One-Dimensional Impurity Bands

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The density of states of one-dimensional crystals consisting of δ functions randomly distributed has been calculated on the IBM 650 computer. The chains contained 500-1000 impurity atoms, and the most probable error in the integrated density of states at various energies was estimated to be at most $\frac{1}{2}\%$. Calculations were performed for various values of the parameter $\epsilon = n/\kappa_0$, where n is the density of atoms and κ_0 the attenuation constant appropriate to the isolated bound state. The results at different densities are compared with those obtained from various physical models. At low densities the machine results display a singularity in the density of states at the isolated atom energy. For $\epsilon \ll 1$, a simple pair theory fits the machine results quantitatively in the wings and displays a similar singularity. At high density ($\epsilon \gg 1$) the machine results are smooth and fitted well by a crude optical model, except for a tail below the band edge omitted by the latter. An optical model containing local density fluctuations provides a qualitative understanding of the tail and a fair over-all fit for $\epsilon \gtrsim 1$.

1. INTRODUCTION

X/**E** are concerned here with the distribution of oneelectron energy levels of an impurity band. The impurities are taken to be of a single kind, but randomly distributed, so that the translational periodicity characteristic of most energy bands is absent. The energy bands of disordered crystals have been treated by several authors.¹ Nearly all these treatments have been based on Nordheim's¹ virtual-crystal approximation; random deviations from the "average" potential are then treated by perturbation theory. As several of these authors recognized, this perturbational approach will not yield the localized negative energy states associated with the impurity band.

One evidently needs, in this problem, a method that is not perturbational in character and yet is readily applied in three dimensions. The multiple scattering treatment provides a means of attack that satisfies these requirements. In general the multiple scattering equations must then be solved by approximate procedures. The nature of our approximations, however, is independent of the dimensionality of the crystal. This suggests checking our ideas by specializing our treatment to the one-dimensional case. Numerical solutions are easily obtained for one-dimensional crystals, and in a way that is suitable for machine computation.

We were thus led to consider here the impurity bands of suitable one-dimensional crystals. We were primarily interested in the effect of the random distribution on the density of states. This effect was expected to be large in the low density or tight-binding limit, and to decrease as the density increased.

Several workers² have previously carried out machine calculations. We found that their results were insuffi-

cient for our purposes. This came about either because the calculations were done only at one density (James and Ginzbarg) or because the constituent concentrations considered were more appropriate for the study of alloys (Landauer and Helland).

The crystals studied by these authors consisted of two different kinds of square wells randomly distributed. The width and depth of each well constitutes two parameters each, the lattice constant is a fifth parameter, the density of impurities is a sixth and the energy is a seventh parameter. Clearly, it is impossible to make an adequate numerical exploration of these parameters to obtain qualitative understanding of the role of each parameter. Moreover, the chains used by Landauer and Helland were 150 atoms long, so that the number of nodes, N_{max} , associated with a minority constituent (at the "top" of the band) was of order 100, and the random error³ in this number is of order $(100)^{\frac{1}{2}}$. To get accuracies of order 1% it is clear that chains containing 500 to 1000 impurity atoms are necessary.3

In view of these considerations several simplifications were introduced.

1. We make the effective-mass approximation. This is valid for wavelengths large compared to the lattice spacing. Since the relevant wavelengths in an impurity band are comparable to or larger than the mean separation 1/n between impurities and the latter separation is large compared to the lattice constant for an impurity band (as contrasted with an alloy), the effective-mass approximation is automatically valid for our problem. This implies that we may neglect the periodic structure of the host lattice altogether. Thus we may set the host

¹L. Nordheim, Ann. Physik 9, 607 and 641 (1931); T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 34, 377 (1938); R. H. Parmenter, Phys. Rev. 97, 587 (1955). ²H. M. James and A. S. Ginzbarg, J. Phys. Chem. 57, 840 (1953); R. Landauer and J. C. Helland, J. Chem. Phys. 22, 1655 (1954).

³ For negative energies no more than one zero can occur between impurities. If there were N_{\max} impurities and if the zeros occurred impurities. If there were N_{\max} impurities and if the zeros occurred at random with probability p, for a given energy, the expected number of zeros would be $N = N_{\max}p$, and the standard deviation would be $[N_{\max}p(1-p)]^{\frac{1}{2}} = [N(1-p)]^{\frac{1}{2}}$. We find in practice (see Table II) that the errors are of this order (actually smaller by a factor of 2). Errors in estimating the differential density of states by taking differences between numbers of zeros at different energies can be (and were in our case) reduced by using the same random sequence of atoms at all energies.

potential equal to zero and allow the impurity atoms to assume random positions on a continuous domain.

2. The square wells of the impurities are replaced by delta functions.^{4,5} This is a good approximation if the width of the potential is small compared to the mean separation between impurities, and to the range $1/\kappa_0$ of the bound state wave function. It also has the advantage of leaving us with only the parameter of most interest, the density n, so that the effect of randomness can be studied as a function of the dimensionless parameter $\epsilon = n/\kappa_0$. The parameter ϵ gives approximately the mean number of impurities within range of a given impurity.

In Sec. 2 we describe the procedure used by the machine to calculate the density of states. Later sections present the results of the calculations and compare them with various physical models. Each of the models can be used for three-dimensional problems as well as one-dimensional ones, so that the results also suggest the range of validity of the models for three-dimensional problems.

2. SOLUTION OF THE DIFFERENTIAL EQUATION

The discussion in the previous section has indicated that the impurity bands associated with localized potentials in one dimension can be adequately investigated by considering the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + |V_0|\sum_j \delta(x-x_j)\right]\psi(x) = E\psi(x), \quad (2.1)$$

where the x_j 's are uniformly distributed with density n. By introducing the definitions

$$\kappa_0 = (m |V_0|)/\hbar^2; \quad E = -(\hbar \kappa)^2/(2m) = (\hbar k)^2/(2m), \quad (2.2)$$

we find Eq. (2.1) reduces to the simpler form,

$$\left[\frac{d^2}{dx^2} + 2\kappa_6 \sum_j \delta(x - x_j)\right] \psi(x) = \kappa^2 \psi(x). \qquad (2.3)$$

The wave function associated with an isolated δ function is given by $\psi_0 \sim \exp(-\kappa_0 |x-x_0|)$ and its energy is given by $E_0 = -(\hbar^2/2m)\kappa_0^2$. Thus κ_0 may be interpreted as the range of the bound state. Equation (2.3) holds for negative energies; according to (2.2) a corresponding equation holds for positive energies, with κ replaced by -ik.

If a transformation were made to a new independent variable u=nx, one would find from Eq. (2.3) that the only relevant parameters are κ/κ_0 , a dimensionless square-root energy, and

$$\epsilon = n/\kappa_0, \qquad (2.4)$$

a dimensionless density. The study of a particular crystal involves a given density ϵ and a variety of energies κ/κ_0 .

The simplicity of the calculation of the density of states in one dimension derives from the fact, first emphasized in connection with this problem by James and Ginzbarg,² that the number of nodes in a solution of the wave equation with energy E determines how many states of the system have energies lower than E. In previous calculations² the wave equation was solved in each cell, with ψ and ψ' being made continuous at the boundaries of each square well. Our choice of zero potential for the host cells requires us to calculate ψ and ψ' only at the δ function themselves, which for low concentrations greatly shortens the calculations. An equally significant gain results from the fact that, as we shall show below, it is not necessary to consider ψ and ψ' separately, which requires a matrix solution, but only their ratio ψ'/ψ . As a consequence of this saving we are able to study chains of 1000 impurity atoms (or the equivalent of 100 000 cells, at 1% impurity concentration) in a comparatively small amount of IBM 650 machine time.

Consider the configuration of δ functions shown in Fig. 1. The δ functions are represented schematically by deep, narrow wells and the coordinate just to the right or left of point x is denoted by x^{\pm} , respectively. Since V=0 between wells, we have for negative energies

$$\psi(x_2^{-}) = \psi(x_1^{+}) \cosh[\kappa(x_2 - x_1)] \\ + \kappa^{-1} \psi'(x_1^{+}) \sinh[\kappa(x_2 - x_1)], \quad (2.5)$$

$$\psi'(x_2^{-}) = \psi'(x_1^{+}) \cosh[\kappa(x_2 - x_1)] \\ + \kappa \psi(x_1^{+}) \sinh[\kappa(x_2 - x_1)]. \quad (2.6)$$

The δ -function potential produces a jump in ψ'/ψ given by

$$\psi'(x_2^+)/\psi(x_2^+) = \psi'(x_2^-)/\psi(x_2^-) - 2\kappa_0.$$
 (2.7)

These results can be simplified by introducing $a_n = \psi'(x_n^-)/\kappa\psi(x_n^-)$ and $b_n = \psi'(x_n^+)/\kappa\psi(x_n^+)$. The connection formulas (2.5) – (2.7) now assume the form

$$b_n = a_n - 2\kappa_0 / \kappa, \tag{2.8}$$

$$a_{n+1} = (b_n + \tanh \kappa x) / (1 + b_n \tanh \kappa x).$$
(2.9)



FIG. 1. The locations of x_1^{\pm} and x_2^{\pm} which appear in Eqs. (2.5) and (2.6).

⁴ The use of δ functions for studying disordered crystals has been criticized by Allen⁵ on the ground that contacts between two bands will not occur in this case, though they do occur in general. However, we are not concerned here with such interband effects.

⁵ G. Allen, Phys. Rev. 91, 531 (1953).

At low densities $\kappa x \gg 1$ and $\tanh \kappa x \simeq 1$. In addition, the density of states may be very large for $\kappa \simeq \kappa_0$. Thus, a considerable gain in the number of significant figures results when (2.8) and (2.9) are rearranged in the following way:

$$b_n' = a_n' - 2(\kappa/\kappa_0 - 1), \qquad (2.10)$$

$$a_{n+1}' = -\left[2(2-b_n')e^{-2\alpha u_n}\right] / \left[b_n' + (2-b_n')e^{-2\alpha u_n}\right]. \quad (2.11)$$

Here $a_n'=a_n-1$, $b_n'=b_n+1$, and $\alpha = \kappa(\kappa_0\epsilon)^{-1}$. The dimensionless parameter $u_n = x_n/\langle x \rangle = nx_n$ is a random variable, independent of density, so that the same set of u's can be used for different densities.

We now count the nodes, i.e., the sign changes of ψ occurring between δ functions. If the sign $(a_{n+1}b_n) < 0$, ψ'/ψ has changed sign. Inspection of Eq. (2.9) shows that ψ can change sign only if $b_n < -1$, and that at most one node can occur. Furthermore, when $b_n < -1$ no sign change in ψ' is possible. The conditions $b_n < -1$, $sign(a_{n+1}b_n) < 0$ are then both necessary and sufficient for one zero of ψ to have occurred in the interval.

A similar procedure can be developed for positive energies. In this case $E = \hbar^2 k^2/2m$, and defining a_n and b_n as before, except with κ replaced by k, we find the connection formulas assume the form

$$b_n = a_n - 2\kappa_0/k, \qquad (2.12)$$

$$a_{n+1} = (b_n - \tan k x_n) / (1 + b_n \tan k x_n).$$
 (2.13)

Now let $b_n = -\tan \varphi_n$, $a_{n+1} = -\tan \chi_{n+1}$. Then Eq. (2.13) becomes

$$\chi_{n+1} = \varphi_n + k x_n, \qquad (2.14)$$

and the number of nodes ψ is given by $\left[(\chi_{n+1}/\pi) + \frac{1}{2} \right]$ $-[(\varphi_n/\pi)+\frac{1}{2}]$, when [] denotes "greatest integer contained in.'

We present the results of the machine calculations for negative and positive energies separately. Most of the calculations have been concerned with the negative energy range, and it is these we present first.

3. NEGATIVE ENERGIES: LOW DENSITIES

It is reasonable to expect that at low densities the broadening of the isolated bound level will be produced mainly by pair interactions. We shall calculate this effect using the multiple scattering formalism, which for δ functions is easy to use, and which we shall need later in any case. It is shown in Appendix A that for our problem the multiple scattering equations reduce to N linear homogeneous equations

$$c_i = \sum_{j=1}^{N} A_{ij} c_j \quad (i = 1, \dots, N), \qquad (3.1)$$

where $A_{ii}=0$ and $A_{ij}=(\kappa/\kappa_0-1)^{-1}\exp(-\kappa|x_i-x_j|)$. If atoms m and n form a pair, we may expect that solutions localized about them have $c_m, c_n \gg c_j, j \neq m, n$.

Thus $c_m = A_{mn}c_n$ and $c_n = A_{nm}c_m$, so that

$$\kappa/\kappa_0 - 1 = \pm e^{-\kappa|x_m - x_n|}.$$
 (3.2)

The probability that the nearest neighbor of an atom located at the origin lies between x and x + dx is $2ne^{-2n|x|}$, and the probability that the nearest neighbor distance is less than x is e^{-2nx} . Thus, according to the pair theory, the fraction of states for which κ/κ_0 is larger than the indicated value is given by

$$1 \le \kappa/\kappa_0 \le 2 : N(\kappa/\kappa_0) = \frac{1}{2} - \frac{1}{2} |\kappa/\kappa_0 - 1|^{2n/\kappa}, \quad (3.3)$$

$$0 \le \kappa/\kappa_0 \le 1: N(\kappa/\kappa_0) = \frac{1}{2} + \frac{1}{2} |\kappa/\kappa_0 - 1|^{2n/\kappa}. \quad (3.4)$$

In the neighborhood of $\kappa/\kappa_0=1$, Eqs. (3.3) and (3.4) imply that the differential density of states is approximately

$$n(\kappa/\kappa_0) = dN(\kappa/\kappa_0)/d(\kappa/\kappa_0) \simeq 2\epsilon |\kappa/\kappa_0 - 1|^{1-2\epsilon}. \quad (3.5)$$

This distribution exhibits a long tail, leading to a first moment proportional to ϵ , although any fixed fraction of the states are confined to a neighborhood of $\kappa/\kappa_0 = 1$ of order $\exp(-1/\epsilon)$. For a regular lattice, the band width is proportional to the overlap and also varies as $\exp(-1/\epsilon)$. At low densities the introduction of randomness modifies the shape of the central region, introducing a singularity at $\kappa/\kappa_0 = 1$, and adds a long tail as compared with the regular arrangement.

The pair theory is correct to order ϵ in the sense that it yields all the moments⁶ of $dN/d\kappa$ correct to order ϵ . The moments, however, are insensitive to the behavior of N in the region $|\kappa/\kappa_0-1| \leq \exp(-1/\epsilon)$, which is the region containing much of the band at low densities. Schmidt⁷ has recently obtained a solution for the onedimensional problem which is accurate to order ϵ in this region as well. His result, which follows from solving an integral equation analogous to the procedure we have used in the machine calculation, is, in our notation⁸ (here $c = \kappa/\kappa_0 - 1$):

$$1 \le \kappa/\kappa_0 \le 2: N(\kappa/\kappa_0) = \frac{1 - |c|^{\epsilon}}{(\frac{3}{2} - \frac{1}{2}|c|^{\epsilon})^2}, \qquad (3.6)$$

$$0 \leq \kappa/\kappa_0 \leq 1: N(\kappa/\kappa_0) = \frac{1}{(\frac{3}{2} - \frac{1}{2} |c|^{\epsilon})^2}.$$
 (3.7)

Better results are obtained if one replaces ϵ in (3.6) and (3.7) by n/κ . In our comparisons with Schmidt we have always evaluated his formula with this improvement. Machine results for $\epsilon = 0.01$ and 0.1 are compared in Tables I and II with the pair theory and Schmidt's formula; the results for $\epsilon = 0.1$ are also shown in Fig. 2. Table II presents results obtained when 500 atoms were

⁶ Details of this and other calculations will be included in a later paper concerned with the multiple scattering formalism as applied to the impurity band problem.

⁷ H. Schmidt, Phys. Rev. **105**, 425 (1957). ⁸ Schmidt's final equation contains an unfortunate misprint. It should read $\epsilon = q/(2kl)$. Thus his ϵ is equal to our $\epsilon/2$, i.e., $n/(2\kappa_0)$.

TABLE I. Integrated density of states at negative energies, $\epsilon = 0.01$.

κ/κ_0-1	Machine results (%)	Pair theory (%)	Schmidt's formula (%)
-0.999	98.6	99.0	99.0
-10^{-4}	91.4	91.6	91.8
- 10-5	89.3	89.7	89.9
10-6	87.5	87.9	88.0
-10-11	79.7	80.0	81.4
-10^{-20}	70.5	70.0	71.9
-10^{-35}	64.1	60.0	61.3
-10^{-40}	63.3	58.2	59.5
2×10^{-49}	30.6	44.6	36.6
10-35	30.3	40.0	33.7
10^{-20}	26.6	30.0	25.9
10-11	19.1	- 20.0	17.7
10-6	12.2	12.1	11.4
10-5	10.4	10.3	9.9
10-4	8.3	8.4	8.1
1	0.0	0.0	0.0

added to the chain to make a total of 1000 atoms. The error due to the Monte Carlo nature of the calculation is seen to be of order $\frac{1}{2}\%$.

From these results it can be seen that the pair solution is adequate for the wings of the distribution, but that it does not predict the asymmetric shoulder for $\kappa \leq \kappa_0$. Schmidt's solution gives a good fit to the entire distribution, but his method is entirely one-dimensional and his results valid only for $\epsilon \ll 1$.

The following argument suggests the existence of the shoulder. In calculating the density of states on a pair model, we assumed all atoms to be members of pairs. From Fig. 3, we can see that this may easily not be the case. Here 1 and 2 and 4 and 5 form pairs, while 3 remains "isolated". It is a simple calculation however, to show that the energy level of an "isolated" atom with a pair at a distance x is given by

$$\kappa/\kappa_0 = 1 - e^{-\kappa x}, \qquad (3.8)$$



FIG. 2. Integrated density of states versus the dimensionless square root energy κ/κ_0 for $\epsilon=0.1$.

				FIG. 3. An example of an
0	0	0 0	0	"isolated" δ function, as dis-
1	2	3 4	5	cussed in the text at the end
				of Sec. 3.

where $x \approx 1/n$, and $\kappa \simeq \kappa_0$, so that the resulting states lie in a neighborhood of $\exp(-1/\epsilon)$ of the bound level, and always slightly higher in energy. This conclusion is in qualitative agreement with the results of the machine calculations.

4. NEGATIVE ENERGIES: HIGH DENSITIES

At high densities the number of atoms within range of a given one is large, and the fractional fluctuation of this number is small. Thus in the limit $\epsilon \rightarrow \infty$ we expect that $|c_i| = c$, so that we may take $c_i = e^{ik'x_i}c$. One then obtains⁹

$$\kappa/\kappa_0 - 1 = \sum_{j \neq i} e^{-\kappa |x_j - x_i| + ik'(x_j - x_i)}$$
(4.1)

$$= -1 + \sum_{\text{all } j} e^{-\kappa |x_j - x_i| + ik'(x_j - x_i)}. \quad (4.2)$$

At high density $(\epsilon \gg 1)$ the sum on the right, by the "law of large numbers," exhibits relatively small fluctuations, and we may approximate the sum by its ensemble average:

$$\kappa/\kappa_0 - 1 = -1 + \int_{-\infty}^{\infty} n dx e^{-\kappa |x| + ik'x}$$
$$= -1 + (2n\kappa)/(\kappa^2 + k'^2). \tag{4.3}$$

Thus

$$\kappa^2 + k'^2 = 2n\kappa_0.$$
 (4.4)

TABLE II. Integrated density of states at negative energies, $\epsilon = 0.1$.

к/ко	Machine results (%) (500 atoms)	Machine results (%) (1000 atoms)	Pair theory (%)	Schmidt's formula (%)
0.001	89.6	89.2	91.0	90.8
0.67	84.6	84.6	85.7	86.4
0.92	78.6	77.9	78.8	79.4
0.99	70.6	69.7	70.0	71.0
0.997	65.6		65.6	66.9
0.999	62.6		62.6	64.1
0.9995	61.4	61.1	60.9	62.3
0.99968	60.2	59.9	60.0	61.3
0.99985	58.6	58.6	58.5	59.9
0.999995	53.8	53.2	54.4	54.7
0.999999	51.4	51.4	53.0	52.9
1.000000	42.8		50.0	44.4
1.000005	36.6	37.0	45.6	38.5
1.00032	32.8	33.4	40.0	33.8
1.0010	31.2	31.8	37.4	32.0
1.0030	29.0		34.6	28.6
1.01	25.4	25.9	30.0	26.0
1.078	18.6	18.2	18.9	17.2
1.33	6.4	7.7	7.9	7.3
2.00	0.4	0.5	0.0	0.0

⁹ Equation (4.3) can also be obtained directly from (4.1) by replacing the sum by an integral involving the pair distribution function $n(x|x_i)$. Since $n(x|x_i) = \langle \Sigma_{i \neq i} \delta(x_i - x) \rangle = \langle \Sigma_i \delta(x_i - x) \rangle - \delta(x_i - x) = n - \delta(x - x_i)$, the result follows.

The numbers of zeros in $\cos k'x$ in a length L is $(k'L)/\pi$, so that the number of zeros per impurity atom is

$$N(\kappa/\kappa_0) = k'/(\pi n), \qquad (4.5)$$

$$N(\kappa/\kappa_0) = (2n\kappa_0 - \kappa^2)^{\frac{1}{2}}/(\pi n).$$
(4.6)

We often refer to this result as the "optical model," since Eq. (4.3) is a continuum approximation.

Results for $\epsilon = 5$ and $\epsilon = 10$ are presented in Tables III and IV. Figure 4 is a graph of the results for $\epsilon = 10$. The results are compared with the optical model approximation of Eq. (4.6), and it can be seen that the model approximates the results reasonably well, except at the band edge where fluctuations are significant.

Fluctuations may be taken into account by avoiding our previous approximation of taking an ensemble average.⁶ For calculational purposes it is simpler to use the following model, which is suggested by the form of the multiple scattering calculation. Since fluctuations are significant primarily near the band edge where $\kappa \simeq \kappa_1$, we consider fluctuations in

$$F = \sum_{i \neq j} e^{-\kappa_1 |x_i - x_j|}. \tag{4.7}$$

TABLE III. Integrated density of states at negative energies, $\epsilon = 5$.

к/ко	Machine results (%)	Optical model (%)
0.001	20.0	20.1
1.00	19.0	18.1
2,32	13.6	13.6
3.16	9.2	0.0
4.00	2.6	0.0

F is similar to the sum entering the multiple scattering calculation for k'=0, and its distribution P(F) is more easily calculated than that for $k'\neq 0$. In fact, P(F), for any value of ϵ , is calculated in Appendix B. The result is that F has a Poisson-like distribution, which becomes Gaussian at high densities.

Now a particular value of F would also be obtained from a regular lattice with a certain lattice constant a'. In fact, for a regular lattice,

$$G = \sum_{n=-\infty}^{\infty} \sum_{n\neq 0}^{n\neq 0} e^{-\kappa_1 a' |n|} = \frac{2e^{-\kappa_1 a'}}{1 - e^{-\kappa_1 a'}}.$$
 (4.8)

We now represent our density of states as that resulting from an ensemble of lattices having different lattice constants a', where the distribution of a' is such as to make the distribution of G equal that of F. We call this the "local density" model (L. D. in the figures).

The computational advantage of this model is, of course, that the density of states corresponding to a regular lattice of lattice constant a' is easily obtained. For negative energies (an analogous result holds for positive energies), this is the Kronig-Penney dispersion

TABLE IV. Integrated density of states at negative energies, $\epsilon = 10$.

к/ко	Machine results (%)	Optical model (%)	Local density model (%)
0.00001	14.1	14.1	14.1
1.00	13.8	13.8	13.8
2.00	12.4	12.6	12.4
2.83	10.9	10.9	10.5
3.50	9.6	8.8	8.1
4.16	6.7	5.2	4.9
4.47	4.85	0.0	3.4
4.97	3.2	0.0	1.3
5.50	1.5	0.0	0.3
6.00	0.7	0.0	0.0

relation:

$$\cos k' a' = \cosh \kappa a' - (\kappa_0 / \kappa) \sinh \kappa a'. \tag{4.9}$$

Thus the local density model yields the following formula for the integrated density of states:

$$N(x) = \int_{G_{\min}}^{\infty} dGP(G) \frac{k'(x,G)}{\pi n'(G)}.$$
 (4.10)

Here P(G) is given by Eq. B1 for P(F) with F replaced by G and G is related to a' by (4.8). Using (4.9), we can evaluate k' in terms of a' and $x = \kappa/\kappa_0$. Finally G_{\min} is determined from (4.8) and (4.9) with k'=0 or π , for x>1 or x<1, respectively. A short calculation gives $\tanh(\frac{1}{2}\kappa a'_{\max}) = B \equiv \min(x, x^{-1})$ and

$$G_{\min} = \frac{2\alpha}{1-\alpha}, \quad \alpha = \left(\frac{1-B}{1+B}\right)^{\kappa_1/\kappa}. \tag{4.11}$$

Our primary interest in the local density model is as a means for calculating corrections to N(x) as given by the optical model at high densities. However, it may be observed that the model also yields good results at low densities, since for P(F) one then recovers the nearest neighbor distribution, and subsequently obtains the density of states given by the pair theory. Thus one may expect the model to yield qualitatively satisfactory results at all densities, including intermediate ones. This actually turns out to be the case, as we shall see later.



FIG. 4. Integrated density of states versus the dimensionless square root energy κ/κ_0 for $\epsilon = 10$.





At high densities a considerable simplification of the equations results. Thus (4.8) becomes $(a')^{-1}\cong 2^{-1}\kappa_1 G$ and (4.9) reduces to the optical model result (4.4), as it must. In addition P assumes the Gaussian form given by Eq. (B9). If we insert these results in Eq. (4.10) and make the substitution $y = (2\epsilon)^{-\frac{1}{2}}G$, we find the simple

TABLE V. Integrated density of states at negative energies, $\epsilon = 0.25$.

к/ко	Machine results (%)	Pair theory (%)	Schmidt's formula (%)
0.0	76.8	80.3	82.0
0.50	74.6	75.0	75.9
0.90	62.8	68.0	65.4
1.00	40.1	50.0	44.4
1.10	26.4	36.0	23.9
1.50	11.2	10.0	9.8
2.00	0.8	0.0	0.0

TABLE VI. Integrated density of states at negative energies, $\epsilon = 0.5$.

к/ко	Machine results (%)	Pair theory (%)	Schmidt's formula (%)	Local density model (%)
0.001	60.7	68.9	71.3	61.6
0.50	58.0	62.5	64.0	58.4
0.80	52.6	56.7	57.6	51.5
0.90	49.8	53.9	53.8	
1.00	38.8	50.0	44.4	39.7
1.10	32.4	43.9	36.8	
1.20	28.0	36.2	32.0	23.5
1.35	22.2	27.1	23.8	
1.50	17.8	18.5	16.9	7.7
1.75	10.4	7.6	7.2	2.2
2.00	4.6	0.0	0.0	0.5
2.50	0.6	0.0	0.0	0

result,

$$N(x) \simeq \frac{2^{\frac{3}{4}}}{\pi^{\frac{3}{2}} \epsilon^{\frac{1}{4}}} \int_{x^{2}/(2\epsilon)}^{\infty} dy [y - x^{2}/(2\epsilon)]^{\frac{1}{4}} \\ \times \exp[-(2\epsilon)^{\frac{1}{2}} (y - 1)^{2}]. \quad (4.12)$$

If we put $x^2 = 2\epsilon$, we obtain the fraction N_0 of the density which fluctuations have pushed below the band edge of the crystal of uniform density. From (4.12) one finds that N_0 is proportional to $\epsilon^{-5/8}$. Since the fraction below E=0 is proportional to $\epsilon^{-1/2}$, this suggests that the effect of fluctuations on the density of states near the band edge will be significant even for rather large values of ϵ . The ϵ dependence of N_0 , as obtained from the machine calculations, is shown in Fig. 5. From the

TABLE VII. Integrated density of states at negative energies, $\epsilon = 1.0$.

к/ко	Machine results (%)	Optical model (%)	Local density model (1) (%)	Local density model (2) (%)
0.001	45.6	45.0	45.0	45.0
0.800	39.8	37.0	37.0	37.0
1.00	34.3	31.8	31.7	33.5
1.18	30.2	24.8	27.4	28.0
1.37	26.8	11.0	21.9	22.3
1.53	22.3	0.0	17.1	16.6
1.69	18.3	0.0	12.7	11.1
1.84	14.0	0.0	9.1	7.0
2.00	10.3	0.0	5.8	4.4
2.20	6.4	0.0	3.1	1.8
2.50	2.5	0.0	1.1	0.6

TABLE VIII. Integrated density of states at negative energies, $\epsilon = 2$.

Machine results (%)	Optical model (%)
32.0	31.8
30.6	30.9
28.6	27.6
22.8	21.0
15.0	0.0
8.4	0.0
	Machine results (%) 32.0 30.6 28.6 22.8 15.0 8.4

figure one obtains $N_0 \simeq C \epsilon^{-2/3}$, so that the local density model apparently predicts qualitative features of the fluctuations.

Equation (4.12) has also been used to calculate N(x) for $\epsilon = 10$. The results are shown in Fig. 4. The curve for N(x) given by the local density model has the same shape as the curve obtained from the machine results, but the tail is only about half as large.

5. NEGATIVE ENERGIES: INTERMEDIATE DENSITIES

At low densities the density of states is peaked near $\kappa/\kappa_0=x=1$, while at high densities the k'=0 peak occurs near $x=(2\epsilon)^{1/2}$. We expect that the transition between the two cases will occur near $\epsilon=1$. In Tables V-VIII and Figs. 6 and 7 we present the machine results for $\epsilon=\frac{1}{4}, \frac{1}{2}, 1$, and 2. From Tables V and VI and Fig. 6 one sees that $\epsilon = \frac{1}{4}$ and $\epsilon = \frac{1}{2}$ are in the low-density range. The density of states is similar to that predicted by both the pair and Schmidt theories, but the band is broadened by triplet and larger cluster interactions not included in these theories.

On the other hand, $\epsilon = 2$ is still a relatively "high" density, as can be seen from Table VIII. The optical model correctly predicts the density of states, except near the band edge.

Both the high- and low-density peaks are barely discernible at $\epsilon=1$ —see Fig. 6, which also shows the results obtained from the local density model with



FIG. 6. Integrated density of states versus the dimensionless square root energy κ/κ_0 for $\epsilon = \frac{1}{2}$.



FIG. 7. Integrated density of states versus the dimensionless square root energy κ/κ_0 for $\epsilon=1$.

 $\kappa_1 = 2\kappa_0$. [This choice was made because of the large tail present at $\epsilon = 1$. It is tabulated in Table VII in the column headed Local Density Model (1). Results with $\kappa_1 = \kappa_0$ are presented under the heading Local Density Model (2), and it can be seen that this choice of κ_1 yields better results near κ_0 , but poorer results for the tail, as one would have expected.] Again the local density model predicts the shape of the tail correctly, but it yields results only about half as large as those obtained from the machine calculation in this region.

6. POSITIVE ENERGIES

Results obtained for positive energies have been compared with the optical model. For high densities

TABLE IX. Integrated density of states at positive energies, $\epsilon = 10$.

к/ко	Machine results (%)	Optical model (%)
π	17.4	17.4
2π	24.9	24.6
4π	43.1	42.4
6π	62.8	61.7
8π	82.6	81.3
10π	101.8	101.0
20π	203.9	200.6

TABLE X. Integrated density of states at positive energies, $\epsilon = 0.5$.

к/ко	Machine results (%)	Optical model (%)
0	60.7	63.7
0.71	75.2	78.0
1.00	88.4	90.0

the optical model is even more satisfactory at positive energies than it is at negative (see Table IX, which presents results for $\epsilon = 10$).

Indeed, satisfactory agreement is obtained even for ϵ as low as $\frac{1}{2}$ (Table X). However, since the fraction having energies less than zero is $\pi^{-1}(2/\epsilon)^{\frac{1}{2}}$ on the optical model, it is clear that this model must fail as $\epsilon \rightarrow 0$, since the fraction actually can never exceed unity. On the other hand, for sufficiently high energies perturbation theory shows that the optical model must be correct. Both these effects can be discerned in the results for $\epsilon = \frac{1}{4}$ and $\epsilon = \frac{1}{10}$, which are presented in Tables XI and XII. It might be remarked that even for positive energies a correct treatment near zero energy for low densities is not easily obtained from ordinary perturbation theory.

7. SUMMARY

The primary conclusion to be drawn from this work is that the pair theory at low densities and the optical

TABLE XI. Integrated density of states at positive energies, $\epsilon = 0.25$.

к/ко	Machine results (%)	Optical model (%)
0	76.8	90.0
0.20	79.0	93.6
0.35	89.4	100.0
0.50	100.6	110.0
0.71	120.0	117.6
1.00	152.8	155.9

TABLE XII. Integrated density of states at positive energies, $\epsilon = 0.1$.

к/ко	$\begin{array}{c} \mathbf{Machine} \\ \mathbf{results} \ (\%) \end{array}$	Optical model (%)
0	89.2	142
0.05π	104.4	150
0.10π	144.2	174
0.15π	188.8	206.8
0.20π	234.2	244.1

model at high densities give a surprisingly good picture of the density of states in spite of the considerable oversimplification that each involves. The pair model is quantitatively correct in the wings and has the correct type of singularity at the center. The errors in the pair theory occur near the center, where contributions from distant atoms can be expected to be important. For energies greater than that of the band edge of the optical model, the latter theory is in good agreement with the high density machine results. The presence of a tail below the band edge can be ascribed to fluctuations neglected in the optical model. The local density model represents a crude attempt at taking these fluctuations into account and it succeeds in giving a qualitatively correct picture of the tail.

The only presently published general theory of impurity bands that may be compared with our results is that due to Aigrain.¹⁰ Since Aigrain calculates his density of states from a dispersion relation E = E(k')his theory is optical in nature with the usual disadvantages: (1) it is valid only at high density; (2) it omits fluctuation effects and produces no tail. Our dispersion relation is, in a sense, exact⁶ and yields good agreement with the machine results above the band edge. The correctness of Aigrain's theory may then be assessed by comparing his dispersion relation with ours, Eq. (4.4). To obtain comparable results, we must apply Aigrain's procedure to our one-dimensional problem. For his atomic orbital we use $\exp(-\kappa |x|)$ rather than the isolated orbital $\exp(-\kappa_0|x|)$. With this significant improvement (since κ differs appreciably from κ_0 near the band edge) we obtain the dispersion relation

$$(\kappa/\kappa_0)^2 = -2\pi^2 \epsilon^2 [y + \ln(1-y)] + 2\epsilon, \qquad (7.1)$$

where $y = k'/\pi n$. For large ϵ and negative energies Eq. (7.1) can be expanded in powers of y and the dominant term agrees with our dispersion relation, Eq. (4.4). For positive energies erroneous results are obtained.

Improving agreement with machine results at high densities requires a more adequate description of the tail. A more systematic treatment of the tail than that given by the local density model can be based on a multiple-scattering approach including fluctuations. This multiple-scattering treatment will be presented in a future publication.⁶

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APPENDIX A

The multiple-scattering equations can be obtained by specializing the general multiple-scattering equations (3.7) and (3.8) of the review article by Lax¹¹ to the case of one dimension and delta function potentials. Since these general equations were presented without proof we shall present a simple proof for the special case at hand.

By making use of the fact that the operator $\lfloor d^2/dx^2 - \kappa^2 \rfloor^{-1}$ can be represented by the Green's function¹² $(2\kappa)^{-1} \exp(-\kappa |x-x'|)$, Eq. (2.3) can be rewritten in the form

$$\psi(x) = \varphi(x) + (\kappa_0/\kappa)$$
$$\times \int \exp(-\kappa |x - x'|) \sum \delta(x' - x_j) \psi(x') dx', \quad (A1)$$

or

or

or

$$\psi(x) = \varphi(x) + \sum_{j} (\kappa_0/\kappa) \exp(-\kappa |x - x_j|) \psi(x_j), \quad (A2)$$

$$=\varphi(x) + \sum_{j} L_{j}(x), \qquad (A3)$$

where $\varphi(x)$ is the external incident wave (if any), and

$$_{j}(x) = (\kappa_{0}/\kappa) \exp(-\kappa |x - x_{j}|)\psi(x_{j}), \qquad (A4)$$

$$= \exp(-\kappa |x - x_j|) L_j(x_j), \qquad (A5)$$

is the field emitted from scatterer j.

y

L

The effective field ψ^i on scatterer *i* differs from the total field by the field emitted by *i*,

$$\psi^i(x) \equiv \psi(x) - L_i(x), \tag{A6}$$

$$\psi^{i}(x) = \varphi(x) + \sum_{j \neq i} L_{j}(x).$$
 (A7)

Equation (A3), evaluated at $x = x_i$ with $L_i(x_i)$ transposed, is

$$\psi(x_i) - (\kappa_0/\kappa)\psi(x_i) = \psi^i(x_i), \qquad (A8)$$

$$\psi(x_i) = \psi^i(x_i) + (\kappa/\kappa_0 - 1)^{-1} \psi^i(x_i).$$
 (A9)

Comparing with (A6), we find that

$$L_{i}(x_{i}) = (\kappa/\kappa_{0} - 1)^{-1} \psi^{i}(x_{i}), \qquad (A10)$$

or in view of (A5), changing i to j:

$$L_{j}(x) = (\kappa/\kappa_{0} - 1)^{-1} \exp(-\kappa |x - x_{j}|) \psi^{j}(x_{j}), \quad (A11)$$

$$\equiv A(|x - x_{j}|) \psi^{j}(x_{j}).$$

Relation (A11) between the field incident on j and the field emitted by j could also have been obtained by solving a problem involving only one scatterer.

If we set $x = x_i$ in (A7) and use (A11), we obtain an equation for the effective fields:

$$\psi^{i}(x_{i}) = \varphi(x_{i}) + \sum_{j \neq i} A_{ij} \psi^{j}(x_{j}), \qquad (A12)$$

where $A_{ij} = A(|x_i - x_j|)$, and from (A3)

$$\psi(x) = \varphi(x) + \sum_{j} A\left(\left| x - x_{j} \right| \right) \psi^{j}(x_{j}), \quad (A13)$$

¹⁰ P. Aigrain, Physica **20**, 978 (1954).

¹¹ M. Lax, Revs. Modern Phys. 23, 287 (1951), and Phys. Rev. 85, 621 (1952).

¹² See P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1071, with $\kappa = -ik$.

where

$$A(|x|) = (\kappa/\kappa_0 - 1)^{-1} \exp(-\kappa|x|).$$
 (A14)

Equation (A12), with $\psi^i(x_i)$ written for brevity as c_i , reduces to Eq. (3.1) of the text if we set $\varphi(x) = 0$. This choice corresponds to a "self-sustained" solution.

APPENDIX B

The distribution of the variable

$$F = \sum_{i \neq j} \exp(-\kappa_1 |x_i - x_j|)$$

can be computed by using techniques developed for problems in random noise. Rice¹³ gives the following formula:

$$P(F) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left\{-iFu + n \int_{-\infty}^{\infty} (e^{iuf(x)} - 1)dx\right\} du,$$
(B1)

where $f(x) = \exp(-\kappa_1 |x|)$.

This equation can be transformed to an integral equation by the following procedure, which was suggested to us by Pollak and Gilbert.¹⁴ From Eq. (B1), we have

$$nif(y)P(F-f(y)) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-iFu} \exp\left[n \int_{-\infty}^{\infty} (e^{iuf(x)} - 1)dx\right] \times e^{iuf(y)} inf(y)du, \quad (B2)$$

so that

$$ni \int_{-\infty}^{\infty} f(y) P(F - f(y)) dy$$
$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} du e^{-iuF} \frac{d}{du} \left\{ \exp\left[n \int_{-\infty}^{\infty} (e^{iuf(x)} - 1) dx\right] \right\}.$$
(B3)

Integrated by parts; the result on the right-hand side is then recognized as iFP(F). Thus

$$n \int_{-\infty}^{\infty} f(y) P(F - f(y)) dy = FP(F).$$
(B4)

For $f(y) = e^{-\kappa_1 |y|}$ we obtain the simple result

[here
$$x = F - f(y)$$
],
 $FP(F) = \frac{2n}{\kappa_1} \int_{F-1}^{F} P(x) dx,$ (B5)

¹³ S. O. Rice, Bell System Tech. J. 23, 282 (1944) and 24, 46 (1945). Reprinted in *Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, New York, 1954), p. 133. ¹⁴ E. Gilbert and H. Pollak (private communication).



FIG. 8. The distribution P(F) of $F = \sum_{i} e^{-\kappa_{1}|x_{i}|}$ for points x_{i} distributed randomly on a line with density n, plotted for the case $n/\kappa_1 = 1$.

if
$$F \ge 1$$
 and
 $FP(F) = \frac{2n}{\kappa_1} \int_0^F P(x) dx,$ (B6)

if $0 \le F \le 1$. Equations (B5) and (B6) can be rewritten as differential equations:

$$P'(F) + \frac{1 - 2n/\kappa_1}{F} P(F)$$

= - (\kappa_1 F)^{-1} 2n P(F-1), F>1 (B7)
= 0, 0 \le F \le 1.

It is easily verified that $P(F) = CF^{2n/\kappa_1-1}$ is a solution for $0 \le F \le 1$. For larger F, one can use the relation

$$P(F) = F^{(2n/\kappa_1)-1} \bigg\{ \frac{P([F])}{[F]^{(2n/\kappa_1)-1}} - \frac{2n}{\kappa_1} \int_{[F]}^{F} \frac{P(x-1)dx}{x^2} \bigg\},$$
(B8)

where [F] means the greatest integer contained in F. Finally, \overline{C} is determined by the normalization condition

$$\int_0^\infty P(F)dF = 1.$$

The solution obtained in this way for $n/\kappa_1 = 1$ is shown in Fig. 8.

For $\epsilon \gg 1$ a simpler approach is sufficient. In this case Rice shows that P(F) is Gaussian. From his formulas one readily finds $\vec{F} = 2n/\kappa_1$, $\sigma^2 = \langle (F - \vec{F})^2 \rangle_{AV} = n/\kappa_1$. Thus

$$P(F) \simeq (\kappa_1/2\pi n)^{\frac{1}{2}} \exp[-\kappa_1(F-2n/\kappa_1)^2/(2n)].$$
(B9)