alpha d \end{pmatrix},$$

with $\alpha=(2mE)^{1/2}/\hbar$.

Let us first consider a system in which r atoms are distributed over the N cells with the restriction that no more than one atom can be in a given cell. The product matrix for such a system is of the form $\mathbf{P}^i(N,r)=\mathbf{A}_0\mathbf{A}_0\mathbf{A}_1\cdots\mathbf{A}_1\mathbf{A}_0\mathbf{A}_1$, where the order in which the $\mathbf{A}_0$ and $\mathbf{A}_1$ matrices appear in this product is the same as the order in which the empty and filled cells appear in the crystal. The superscript i indicates which of the $\binom{N}{r}$ distinct crystals that can be formed in this way is meant. We know that the eigenvalues for a particular crystal are those energies for which $f^i(E)=\text{trace }\mathbf{P}^i=2$. Although each crystal will have a different set of eigenvalues, we feel sure that in the limit as N and r approach infinity, the distribution of eigenvalues (as described by a density of states or integrated density of states function) will approach a limiting distribution for all but a fraction of the crystals which goes to zero in the limit. We make the statistical assumption that this limiting distribution can be found from the asymptotic form of the ensemble average of the trace functions,

$$\langle f\rangle_{\text{F-D}}=\binom{N}{r}^{-1}\sum_i f^i,$$

and is in fact the distribution of the energy values for which $\lim_{N,r\to\infty}\langle f\rangle_{\text{F-D}}=2$. We will sometimes loosely refer to these energy values as the eigenvalues of the random system. This assumption is also discussed in Sec. I, and possible difficulties with it are given in Sec. IV. The coefficient of z^r in the expansion of $(\mathbf{A}_0+z\mathbf{A}_1)^N$ is the sum of all possible products of $(N-r)$ matrices $\mathbf{A}_0$ with r matrices $\mathbf{A}_1$. Also, the sum of the traces of a set of matrices is the trace of the sum of the matrices. Thus, the average trace can be found from

$$\langle f\rangle_{\text{F-D}}=\text{trace}\langle\mathbf{P}\rangle_{\text{F-D}}\,, \tag{3}$$

where

$$\langle\mathbf{P}\rangle_{\text{F-D}}=\binom{N}{r}^{-1}\frac{1}{2\pi i}\oint(\mathbf{A}_0+\mathbf{A}_1z)^{N}z^{-r-1}dz\,, \tag{4}$$

the contour of integration enclosing the origin. The subscript F-D is used for this case because the scattering atoms are distributed as noninteracting particles obeying Fermi-Dirac statistics.

The r atoms can also be distributed over N cells in such a way that any number of atoms (up to r) can appear in a cell. To describe such distributions by the matrix method it is necessary to use the matrices $\mathbf{A}_q$ of Eq. (2) with $q=0, 1, 2\cdots, r$. The sum of all possible products of N matrices such that $\sum_q q\times$(number of times $\mathbf{A}_q$ appears)$=r$ is given by the coefficient of z^r in the expansion of $(\mathbf{A}_0+\mathbf{A}_1z+\mathbf{A}_2z^2+\mathbf{A}_3z^3+\cdots)^N$, and the number of such products that can be formed is $\binom{N+r-1}{r}$. Thus, the average trace for this case can be found from

$$\langle f\rangle_{\text{B-E}}=\text{trace}\langle\mathbf{P}\rangle_{\text{B-E}}\,, \tag{5}$$

where

$$\langle\mathbf{P}\rangle_{\text{B-E}}=\binom{N+r-1}{r}^{-1}\frac{1}{2\pi i}\oint(\mathbf{A}_0+\mathbf{A}_1z+\mathbf{A}_2z^2+\cdots)^{N}\times z^{-r-1}dz\,. \tag{6}$$

The atoms in this case are distributed as noninteracting Bose-Einstein particles, which accounts for the subscript. It must be admitted that the B-E case has no physical meaning because of the superposition of atomic potentials, but it is useful for discussing some formal questions that have been raised by other treatments of this problem.

The integrals shown in Eqs. (4) and (6) could be used to find $\langle\mathbf{P}\rangle$ for any kind of atomic potential. They simplify considerably for δ functions, however, because of the particularly simple form that the matrices $\mathbf{A}_q$ take for this case. Using Eq. (2) and the Taylor's expansion for $1/(1-z)$ we can rewrite $\langle\mathbf{P}\rangle_{(\text{F-D})}$ and $\langle\mathbf{P}\rangle_{\text{B-E}}$ in the form

$$\begin{aligned}\langle\mathbf{P}\rangle_{\text{F-D}}&=\binom{N}{r}^{-1}\frac{1}{2\pi i}\oint(1+z)^N\mathbf{M}_1{}^Nz^{-r-1}dz\,,\\ \langle\mathbf{P}\rangle_{\text{B-E}}&=\binom{N+r-1}{r}^{-1}\frac{1}{2\pi i}\oint(1-z)^{-N}\mathbf{M}_2{}^Nz^{-r-1}dz\,,\end{aligned} \tag{7}$$

where

$$\begin{aligned}\mathbf{M}_1&=\mathbf{A}_0+z\mathbf{D}/(1+z)\,,\\ \mathbf{M}_2&=\mathbf{A}_0+z\mathbf{D}/(1-z)\,.\end{aligned} \tag{8}$$

There are a number of ways to evaluate the Nth power of the matrices $\mathbf{M}_1$ and $\mathbf{M}_2$, but we will use a method adapted from the work of Luttinger.[11] The matrices $\mathbf{G}_1$ and $\mathbf{G}_2$ are defined by

$$\begin{aligned}\mathbf{G}_1&=(\mathbf{M}_1-\cos p\mathbf{I})/i\sin p\,,\\ \mathbf{G}_2&=(\mathbf{M}_2-\cos q\mathbf{I})/i\sin q\,,\end{aligned}\tag{9}$$

where

$$\cos p=\tfrac{1}{2}\mathrm{trace}\mathbf{M}_1\quad \cos q=\tfrac{1}{2}\mathrm{trace}\mathbf{M}_2\,,\tag{10}$$

and $\mathbf{I}$ is the unit matrix. From Eq. (9) and the fact that $\mathbf{G}_1{}^2=\mathbf{G}_2{}^2=\mathbf{I}$ it can be shown that $\mathbf{M}_1=\exp(ip\mathbf{G}_1)$ and $\mathbf{M}_2=\exp(iq\mathbf{G}_2)$; hence,

$$\begin{aligned}\mathbf{M}_1{}^N&=\cos Np\mathbf{I}+i\sin Np\mathbf{G}_1\,,\\ \mathbf{M}_2{}^N&=\cos Nq\mathbf{I}+i\sin Nq\mathbf{G}_2\,.\end{aligned}\tag{11}$$

These expressions can be inserted in Eqs. (7), and the trace taken to find $\langle f\rangle_{\text{F-D}}$ and $\langle f\rangle_{\text{B-E}}$. Since trace $\mathbf{G}_1=$ trace $\mathbf{G}_2=0$ for all z, the second terms in Eqs. (11) do not contribute. We obtain, then,

$$\begin{aligned}\langle f\rangle_{\text{F-D}}&=K^++K^-\,,\\ \langle f\rangle_{\text{B-E}}&=L^++L^-\,,\end{aligned}\tag{12}$$

with

$$\begin{aligned}K^\pm&=\binom{N}{r}^{-1}\frac{1}{2\pi i}\oint\exp Ng_\pm dz\,,\\ L^\pm&=\binom{N+r+1}{r}^{-1}\frac{1}{2\pi i}\oint\exp Nh_\pm dz\,,\end{aligned}\tag{13}$$

and

$$\begin{aligned}g_\pm&=\pm ip+\ln(1+z)-(\xi+1/N)\ln z\,,\\ h_\pm&=\pm iq-\ln(1-z)-(\xi+1/N)\ln z\,,\end{aligned}\tag{14}$$

where $\xi=r/N$.

Since our primary interest is in infinite crystals, it is natural to use the saddle-point method to evaluate the integrals in Eqs. (13) asymptotically in the limit as N and r approach infinity.

For the F-D case the equations for the saddle points of K^+ and K^-, $dg_\pm/dz=0$, lead to the same quartic equation. After factoring out $1+z$, the following cubic equation is obtained:

$$\begin{aligned}&\sum_{n=0}^{3}F_nz^n=0\,,\\ &F_3=-2R+P(1-2\mathcal{E}),\quad F_0=-2PX^2\mathcal{E}\,,\\ &F_2=-P(1+2\mathcal{E})+2X[2R-P(1-2\mathcal{E})]\,,\\ &F_1=4XP\mathcal{E}-2X^2(R+P\mathcal{E})\,,\end{aligned}\tag{15}$$

where $X=\xi/(1-\xi)$, $R=\alpha d\cot\alpha d$, and $\mathcal{E}=(md^2/\hbar^2P^2)E$. In terms of the dimensionless energy $\mathcal{E}$ introduced above, R can be rewritten in the form $R=(2\mathcal{E})^{1/2}\cot P(2\mathcal{E})^{1/2}$.

If the energy is such that Eq. (15) has one real and two complex-conjugate roots, and investigation of the function $\mathrm{Re}g_+$ shows that the saddle point which must be used to evaluate K^+ is one of the complex roots which we will call t. The Riemann sheets that make $g_\pm$ single valued can be chosen such that $g_-(z^*)=g_+{}^*(z)$. The saddle point for K^- turns out to be t^* and $K^-=(K^+)^*$. The average trace can now be evaluated for this case:

$$\langle f\rangle_{\text{F-D}}=Q_1\cos(N\theta_1+\delta_1)\exp N\gamma_1\,,\tag{16}$$

where

$$\begin{aligned}\theta_1&=\mathrm{Im}g_+(t)\,,\\ Q_1&=2[\xi(1-\xi)]^{1/2}|g_+{}''(t)|^{-1/2}\,,\\ \gamma_1&=\mathrm{Re}g_+(t)-\mu_1\,,\\ \delta_1&=-\tfrac{1}{2}\arg g_+{}''(t)\,.\end{aligned}\tag{17}$$

The quantity μ_1 and other factors in these equations were taken from an asymptotic expression for $\binom{N}{r}$ which can be found from Stirling's approximation or the saddle-point method

$$\begin{aligned}\binom{N}{r}&=[2\pi N\xi(1-\xi)]^{-1/2}\exp N\mu_1\,,\\ \mu_1&=-(1-\xi)\ln(1-\xi)-\xi\ln\xi\,.\end{aligned}$$

From the fact that the saddle-point method gives the leading term in an asymptotic expansion, it follows that γ_1 must be positive. Also, although it has no effect on the value of the integral in Eq. (16), it is convenient to choose our Riemann sheets in such a way that θ_1 is a nondecreasing function of the energy.

If the energy is such that Eq. (15) has three real roots, it can be shown that $|\langle f\rangle_{\text{F-D}}|$ is greater than 2. We will call such energies forbidden. Energies for which Eq. (15) has one real and two complex roots will be called allowed.

In accordance with our statistical assumption, we take the eigenvalues of the random system to be those energies for which $\langle f\rangle_{\text{F-D}}=2$. From the form of Eq. (16) it can be seen that if θ_1 is a nondecreasing function of the energy then the number of eigenvalues of the system having energies less than some allowed energy $\mathcal{E}$ is $N\theta_1(\mathcal{E})/\pi$. In order to compare with other work, we will be interested in the number of states *per atom* having an energy less than $\mathcal{E}$, i.e., the integrated density of states

$$N_1(\mathcal{E})=(1/\pi\xi)\theta_1(\mathcal{E})\,.\tag{18}$$

Since there are no eigenvalues in the forbidden energy regions, the above definition can be extended if we define θ_1 in such a region to be a constant equal to the maximum value that it took on in the preceding allowed region. Thus, by solving Eq. (15) for a large number of energies and using the saddle points to evaluate θ_1, we can plot the integrated density of states as a function of the energy. The energy dependence of other functions in Eqs. (17), such as γ_1, can also be investigated, but we will not make use of them in this paper.

It is useful to notice that the density of states $\rho_1(\mathcal{E})=dN_1/d\mathcal{E}$ can be found from the saddle points

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[11] J. M. Luttinger, Phillips Res. Rept. 6, 303 (1951).

without going through the process of numerically differentiating $N_1(E)$. Using Eq. (17), we have

$$\frac{d\theta_1}{d\mathcal{E}}=\mathrm{Im}\left(\frac{dg_+}{d\mathcal{E}}\right)=\mathrm{Im}\left(\frac{\partial g_+}{\partial t}\frac{dt}{d\mathcal{E}}+\frac{\partial g_+}{\partial \mathcal{E}}\right),$$

but $\partial g_+/\partial t=0$ because this is just the equation that defines the saddle-point t. The only explicit energy dependence of the function g_+ comes from the function p defined in Eq. (10). Carrying through the differentiation, we have

$$\rho_1(\mathcal{E})=(P/\pi\xi)\times\mathrm{Re}\{[1+(R-1)t/2P\mathcal{E}(1+t)]f_1^{-1/2}\}, \quad (19)$$

where

$$f_1=2\mathcal{E}+2Rt/P(1+t)-t^2/(1+t)^2,$$

and R was defined following Eq. (15).

An analysis similar to the above can be carried out for the B-E case. The equations for the saddle points of L^+ and L^-, $dh_\pm/dz=0$, again lead to the same quartic equation. After factoring out $1-z$, the following cubic equation is obtained:

$$\sum_{n=0}^{3} B_n z^n=0,$$

$$\begin{aligned}&B_3=-2R-P(1-2\mathcal{E}),\quad B_0=-2PY^2\mathcal{E},\\&B_2=-P(1+2\mathcal{E})+2Y[2R+P(1-2\mathcal{E})],\\&B_1=4YP\mathcal{E}-2Y^2(R-P\mathcal{E}),\end{aligned}\quad (20)$$

where $Y=\xi/(1+\xi)$ and the other quantities were defined for Eq. (15). The energies for which this equation has one real and two complex-conjugate roots are called allowed, while those for which it has three real roots are called forbidden. For all forbidden energies, $|\langle f\rangle_{\text{B-E}}|>2$. The saddle point that is used to evaluate L^+ for allowed energies is one of the complex roots of Eq. (20) which we will call u. The corresponding saddle point of L^- is u^*, and $L^-=(L^+)^*$. The average trace for this case is

$$\langle f\rangle_{\text{B-E}}=Q_2\cos(N\theta_2+\delta_2)\exp N\gamma_2, \quad (21)$$

where

$$\begin{aligned}&\theta_2=\mathrm{Im}h_+(u),\\&Q_2=2[\xi(1+\xi)]^{1/2}|h_+''(u)|^{-1/2},\\&\gamma_2=\mathrm{Re}h_+(u)-\mu_2,\\&\delta_2=-\tfrac{1}{2}\arg h_+''(u).\end{aligned}\quad (22)$$

We have used the asymptotic expression

$$\binom{N+r-1}{r}=[2\pi N\xi(1+\xi)]^{-1/2}\exp N\mu_2,$$

where

$$\mu_2=(1+\xi)\ln(1+\xi)-\xi\ln\xi.$$

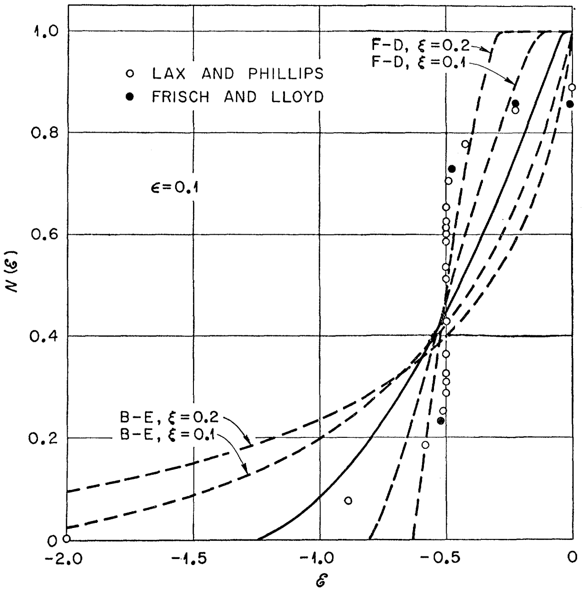

FIG. 1. Integrated density of states for negative energies, $\epsilon=0.1$. The solid curve is calculated from Eqs. (25) and (26) and represents the continuum case.

The integrated density of states for this case is given by

$$N_2(\mathcal{E})=(1/\pi\xi)\theta_2(\mathcal{E}), \quad (23)$$

and the density of states can be calculated from

$$\rho_2(\mathcal{E})=\frac{P}{\pi\xi}\mathrm{Re}\{[1+(R-1)u/2P\mathcal{E}(1-u)]f_2^{-1/2}\}, \quad (24)$$

where

$$f_2=2\mathcal{E}+2Ru/P(1-u)-u^2/(1-u)^2.$$

III. RESULTS OF CALCULATIONS

We will describe our calculations in terms of the dimensionless variables, ϵ and $\mathcal{E}$, used in Refs. 1, 3, and 4. It is easy to show that the average number of atoms per unit length in the models we are considering is given by $n=\xi/d$. The wave function and energy of the bound state of an isolated δ-function atom as is used in Sec. II are given by $\psi_0\propto\exp(-\kappa_0|x|)$ and $E_0=-(\hbar^2/2m)\kappa_0^2$, where $\kappa_0=P/d$. The dimensionless density ϵ is defined by $\epsilon=n/\kappa_0=\xi/P$. We have already used the dimensionless energy $\mathcal{E}=-\tfrac{1}{2}E/E_0$ in Sec. II.

Inserting $P=\xi/\epsilon$ into the expressions of Sec. II we have calculated the integrated density of states as a function of $\mathcal{E}$ for F-D and B-E models using various values of ξ and ϵ. Some of these calculations, for $\epsilon=0.1$, are shown in Fig. 1. It can be seen that the curves for the F-D and B-E cases approach the same limiting curve as ξ approaches zero. This approach is even more rapid in the positive energy region which is not shown in the figure. From the construction of our models it is clear that the distribution of scattering

TABLE I. Integrated density of states for positive energies $\epsilon=0.1$.

$(2\mathcal{E})^{1/2}$	Lax and Phillips	Continuum case
$0.05\,\pi$	1.044	1.0607
$0.10\,\pi$	1.442	1.4428
$0.15\,\pi$	1.882	1.8767
$0.20\,\pi$	2.342	2.3283

atoms approaches a continuous distribution if ξ and d approach zero in such a way as to keep n fixed. We will call this the continuum case.

Under the assumption that ξ is very small the expressions of Sec. II simplify. The quantity R can be expanded in a Taylor's series, $R=1-\frac{2}{3}\xi^2\mathcal{E}/\epsilon^2+\cdots$. The saddle points for the F-D and B-E cases become equal and proportional to ξ. Thus, $t=u=\xi v$, where v is a complex root of

$$2\epsilon v^3+(1+2\mathcal{E}-4\epsilon)v^2+2(\epsilon-2\mathcal{E})v+2\mathcal{E}=0. \quad (25)$$

The density of states and integrated density of states are given by

$$\begin{aligned}\rho(\mathcal{E})&=1/\pi\epsilon\,\mathrm{Re}f^{-1/2},\\ N(\mathcal{E})&=1/\pi\epsilon\,\mathrm{Re}f^{1/2}+1/\pi\,\mathrm{Im}(v-\ln v),\end{aligned} \quad (26)$$

where

$$f=2(\mathcal{E}+\epsilon v).$$

We have no doubt that this limiting process is convergent because the integrated density-of-states curve calculated from Eqs. (18) and (23) for $\epsilon=0.1$ and $\xi=0.01$ is so close to the one calculated from Eq. (26) that it could not be displayed in Fig. 1. In the next section we will show that this expression for the density of states for the continuum case is identical with one obtained by Klauder using the Brueckner approximation.

Klauder has already compared his results with the exact results of Refs. 1 and 3 so only a few points will be touched on here. It seems certain that the distribution of scattering atoms is the same for our continuum model as in the Poisson model.

For $\epsilon\gtrsim 1$ our $N(\mathcal{E})$ curves for the continuum case agree very well with the exact results for both positive and negative energies except that their curves show a small tail extending down to arbitrarily low energies. The occurrence of very low energy eigenvalues that would cause such a tail has been attributed to the superposition of atomic potentials. For finite ξ we do get a tail extending toward low energies for our B-E model, but this disappears as ξ approaches zero. Since the results for the B-E and F-D models become identical as $\xi\to 0$, it can be seen that the superposition of atoms has no effect on the integrated density of states *per atom* for the continuum case in our results.

For $\epsilon\lesssim 1$ our continuum results agree with the exact results for positive energies as is shown for $\epsilon=0.1$ by the values of $N(\mathcal{E})$ given in Table I. For negative energies, however, there are serious discrepancies. To illustrate this we plot the data points from Refs. 1 and 3 for $\epsilon=0.1$ in Fig. 1. The disagreement between these curves can be discussed in terms of three main features: (1) The exact results predict an infinity in the density-of-states function for $\mathcal{E}=-\frac{1}{2}$ (the energy of the bound state of the δ-function atoms in dimensionless units). This agrees with a formula first derived by Schmidt[9] and improved by Lax and Phillips. The Schmidt formula was also derived from Frisch and Lloyd's expressions by Morrison.[12] According to our calculations the density of states for the continuum case has a maximum in the negative energy region for $\epsilon<\frac{1}{8}$. For $\epsilon=0.1$, the maximum value $\rho_{\max}=1.35259$ occurs at an energy $\mathcal{E}=-0.124$; for $\epsilon=0.01$, $\rho_{\max}=3.25318$ at $\mathcal{E}=-0.456$; and for $\epsilon=0.001$, $\rho_{\max}=10.08699$ at $\mathcal{E}=-0.496$. From the trend shown by these numbers, it can be seen that our results agree with the exact ones only in the limit as $\epsilon\to 0$. (2) Klauder has already pointed out that the integrated density of states for the continuum case at $\mathcal{E}=0$, $N(0)$, becomes equal to 1 for all $\epsilon\leqq\frac{1}{8}$. Since we have an expression for $N(\mathcal{E})$ [Eq. (26)] we can go even further to show that for any ϵ

$$N(0)=(\psi+\sin\psi)/\pi, \quad (27)$$

where

$$\cos\psi=1-\tfrac{1}{4}\epsilon.$$

In Table II we compare the exact values for $N(0)$ with those obtained from Eq. (27). We also show calculations of this quantity based on the Schmidt approximation mentioned above and the optical model proposed by Lax and Phillips and rederived from their respective points of view by Frisch and Lloyd, and Klauder. Our expression for $N(0)$ becomes identical with the optical model for large ϵ. It can be seen from this table that the results of Eq. (27) agree better with the exact results over the whole range of ϵ than those of either of the approximation methods, but the agreement is still not good. Our results also show a band of forbidden energies in the neighborhood of $E=0$ for $\epsilon<\frac{1}{8}$ that is not found in the exact results. (3) The

TABLE II. Integrated density of states for $\mathcal{E}=0$ and various ϵ.

ϵ	Lax and Phillips	Continuum case	Schmidt	Optical model
0.01	0.986	1.0000	0.9901	4.5016
0.10	0.892	1.0000	0.9112	1.4235
0.25	0.768	0.8183	0.8107	0.9003
0.50	0.607	0.6090	0.6982	0.6366
1.00	0.456	0.4406	0.5774	0.4502
2.00	0.320	0.3150	0.4874	0.3183
5.00	0.200	0.2005	0.4465	0.2013
10.00	0.141	0.1421	0.4445	0.1424

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[12] J. A. Morrison, J. Math. Phys. **3**, 1 (1962).

tail on the integrated density-of-states curve extending into negative energies becomes more pronounced for smaller ϵ. A similar effect occurs for our B-E case for finite ξ, but it vanishes as ξ approaches zero.

IV. DISCUSSION

An alternate approach to this problem is provided by the fact that the density of states for an electron moving in an array of scattering centers is proportional to the trace of the Green's function for the system. Klauder used this approach, making the statistical assumption that the density of states for a random system can be obtained from the ensemble average Green's function. He was then able to recast the problem into the form of a Fermi field (the electron) interacting with a Bose field (the scattering atoms). Diagrammatic methods can be used to analyze the calculation by perturbation theory of the Green's function for such a system. This problem is simpler than the ones that normally occur in solid-state theory because the bosons do not interact with each other and there is only one fermion.

For the one-dimensional problem with δ-function potentials Klauder was able to calculate the density of states for five different types of restricted diagram summations. He called his highest order approximation the Brueckner approximation because of the structure of the terms included. In this approximation he obtained

$$\rho(\mathcal{E})=\mathrm{Im}\Sigma_5/(\pi\epsilon)\,, \tag{28}$$

where Σ_5 is a root of the cubic equation

$$2\mathcal{E}\Sigma_5^3-2(\mathcal{E}+\epsilon)\Sigma_5^2+\Sigma_5-1=0\,. \tag{29}$$

Comparing Eqs. (26) and (28) it can be seen that the results for our limiting case are the same as Klauder's if the identification

$$\Sigma_5=i[2(\mathcal{E}+\epsilon v)]^{-1/2} \tag{30}$$

can be made. Substituting this expression for Σ_5 into Eq. (29) leads to an equation for v that is identical with Eq. (25).

It is interesting to note that the expression for the density of states obtained from Eqs. (30) and (28) has the same form as that of the optical model of Lax and Phillips except that the quantity ϵv in Σ_5 is replaced in their expression with ϵ. Their optical model describes the motion of an electron in a constant average potential which, in dimensionless units, is just ϵ. Replacing ϵ with ϵv is equivalent to using an average potential that is both complex and energy-dependent. We are thus led in a natural way to a formulation of our results and Klauder's that is like the optical model used in scattering theory.

For the problems that we have been considering here, the primary difference between the Green's function method and the matrix method is that the two-point boundary conditions for the eigenvalue problem are incorporated into the Green's function at the outset, whereas boundary conditions at only one point (e.g., defining the solution and its derivative at one point) are used in the matrix method. Since the Kramers' matrix gives the solution and its derivative at one end of the crystal in terms of the values at the other end, the two-point boundary conditions that serve to define the eigenvalues can be invoked at a later stage of the calculation.

At the present time, we do not know why the results that we get by treating an average trace function in a manner that appears to be exact in the asymptotic limit are identical with the results Klauder obtained by leaving out certain terms in the evaluation of an average Green's function. This Brueckner approximation seems to occupy a special position in the hierarchy of approximations to the Green's function in that the technical difficulties encountered in trying to go beyond it appear rather fundamental. From the comparison of our results with the exact calculations, it appears that averaging the trace functions performs a smoothing process on the density-of-states function. If one assumes that the average Green's function will give the exact density of states if it can be completely evaluated, it follows that the omission of diagrams which lead to the Brueckner approximation performs exactly the same smoothing process as averaging the trace function. Such a relationship is surprising, and an investigation of it might lead to a better understanding of the meaning of the Brueckner approximation for this problem. There is also the question as to whether the saddle-point approach will give the same results for other one-dimensional problems as the Green's function method when the latter is evaluated to the level of approximation discussed here. An affirmative answer to this question will mean that we have a simple method to investigate the gross features of the density of states and integrated density of states for a large variety of one-dimensional problems as described in I. On the other hand, the possibility cannot be ruled out that averaging the Green's function performs the same smoothing process on the density of states as averaging the trace function. This would provide the simplest explanation for the identity of the results, but it would mean that the ensemble average Green's function could not be used even in principle to find the exact density of states for a random system. It is harder to see how this smoothing would arise in the manipulation of Green's function than with trace functions.

Since the results of Frisch and Lloyd for infinite systems agree almost exactly with those of Lax and Phillips for systems made up of only 500 atoms, it is clear that the density of states per atom for most random chains having a given density ϵ must converge very rapidly to the asymptotic function for chains with that density. Since our results do not agree with theirs, it follows that the trace functions do not converge. From general theorems[7] about the trace functions, we know that they must oscillate rapidly as the energy traverses an allowed region with periods of the order of $1/N$, maxima greater than 2, and minima less than -2. From our calculations on specific systems, we know that the trace functions for the individual chains f^i are given by

$$f^i = 2C^N \cos(N\theta+\delta)+\nu_i\,, \tag{31}$$

where

$$\lim_{N,r\to\infty} \langle \nu_i \rangle = 0\,, \tag{32}$$

and C is larger than 1. There is nothing in the restriction of Eq. (32) that requires $\lim_{N,r\to\infty}\nu_i=0$ or that prevents the ν_i from making a systematic contribution to the density of states. The only conclusion that can be drawn is that the ν_i must be of the same order of magnitude and must oscillate as rapidly as the cosine term in Eq. (31). Although it is fairly simple to devise a general argument that explains why our procedure does not give exact results, it is more difficult to devise one that also explains why it gives as good an approximation as it does.

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Electronic Structure of Alloys*

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A theory of the electronic structure of alloys is presented which takes proper account of the symmetries present or absent in the alloy and does not rely on using Bloch's theorem either for the alloy or for the host metal. The band structure is worked out in an approximation which is exact for an ordered alloy and which gives a simple picture for a disordered substitutional alloy. Using this theory the band structure for the *d* electrons of the transition metal alloys is qualitatively discussed. The rigid band model is shown to fail for alloy constituents having a large valency difference and it is shown that the theory of this paper agrees with the experimental results both for magnetic moments and specific heats in such cases. A simple physical interpretation of these results is given using arguments similar to those of the conventional tight binding approximation. It is suggested that the difference between NiAl and FeAl alloys might be due to the aluminum conduction band lying above the nickel *d* band so that the latter fills, whereas the iron *d* band does not lie below the aluminum conduction band. No reference is made to theories of ferromagnetism, though it is possible that the methods used in this paper could be used to obtain a great deal more information from alloys of the transition metals than is available at the moment.

I. INTRODUCTION

THE purpose of this paper is to propose a theory of the electronic structure of alloys which is based on earlier work of Edwards and the author.[1–4] In this earlier work, the electronic structures of various disordered systems were discussed using a model of independent electrons moving in a total potential formed from individual ionic potentials which do not overlap each other. The positions of the ions are supposed to be given by some probability distribution. For example, in the case of a liquid the probability distribution can be taken as the distribution of given ionic positions as the liquid changes in time. The density of states can then be written down in terms of an average of the independent electron propagator over the distribution of systems. The averaging process can only be done approximately, but the approximation used is actually exactly true for a perfectly ordered system. The results obtained, therefore, give the correct limit in the case when the substance being considered has the form of a perfect crystal. The formalism is discussed in more detail later in this section. In the case of a perfect lattice this formalism is identical with that of Kohn and Rostoker,[5] which in the manner it will be applied in this paper avoids some of the difficulties usually associated with *d* electron band structure calculations. In such a formalism it is not necessary to distinguish whether the electrons are localized or free, though it is always helpful if they do belong to one of the limiting

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