Impurity-Band Tails in the High-Density Limit. I. Minimum Counting Methods

B. I. HALPERIN AND MELVIN LAX

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 7 March 1966)

A new approximate method is presented for calculating the density of states and one-electron Green's function in the low-energy tail of a high-density impurity band. Such states occur in regions of large attractive potential produced by unusually high (random) concentrations of attractive centers and/or unusually low concentrations of repulsive centers. These well-separated deep wells each have one bound state of lowest energy. The distribution of these lowest levels yields the low-energy tail. For any one well, a bound-state energy $E(\mathbf{x}_0)$ is estimated variationally using $\psi(\mathbf{x}) = f(\mathbf{x} - \mathbf{x}_0)$, where $f(\mathbf{x})$ has any fixed form. The best energy for any well is obtained by minimizing $E(\mathbf{x}_0)$ with respect to $\mathbf{x}_0$ in the vicinity of that well. The number of wells that contribute to the density of states at energy E is given by the number of local minima in $E(\mathbf{x}_0)$ that occur at the level E. In the high-density limit, Gaussian statistics are adequate for treating the potential fluctuations and the expectation value for the density of states is easily calculated. At low energies the best choice for the function f is that which maximizes the expected density of states. Application to an exactly soluble one-dimensional model, a Gaussian "white noise" potential, yields the correct asymptotic form $\rho(E) = \text{const}\,|E|\exp[-(\tfrac{4}{3})\,|2E|^{3/2}]$. In three dimensions, the density of states in the Gaussian approximation is found to have the form $\rho(E) = [A(E)/\xi^2]\exp[-B(E)/(2\xi)]$, where ξ is proportional to the concentration of impurities and to the square of the strength of the impurity potential. For screened, charged impurities, $B(E) = E_Q{}^2 b(\nu)$, $A(E) = Q^3 E_Q{}^3 a(\nu)$, where $E_Q = \hbar^2 Q^2/(2m^*)$, $(1/Q)$ is the screening radius, and $\nu = (E_0 - E)/E_Q$ is the energy below the mean potential E_0 in units of E_Q. Computer-calculated curves are provided for the "universal" dimensionless functions $a(\nu)$ and $b(\nu)$. The exponent $b(\nu)$ behaves like $\nu^{1/2}$ when ν is small (strong screening) and behaves like ν^2 when ν is large (weak screening).

1. INTRODUCTION

A. Comparison with Previous Work

A NUMBER of recent experiments on tunneling,[1] optical absorption,[2] and luminescence[3] have yielded experimental evidence for a tail in the density of states associated with impurities in degenerate semiconductors.

The theory of impurity-band density of states in the high-density limit has passed through several stages: (1) a calculation of the shift of the band edge by Stern and Talley,[4] and Baltensberger[4] placing the impurities on a suitable sublattice; (2) the virtual crystal approximation has been combined with second-order perturbation theory by Parmenter[5] to calculate a real, perturbed,

$E(\mathbf{k})$ relationship from which the density of states can be obtained; (3) multiple-scattering techniques using unmodified propagators have been used by Lax[6] and Edwards[7]; (4) the improvement of modified propagator techniques over unmodified propagator techniques has been demonstrated by Klauder,[8] by comparison with exact calculations for a one-dimensional model by Lax and Phillips,[9] and by Frisch and Lloyd.[10] However, all perturbation and propagator techniques lead to tails that cut off sharply. (5) A many-electron treatment of Wolff's[11] shows that, aside from a small rigid shift of the bands (and a slight modification of the effective mass) due to exchange effects, electron-electron interactions can be ignored provided single electrons are treated as moving in the screened fields of the impurities; (6) Wolff[11] and Kane[12] both demonstrated the inadequacy of perturbation methods, particularly in the tail. (7) When the potential varies slowly enough, the fluctuations in the energies of states mirror the fluctuations in the potential energy. This approach has been discussed

[1] R. A. Logan and A. G. Chynoweth, Phys. Rev. **131**, 89 (1963); for photon-assisted tunneling, see J. I. Pankove, Phys. Rev. Letters **9**, 283 (1962) and R. J. Archer, R. C. C. Leite, A. Yariv, S. P. S. Porto, and J. M. Whelan, *ibid.* **10**, 483 (1963).

[2] I. Kudman and T. Seidel, J. Appl. Phys. **33**, 771 (1962); Dale E. Hill, Phys. Rev. **133**, A866 (1964); G. Lucovsky, Appl. Phys. Letters **5**, 37 (1964); G. Lucovsky, Solid State Commun. **3**, 105 (1965); J. I. Pankove, Phys. Rev. **140**, A2059 (1965).

[3] M. I. Nathan, G. Burns, S. E. Blum, and J. C. Marinace, Phys. Rev. **132**, 1482 (1963); G. Burns and M. I. Nathan, Proc. IEEE **52**, 770 (1964); J. I. Pankove, J. Appl. Phys. **35**, 1890 (1964); V. S. Bagaev, Y. M. Berozashvili, L. V. Keldysh, A. P. Shotov, B. M. Vul, and E. I. Zavaritskaya, in *Proceedings of the International Symposium on Radiative Recombination in Semiconductors* (Dunod Cie, Paris, 1965), p. 149; and Fiz. Tverd. Tela **6**, 1399 (1964) [English transl.: Soviet Phys.—Solid State **6**, 1093 (1964)]; J. C. Sarace, R. H. Kaiser, J. M. Whelan, and R. C. C. Leite, Phys. Rev. **137**, A623 (1965); T. N. Morgan, M. Pilkuhn, and H. Rupprecht, *ibid.* **138**, A1551 (1965); T. N. Morgan, *ibid.* **139**, A343 (1965).

[4] F. Stern and R. M. Talley, Phys. Rev. **100**, 1638 (1955); W. Baltensberger, Phil. Mag. **44**, 1355 (1953).

[5] R. H. Parmenter, Phys. Rev. **97**, 587 (1955); **104**, 22 (1956).

[6] M. Lax, Rev. Mod. Phys. **23**, 287 (1951); Phys. Rev. **85**, 621 (1952). See also Ref. 9.

[7] S. F. Edwards, Phil. Mag. **6**, 617 (1961).

[8] J. R. Klauder, Ann. Phys. (N. Y.) **14**, 43 (1961).

[9] M. Lax and J. C. Phillips, Phys. Rev. **110**, 41 (1958).

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

[11] P. A. Wolff, Phys. Rev. **126**, 405 (1962) and *Proceedings of the International Conference on Semiconductor Physics, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1963), p. 220.

[12] E. O. Kane, Phys. Rev. **131**, 1532 (1963). This paper combines moment and perturbation methods.

by Lifschitz[13] and by Bonch-Bruevich.[14] Kane[15] has combined the potential energy fluctuations with the Thomas-Fermi method to calculate the density of states. Kane's procedure has also been compared with experiment by Morgan.[3]

Since the potential energy fluctuations at high concentrations are Gaussian, the tail found by Kane is Gaussian. This is a disadvantage, since simple exponential tails are often found. The present paper, when applied to the screened Coulomb impurity case, in the Gaussian approximation, leads to a density of states $\rho(E) \approx \exp[-\beta(E)]$, where $\beta(E)$ varies from $|E|^{1/2}$ to E^2; see Fig. 1. Over any reasonable energy range, $\rho(E)$ will behave roughly as $\exp[-|E|^n]$ where n is some number between $\frac{1}{2}$ and 2. The value of n, in any given experiment, will be determined by a combination of relevant physical parameters: the carrier and impurity concentrations, the degree of compensation, the effective mass of the observed carrier and of the screening carrier, and the dielectric constant. See Figs. 2 and 3 and Table I.

Our method of calculation is nonperturbative. We do not treat potential energy fluctuations as perturbations, but require the electron to respond to these fluctuations. This is similar to the spirit of Kane's approach. But the electron cannot follow very short-range fluctuations. We therefore smooth (or "filter") the potential and calculate eigenstates of the smoothed potential. As the binding energy increases, the electron wave function tightens up, and can follow shorter range fluctuations. Thus the appropriate "filter" acquires a narrower range with increasing binding energy. But as the range is narrowed, the probability of smoothed potential fluctuations of a given amount is increased in an energy-dependent way, and the tail falls off less rapidly than Gaussian.

Our results also differ from those of the Fermi-Thomas procedure because we include properly the kinetic energy of localization omitted in the former method.

B. Qualitative Discussion of the Present Method

In impurity-band problems one is generally interested in statistical properties of the eigenstates of an electron

[13] I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **44**, 1723 (1963) [English transl.: Soviet Phys.—JETP **17**, 1159 (1963)]; Advan. Phys. **13**, 483 (1964); Nuovo Cimento Suppl. **3**, 716 (1956); Usp. Fiz. Nauk **83**, 617 (1964) [English transl.: Soviet Phys.—Usp. **7**, 549 (1965)].

[14] V. L. Bonch-Bruevich, in *Proceedings of the International Conference on Physics, Exeter, 1962* (The Institute of Physics and The Physical Society, London, 1963), p. 216; V. L. Bonch-Bruevich and A. G. Mironov, Fiz. Tverd. Tela **3**, 3009 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2194 (1962)]. See also I. V. Andreev, Zh. Eksperim. i Teor. Fiz. **48**, 1437 (1965) [English transl.: Soviet Phys.—JETP **21**, 961 (1965)] and A. B. Almazov, Fiz. Tverd. Tela **5**, 1320 (1963) [English transl.: Soviet Phys.—Solid State **5**, 962 (1963)].

[15] E. O. Kane, *Proceedings of the International Conference on Semiconductor Physics, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1963), p. 252; Phys. Rev. **131**, 79 (1963.) See also T. N. Morgan, Ref. 3, who has simply assumed that the density of states mirrors the potential energy fluctuations.
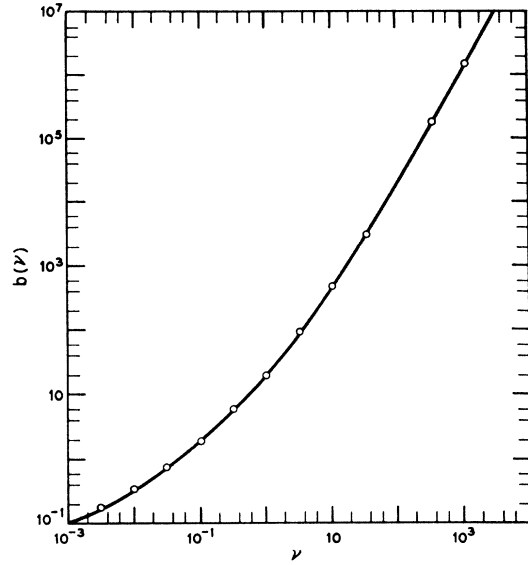

FIG. 1. The density of states deep in the tail of an impurity band, for a density of impurities high enough to use Gaussian statistics has the form

$$\rho_1(E) = \frac{Q^3}{E_Q} \frac{a(\nu)}{(\xi')^2} \exp[-b(\nu)/2\xi'],$$

where $\nu = (E_0 - E)/E_Q$ is an energy measured relative to the mean potential energy E_0 (using the unperturbed band edge as origin) in units $E_Q = \hbar^2 Q^2/(2m^*)$ where Q is the inverse screening radius. The parameter

$$\xi' = \frac{8\pi e^4 (m^*)^4}{\hbar^4 \epsilon_0^2 Q^5} \sum_a \bar{n}_a Z_a^2,$$

if $\bar{n}_a$ is the concentration of impurities of charge $Z_a e$, m^* is the effective mass in the band from which the impurity band is formed, and ϵ_0 is the dielectric constant. The figure shows the "universal" function $b(\nu)$ which varies from $\nu^{1/2}$ at small ν to ν^2 at large ν.

in a random potential. Two of the simplest and most important properties of an impurity band are the total density of electronic states $\rho(E)$, and the spectral density $A(\mathbf{k},E)$, which is a function of the wave vector $\mathbf{k}$ as well as of the energy E. In the present paper, we present an approximate method for calculating these
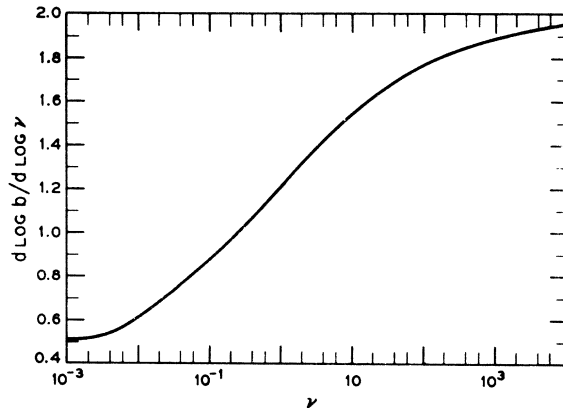

FIG. 2. The logarithmic derivative $n = [d \log b(\nu)]/[d \log \nu]$ of the exponent $b(\nu)$ in the density of states is plotted and is shown to vary smoothly from $n = \frac{1}{2}$ to 2.

TABLE I. Summary of numerical results. The density of states at "energy" ν is given in dimensionless units by $a(\nu) \exp[-b(\nu)/2\xi']$. The eigenvalue μ determines the potential energy $-\mu U(r)$. The mean potential energy is $-\mu\sigma_0^2$, and $T=\mu\sigma_0^2-\nu$ is the mean kinetic energy. All symbols are defined in Eqs. (5.12)–(5.19), and (3.16)–(3.19). [Small errors (a few percent) for $\nu\ll1$ due to insufficient iteration will be corrected in paper III of this series.]

log ν	ν	μ	b	a	T	σ_0^2	σ_1^2
3	1000	1354	1.444×10^6	3.098×10^8	65.60	0.7866	2.7
2.75	562	810	4.912×10^5	4.645×10^7	44.49	0.7478	2.1
2.5	316.2	491.3	1.702×10^5	7.250×10^6	30.29	0.7052	1.64
2.25	178	302.1	6.00×10^4	1.153×10^6	20.60	0.6573	1.23
2.00	100	188.6	2.150×10^4	1.888×10^5	14.00	0.6044	0.91
1.75	56.2	120.2	7.808×10^3	3.223×10^4	9.53	0.5471	0.67
1.50	31.6	78.4	2.988×10^3	5.781×10^3	6.51	0.4864	0.48
1.25	17.8	52.5	1.167×10^3	1.094×10^3	4.44	0.4237	0.336
1.0	10	36.2	4.716×10^2	2.197×10^2	3.03	0.3602	0.230
0.75	5.62	25.78	1.983×10^2	4.689×10	2.07	0.2984	0.152
0.50	3.16	19.06	8.720×10	1.078×10	1.46	0.2400	0.097
0.25	1.78	14.71	4.043×10	2.793	0.969	0.1869	0.0596
0.00	1.00	11.99	1.956×10	7.259×10^{-1}	0.659	0.1407	3.01×10^{-2}
−0.25	0.562	9.96	1.008×10	2.157×10^{-1}	0.450	0.1015	1.965×10^{-2}
−0.50	0.316	8.79	5.456	5.957×10^{-2}	0.3044	7.06×10^{-2}	1.05×10^{-2}
−0.75	0.178	8.12	3.108	2.423×10^{-2}	0.2047	4.71×10^{-2}	5.33×10^{-3}
−1.00	0.100	7.83	1.846	8.906×10^{-3}	0.1358	3.012×10^{-2}	2.53×10^{-3}
−1.25	0.0562	7.912	1.151	3.532×10^{-3}	0.0893	1.84×10^{-2}	1.13×10^{-3}
−1.0	0.0316	8.390	0.7516	1.485×10^{-3}	0.0580	1.07×10^{-2}	4.73×10^{-4}
−1.75	0.0178	9.19	0.5006	5.407×10^{-4}	0.03696	5.99×10^{-3}	1.79×10^{-4}
−2.0	0.01	10.34	0.343	2.834×10^{-4}	0.02316	3.20×10^{-3}	6.9×10^{-5}
−2.25	0.00562	12.244	0.2464	1.29×10^{-5}	0.041211	1.596×10^{-3}	2.24×10^{-5}
−2.50	0.00316	15.46	0.1806	5.89×10^{-5}	0.0085	7.57×10^{-4}	6.71×10^{-6}

two functions when the energy is in the low-energy tail of the impurity band and when the density of impurities is sufficiently high.

The high-density limit occurs when many impurity atoms are found within a volume characteristic of the "spread" or "width" of a typical wave function. Thus we do not, in the high-density limit, think of a wave function as localized on a single impurity atom; the wave function is localized in a region in space in which many impurities are present, and no one impurity is very important. The high-density limit is in fact approached in semiconductors, where the average distance between impurities may be much smaller than the

FIG. 3. At the ν for which $b(\nu) = 10\xi'$ [and the exponential factor in the density of states is $\exp(-5)$], $b(\nu)$ varies roughly as ν^n where $n=[d \log b(\nu)]/d \log\nu$ is obtained from Fig. 2. The result is the plot of n versus $\xi'=b(\nu)/10$ shown above, where

$$\xi' = \frac{8\pi e^4(m^*)^2}{\hbar^4\epsilon_0Q^5} \sum \bar{n}_a Z_a.$$

effective Bohr radius, yet large compared to the lattice spacing. Thus our wave functions will vary slowly from one cell to the next, and the effective-mass approximation will be assumed in this paper. Impurity ions are represented by a model potential which includes properly the effective intraband matrix elements of the original Hamiltonian.

The simplest approximation that one can make in the high-density limit is that the electron (or hole) moves in a uniform potential equal to the average potential of the impurity atoms. The eigenstates in this approximation are plane waves; and the density of states in this approximation vanishes completely for energies below a minimum energy E_0, which is equal to the average impurity potential plus the energy of the $\mathbf{k}=0$ state in the pure crystal. In the real crystal, however, we know that the density of states does not vanish below the energy E_0. Because of the random nature of the impurity distribution, there will always be some region of a macroscopic crystal in which we find an unusually high number of attractive impurities or an unusually small number of repulsive impurities. The average potential in this region will be lower than the average of the crystal as a whole. If the region in question is sufficiently large and the potential sufficiently low, then we expect to find a bound state, localized in this region, with energy less than E_0. The probability of finding a fluctuation of sufficient magnitude to produce a bound state of energy E decreases very rapidly as E becomes much lower than E_0, and hence the density of states $\rho(E)$ becomes very small for E_0-E sufficiently large. The region of energy with small density of states is called the "low-energy tail," and is the region of interest in the present paper.
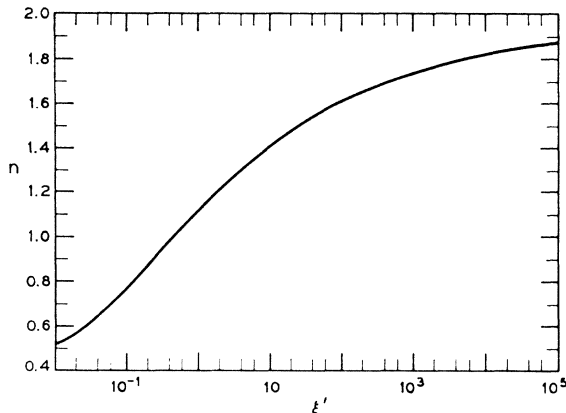
A crude description of the most important factors which determine the density of states in the low-energy tail may be given as follows: We discuss the properties of a "typical" wave function with a given energy E. For the sake of simplicity of discussion, we may assume that the range of a single impurity potential is small compared with the width of the wave function, and that the impurities are attractive. In order to have a wave function of energy $E \ll E_0$, we must have an unusually high number of attractive impurities in the region where the wave function is large. The necessary density of excess impurities in the region depends on the size of the wave function. If the wave function is very spread out, its kinetic energy of localization will be very small, and the potential energy of the wave function differs from the average potential energy in the crystal by the amount $E - E_0$. The required average density of impurities in the region of the wave function exceeds the average density in the crystal as a whole by the number of impurities per unit volume necessary to give an average potential of $E - E_0$. On the other hand, if we assume that the wave function is very narrow, then the kinetic energy of localization will be very large; consequently the potential energy of the wave function must be very negative, and the excess density of impurities required in the region of the wave function must be very high.

In general, if the wave function is assumed to be too narrow, the probability of finding the required excess density of impurities in a region the size of the wave function becomes extremely small. On the other hand the probability of finding any given excess density of impurities, throughout a region, decreases rapidly when the region becomes large. It may therefore be readily seen that if the wave function is assumed to be too spread out in space, the probability of having the necessary excess impurity density to produce the energy E again becomes extremely small. We expect, therefore, that there will be a most probable shape for the wave function, not too narrow and not too spread out, and we may expect that the probability of great deviations from this optimum wave function should be rather small. The dominant factor in the density of states $\rho(E)$ is the probability of finding an impurity fluctuation of the necessary magnitude in a region the size of the optimum wave function.

In Sec. 2 of this paper we show how the density of states at a given energy E in the low-energy tail could be estimated if the shape of the typical wave function at energy E were known. Using a variational principle, we show how to make a best choice for the shape of the wave function and thus for the density of states. An approximation for calculating $A(\mathbf{k}, E)$ is also described. In Sec. 3 we discuss in detail how to carry out these calculations when the density of impurities is sufficiently high that it is permissible to use Gaussian statistics for the potential energy fluctuations. When Gaussian statistics are applicable we find that the density of

states has the form (in three dimensions):

$$[A(E)/\xi^2] \exp[-B(E)/2\xi], \qquad (1.1)$$

where ξ is a parameter proportional to the concentration of impurities and to the square of the strength of the individual impurity atoms, B is a function of the energy E and, implicitly, of the "shape" of the individual impurity potentials, while the function $A(E)$ is slowly varying, in the low-energy tail, relative to the exponential factor.

In Sec. 4 we apply these procedures to a one-dimensional model of an infinite density of very weak point scatterers, for which the density of states and spectral density can be exactly calculated.[10,16,17] The density of states for this model, in appropriately chosen units, has the simple asymptotic form, as $E \to -\infty$, of

$$\rho(E) \sim \frac{8}{\pi} \frac{|E|}{\xi} \exp\left[-\frac{4}{3} \frac{|2E|^{3/2}}{\xi}\right]. \qquad (1.2)$$

The approximate method gives the asymptotic form exactly, except for a factor of approximately 2 in the constant in front. [See Equation (4.9).] The approximate ratio of $A(k, E)$ to $\rho(E)$, calculated by the methods of Sec. 2, agrees with the exact asymptotic form of this ratio.

In a forthcoming paper, paper II of this series, we shall show how to improve the approximation of Secs. 2 and 3 by the inclusion of an average-second-order correction. When this correction is applied to the calculations of the one-dimensional model of Sec. 4, the overall constant in the asymptotic form of the density of states is obtained correctly to within 8% of the exact value.

In Sec. 5 of the present paper we study the three-dimensional case of screened Coulomb impurities. The value of $d \log B(E)/d \log E$ is found to vary smoothly from $\frac{1}{2}$ to 2. In paper III of this series we shall show that the proportionality of $B(E)$ to $|E|^{1/2}$ is characteristic of the short range potentials, whereas the E^2 dependence is characteristic of long range potentials. In Secs. 6 and 7, we discuss some details necessary for the application of the Coulomb model to real crystals.

The techniques of these papers can also be adapted to study the low-energy tail of an exciton absorption band due to interactions with thermal phonons in an otherwise perfect crystal.[18]

2. GENERAL METHOD

A. The Impurity-Band Model

We consider a model in which the electron (or hole) obeys a Hamiltonian of the form

$$H = T + V(\mathbf{x}). \qquad (2.1)$$

[16] B. I. Halperin, Phys. Rev. **139**, A104 (1965).
[17] M. Lax, Rev. Mod. Phys. **38**, 541 (1966), Sec. 4.
[18] B. I. Halperin, Ph.D. thesis, University of California, 1965 (unpublished). (Available from University Microfilms, Inc., Ann Arbor, Michigan.)

The operator T is the "kinetic energy" of the particle, and is invariant under spatial translations. For an electron in a nondegenerate isotropic band, T has the simple form

$$T = -\hbar^2\nabla^2/2m^* + E_0, \tag{2.2}$$

but the following discussion is not restricted to this case. The potential $V(\mathbf{x})$ is the random potential due to the impurity atoms. We assume here that $V(\mathbf{x})$ is diagonal in the electronic position, in order to simplify our equations, but the discussion may be readily generalized to the case of a nonlocal potential.

Although we shall use notations appropriate to a three-dimensional crystal, almost everything we say will be equally applicable to one-dimensional models of impurity bands with the trivial substitution of scalar for vector variables. For those equations which require more serious modifications in the one-dimensional case we shall indicate the necessary changes.

We assume $V(\mathbf{x})$ to be the sum of the individual impurity potentials, and it may be written in the form

$$V(\mathbf{x}) = \eta \sum_a \int v_a(\mathbf{x}-\mathbf{z})[n_a(\mathbf{z}) - \bar{n}_a]d\mathbf{z}, \tag{2.3}$$

where the index a denotes the type of impurity, the quantity $\eta v_a(\mathbf{x}-\mathbf{z})$ is the potential at point $\mathbf{x}$ which would result from an a-type impurity at point $\mathbf{z}$, and the quantity $\bar{n}_a$ is the average concentration of a-type impurities. The function $n_a(\mathbf{z})$ is the actual distribution function of the impurities, thus

$$n_a(\mathbf{z}) = \sum_i \delta(\mathbf{z} - \mathbf{z}_{ai}), \tag{2.4}$$

where $\mathbf{z}_{ai}$ is the position of the ith impurity of type a. The quantity η in Eq. (2.3) is an over-all strength parameter, which we have introduced in order to discuss more easily the behavior of the density of states as a function of the strength of the impurity potentials. Note that, as defined here, the expectation value of the random potential $V(\mathbf{x})$ is zero; the average potential of the impurities is assumed to have been included in E_0.

The statistical distribution of the impurities may be described by the concentrations n_a, and the correlation functions $\langle n_a(\mathbf{z})n_{a'}(\mathbf{z}')\rangle$, $\langle n_a(\mathbf{z})n_{a'}(\mathbf{z}')n_{a''}(\mathbf{z}'')\rangle$, etc., where $\langle \cdots \rangle$ denotes the expectation value for the statistical ensemble. In this paper, except where otherwise stated, we shall assume all the impurity atoms to be statistically independent. The two point correlations are then given by

$$\langle n_a(\mathbf{z})n_{a'}(\mathbf{z}')\rangle = \bar{n}_a\bar{n}_{a'} + \bar{n}_a\delta_{aa'}\delta(\mathbf{z}-\mathbf{z}'), \tag{2.5}$$

or, equivalently,

$$\langle [n_a(\mathbf{z}) - \bar{n}_a][n_{a'}(\mathbf{z}') - \bar{n}_{a'}]\rangle = \bar{n}_a\delta_{aa'}\delta(\mathbf{z}-\mathbf{z}'). \tag{2.6}$$

Similar relations can be written for the higher correlation functions.[19]

The density of states is defined by

$$\rho(E) = \frac{1}{\Omega}\langle \sum_i \delta(E - E_i)\rangle, \tag{2.7}$$

where E_i is the energy of the ith eigenstate of the Hamiltonian H, and Ω is the volume of the crystal. The spectral density $A(\mathbf{k},E)$ is defined by

$$A(\mathbf{k},E) = \frac{1}{\Omega}\langle \sum_i |\psi_i(\mathbf{k})|^2\delta(E-E_i)\rangle, \tag{2.8}$$

where $\psi_i(\mathbf{k})$ is the $\mathbf{k}$th Fourier component of the ith eigenstate,

$$\psi_i(\mathbf{k}) = \int e^{-i\mathbf{k}\cdot\mathbf{x}}\psi_i(\mathbf{x})d\mathbf{x}. \tag{2.9}$$

The spectral density is proportional to the imaginary part of the Green's function[20] for an electron in the impurity band.

When the energy E is sufficiently far below E_0, the density of states $\rho(E)$ decreases very rapidly with decreasing E. Because the average value of $|\psi_i(\mathbf{k})|^2$ is a relatively slowly varying function of the energy, we expect that the behavior of $A(\mathbf{k},E)$ will be principally determined by the behavior of the density of states, and our first task will be to determine the approximate form of $\rho(E)$.

The approximations we will make will be valid in the low-energy tail. For the time being we shall not be precise about the meaning of the low-energy tail—that is, we shall not specify just how far below E_0 one must be. We *do* state that the energy must be sufficiently low that the ratio $\rho(E)/\rho(E_0)$ must be much smaller than 1. This means that $|E-E_0|$ must be large compared to the energy easily obtainable from the potential fluctuations. Note that the low-energy tail may be reached in two ways, by keeping the fluctuations fixed and letting $E-E_0 \to -\infty$, or by holding $E-E_0$ fixed at a given negative value and letting the fluctuations become small, i.e., $\eta \to 0$.

B. The Density of States

The crucial assumption we make is that at a given energy E, in the low-energy tail, almost all of the energy eigenfunctions have approximately the same shape. Specifically let us assume that whenever $E_i \approx E$ we find

$$\psi_i(\mathbf{x}) \approx f(\mathbf{x}-\mathbf{x}_0), \tag{2.10}$$

where f is a fixed function (for each E), and $\mathbf{x}_0$ is a position variable which may be anywhere in the crystal and will be different for each eigenstate. It is no restriction to assume that f has its maximum when its argument is zero. States in the low-energy tail will generally

[19] See for example Eq. (12.27) of M. Lax, Rev. Mod. Phys. **32**, 25 (1960) and Sec. 9 of Ref. 17.

[20] See for example D. Pines, *The Many Body Problem* (W. A. Benjamin, Inc., New York, 1961), p. 31.

be highly localized in a region of low potential, and it is clear that f must be rapidly decreasing when its argument becomes large. We also require that $f(\mathbf{x})$ obey the normalization condition imposed on the wave function ψ_i,

$$\int f(\mathbf{x})^2 d\mathbf{x} = 1. \tag{2.11}$$

[Since we find that f is real, we can simplify our notation by assuming this from the start.]

For the present, let us assume that the function f is known—we shall discuss later the best method for finding this function. Let us use the right-hand side of (2.10) in a variational estimate of the energy E_i. The variational estimate, for a particular choice of $\mathbf{x}_0$, is defined by

$$E(\mathbf{x}_0) \equiv \int f(\mathbf{x}-\mathbf{x}_0) H f(\mathbf{x}-\mathbf{x}_0) d\mathbf{x}. \tag{2.12}$$

The variational energy can be written as the sum of two terms

$$E(\mathbf{x}_0) = \theta + V_s(\mathbf{x}_0), \tag{2.13}$$

where

$$\theta = \int f(\mathbf{x}-\mathbf{x}_0) T f(\mathbf{x}-\mathbf{x}_0) d\mathbf{x},$$
$$\tag{2.14}$$
$$V_s(\mathbf{x}_0) = \int f(\mathbf{x}-\mathbf{x}_0)^2 V(\mathbf{x}) d\mathbf{x}.$$

Note that the kinetic energy θ is independent of the choice of $\mathbf{x}_0$, because the operator T is translationally invariant. The potential energy $V_s(\mathbf{x}_0)$ is an average of the potential $V(\mathbf{x})$ in a region about $\mathbf{x}=\mathbf{x}_0$. As $\mathbf{x}_0$ is permitted to vary throughout the crystal, $V_s(\mathbf{x}_0)$ will fluctuate about an average value of zero, and at various places in the crystal $V_s(\mathbf{x}_0)$ will exhibit an unusually large negative fluctuation. These places correspond to regions of very low $V(\mathbf{x})$, and hence to places where we expect to find a low-energy eigenstate $\psi_i(\mathbf{x})$. We know that a variational estimate of the ground-state energy of a system always overestimates this energy. Hence, we expect that $E(\mathbf{x}_0)$, in a region of negative fluctuations, will always be larger than the true energy E_i of the local low-energy eigenstate. The best estimate of the energy E_i is thus obtained by choosing $\mathbf{x}_0$ so that $E(\mathbf{x}_0)$ is as small as possible, i.e., so that $E(\mathbf{x}_0)$ is a local minimum. In general, $E(\mathbf{x}_0)$ at this minimum may be considerably larger than E_i; however, if the assumption (2.10) holds, we expect $E(\mathbf{x}_0)$ to be a good approximation to E_i whenever $E_i \approx E$. It may also be seen that, in general, if $E(\mathbf{x}_0)$ is close to E, then E_i will be close to E, and hence $E(\mathbf{x}_0)$ will again be a good approximation to E_i. (This last statement follows from the fact that the density of states is rapidly falling with decreasing energy, and thus almost all of the eigenstates with energy less than E have energy close to E.)

It may be objected that the variational principle rigorously tells us that $E(\mathbf{x}_0)$ is greater than E_i only if ψ_i is the ground state of the particle for the whole crystal. In order for $E(\mathbf{x}_0)$ to be smaller than E_i, however, the trial function $f(\mathbf{x}-\mathbf{x}_0)$ must mix in another wave function ψ_j whose energy is lower than E_i. In the low-energy tail, where the density of states is very small, energy eigenstates are (spatially) few and far between, and the possibility of simultaneous overlap between $f(\mathbf{x}-\mathbf{x}_0)$ and two different eigenstates is quite negligible.

If, as we claim, there is a close one-to-one correspondence between local minima in $E(\mathbf{x}_0)$ and the energies of eigenstates in the vicinity of E, then the number of eigenstates with energy E is approximately equal to the number of local minima in $E(\mathbf{x}_0)$ with value E. Thus we have the following approximation to the density of states in the volume Ω:

$$\rho_f(E) = \frac{1}{\Omega dE} \quad \begin{array}{l}\text{[Number of local minima in}\\ E(\mathbf{x}_0) \text{ such that at the mini-}\\ \text{mum } E \leq E(\mathbf{x}_0) \leq E + dE.]\end{array} \tag{2.15}$$

We have placed the subscript f on the density of states to remind us that the validity of the estimate will depend on the correct choice of f.

Until now, we have used the words "local minimum" loosely to mean the minimum value of $E(\mathbf{x}_0)$ in some region. For purposes of computation we wish to define a local minimum as any point where $\nabla E(\mathbf{x}_0)$ equals zero and the second derivatives are positive. If two points with vanishing first derivatives occur very close together, then the use of this new definition may destroy the one-to-one correspondence between local minima and eigenstates, because the same eigenstate may be counted twice. It may be shown, however, that in the low-energy tail, the probability of occurrence of two points close together, with $\nabla E(\mathbf{x}_0)=0$ and $E(\mathbf{x}_0) \leq E$ at each point, is extremely small. Furthermore, if there is only one such point in a region, it must be a local minimum, so that the second derivatives are automatically positive. Hence, we may substitute for the words "local minimum in $E(\mathbf{x}_0)$," in Eq. (2.15), the words "point where $\nabla E(\mathbf{x}_0)=0$."

C. Determination of the Best Trial Function

Let us now consider the problem of finding the best trial function f. We know that regardless of the choice of f, the variational estimates of the energies of the eigenstates will be high. In the low-energy tail, where the density of states is rapidly falling, any approximation which systematically overestimates the energies of all the eigenstates is bound to underestimate the density of states. Thus we claim that in the low-energy tail, no matter what the choice of f, $\rho_f(E)$ will be smaller than the true density of states, $\rho(E)$. Clearly the best choice of f, for any given energy E, is that which maximizes

$\rho_f(E)$. We call the density of states obtained by this optimum choice "$\rho_1(E)$"; i.e., we have

$$\rho_1(E) = \max_f[\rho_f(E)]. \qquad (2.16)$$

D. The Spectral Density

Thus far we have discussed only the total density of states $\rho(E)$. In order to calculate the optical absorption, one needs to know the spectral density $A(\mathbf{k},E)$. The spectral density is, by definition, the product of the density of states $\rho(E)$ times the expectation value of the absolute square of the kth Fourier component of the wave functions at the given energy. If our assumption is correct, that almost all the wave functions at energy E have the approximate form $f(\mathbf{x}-\mathbf{x}_0)$, then the absolute square of their Fourier transforms must be approximately $|f(\mathbf{k})|^2$. Thus we claim that in the low-energy tail,

$$A(\mathbf{k},E) \approx |f(\mathbf{k})|^2\rho(E), \qquad (2.17)$$

where f is the function which maximizes $\rho_f(E)$. To compute $A(\mathbf{k},E)$ when we do not know the exact density of states $\rho(E)$, we use the approximate density of states, $\rho_1(E)$.

3. METHOD OF CALCULATION

A. General Statistics

The method we use to calculate $\rho_f(E)$ is essentially a generalization to three dimensions of a method used by Rice in random noise problems.[21] Equation (2.15) may be written

$$\rho_f(E) = \frac{1}{\Omega} \int d\mathbf{y} \langle \sum_j \delta(\mathbf{y}-\mathbf{y}_j)\delta[E-\theta-V_s(\mathbf{y})]\rangle, \qquad (3.1)$$

where $\{\mathbf{y}_j\}$ is the set of all points satisfying

$$\nabla V_s(\mathbf{y}_j) = 0. \qquad (3.2)$$

When the indicated average over all potential configurations has been taken, the quantity in brackets in (3.1) becomes independent of $\mathbf{y}$, and the integration over $\mathbf{y}$ merely yields a factor of Ω. Thus we may write

$$\rho_f(E) = \langle \sum_j \delta(\mathbf{y}-\mathbf{y}_j)\delta[E-\theta-V_s(\mathbf{y})]\rangle, \qquad (3.3)$$

where $\mathbf{y}$ is any point in the crystal. We next make a transformation from the variable $\mathbf{y}$ to the variable $\nabla V_s(\mathbf{y})$ by writing

$$\sum_j \delta(\mathbf{y}-\mathbf{y}_j) = \delta[\nabla V_s(\mathbf{y})]|\det\nabla\nabla V_s(y)|. \qquad (3.4)$$

The determinant of the second derivatives in (3.4) arises as the Jacobian of the transformation. Equation (3.3) can now be written

$$\rho_f(E) = \langle \delta[E-\theta-V_s(\mathbf{y})]$$
$$\times \delta[\nabla V_s(\mathbf{y})]\det\nabla\nabla V_s(\mathbf{y})\rangle. \qquad (3.5)$$

[21] S. O. Rice, in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, Inc., New York, 1954).

In (3.5) we have dropped the absolute value sign from the determinant because, as mentioned earlier, almost all the critical points of $V_s(\mathbf{y})$ with $V_s(\mathbf{y})=E-\theta$ have positive second derivatives. The quantity $\rho_f(E)$ is then determined by the 10-variable joint probability distribution of V_s and its first and second derivatives at a single point.

In the case of a one-dimensional model of an impurity band, we have instead of (3.5), the relation

$$\rho_f(E) = \langle \delta[E-T-V_s(y)]\delta[V_s'(y)]V_s''(y)\rangle. \qquad (3.6)$$

The density of states $\rho_f(E)$, defined by (3.5), may be written as the product of three factors

$$\rho_f(E) = p(E-\theta)p_3(0|E-\theta)\chi(E-\theta, 0), \qquad (3.7)$$

where the function $p(\lambda)$ is the probability density for $V_s(\mathbf{y})$ to take on the value λ at an arbitrary point $\mathbf{y}$; $p_3(\mathbf{\Lambda}|\lambda)$ is the conditional probability density for $\nabla V_s(\mathbf{y})$ to take on the value $\mathbf{\Lambda}$, when it is specified that $V_s(\mathbf{y})=\lambda$; and $\chi(\lambda,\mathbf{\Lambda})$ is the conditional expectation value of $\det\nabla\nabla V_s(\mathbf{y})$, when it is specified that $V_s(\mathbf{y})=\lambda$ and $\nabla V_s(\mathbf{y})=\mathbf{\Lambda}$. In (3.7), we are interested in the functions p, p_3, and χ when $\lambda=E-\theta$ and $\mathbf{\Lambda}=0$.

As a preliminary to estimating the probability functions in (3.7), we need to know the two-point auto-correlation function $\langle V_s(\mathbf{y})V_s(\mathbf{y}')\rangle$. This autocorrelation function may be expressed in terms of the autocorrelation function $\langle V(\mathbf{x})V(\mathbf{x}')\rangle$ of the original potential, which in turn may be expressed in terms of the autocorrelation function of the impurities. Thus we have

$$\langle V_s(\mathbf{y})V_s(\mathbf{y}')\rangle = \int f^2(\mathbf{x}-\mathbf{y})f^2(\mathbf{x}'-\mathbf{y}')$$
$$\times\langle V(\mathbf{x})V(\mathbf{x}')\rangle d\mathbf{x}d\mathbf{x}', \qquad (3.8)$$

and

$$\langle V(\mathbf{x})V(\mathbf{x}')\rangle = \eta^2\sum_{aa'}\int v_a(\mathbf{x}-\mathbf{z})v_{a'}(\mathbf{x}'-\mathbf{z}')$$
$$\times\langle[n_a(\mathbf{z})-\bar{n}_a][n_{a'}(\mathbf{z}')-\bar{n}_{a'}]\rangle d\mathbf{z}d\mathbf{z}', \qquad (3.9)$$

or

$$\langle V(\mathbf{x})V(\mathbf{x}')\rangle = \eta^2\sum_a \bar{n}_a\int v_a(\mathbf{x}-\mathbf{z})v_a(\mathbf{x}'-\mathbf{z})d\mathbf{z}. \qquad (3.10)$$

In Eq. (3.9), correlations between atom positions are still included. Equation (3.10) specializes to the uncorrelated case, using Eq. (2.6).

In order to exhibit explicitly the dependence of these moments on the concentration of impurities and the strength of the potential, we introduce a parameter

$$\xi = \eta^2\bar{N}, \qquad (3.11)$$

where $\bar{N}$ is the total concentration of impurities, $\bar{N} = \sum_a \bar{n}_a$. Thus we write

$$\langle V(\mathbf{x}) V(\mathbf{x}') \rangle = \xi W(\mathbf{x} - \mathbf{x}') , \qquad (3.12)$$

$$\langle V_s(\mathbf{y}) V_s(\mathbf{y}') \rangle = \xi G(\mathbf{y} - \mathbf{y}') , \qquad (3.13)$$

where

$$W(\mathbf{x} - \mathbf{x}') = \sum_a \frac{\bar{n}_a}{\bar{N}} \int v_a(\mathbf{x} - \mathbf{z}) v_a(\mathbf{x}' - \mathbf{z}) d\mathbf{z} , \qquad (3.14)$$

$$G(\mathbf{y} - \mathbf{y}') = \int f^2(\mathbf{x} - \mathbf{y}) f^2(\mathbf{x}' - \mathbf{y}') W(\mathbf{x} - \mathbf{x}') d\mathbf{x} d\mathbf{x}' . \quad (3.15)$$

B. Gaussian Statistics

The calculation of $\rho_1(F)$ is greatly simplified when the concentration of impurities is sufficiently high that the random variable $V_s(\mathbf{y})$ obeys Gaussian statistics. The value of $V_s(\mathbf{y})$ is the sum of independent contributions from all the impurity atoms in the crystal. The impurity atoms which contribute heavily to $V_s(\mathbf{y})$ are those which fall in a sphere about $\mathbf{y}$ whose radius is roughly the width of the wave function f or the range of a single impurity potential, whichever is larger. When the concentration of impurities is sufficiently high so that there are many impurities in this region, we know by the central limit theorem that Gaussian statistics apply. Henceforth, we shall assume that Gaussian statistics can be used. This is mathematically equivalent to studying the impurity band in the limit that the strength parameter η of the impurity potentials approaches zero and the concentrations $\bar{n}_a$, approach infinity in such a manner that the products $\eta^2 \bar{n}_a$ remain constant.

The statistical properties of $V_s(\mathbf{y})$, in the Gaussian case, are completely determined by the two-point autocorrelation function $\langle V_s(\mathbf{y}) V_s(\mathbf{y}') \rangle$. The function $p(\lambda)$ of Eq. (3.7) is a Gaussian distribution,

$$p(\lambda) = (2\pi \xi \sigma_0^2)^{-1/2} \exp(-\lambda^2 / 2\xi \sigma_0^2) , \qquad (3.16)$$

with variance

$$\xi \sigma_0^2 \equiv \langle V_s(\mathbf{y})^2 \rangle = \xi G(0) . \qquad (3.17)$$

The covariance of $V_s(\mathbf{y})$ with its first derivatives is given by

$$\langle V_s(\mathbf{y}) \nabla V_s(\mathbf{y}) \rangle = \xi \nabla_{\mathbf{y}'} G(\mathbf{y} - \mathbf{y}') |_{\mathbf{y}' = \mathbf{y}} .$$

Because the function G, by definition, is an even function of its argument, the right-hand side vanishes identically. But Gaussian variables (of mean zero) are completely described by their second moments, so that uncorrelated variables such as $V_s(\mathbf{y})$ and $\nabla V_s(\mathbf{y})$ are statistically independent. Thus the conditional distribution $p_3(\mathbf{\Lambda} | \lambda)$ is independent of λ and reduces to the ordinary probability distribution of $\nabla V_s(\mathbf{y})$.

The covariances of the derivatives among themselves are given by

$$\langle [\nabla V_s(\mathbf{y})][\nabla V_s(\mathbf{y})] \rangle = -\xi \nabla \nabla G(0) . \qquad (3.18)$$

It is convenient to choose the coordinate axes such that the matrix of second derivatives of G is diagonal, with the form

$$\nabla \nabla G(0) = - \begin{vmatrix} \sigma_1^2 & 0 & 0 \\ 0 & \sigma_2^2 & 0 \\ 0 & 0 & \sigma_3^2 \end{vmatrix} . \qquad (3.19)$$

In this case, the three components of $\nabla V_s(\mathbf{y})$ are uncorrelated, and the function p_3 is simply the product of three Gaussians:

$$p_3(\mathbf{\Lambda} | \lambda) = (2\pi\xi)^{-3/2} (\sigma_1 \sigma_2 \sigma_3)^{-1}$$

$$\times \exp \left[-\frac{\Lambda_1^2}{2\xi \sigma_1^2} - \frac{\Lambda_2^2}{2\xi \sigma_2^2} - \frac{\Lambda_3^2}{2\xi \sigma_3^2} \right] . \quad (3.20)$$

We now must find $X(E - \theta, 0)$, the conditional expectation value of the determinant of the second derivatives of $V_s(\mathbf{y})$. Each of the second derivatives may be written as the sum of a term proportional to $V_s(\mathbf{y})$ and a term uncorrelated with $V_s(\mathbf{y})$; that is,

$$\nabla \nabla V_s(\mathbf{y}) = V_s(\mathbf{y}) \mathbf{M} + \mathbf{X} , \qquad (3.21)$$

where $\mathbf{M}$ is a constant matrix, and $\mathbf{X}$ is a matrix of variables, uncorrelated with $V_s(\mathbf{y})$, which have mean zero and variances proportional to ξ. (See Appendix A.) The matrix $\mathbf{M}$ is given by

$$\mathbf{M} = \frac{\langle V_s(\mathbf{y}) \nabla \nabla V_s(\mathbf{y}) \rangle}{\langle V_s(\mathbf{y})^2 \rangle} = \frac{\nabla \nabla G(0)}{G(0)} . \qquad (3.22)$$

Note that $\mathbf{M}$ is independent of ξ. Thus, when $V_s(\mathbf{y}) = E - \theta$, the second derivatives are equal to $(E - \theta)\mathbf{M}$ plus terms which disappear as $\xi \to 0$. The determinant of the second derivatives is therefore equal to $(\theta - E)^3 \sigma_1^2 \sigma_2^2 \sigma_3^2 / \sigma_0^6$ plus terms which are negligible in the low-energy tail.[22] See Sec. 7D for an exact evaluation of these terms. Since $\mathbf{M}$ is negative definite, and $V_s(\mathbf{y})$ is negative, the second derivative $\nabla \nabla V_s(\mathbf{y})$ is certainly positive definite if we are deep enough in the low energy, so that we may neglect $\mathbf{X}$. This confirms our earlier claim that almost all the critical points of V_s are local minima when V_s is sufficiently negative.

Combining our results for p, p_3, and X, we find

$$\rho_f(E) = \frac{\sigma_1 \sigma_2 \sigma_3 (\theta - E)^3}{(2\pi)^2 \xi^2 \sigma_0^7} \exp \left[-\frac{(\theta - E)^2}{2\xi \sigma_0^2} \right] . \quad (3.23)$$

In the one-dimensional case, we have instead of

---

[22] As remarked at the end of Sec. 2A, the low-energy tail can be reached in two equivalent ways, by letting $E \to -\infty$, or by keeping E constant and reducing the magnitude of the potential fluctuations by letting $\xi \to 0$.

Eq. (3.23),

$$\rho_f(E) = \frac{\sigma_1(\theta - E)}{2\pi\xi\sigma_0^3} \exp\left[-\frac{(\theta - E)^2}{2\xi\sigma_0^2}\right], \quad (3.24)$$

where

$$\xi\sigma_1^2 \equiv \langle [V_s'(y)]^2 \rangle = -\xi G''(0). \quad (3.25)$$

We must now choose f so as to maximize Eq. (3.23). When $\xi \to 0$, it is clear that the exponential factor will become extremely sensitive to the choice of f, while the other factors are much more slowly varying. Hence, the best choice of f is that which maximizes the exponential factor in (3.23), or equivalently, that which minimizes the expression

$$\Gamma \equiv \frac{(\theta - E)^2}{\sigma_0^2} = \frac{[E - \int f(\mathbf{x}) \mathcal{T}f(\mathbf{x})d\mathbf{x}]^2}{\int f(\mathbf{x})^2 f(\mathbf{x}')^2 W(\mathbf{x} - \mathbf{x}')d\mathbf{x}d\mathbf{x}'}. \quad (3.26)$$

Note that in the low-energy tail the choice of f is independent of ξ. Hence the factors σ_0, σ_1, σ_2, σ_3, and θ will also be chosen independent of ξ, and the concentration dependence of $\rho_1(E)$ will just be contained in the explicit ξ dependence[23] of Eq. (3.23):

$$\rho_1(E) = A(E)\xi^{-2} \exp[-B(E)/2\xi]. \quad (3.27)$$

For the one-dimensional case, ρ_1 has the form

$$\rho_1(E) = A(E)\xi^{-1} \exp[-B(E)/2\xi]. \quad (3.28)$$

In either case, $B(E)$ is the minimum value of Γ, Eq. (3.26), at the specified E:

$$B(E) = \Gamma_{\min} = \min[(\theta - E)^2/\sigma_0^2]. \quad (3.29)$$

We can show that $B(E)/(E_0 - E)^2$ decreases monotonically as $E \to -\infty$, so that the density of states falls off less rapidly than a Gaussian. Note that $\Gamma/(E_0 - E)^2$, which varies as $(\theta - E)^2/(E_0 - E)^2$, is monotonically decreasing as $E \to -\infty$ for any fixed f. Let f_j be the best f at energy E_j. If $E_2 < E_1$,

$$B(E_2) \equiv \Gamma[f_2, E_2] \leq \Gamma[f_1, E_2], \quad (3.30)$$

$$\frac{B(E_2)}{(E_0 - E_2)^2} \leq \frac{\Gamma(f_1, E_2)}{(E_0 - E_2)^2} \leq \frac{\Gamma[f_1, E_1]}{(E_0 - E_1)^2} \equiv \frac{B(E_1)}{(E_0 - E_1)^2}. \quad (3.31)$$

A similar argument shows that $B(E)$ increases as $E \to -\infty$, i.e., as the density of states decreases.

The problem of minimizing Eq. (3.26) can be reduced to the solution of a nonlinear integral equation. Let us multiply the quantity E in Eq. (3.26) by the normalization integral $\int f(\mathbf{x})^2 d\mathbf{x}$ in order to make the expression homogeneous in f. Expression (3.26) is then independent of the normalization of f, and may be minimized by holding the denominator fixed at any constant value, and varying f to minimize the numerator. Introducing a Lagrange multiplier μ, we find by the methods

of variational calculus

$$\mathcal{T}f(\mathbf{x}) - \mu f(\mathbf{x})\int f(\mathbf{x}')^2 W(\mathbf{x} - \mathbf{x}')d\mathbf{x}' = Ef(\mathbf{x}). \quad (3.32)$$

This equation looks like the Hartree equation for a particle bound in its own self-consistent field, with an interaction $-\mu W(\mathbf{x} - \mathbf{x}')$; the only difference between Eq. (3.32) and Hartree's equation is that in the present case we have specified E and consider μ as the eigenvalue to be found. Equation (3.32) can be solved on a computer using the techniques developed by Hartree[24] for solving his self-consistent equations. Essentially, one assumes a potential, solves the Schrödinger equation for the wave function of a particle in that potential, and then uses this wave function to obtain a better shape for the self-consistent potential.

An alternative procedure for minimizing (3.26) is simply to introduce a trial function with several parameters and to minimize with respect to these parameters. If $\mathcal{T}$ and W are sufficiently simple, the necessary integrals can be done explicitly for a well-chosen trail function, and a minimization with respect to a small number of parameters may even be carried out by hand.

That a minimum value for (3.26) exists is pretty clear. We know that (3.26) is always greater than zero and that it becomes large if f is either too spread out in space or too confined. It also becomes large if f is not smooth. It is very hard to imagine any situation other than that (3.26) achieves its greatest-lower-bound for some well-behaved, smooth f.

The question of the uniqueness of the optimizing function f is a difficult one to answer. To be more specific, let us assume that $\mathcal{T}$ and the function W are spherically symmetric. (Spherical symmetry of v_a, and spherical correlation functions imply that W is spherical.) There will then always be a spherically symmetric solution of the Hartree equation (3.32), because (3.32) is the same equation which occurs if one wishes to find the *spherically symmetric function* f which minimizes Eq. (3.26). On the other hand, the Hartree equation is nonlinear, and we must worry about the possibility of a "lower" solution with "broken symmetry," i.e., a solution which is not rotationally invariant. If the "lowest" solution is not rotationally invariant, then there is not one optimum choice of f but a continuous family of solutions, obtained by arbitrary rotations of any one solution. [Actually, we already have one broken symmetry: Eq. (3.32) is translationally invariant, but we know that the best choice of f must be localized in space. The translational degeneracy of the solution has been removed by specifying that $f(\mathbf{x})$ have its maximum at $\mathbf{x} = 0$.] Although it is difficult to see why a nonsymmetric solution would give a lower value for Eq. (3.26) than would a symmetric solution, we have not

---

[23] For the case of screened charged impurities, the screening length, which appears in $W(\mathbf{x} - \mathbf{x}')$, is also concentration-dependent.

[24] D. R. Hartree, *The Calculation of Atomic Structures*, (John Wiley & Sons, Inc., New York, 1957), pp. 63–100.

been able to disprove this possibility. If it should occur that the function f is infinitely degenerate, it is necessary to modify our basic assumption that all wave functions have the form $f(\mathbf{x}-\mathbf{x_0})$ by including parameters α, β, and γ which describe the orientation of the function f. The best variational estimate to the energy of an eigenstate would then be the value of $E(\mathbf{x_0},\alpha,\beta,\gamma)$ taken at a local minimum in *all* the parameters.

In the three-dimensional calculations we have done, we have always assumed that the correct solution for f is spherically symmetric.

4. APPLICATION TO ONE-DIMENSIONAL WHITE-GAUSSIAN-NOISE MODEL

In order to check our approximation method, we have applied it to a one-dimensional model for which the density of states and spectral density may be exactly calculated, the model of a particle in a "white-Gaussian-noise" potential.[10,16,17] It also turns out that our approximate method is especially simple in this case; all quantities of interest can be obtained analytically, without the need of a computer.

The White-Gaussian-noise potential is the random potential which arises in the limit of an infinite density of very weak δ-function scatterers. This potential is characterized by Gaussian statistics, with the autocorrelation function

$$\langle V(x)V(x')\rangle = \tfrac{1}{2}\xi\delta(x-x').\tag{4.1}$$

If the individual scattering potentials in (2.3) are written in the form

$$\eta v_a(x-z) = \eta u_a\delta(x-z),\tag{4.2}$$

then Eq. (4.1) in comparison with (3.10) and (3.11) corresponds to the normalization

$$2\sum \bar{n}_a u_a{}^2 = \bar{N} \equiv \sum \bar{n}_a.\tag{4.3}$$

We shall choose units where h and the effective mass are equal to unity, and we shall choose the zero of energy such that $E_0 = 0$. The kinetic energy operator is then given by

$$T = -\frac{1}{2}\frac{d^2}{dx^2}.\tag{4.4}$$

For the Gaussian-white-noise model, the "Hartree equation," Eq. (3.32), takes the simple form

$$-\tfrac{1}{2}f''(x)-\tfrac{1}{2}\mu f(x)^3 = Ef(x).\tag{4.5}$$

With the conditions that $f(x)$ be properly normalized and that $f(x)$ be maximum when $x=0$, Eq. (4.6) has the solution obtained in Appendix B:

$$f(x) = (\kappa/2)^{1/2}\operatorname{sech}\kappa x,\tag{4.6}$$

$$\mu = 4\kappa,\tag{4.7}$$

where κ is defined by

$$E = -\tfrac{1}{2}\kappa^2.\tag{4.8}$$

In Appendix B we show that this solution is, in fact, unique, and we discuss the procedure for evaluating the constants in (3.24) for this choice of f. We find that

$$\rho_1(E) = \frac{1}{\sqrt{5}}\frac{4\kappa^2}{\pi\xi}\exp\left(-\frac{4}{3}\frac{\kappa^3}{\xi}\right).\tag{4.9}$$

The true density of states, for the Gaussian-white-noise model, may be expressed analytically in terms of Airy functions.[16,17] In the limit $E\to -\infty$, or equivalently $\xi\to 0$, the density of states has the exact asymptotic form

$$\rho(E)\sim\frac{4\kappa^2}{\pi\xi}\exp\left(-\frac{4}{3}\frac{\kappa^3}{\xi}\right).\tag{4.10}$$

The agreement between ρ_1 and the exact asymptotic form of ρ is remarkably good. The power of κ in the exponent is correct, the factor $\tfrac{4}{3}$ is exactly correct, and the power of κ in front of the exponential is correct. The over-all constant in ρ_1 is too small by a factor of $\sqrt{5}$; in the low-energy tail, where the density of states may change by many orders of magnitude, this error is not very significant. Even this error may be greatly reduced, however. If one includes the "average higher order-energy correction," described in a forthcoming paper, II, the factor $1/\sqrt{5}$ in Eq. (4.9) is removed and replaced by the factor 0.921. Thus we can reproduce the exact asymptotic form with an error of less than 8%.

We may also compare the form for $A(k,E)$ predicted by the approximate theory with the exact asymptotic form for the spectral density found in Ref. 16. It was shown that in the limit $E\to -\infty$, with k/κ held constant, or equivalently with k and E held fixed and $\xi\to 0$, one has

$$A(k,E)/\rho(E)\sim(\pi^2/2\kappa)\operatorname{sech}^2(k\pi/2\kappa).\tag{4.11}$$

Our approximate theory says that the ratio (4.11) should be $|f(k)|^2$. If we take the Fourier transform of $(\kappa/2)^{1/2}\operatorname{sech}\kappa x$, we indeed find

$$|f(k)|^2 = (\pi^2/2\kappa)\operatorname{sech}^2(k\pi/2\kappa).\tag{4.12}$$

The good agreement between the results of our approximate theory and the exact asymptotic forms of $\rho(E)$ and $A(k,E)$, for the white-Gaussian-noise model, provides striking confirmation of the validity of the approximate theory in the low-energy tail. One may still ask, however, where the low-energy tail begins: we must be sure that the exact functions $\rho(E)$ and $A(k,E)$ achieve their asymptotic forms at energies high enough to make the asymptotic forms useful.

In Fig. 4 we have compared the exact value of $\rho(E)$ with its asymptotic form, Eq. (4.10), The error in the asymptotic form is found to be 27% when $E/\xi^{2/3} = -1$, approximately 6% when $E/\xi^{2/3} = -2$, and $\approx 3\%$ when $E/\xi^{2/3} = -3$. The values of $\rho(E)/\rho(0)$ at these three points are 0.15, 3×10^{-4}, and 7×10^{-8}, respectively. Thus, over most of the range of interest, the error in the
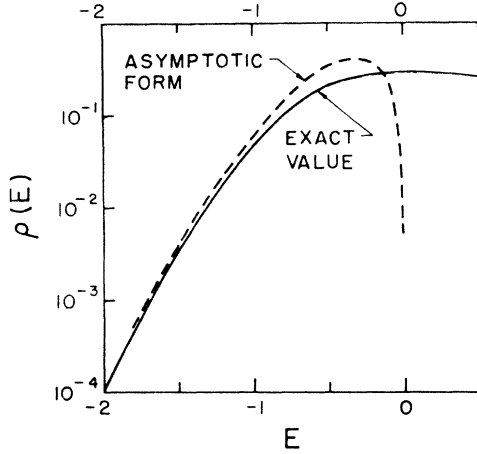
FIG. 4. Density of states for one-dimensional white noise model: Comparison of the *exact* $\rho(E)$ with the asymptotic form of the *exact* $\rho(E)$, namely $\rho_{AS}(E) = [8|E|/\pi\xi] \exp[-4|2E|^{3/2}/3\xi]$ (when $\hbar = m^* = 1$). The energy is plotted in units of $\xi^{2/3}$, the density of states in units of $\xi^{-(1/3)}$, i.e., $(\rho/\xi^{-(1/3)})$ is plotted against $(E/\xi^{2/3})$ as a universal curve. Including second-order corrections, the density computed in this paper is $\rho_2(E) = 0.92\rho_{AS}(E)$.

asymptotic form is of the same order of magnitude as the discrepancy between the asymptotic form and the approximate theory, when the average higher energy correction is included in the latter.

We have also made comparisons, at several points, between the exact value of the ratio $A(k,E)/\rho(E)$ and its asymptotic form, Eq. (4.11). The results of these comparisons are shown in Fig. 5.

5. SCREENED COULOMB POTENTIALS

We now turn our attention to the important example of screened Coulomb impurity potentials. We assume
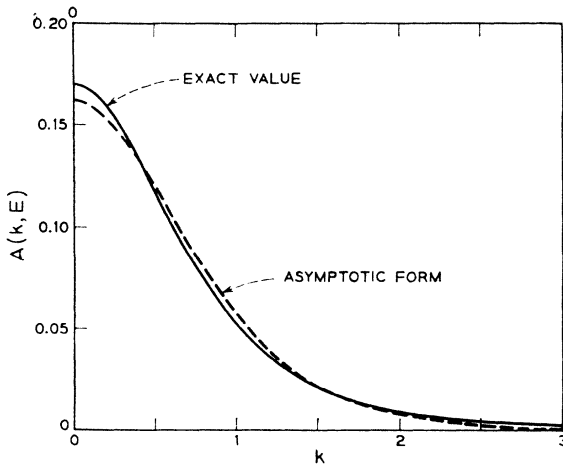
FIG. 5. Momentum dependence of spectral density for one-dimensional white noise model, at energy $E = -\xi^{2/3}$. Comparison of $A(k,E)$ and its asymptotic form $|f(k)|^2\rho(E)$, where $|f(k)|^2 = (\pi^2/2k) \operatorname{sech}^2(\pi k/2\kappa)$, and $\kappa = |2E|^{1/2}$. We plot the spectral density in units of $\xi^{-(2/3)}$ against wave number in units of $\xi^{1/3}$, i.e., we plot $A(k,E)/\xi^{-(2/3)}$ versus $k/\xi^{1/3}$. We have assumed $\hbar = m^* = 1$.

impurity potentials of the form

$$\eta v_a(\mathbf{x} - \mathbf{z}) = -Z_a \frac{e^2}{\epsilon_0 |\mathbf{x} - \mathbf{z}|} \exp(-Q|\mathbf{x} - \mathbf{z}|), \quad (5.1)$$

where e is the electronic change, ϵ_0 is the dielectric constant of the pure semiconductor, Q is the reciprocal screening length, and $Z_a e$ is the charge of the a-type impurities. We assume that the impurities are randomly distributed. The autocorrelation function for the potential fluctuations can be evaluated by working with the Fourier transform of Eq. (3.14). One finds after straightforward calculation that

$$\langle V(\mathbf{x}) V(\mathbf{x}') \rangle = \xi \exp(-Q|\mathbf{x} - \mathbf{x}'|), \quad (5.2)$$

where

$$\xi = \frac{2\pi}{Q} \frac{e^4}{\epsilon_0^2} \sum_a \bar{n}_a Z_a^2. \quad (5.3)$$

We assume that Gaussian statistics may be used.

The kinetic energy operator T for the model is assumed to be of the isotopic, effective mass form, Eq. (2.2). We assume that the optimum choice of f is a spherically symmetric function. Let

$$f(\mathbf{x}) = (4\pi)^{-1/2} S(r)/r, \quad (5.4)$$

where $r = |\mathbf{x}|$.

If one averages the function $\exp(-Q|\mathbf{x} - \mathbf{x}'|)$ with respect to the angular coordinates of the variable $\mathbf{x}'$, one finds

$$\frac{1}{2} \int_{-1}^{1} \exp[-Q(r^2 + r'^2 + 2rr'\mu)^{1/2}] d\mu \equiv K(r,r')$$

$$= \frac{1}{Qrr'} e^{-Qr_>} [(r_> + Q^{-1}) \sinh Qr_< - r_< \cosh Qr_<], \quad (5.5)$$

where $r_>$ and $r_<$ are the greater and lesser, respectively, of the two numbers r' and r. The Hartree-type eigenvalue equation, (3.32), is equivalent to the pair of equations

$$\left[-\frac{\hbar^2}{2m^*} \frac{d^2}{dr^2} - \mu U(r) \right] S(r) = (E - E_0) S(r), \quad (5.6)$$

$$U(r) = \int K(r,r') S(r')^2 dr'. \quad (5.7)$$

The function $S(r)$ is required to vanish at $r = 0$ and $r = \infty$.

Equations (5.6) and (5.7) have been solved iteratively on a digital computer for a range of values of the parameter $E - E_0$. For each value of $(E - E_0)$, a trial function was first used for $S(r)$ in Eq. (5.7); then the value of $U(r)$ so obtained was substituted in (5.6). The value of μ is varied until the solution $S(r)$ of (5.6) satisfies the required boundary conditions and the function S thus obtained is used as a new trial function in (5.7). The

iteration process was found to converge rapidly. The wave function finally obtained was then used to calculate the constants $T=\theta-E_0$, σ_0, and σ_1, and the functions $A(E)$ and $B(E)$ of Eq. (3.27). The results are presented in Table I. Typical wave functions $S(r)$ and potentials $U(r)$ are shown in Figs. 6–8.

The parameters which can enter the density of states, in the present model, are Q, ξ, $(\hbar^2/2m^*)$, and $(E-E_0)$. Note that ξ has the dimensions of (energy)^2. We know that the dependence of the density of states $\rho_1(E)$ on the parameter ξ must be given by Eq. (3.27). Hence, by dimensional arguments, ρ_1 must have the form

$$\rho_1(E)=(E_Q{}^3Q^3/\xi^2)a(\nu)\,\exp[-(E_Q{}^2/2\xi)b(\nu)], \quad (5.8)$$

where $a(\nu)$ and $b(\nu)$ are universal dimensionless functions; E_Q is the energy unit:

$$E_Q\equiv\hbar^2Q^2/2m^*, \quad (5.9)$$

and ν is the dimensionless energy,

$$\nu\equiv(E_0-E)/E_Q>0. \quad (5.10)$$
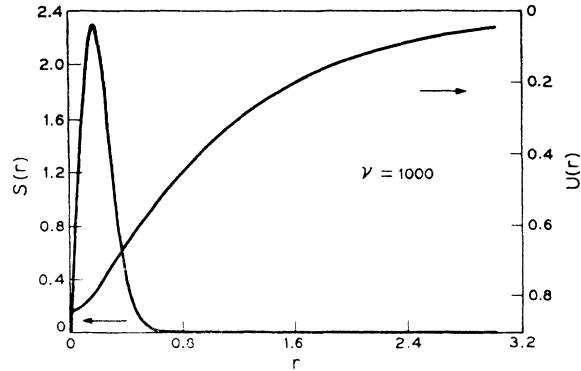
FIG. 6. The wave function $S(r)$ of (5.6) and potential $U(r)$ of (5.7) are plotted against r, using as units $E_Q=\hbar^2Q^2/(2m^*)=1$, $Q=1$, for the case $\nu=(E_0-E)/E_Q=1000$. (These are plots of $Q^{-1/2}S$ and U/E_Q versus Qr.)

For the conduction band we must take

$$E_0=E_c+\bar{V}; \quad \nu=(E_c+\bar{V}-E)/E_Q, \quad (5.11)$$

where E_c is the conduction-band-edge energy. For the "high-energy tail" of the valence band, we must take

$$\nu=[E-(E_v+\bar{V})]/E_Q, \quad (5.12)$$

where E_v is the valence-band edge. In both cases, $\bar{V}$ is the mean of the original potential [see (5.1)]:

$$\bar{V}=-\Big\langle\sum_{a,i}\frac{Z_ae^2}{\epsilon_0|\mathbf{x}-\mathbf{z}_{ai}|}\exp[-Q|\mathbf{x}-\mathbf{z}_{ai}|]\Big\rangle$$

$$=-\frac{4\pi e^2}{\epsilon_0Q^2}\sum_a Z_a\bar{n}_a. \quad (5.13)$$

The behavior of ρ_1 is, of course, dominated, in the low-
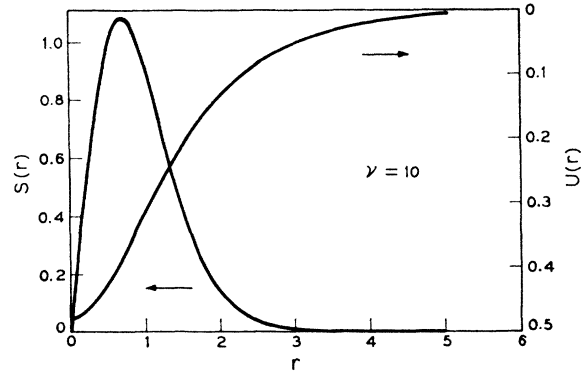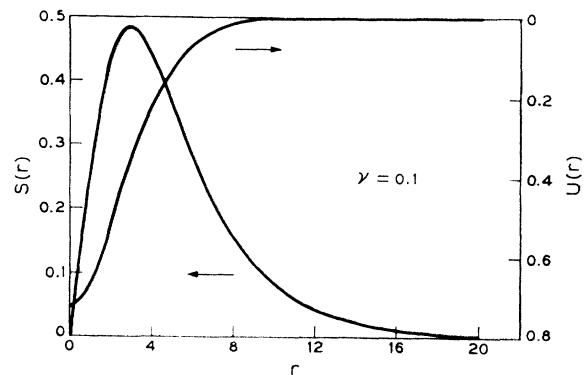

FIG. 7. The wave function $S(r)$ and potential $U(r)$ of Eqs. (5.6)–(5.7) are plotted against r in dimensionless units (see Fig. 6 legend) for $\nu=10$.

energy tail, by the exponential factor in (5.8). The functions $a(\nu)$ and $b(\nu)$ are equal to the functions $A(E)$ and $B(E)$ in units where $Q=\hbar^2/2m^*=1$. Our actual computational procedure thus consists in picking ν and solving

$$[-d^2/dr^2-\mu U(r)]S(r)=-\nu S(r) \quad (5.14)$$

jointly with (5.7) [using $Q=1$ in (5.5)] to obtain μ and $S(r)$. Then using Eqs. (3.17), (3.15), and (3.32), we obtain

$$\sigma_0{}^2=\int_0^\infty S^2(r)U(r)dr\equiv(f,Uf); \quad (5.15)$$

and using (3.19), (3.15), and (3.32), we get

$$\sigma_1{}^2=-\frac{1}{3}\int U(\mathbf{x})\nabla^2[f(\mathbf{x})]^2d\mathbf{x}$$

$$=-\frac{1}{3}\int_0^\infty rU(r)dr[S^2(r)/r]''$$

$$=-\frac{1}{3}\int_0^\infty [S^2(r)/r]dr[rU(r)]'', \quad (5.16)$$

FIG. 8. The wave function $S(r)$ and potential $U(r)$ of Eqs. (5.6)–(5.7) are plotted against r in dimensionless units (see Fig. 6 legend) for $\nu=0.1$.
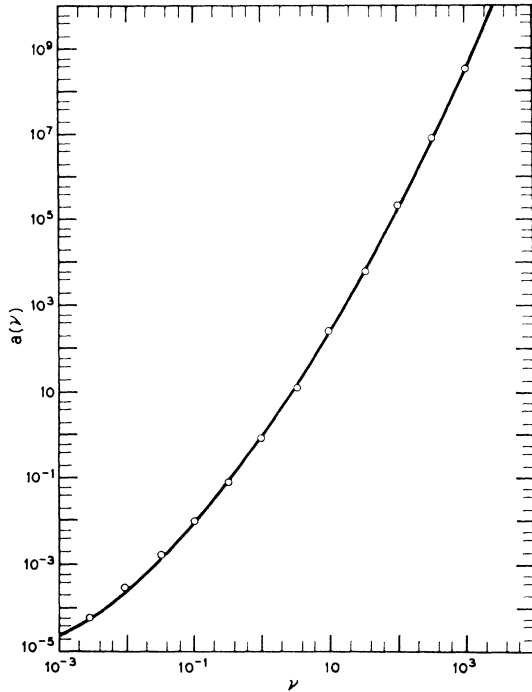
Fig. 9. The prefactor $a(\nu)$ in the density of states, Eq. (5.8), is plotted against $\nu = (E_0 - E)/E_Q$. (See Fig. 1 legend.)

where $''$ denotes the second derivative d^2/dr^2. Since $\theta - E = -$ (potential energy), we have

$$\theta - E = T + \nu = \mu(f, Uf) = \mu \sigma_0^2 \qquad (5.17)$$

where $T = -(f, \nabla^2 f)$ is the mean kinetic energy. Equation (3.23) now yields the universal functions

$$b(\nu) = (T + \nu)^2/\sigma_0^2 = \mu^2 \sigma_0^2, \qquad (5.18)$$

$$a(\nu) = (T + \nu)^3 \sigma_1^3 / [(2\pi)^2 \sigma_0^7] = \mu^3 \sigma_1^3 / [(2\pi)^2 \sigma_0], \qquad (5.19)$$

when σ_0, σ_1 and μ are evaluated for each ν. The results of our computer calculations for $b(\nu)$ and $a(\nu)$ are plotted in Figs. 1 and 9. In Fig. 2, we have plotted the quantity

$$n(\nu) \equiv d \log b(\nu)/d \log \nu. \qquad (5.20)$$

As may be seen from Fig. 2, $n(\nu)$ varies smoothly from $\frac{1}{2}$ to 2 as ν increases. That this is the correct behavior to be expected, will be established in paper III.

Note that the argument ν in Figs. 1, 2, and 9 is plotted on a logarithmic scale, with ν varying over many orders of magnitude. We would not expect to see all regions of these curves in any one type of crystal. At energies which are too close to E_0, we will not be in the low-energy tail, and the approximation $\rho_1(E)$ will not be of value. On the other hand, when E is too far in the low-energy tail, Gaussian statistics will certainly not be valid, and Eq. (5.8) will be incorrect. Thus in any one material the interesting range of ν is probably restricted to considerably less than one decade. However, by considering models with different values of the screening

length, of the impurity concentration, and of the effective mass m^*, we may hope to reach different regions of Figs. 1, 2, and 9. The requirements that limit the region of validity of Eq. (5.8) are discussed in Sec. 7.

The region of Figs. 1, 2, and 9 of importance for a particular material depends on the dimensionless parameter

$$\xi' \equiv \xi/E_Q^2 = 8\pi n_D/(a^2 Q^5), \qquad (5.21)$$

where

$$a \equiv \epsilon_0 \hbar^2/m^* e^2 \qquad (5.22)$$

is the hydrogenic Bohr radius in the solid for a singly charged impurity, and

$$n_D \equiv \sum_a \bar{n}_a Z_a^2. \qquad (5.23)$$

(The density n_D reduces to the concentration n of free carriers in an uncompensated sample of singly charged impurities. Otherwise $n_D > n$.)

The low-energy tail for any material begins, roughly, at an energy where $b(\nu)/2\xi' \approx 3$. A typical measurement in the low-energy tail will be made at an energy where $b(\nu) \approx 10\xi'$. Hence, when ξ' is known the corresponding value of ν may be determined from Fig. 1, and the resulting $n(\nu)$ from Fig. 2. The result is the plot of n versus ξ' shown in Fig. 3.

In Figs. 10 through 13 we show semilog plots of the complete function $\rho_1(E)$ for several values of the
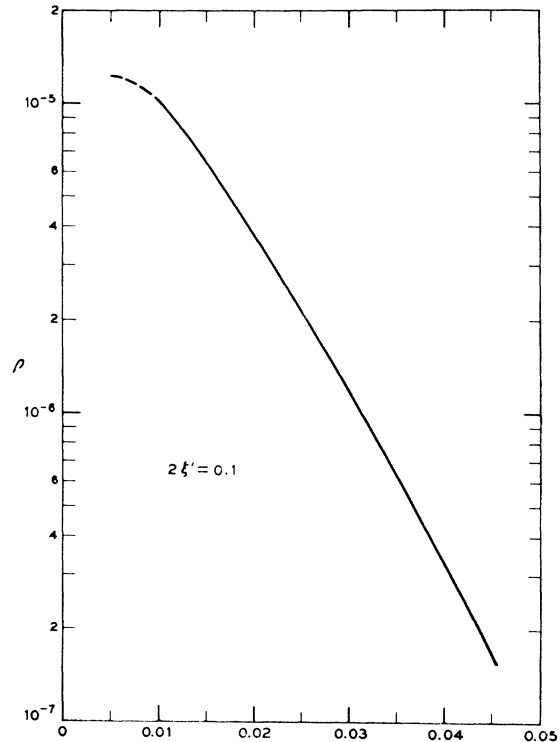

Fig. 10. The density of states ρ_1, in dimensionless form, $a(\nu) \exp[-b(\nu)/2\xi']$, is plotted against $\nu = (E_0 - E)/E_Q$ for $2\xi' = 0.1$ (See Fig. 1 legend.) The dashed region is not deep enough in the tail for our approximations to be valid. See (7.6).

parameter $\xi' = \xi/E_Q^2$. For ξ' near one, $\rho_1(E)$ displays a behavior close to simple exponential.

6. SCREENING

In order to implement the formulas in Sec. 5, it is necessary to estimate the screening length, Q^{-1}. It should be remembered that the screening carriers need not belong to the band whose low-energy tail we are studying. For example, in certain optical experiments, one may be interested in the low-energy tail of the conduction band in a p-type semiconductor.

In the following, we shall assume that all the screening comes from one band. We shall give formulas for the case where the screening carriers are electrons in the conduction band. The formulas are directly applicable to p-type semiconductors, with the appropriate sign convention for holes. In any situation where there are carriers in several bands, we may write

$$Q^2 = \sum_\alpha Q_\alpha^2 \qquad (6.1)$$

where Q_α^2 is the contribution from band α, computed according to the formulas below.

If we make the Fermi-Thomas approximation[25] to estimate the screening charge, and moreover linearize the result in the potential V, the screening constant is
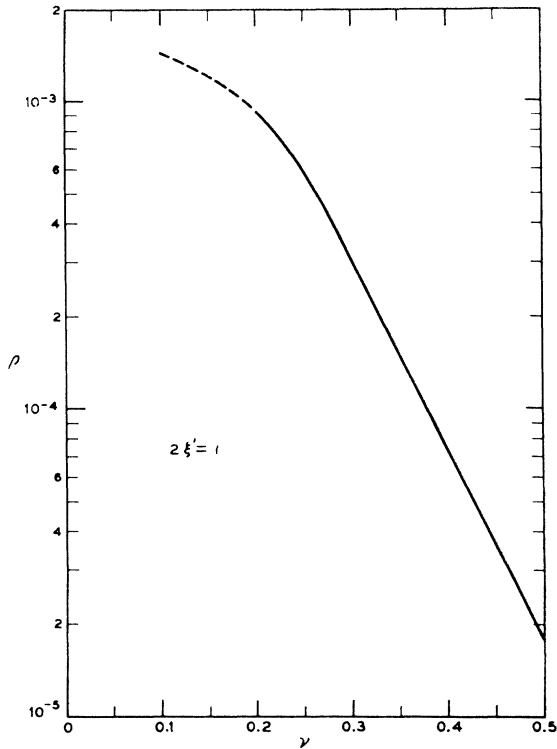

Fig. 11. The density of states ρ_1, in dimensionless form, $a(\nu)\exp[-b(\nu)/2\xi']$, is plotted against ν for $2\xi' = 1$. (See Fig. 1 legend.)

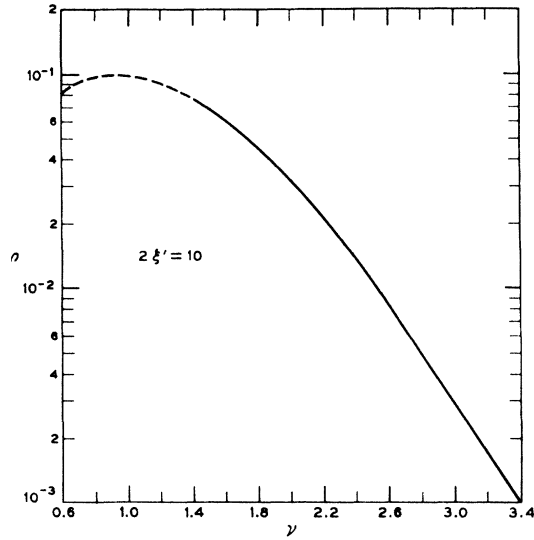[25] See for example J. C. Slater, Phys. Rev. **76**, 1592 (1949); R. B. Dingle, Phil. Mag. **46**, 831 (1955).

Fig. 12. The density of states ρ_1, in dimensionless form, $a(\nu)\exp[-b(\nu)/2\xi']$, is plotted against ν for $2\xi' = 10$.

found to be

$$Q^2 = (4\pi e^2/\epsilon_0)\int \rho_c(E)dE[-\partial f_0(E)/\partial E], \qquad (6.2)$$

where $\rho_c(E)$ is the density of states in the conduction band (including the impurity-band tail) and $f_0(E)$ is the Fermi occupancy factor

$$f_0(E) = \{\exp[(E-E_n)/kT]+1\}^{-1}, \qquad (6.3)$$

where E_n is the electron quasi-Fermi level.[26]

At high temperatures, when Boltzmann statistics are applicable (6.2) reduces to

$$Q^2 = 4\pi e^2 n/(\epsilon_0 kT), \qquad (6.4)$$

where n is the concentration of free electrons. For temperatures below the degeneracy temperature,[26] $\partial f_0/\partial E$ can be approximated by a delta function and

$$Q^2 \approx 4\pi e^2 \rho_c(E_n)/\epsilon_0. \qquad (6.5)$$

If the quasi-Fermi level is not the tail, we can approximate $\rho_c(E)$ by the unperturbed "free-carrier" density:

$$\rho_c(E) \approx \rho_0(E) = (2\pi^2)^{-1}(2m_s/\hbar^2)^{3/2}(E-E_0)^{1/2}, \qquad (6.6)$$

where m_s is the mass of the screening carrier and is not necessarily the same as m^* the mass in the observed band whose low-energy tail we wish to calculate. The quasi-Fermi level can then be approximated by

$$E_n - E_0 = \hbar^2(3\pi^2 n)^{2/3}/(2m_s), \qquad (6.7)$$

so that Q^2 reduces to the "free" electron value

$$Q^2 \approx [4m_s e^2/(\epsilon_0 \hbar^2)](3n/\pi)^{1/3},$$

or

$$Q^2 \approx 4n^{1/3}/a_s; \quad a_s = \epsilon_0 \hbar^2/(m_s e^2). \qquad (6.8)$$

[26] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).
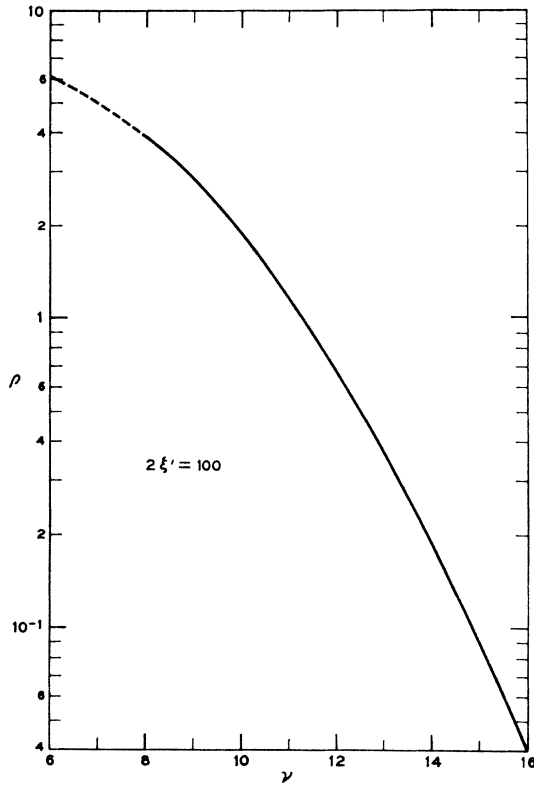
FIG. 13. The density of states ρ_1, in dimensionless form, $a(\nu) \exp[-b(\nu)/2\xi']$, is plotted against ν for $2\xi' = 100$.

In the presence of nearly perfect compensation, E_n will move into the tail of the density of states, and it will no longer be valid to approximate $\rho_c(E_n)$ by $\rho_0(E_n)$. There is, however, a worse difficulty, which arises in compensated semiconductors: linearization in V may no longer be possible, and the potential $V(\mathbf{x})$ is no longer strictly a superposition of screened Coulomb interactions.

The criterion for linear screening is that the potential $V(\mathbf{x})$ be small compared to the Fermi energy $(E_n - E_0)$. For linear screening to be valid the root mean square fluctuation in $V(\mathbf{x})$ should be small compared to the Fermi energy, or

$$\xi^{1/2} < E_n - E_0. \tag{6.9}$$

It is convenient to express Eq. (5.3) [or (5.21)] for ξ as

$$\xi = \frac{8\pi n_D}{a^2 Q}\left(\frac{\hbar^2}{2m^*}\right)^2 = \frac{8\pi n_D}{a_s^2 Q}\left(\frac{\hbar^2}{2m_s}\right)^2. \tag{6.10}$$

If we use Eq. (6.8) to approximate Q, Eq. (6.10) becomes

$$\xi = \frac{4\pi n_D}{n^{1/6}(a_s)^{3/2}}\left(\frac{\hbar^2}{2m_s}\right)^2, \tag{6.11}$$

and thus condition (6.9) is equivalent to

$$1 < \frac{(3\pi^2)^{2/3}}{(4\pi)^{1/2}}\frac{(na_s)^{3/4}}{(n_D)^{1/2}} \sim 3\left(\frac{n}{n_D}\right)^{1/2}(na_s^3)^{1/4}. \tag{6.12}$$

Inequality (6.12) gives the condition for validity of linear screening when the magnitude of the potential fluctuation is equal to the root-mean-square fluctuation of $V(\mathbf{x})$. In the low-energy tail we may be interested in potential fluctuations which are larger than the root mean-square fluctuations in $V(\mathbf{x})$. If we are in the region $\xi' \gg 1$ where the range of the wave function $Q^{-1}\nu^{-1/2}$ is small compared to the screening radius, the condition $b(\nu) \approx 10\xi'$ means that we are interested in potential fluctuation with $|V(\mathbf{x})| \approx 3\xi^{1/2}$. In the range where $\xi' \ll 1$, the wave function averages $V(\mathbf{x})$ over a region large compared to the screening length; the low-energy tail in this case arises when $V(\mathbf{x})$ is attractive over a large region, but $|V(\mathbf{x})|$ will not be much larger than $\xi^{1/2}$ in this region. Condition (6.12) may thus be more properly written

$$1 < 3\left(\frac{n}{n_D}\right)^{1/2}(na_s^3)^{1/4}\gamma \tag{6.13}$$

where γ depends on ξ' and varies between $\frac{1}{3}$ (for $\xi' \gg 1$) and 1 for ($\xi' \ll 1$).

It should be remembered that the parameters ξ' depends on m^* as well as m_s. If the screening constant is given by (6.8), then Eq. (5.21) may be written

$$\xi' = \frac{\pi}{4}(na^3)^{1/6}\left(\frac{n_D}{n}\right)\left(\frac{m^*}{m_s}\right)^2 \tag{6.14}$$

If inequality (6.13) does not hold we cannot use linear screening, and all our problems become much more difficult. It is probable then that some further approximations will have to be made.

It is also useful to re-express the condition of linear screening in the form

$$\xi' > \left(\frac{1}{3\gamma}\right)^{2/3}\frac{\pi}{4}\left(\frac{n_D}{n}\right)^{4/3}\left(\frac{m^*}{m_s}\right)^2. \tag{6.15}$$

In the absence of compensation, when $m_s \sim m^*$ this condition is roughly $\xi' > 1$. Only if $m^* \ll m_s$, will this condition be weakened.

7. VALIDITY REGIONS OF $\rho(\nu)$ FOR SCREENED COULOMB CASE

A. Gaussian Statistics

Our "smoothed potential" can be written as a sum

$$V_s(\mathbf{x}) = \sum_{a,i} R(\mathbf{x} - \mathbf{z}_{ai}), \tag{7.1}$$

$$R(\mathbf{x} - \mathbf{z}_{ai}) = \int f^2(\mathbf{x} - \mathbf{x}')e^{-Q|\mathbf{x}' - \mathbf{z}_{ai}|}/|\mathbf{x}' - \mathbf{z}_{ai}|\,d\mathbf{x}'. \tag{7.2}$$

Gaussian statistics are adequate in dealing with the sum (7.1), provided the average number of centers within the range of $R(\mathbf{x})$ is large compared to 1, and provided we are not too far in the low-energy tail. Since the range of $f^2(\mathbf{x})$ is $[\hbar^2/(2m^*|E|)]^{1/2}$, and this function is convoluted with a function of range Q^{-1}, we can combine these ranges and write our condition roughly as

$$n_D[\hbar^2/(2m^*|E|)^{1/2}+Q^{-1}]^3 \gg 1,$$

or

$$(\nu^{-1/2}+1)^3 \gg Q^3/n_D. \quad (7.3)$$

If the number of centers within a screening radius Q^{-1} is large compared to 1,

$$n_D Q^{-3} \equiv (2\xi'/\pi)^3(n/n_D)^2(m_s/m^*)^6 \gg 1, \quad (7.4)$$

then (7.3) is satisfied for all ν. Note, moreover, that when the condition (6.15) for linear screening is obeyed, (7.4) is also likely to be obeyed. If, however, $(2\xi'/\pi) \times (n/n_D)^{2/3}(m_s/m^*)^2 < 1$, then Gaussian statistics are valid when Eq. (7.3) is obeyed:

$$\nu < \frac{(n_D Q^{-3})^{2/3}}{[1-(n_D Q^{-3})^{1/3}]^2},$$

or

$$\nu < \frac{(2\xi'/\pi)^2(n/n_D)^{4/3}(m_s/m^*)^4}{[1-(2\xi'/\pi)(n/n_D)^{2/3}(m_s/m^*)^2]^2}. \quad (7.5)$$

If we attempt to go too far into the low-energy tail, Gaussian statistics will inevitably break down, whether or not Eq. (7.4) holds. Moreover, the criterion (7.3) is a sensitive one, and a more careful evaluation of the effective radius of $R(\mathbf{x})$ is needed. We hope to return to these points in a future discussion of non-Gaussian statistics.

B. Use of Ground State Only

Our calculation neglects the presence of excited states in each minimum. If we are deep enough in the tail for the ground state at energy ν to be moderately unlikely, say

$$b(\nu) > 6\xi', \quad (7.6)$$

[which makes $\exp[-b/2\xi'] = \exp(-3)$], then the probability of a potential fluctuation deep enough to produce an *excited* state at ν will be quite small. Thus we adopt (7.6) as an interim condition for the validity of our calculations. The dashed portions of Figs. 10–13 were indicated in this way, because they violate (7.6).

It is, of course, preferable to use (7.6) directly, with Fig. 1 or Table I, but for small and large ν we have the approximate formulas (see paper III)

$$b(\nu) \approx 3\nu^{1/2}, \quad \nu \ll 1,$$
$$b(\nu) \approx \nu^2, \quad \nu \gg 1, \quad (7.7)$$

so that Eq. (7.6) is roughly equivalent to

$$\nu > 4(\xi')^2, \quad \xi' \ll 1, \quad (7.8)$$
$$\nu > (6\xi')^{1/2}, \quad \xi' \gg 1. \quad (7.9)$$

Summary of Conditions for Small ξ'

If $n \approx n_D$, $m_s \approx m^*$, the condition (7.5) $\nu < (2\xi'/\pi)^2$, (roughly), is incompatible with Eq. (7.8). A direct use of Eq. (7.6) rather than the less precise Eq. (7.8) requires

$$b(4\xi'^2/\pi^2) \geq 6\xi', \quad \text{or} \quad \xi' \gtrsim 1, \quad (7.10)$$

if there is to be any region of ν for which Eqs. (7.6) and (7.5) are compatible. Smaller values of ξ' can thus lead to a valid region only if $m_s > m^*$.

Summary of Conditions for Large ξ'

If $\xi' \gg 1$, and $m_s = m^*$, $n = n_D$ both the condition (6.15) for linear screening, and Eq. (7.4) for Gaussian statistics will be obeyed. In this case, our computed results are valid for $b(\nu) > 6\xi'$, i.e., the solid portions of the curves in Figs. 12 and 13. If $m_s < m^*$, larger values of ξ' are needed to satisfy Eqs. (6.15) and (7.4). If $m_s > m^*$, our results can be valid for ξ' considerably smaller than unity.

C. Use of Minimum Counting Methods

A one-to-one correspondence between energy states and minima is only valid if the spread of the wave function associated with each minimum is small compared to the mean separation between minima, i.e., if

$$\{\hbar^2/[2m^*(E-E_0)]\}^{1/2} \ll \left(\int_{-\infty}^{E_1} \rho(E)dE\right)^{-1/3}, \quad (7.11)$$

where only minima below some cutoff energy E_1 are to be counted. Using Eqs. (5.8)–(5.10), we rewrite this condition in the form

$$\nu > \left[\int_{\nu_1}^{\infty} a(\nu) \exp[-b(\nu)/2\xi']d\nu/(\xi')^2\right]^{2/3}. \quad (7.12)$$

In particular, this condition must be obeyed even at $\nu = \nu_1$. A "safe" condition can therefore be written in the form

$$\nu \geq \nu_1 > \left[\int_0^{\infty} a(\nu) \exp[-b(\nu)/2\xi']d\nu/(\xi')^2\right]^{2/3}. \quad (7.13)$$

By introducing the approximate forms

$$a(\nu) = A\nu^\mu, \quad b(\nu) = B\nu^n, \quad (7.14)$$

we obtain an approximate evaluation of Eq. (7.13):

$$\nu_1 \geq \{A\Gamma(m)/[n(B/2)^m]\}^{2/3}(\xi')^{2(m-2)/3}, \quad (7.15)$$

where $m = (\mu+1)/n$.

For small ξ', the region of small ν is important, and then from Figs. 1, 2, and 9 or from paper III, we can conclude that

$$a(\nu)\approx 0.4\nu^{3/2}; \quad b(\nu)\approx 3\nu^{1/2} \quad (7.16)$$

so that

$$\nu_1 > 1.6(\xi')^2, \quad (7.17)$$

a condition less stringent than Eq. (7.9). From the same sources, we can conclude that for large ξ' and ν,

$$a(\nu)\approx 10^{-2}\nu^{7/2}; \quad b(\nu)\approx \nu^2. \quad (7.18)$$

Using this information in Eq. (7.15), we find that in large ξ'

$$\nu > 0.1(\xi')^{1/6}, \quad (7.19)$$

a condition far less stringent than Eq. (7.10). For intermediate values of ξ', by using the exponents n and μ appropriate for the relevant values of ν [say at $b(\nu)\approx 10\xi'$], we again find that the condition (7.15) is considerably less stringent than the condition (7.6): $b(\nu)>6\xi'$ required for excited states to be unimportant.

Thus we may conclude that *if we are deep enough in the tail for excited states to be unimportant, the use of minimum counting methods should be quite valid.*

D. Exact Evaluation of the Mean Determinant

In Sec. 3, Eq. (3.21), we evaluated the dominant term in the conditional mean of $\det\partial^2 V_s(\mathbf{y})/\partial y_i\partial y_j$. In this section, we shall make an *exact* evaluation of the mean of *all* terms in the determinant. Using Eq. (3.21) this determinant can be written

$$\det = V_s{}^3 M_{11}M_{22}M_{33}+[V_s{}^2 M_{22}M_{33}X_{11}+\text{cyclic}]$$
$$+ V_s[M_{11}(X_{22}X_{33}-X_{23}X_{32})+\text{cyclic}]+\det X_{ij}. \quad (7.20)$$

As before, we want the mean conditional on $V_s=E-\theta$. (It is also conditional on $\nabla V_s=0$; but, as the second derivatives are uncorrelated with the first, this condition can be ignored.) Thus V_s is fixed, and the X_{ij} are Gaussian random variables of mean zero. Hence, only polynomials of even degree in X_{ij} survive the average, namely the first term in (7.20), which we have already evaluated, and the third which we shall proceed to evaluate. According to (3.21)

$$X_{ij}=\nabla_i\nabla_j V_s-\langle\langle\nabla_i\nabla_j V_s\rangle\rangle, \quad (7.21)$$

where $\langle\langle\ \rangle\rangle$ is the mean conditional on $V_s=E-\theta$. Equation (A9) now yields

$$\langle\langle X_{ij}X_{kl}\rangle\rangle$$
$$=\langle(\nabla_i\nabla_j V_s)\nabla_k\nabla_l V_s\rangle-\langle(\nabla_i\nabla_j V_s)V_s\rangle\langle V_s\nabla_k\nabla_l V_s\rangle/\langle V_s{}^2\rangle$$
$$=-\nabla_i\nabla_j\nabla_k\nabla_l G(0)-M_{ij}M_{kl}\langle V_s{}^2\rangle. \quad (7.22)$$

The second term, which follows from Eq. (3.22) can be simplified using Eqs. (3.19) and (3.17):

$$M_{ij}=-\delta_{ij}(\sigma_i{}^2/\sigma_0{}^2); \quad \langle V_s{}^2\rangle=\xi\sigma_0{}^2. \quad (7.23)$$

Thus we obtain the simple results

$$\langle\langle X_{22}X_{33}\rangle\rangle=-\nabla_2{}^2\nabla_3{}^2 G(0)-M_{22}M_{33}\langle V_s{}^2\rangle, \quad (7.24)$$

$$\langle\langle X_{23}X_{32}\rangle\rangle=-\nabla_2{}^2\nabla_3{}^2 G(0), \quad (7.25)$$

so that including the cyclic terms,

$$\langle\langle\det\rangle\rangle= V_s{}^3 M_{11}M_{22}M_{33}-3V_s M_{11}M_{22}M_{33}\langle V_s{}^2\rangle$$
$$=(E-\theta)^3 M_{11}M_{22}M_{33}\left[1-3\frac{\langle V_s{}^2\rangle}{(E-\theta)^2}\right]; \quad (7.26)$$

$$\langle\langle\det\rangle\rangle=[E_Q{}^3(\nu+T)^3\sigma_1{}^2\sigma_2{}^2\sigma_3{}^2/\sigma_0{}^6][1-3\xi'\sigma_0{}^2/(\nu+T)^2].$$

For large ν, we show in paper III that

$$\sigma_0{}^2\to 1, \quad T/\nu\to 0, \quad (7.27)$$

so that our fractional error is

$$3\xi'/\nu^2<\tfrac{1}{2}, \quad (7.28)$$

if we obey (7.10) and require $\nu^2>6\xi'$. For small ν, we show in paper III that

$$\sigma_0{}^2\approx 5.4\nu^{3/2}, \quad T\approx 3\nu, \quad (7.29)$$

so that our fractional error is

$$3\xi'(5.4\nu^{3/2})/(16\nu^2)\approx\xi'/\nu^{1/2}<\tfrac{1}{2}, \quad (7.30)$$

when we follow Eq. (7.9) and require $\nu>4(\xi')^2$.

Thus as long as we are deep enough in the tail, this error is unimportant. When it becomes important, we should evaluate $\langle\langle|\det|\rangle\rangle$, the conditional mean of the absolute value of the determinant, rather than $\langle\langle\det\rangle\rangle$. Moreover, when Eq. (7.6) is violated, excited states become important.

E. Single Shape for All Wave Functions

The assumption in this paper which underlies our work is that all the wave functions of the system *at a given energy* (in the low-energy tail) have the same shape. When Gaussian statistics are applicable, the most important corrections to this assumption are included in the average second-order energy correction, which will be discussed in paper II. When the density of impurities is not high enough for Gaussian statistics to be employed, it is more difficult to analyze this assumption. It is clear that, if the wave function is bound to a cluster of three or four impurities, its shape will depend on the positions of these impurities. It is probable that there will be situations where Gaussian statistics are invalid but where the general approach of this paper can still be used.

For example, if the density of impurities is low enough that any electron bound in the tail is localized on a single impurity, a single-shape wave function is again likely to be a good approximation. Gaussian statistics are then likely to be invalid (except in the case of very weak screening). However, the counting procedure is

trivial: There is one minimum at each impurity. Energy fluctuations are produced by the potential energy contributions of the *other sites*. The distribution of such energy fluctuations can be treated by Markoff's method.[27] At low densities, the nearest-neighbor contributions will predominate, and we expect the density of states to have an analytic behavior near the energy E_i of an isolated impurity similar to that produced by the pair approximation.[9,28]

8. SUMMARY

We have developed a method for calculating the density of states in the low-energy tail of an impurity band in the high-density limit based upon counting minima in an appropriately smoothed version of the random potential.

We have tested our theory on an exactly solvable one-dimensional Gaussian model and have found that our approximate results yield the correct form, Eq. (1.2), and, when appropriate second-order corrections are applied, the correct numerical coefficient within 8%.

We have applied our results to the case of screened, charged impurities, in a Gaussian approximation, and have found

$$\rho_1(E) = [(QE_Q)^3/\xi^2]a(\nu) \exp[-E_Q{}^2 b(\nu)/2\xi], \quad (8.1)$$

where

$$\xi = \frac{2\pi}{Q}\frac{e^4}{\epsilon_0{}^2}\sum_a \bar{n}_a Z_a{}^2, \quad (8.2)$$

$$E_Q = \hbar^2 Q^2/(2m^*), \quad (8.3)$$

$$\nu = (E_0 - E)/E_Q, \quad (8.4)$$

$$E_0 = -\frac{4\pi e^2}{\epsilon_0 Q^2}\sum_a Z_a \bar{n}_a, \quad (8.5)$$

where $\bar{n}_a$ is the concentration of impurities of charge $Z_a e$, ϵ_0 is the dielectric constant, and m^* is the effective mass of the carrier whose impurity band is under study. The determination of the reciprocal screening length Q is discussed in Sec. 6. The numerical functions $b(\nu)$ and $a(\nu)$ are given in Figs. 1 and 9, respectively.

ACKNOWLEDGMENTS

The authors wish to thank Miss Rosemary Cox for programming the necessary computer calculations.

[27] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943); see also Ref. 21.

[28] In one dimension, there is an algebraic singularity as given in Eq. (3.5) of Ref. 9. In three dimensions, the density of states is concentrated within a region

$$|E/E_i - 1| \lesssim \exp(-\epsilon^{1/3}),$$

where $\epsilon \ll 1$ is the average number of impurities within a Bohr radius, i.e., in the volume $4\pi a^3/3$. However, the differential density of states vanishes at $E = E_i$ faster than any power. See Eq. (49) of M. Lax and H. L. Frisch, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952), Chap. 6.

APPENDIX A: CONDITIONAL EXPECTATION VALUES IN GAUSSIAN STATISTICS

Let $Z_1, Z_2, \cdots, Z_n$ be n independent Gaussian variables of mean zero. Let X and Y be Gaussian variables of mean zero that may be dependent on the Z_r. Then we can write

$$X = A + \sum_r a_r Z_r, \quad (A1)$$

and impose the condition that A be uncorrelated with the Z_r:

$$\langle A Z_r \rangle = 0, \quad r = 1, \cdots, n \quad (A2)$$

by choosing the numerical coefficients according to

$$a_r = \langle X Z_r \rangle / \langle Z_r{}^2 \rangle. \quad (A3)$$

The coefficient a_r is analogous to the "component" of the "vector" X in the direction Z_r. The variable A is a linear combination of X and Z_r and is thus a Gaussian variable of mean zero. Because a set of Gaussian variables which are uncorrelated are statistically independent, A is independent of the Z_r.

Let the symbol $\langle\langle \cdots \rangle\rangle$ denote the conditional expectation value of a variable when $Z_1, \cdots, Z_n$ are specified to have the values $z_1, \cdots, z_n$. Since A is independent of the Z_r, the conditional expectation value of A is the same as the ordinary expectation value, namely, 0. It follows that

$$\langle\langle X \rangle\rangle = \sum a_r z_r. \quad (A4)$$

Similarly we may write

$$Y = B + \sum b_r Z_r, \quad (A5)$$

where

$$b_r = \langle Y Z_r \rangle / \langle Z_r{}^2 \rangle \quad (A6)$$

and B is independent of the Z_r. As in (A4), the conditional expectation value (for fixed Z_r) can be written

$$\langle\langle Y \rangle\rangle = \sum b_r z_r. \quad (A7)$$

The conditional expectation value of the product $[X - \langle\langle X \rangle\rangle][Y - \langle\langle Y \rangle\rangle]$ is just the conditional expectation value $\langle\langle AB \rangle\rangle$. Since A and B are independent of the specified variables, the conditional expectation value $\langle\langle AB \rangle\rangle$ is equal to the ordinary expectation value $\langle AB \rangle$. This in turn may be related to the ordinary expectation value $\langle XY \rangle$ by

$$\langle XY \rangle = \langle AB \rangle + \sum a_r b_r \langle Z_r{}^2 \rangle. \quad (A8)$$

Hence, using (A3) and (A6), we have

$$\langle\langle[X-\langle\langle X\rangle\rangle][Y-\langle\langle Y\rangle\rangle]\rangle\rangle$$
$$=\langle XY\rangle-\sum_r\frac{\langle XZ_r\rangle\langle Z_rY\rangle}{\langle Z_r^2\rangle}. \quad (A9)$$

APPENDIX B: EVALUATION OF FORMULAS IN THE ONE-DIMENSIONAL MODEL

Equation (4.5) for $f(x)$ may be written

$$-\tfrac{1}{2}f''(x)-\tfrac{1}{2}\mu f(x)^3=-\tfrac{1}{2}\kappa^2 f(x). \quad (B1)$$

Multiplying by $f'(x)$ and integrating, we have

$$[f'(x)]^2=\kappa^2 f(x)^2-\tfrac{1}{2}\mu f(x)^4+\text{const}. \quad (B2)$$

Since $f'(x)=f(x)=0$ when $x=\infty$, the constant in (B2) must equal zero. We have chosen our origin so that $f(0)$ is a maximum and hence, $f'(0)=0$. Equation (B2) thus implies

$$\tfrac{1}{2}\mu f(0)^2/\kappa^2=1. \quad (B3)$$

If we define

$$u(x)\equiv f(\kappa^{-1}x)/f(0), \quad (B4)$$

then we have $u(0)=1$, and

$$u'(x)=-[u(x)^2-u(x)^4]^{1/2} \quad \text{for} \quad x\geq0. \quad (B5)$$

The sign of (B5) is fixed by noting that $u(x)$ is a maximum at $x=0$. From (B5) it follows that for $x\geq0$,

$$x=\int_u^1\frac{dv}{v(1-v^2)^{1/2}}=\tanh^{-1}[(1-u^2)^{1/2}]=\operatorname{sech}^{-1}u. \quad (B6)$$

Similar procedures may be used for $x<0$, and we find that for all x,

$$u(x)=\operatorname{sech}x. \quad (B7)$$

The normalization of $f(x)$ requires that

$$f(x)=(\kappa/2)^{1/2}\operatorname{sech}\kappa x, \quad (B8)$$

$$f(0)=(\kappa/2)^{1/2}, \quad (B9)$$

$$\mu=4\kappa. \quad (B10)$$

The normalization integral, and most other integrals involving $f(x)$, can be performed by changing the variable of integration from x to $e^{-2\kappa r}$. We also use the fact that $d\operatorname{sech}x/dx=-\operatorname{sech}x\tanh x$. We find

$$\langle V_s(y)^2\rangle=\frac{\xi}{2}\int_{-\infty}^\infty f^4(x)dx$$
$$=\frac{\xi}{6}\kappa, \quad (B11)$$

$$\langle V_s'(y)^2\rangle=\frac{\xi}{2}\int_{-\infty}^\infty \{d[f(x)]^2/dx\}^2dx$$
$$=\frac{2\xi}{15}\kappa^3, \quad (B12)$$

$$\theta=\frac{1}{2}\int_{-\infty}^\infty f'(x)^2dx=\tfrac{1}{6}\kappa^2. \quad (B13)$$

The Fourier transform of $f(x)$ is computed by a different method. In the integral

$$f(k)=\int_{-\infty}^\infty e^{-ikx}f(x)dx, \quad (B14)$$

we can close the contour of integration in the upper or lower half-plane according to the sign of k. Poles of $f(x)$ occur when $x=i\pi\kappa^{-1}(n+\tfrac{1}{2})$, where n is any integer. The residues of the integrand at these poles form a geometric series which may be easily summed, giving

$$f(k)=\pi(2\kappa)^{-1/2}\operatorname{sech}(k\pi/2\kappa). \quad (B15)$$