

THE DENSITY OF ELECTRON ENERGY LEVELS IN THE FIELD OF
RANDOMLY DISTRIBUTED SCATTERING CENTERS

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The energy level density of a particle $\rho(E)$ is studied in the resonance scattering approximation for the limiting cases of low and high scatterer densities. The existence of "self-similar" laws for $\rho(E)$ in certain energy ranges is demonstrated. The relaxation lengths are estimated. It is shown that in the long-wave limit the problem reduces to that of determining the density of eigenvalues of the Schrödinger equation with a random potential due to a fluctuating scatterer density.

THE energy level density of an electron in a crystal containing impurities has been considered theoretically by many authors. The problem is important for spectroscopy and plays an essential role in the problem of the conductivity of semiconductors and conducting gases. The single-particle aspect of this problem is treated in the review of I. Lifshitz^[1] in which one can find a bibliography of this subject, and in the work of Jonezawa and Matsubara which has appeared recently.^[2]

The purpose of this paper is to indicate certain "self-similar" laws for the level densities and to refine the criteria for the applicability of previously known results.

We consider the simplest model in which the scatterers occupy arbitrary positions, and consequently do not take into account lattice effects (see, for example, ^[1], Sec. 2). Furthermore we assume that the scattering for the s-wave is of a resonance nature. This assumption allows us to disregard the angular dependence of the scattering amplitude f and consider it to be (see ^[3], Sec. 131)

$$f = -(\alpha + ik)^{-1}, \quad k = \sqrt{2mE}. \tag{1}$$

The resonance scattering can be taken into account by means of the effective boundary condition at the center of the scatterer $r = 0$ (see, for example, ^[3]):

$$\frac{d}{dr} \ln(r\psi) |_{r=0} = -\alpha. \tag{2}$$

Outside the scatterers the wave function ψ can be written in the form of a superposition of scattered waves:

$$\psi = \sum_n a_n \frac{\exp\{ik|\mathbf{r} - \mathbf{R}_n|\}}{|\mathbf{r} - \mathbf{R}_n|} \equiv \sum G_0(\mathbf{r} - \mathbf{r}_n) a_n. \tag{3}$$

Here a_n is the amplitude of the wave scattered by the n th center.

Let us write the boundary condition (2) for each center. We obtain a system of equations for a_n :

$$(ik + \alpha)a_n + \sum_{m \neq n} \frac{\exp\{ik|\mathbf{R}_n - \mathbf{R}_m|\}}{|\mathbf{R}_n - \mathbf{R}_m|} a_m = 0, \quad n = m = 1. \tag{4}$$

In the system (4) the quantity k plays the role of an eigen number. The problem consists in determining for

a given interval dk the number of solutions of the system (4) averaged over the volume or all possible locations of the centers.

The system (4) has been investigated in ^[1] using a somewhat different notation. However, for clarity and completeness of presentation we shall carry out a general investigation of Eq. (4) and its related level densities and relaxation lengths.

Let us first consider the case of low densities $n/\alpha^3 \ll 1$. For sufficiently high energies the aggregate of scatterers can be replaced by a complex energy-dependent potential $V = 4\pi n f(E)$ (see ^[3], Sec. 139). With an accuracy up to small corrections the level density can be written in the form

$$\rho(E) = \frac{1}{\sqrt{2}\pi^2} \sqrt{E - E_0}, \quad E_0 = \frac{4\pi n}{\alpha}, \tag{5}$$

and the mean free path is given by the formula from the kinetic theory of gases

$$l = (n\sigma)^{-1} = (4\pi n |f|^2)^{-1}. \tag{6}$$

Equations (5) and (6) can be obtained from (4) in the following way. We multiply both sides of (4) by $G_0(\mathbf{x} - \mathbf{R}_n)$ and sum over n , obtaining

$$(4\pi f)^{-1} \Psi(\mathbf{r}) = \sum_n \tilde{\Psi}(\mathbf{R}_n) G_0(\mathbf{r} - \mathbf{R}_n), \tag{7}$$

where

$$\tilde{\Psi}(\mathbf{R}_n) = -4\pi \sum_{m \neq n} G_0(\mathbf{R}_n - \mathbf{R}_m) a_m. \tag{8}$$

Then we average both sides of (7) over all possible positions of the impurities. The average of the product of the right-hand side of (7) can be represented in the form of a product of the averages, since the phases of $\tilde{\Psi}(\mathbf{R}_n)$ and $G_0(\mathbf{x} - \mathbf{R}_n)$ are independent. Finally, in the absence of an impurity at the point \mathbf{R}_n the average value of $\tilde{\Psi}(\mathbf{R}_n)$ is equal to $\overline{\tilde{\Psi}(\mathbf{R}_n)}$. But in the limit of a large volume these quantities are equal. Thus averaging of (7) yields

$$(4\pi f)^{-1} \overline{\Psi(\mathbf{r})} = n \int G_0(\mathbf{r} - \mathbf{r}') \overline{\tilde{\Psi}(\mathbf{r}')} d^3r'. \tag{9}$$

Going over to the momentum representation, we find the dispersion equation

$$f^{-1} = \frac{4\pi n}{k^2 - p^2}, \tag{10}$$

which is equivalent in the region $|E| \ll \alpha^2$ to (5) and (6). We emphasize that for $E \gtrsim \alpha^2$ the retention of E_0 in Eq. (5) exceeds the accuracy, and Eq. (5) should be considered an interpolation formula.

Equations (5) and (6) are applicable only in the case when multiple scattering can be disregarded (the criterion will be presented below).

The criterion of the applicability of (5) and (6) is obviously connected with the correlation relations of the scatterers. Indeed, in the case when the scatterers form a regular lattice the spectrum has, as is well known, a band structure, and for stationary states the free path is infinite.

Below we shall only consider a system without long-range order. For $k \ll n^{1/3}$ the system of scatterers can be considered as a continuous medium characterized by a density $n(\mathbf{r})$. We note that the limiting energy of this region is $\sim n^{2/3} \gg E_0$.

We introduce a function $a(\mathbf{R})$ whose values at the points \mathbf{R}_n coincides with a_n and for arbitrary \mathbf{R} is given by the formula

$$(a + ik)a(\mathbf{R}) = - \int G_0(\mathbf{R} - \mathbf{R}') a(\mathbf{R}') n(\mathbf{R}') d^3\mathbf{R}' + a(\mathbf{R}) \int_{V_0} G_0(\mathbf{R} - \mathbf{R}') n(\mathbf{R}') d^3\mathbf{R}'. \quad (11)$$

Here $n(\mathbf{R}) = \sum_n \delta(\mathbf{R} - \mathbf{R}_n)$ is the density of scatterers, and V_0 is a region about the point \mathbf{R} such that

$$\int_{V_0} n(\mathbf{R}') d^3\mathbf{R}' = 1. \quad (12)$$

Setting $\mathbf{R} = \mathbf{R}_n$, we obtain the system of equations (4). For $k \ll n^{1/3}$ one can consider $a(\mathbf{R})$ to be a slowly varying function of the coordinates.¹⁾ Further one can replace in the integral over the region V_0 the quantity $G_0(\mathbf{R} - \mathbf{R}')$ by $1/|\mathbf{R} - \mathbf{R}'| + ik$. Thus we obtain from (12):

$$aa(\mathbf{R}) + \int G_0(\mathbf{R} - \mathbf{R}') a(\mathbf{R}') n(\mathbf{R}') d^3\mathbf{R}' = 0 \quad (13)$$

(a quantity of the order of $n^{1/3}$ has been neglected by comparison with α).

In Eq. (13) and below we understand $n(\mathbf{R})$ to be a density averaged over a region of dimensions larger than $n^{-1/3}$ but smaller than the wavelength. Equation (13) is equivalent to the Schrödinger equation

$$(\Delta + k^2 - 4\pi n(\mathbf{R})/\alpha)a(\mathbf{R}) = 0. \quad (14)$$

Equation (14) describes the propagation of a plane wave which is weakly damped because of the scattering by fluctuations of the density $n(\mathbf{R})$. We introduce the notation $n(\mathbf{r}) = \bar{n} + \nu(\mathbf{r})$, and define the correlation function

$$\langle \nu(\mathbf{r})\nu(\mathbf{r}') \rangle = \langle \nu^2(0) \rangle w(\mathbf{r} - \mathbf{r}'). \quad (15)$$

Equation (14) leads to a relaxation time τ given by the equation

$$\frac{1}{\tau} = \frac{\langle \nu^2 \rangle}{\alpha^2} \int w(\mathbf{r}) \frac{\sin \kappa r}{r} d^3\mathbf{r}, \quad \kappa = \sqrt{2(E - E_0)}. \quad (16)$$

¹⁾Except in cases when there appear in the vicinity of the point \mathbf{R} two or more centers that are accidentally at distances much smaller than the average. The limitations imposed by this situation will be considered below.

Equation (14) itself is approximate. In deriving it we omitted terms of the form $n^{-2/3} k^3 a(\mathbf{R})$ which lead to a contribution of the order of $n^{1/3} k^3 \alpha^{-2}$ to $1/\tau$. Comparing it with (16), we conclude that Eq. (16) is correct only for $k \ll (\langle \nu^2 \rangle n^{-1/3})^{1/5}$. In the case of a Poisson distribution $\langle \nu^2 \rangle \sim n^2$ and the above estimate coincides with $k \ll n^{1/3}$. In the range of sufficiently low energies when the wavelength λ becomes very much larger than the correlation length r_c , Eq. (15) can be written in the form

$$\langle \nu(\mathbf{r})\nu(\mathbf{r}') \rangle = \mu \delta(\mathbf{r} - \mathbf{r}'), \quad \mu = \frac{\langle N^2 \rangle - \langle N \rangle^2}{V}, \quad (15')$$

and we obtain from (16)

$$\frac{1}{\tau} = \frac{\mu}{\alpha^2} \kappa. \quad (16')$$

Thus in the region $\kappa \ll r_c^{-1}$ only two parameters enter in Eq. (14): $1/2 \kappa^2 = E - 4\pi \bar{n}/\alpha = E - E_0$ and μ/α^2 (since any averages of products of $\nu(\mathbf{r})$ break up for $|\nu(\mathbf{r})| \ll \bar{n}$ into a product of pair averages or vanish). Therefore the level density can be represented in the form

$$\rho(E) = \mu a^2 f\left(\frac{E - E_0}{(\mu a^2)^2}\right), \quad a = \frac{1}{\alpha}, \quad (17)$$

where $f(x)$ is a standard function of its argument. The region $x \equiv E - E_0 / (\mu a^2)^2 \sim 1$ represents the smearing out of the shifted edge of the band due to the damping of plane waves. Of course, for $x \sim 1$ Eq. (16') loses its meaning.

The asymptotic behavior of $f(x)$ for $x \rightarrow +\infty$ is determined from the physical requirement that the level density be given by (5) (region of weak damping). This yields

$$f(x) \rightarrow \sqrt{x} / \sqrt{2\pi^2} \quad \text{when } x \rightarrow +\infty.$$

The same result can be obtained directly from (14).

The asymptotic behavior of $f(x)$ for $x \rightarrow -\infty$ can be obtained qualitatively by means of the following estimates. For a given $|E - E_0| \gg (\mu a^2)^2$ the energy level can only appear as a result of a sufficiently large fluctuation $n(\mathbf{r})$. The probability w of the occurrence of a fluctuation $n(\mathbf{r})$ in a region of volume V is given by the Gaussian distribution:

$$w \sim \exp\left\{-\frac{(N - \bar{N})^2 / 2\bar{\mu}V}{2\bar{\mu}V}\right\} = \exp\left\{-\left(\int (n - \bar{n}) dV\right)^2 / 2\bar{\mu}V\right\}, \quad (18)$$

where N and \bar{N} are the actual and average numbers of particles in the region of the fluctuation. Obviously, a fluctuation with a given value of the energy $E < E_0$ is most probable if this level is the ground level in the resulting potential well. The relation $(4\pi/\alpha)(n - \bar{n})R^2 \sim 1$ where $R \sim V^{1/3}$ is the well dimension should therefore be satisfied. The order of magnitude of the exponent in (18) can therefore be estimated accurate to within a constant factor as $\alpha^2/R\mu$. The uncertainty relation restricts the value of R from above with $\lambda = \kappa^{-1}$. Consequently,

$$\rho(E) \sim \exp\left\{-\text{const} \frac{\alpha^2 |\kappa|}{\mu}\right\}$$

and for $x \rightarrow -\infty$

$$f(x) \sim \exp\{-\text{const} \sqrt{-x}\}. \quad (19)$$

In order to determine the constant in the exponent and the pre-exponential factor, one must minimize exactly the fluctuation probability for a given ground level; this constitutes a rather complex mathematical problem.²⁾

Equation (19) makes it possible to estimate the order of magnitude of the level density $\rho(E) \sim \mu a^2$ and the total number of levels $N(E) \sim (\mu a^2)^3$ in the "diffusion" region $|E - E_0| \sim (\mu a^2)^2$. We note that the asymptotic behavior of (19) for the level density is only valid in the region $|E - E_0| \ll 4\pi n/\alpha$. This follows from the inequality $|n - \bar{n}| \ll \bar{n}$; when the latter is satisfied the fluctuations obey a Gaussian distribution.

There exists, however, a stricter limitation. Let us consider the role of states with a negative energy which appear in individual groups of scattering centers. These states are not described by Eq. (14) which contains a continuous function of the density. Let us consider again the system (4) with the notation $ik = \kappa$. In addition to the energy level characterizing an individual center ($\kappa = \alpha$) there appear states that are localized on several centers. For $\kappa \gg n^{1/3}$ one need consider in the principal term in the concentration (in the parameter n/α^3) only states produced by pairs of close centers. From (4) we obtain the characteristic equation

$$\alpha - \kappa = \pm e^{-\kappa R} / R,$$

which is invalid only near the resonance level in a narrow region of width $|\kappa - \alpha| \sim n^{1/3} \exp\{-\alpha/n^{1/3}\}$. The minus sign refers to a symmetric deeper level.

Let us consider the density of states corresponding to the asymmetric terms in more detail. The characteristic equation can be rewritten in the form

$$\frac{\alpha}{\kappa} = 1 + \frac{e^{-\kappa R}}{\kappa R} \equiv f(\kappa R).$$

Hence $R = \kappa^{-1} f^{-1}(\alpha/\kappa)$, and the energy level density with a given κ is determined by the probability that one of these centers is at a distance between R and $R + dR$ from another center.

For a Poisson distribution of centers the energy level density per unit volume is

$$4\pi n^2 R^2 \frac{dR}{dE}; \quad R = \frac{1}{\kappa} f^{-1}\left(\frac{\alpha}{\kappa}\right), \quad \frac{\kappa^2}{2} = -E.$$

Asymptotically for $\kappa \rightarrow 0$ the solution of the characteristic equation is of the form $\kappa^2/2 = \alpha(\alpha - 1/R)$, and the density of states turns out to be a constant, $4\pi n^2/\alpha^5$.

For $\alpha \lesssim n^{1/3}$ one must not restrict oneself only to an account of nearest neighbors. For $\kappa \ll n^{1/3}$ many scattering centers that are no longer in "resonance" with the levels under consideration ($\kappa^2/2 \ll \alpha^2/2$) enter within the radius of the state. They can therefore be considered as a "medium" that merely changes the average energy, i.e., displaces the origin of the energy. The only exception are those centers which form as a result of their proximity a fine level. Now only pairs of centers need to be taken into account, and we obtain for the energy levels (now with a shifted origin of the energy) again the density $4\pi n^2/\alpha^5$. The edge of the continuous spectrum thus joins smoothly with the diffuse

impurity level.

The concentration of pairs of centers with energy levels within the diffusion layer is $\sim n^4/\alpha^9$. The average spacing between them is $\sim n^{-1/3} \alpha^3/n$ which is much larger than the radius of states $\sim \alpha^2/n$. As a result such pairs do not affect appreciably the motion of electrons within the diffusion region, and do not perturb neighboring pairs. The asymptotic behavior (19) will only be correct in a limited region up to energies $\sim (n^2/\alpha^4) \ln^2(n/\alpha^3)$. After this the exponentially decreasing density of states is replaced abruptly (practically at a point) by the constant $4\pi n^2/\alpha^5$ —the tail of the spectrum resulting from the smearing out of the resonance level.

The system of equations (4) is also valid when there is no real resonance level ($\alpha < 0$). The solution of the characteristic equation for the fine energy states is of the form

$$\kappa = 1/2(\alpha + 1/R).$$

For a Poisson distribution of the centers the energy level density $\rho^*(E)$ turns out to be $4\sqrt{2} \pi n^2/\alpha^4 \sqrt{E}$. For $E \sim (n/\alpha^2)^2$ the density $\rho^*(E) \sim n/\alpha^2$, i.e., it is of the same order of magnitude as the density given by Eq. (14). The solution of the problem in the case $\alpha < 0$ requires therefore further investigation.

Let us now consider the opposite case of high densities $n/\alpha^3 \gg 1$. In this case $a(R)$ cannot be a slowly changing function of R . Indeed, assuming the opposite to be true we arrive again at the dispersion relation (10). However, this equation has no roots in the region $p, k \ll n^{1/3}$ if $n \gg \alpha^3$. This means that the characteristic dimension $a(R)$ is $n^{-1/3}$ and the characteristic value $k \sim n^{1/3}$. Therefore one can neglect α in Eq. (4). Going over in (4) to dimensionless variables $x_{mn} = R_{mn} n^{1/3}$, we obtain a standard system of equations which depends formally only on one parameter $kn^{-1/3}$. In the case of a Poisson distribution of the centers when this parameter is the only one that enters in the problem the density of states $\rho(E)$ is of the form

$$\rho(E) = n^{1/3} \varphi(E/n^{1/3}), \quad (20)$$

where $\varphi(x)$ is a standard dimensionless function. The asymptotic behavior of $\varphi(x)$ for large positive x is determined from the requirement that (20) go over into the density of states of a free particle:

$$\varphi(x) \rightarrow \sqrt{x} / \sqrt{2\pi^2}, \quad x \rightarrow +\infty. \quad (21)$$

Negative and large E correspond to negative x , large in absolute value. The asymptotic behavior of $\varphi(x)$ can in this case be obtained from simple physical considerations. Large negative energies appear when a fluctuation causes two or more impurity centers to come close together. Since the radii of the centers are considered to be small compared to the distances between them, only pair collisions need be taken into account in the principal term in the concentration.

A symmetric wave function corresponds to a lower stationary state of the electron in the field of two centers with short-range action; the energy of this state $E = -\kappa^2/2$ is given by the equation

$$\kappa = e^{-\kappa R} / R, \quad (22)$$

where R is the distance between the centers. The

²⁾In principle this problem has recently been solved by Zittartz and Langer, [4] and in a more general form by I. Lifshitz. [15]

probability that the distance is between R and $R + dR$ is $4\pi\bar{n}R^2 dR \exp\{-\frac{4}{3}\pi\bar{n}R^3\}$. Since we are interested in $R \ll n^{-1/3}$, the exponent can be replaced by unity. Hence we find $\rho(E)$ for $E < 0$ and $|E| \gg n^{2/3}$:

$$\rho(E) \approx \frac{\pi\bar{n}^2\gamma^3}{\gamma^2} |E|^{-3/2}, \quad (23)$$

where $\gamma \approx 0.57$ —the root of the equation $\gamma = e^{-\gamma}$. It follows from (23) that

$$\varphi(x) \rightarrow \frac{\pi\gamma^3}{\gamma^2} |x|^{-3/2}, \quad x \rightarrow -\infty. \quad (24)$$

Let us summarize. In the case of a gas $n/\alpha^3 \ll 1$ the density of states $\rho(E)$ corresponds to that of a free particle with a shifted spectrum boundary ($E_0 = 4\pi\bar{n}/\alpha$) in the region $E - E_0 \gg (\mu a^2)^2$. This expression for the shift of the edge of the band is only the first term of an expansion in powers of the concentration, since even in the derivation of (13) we have neglected quantities of the order of $n^{1/3}$ compared with α . In the region $|E| \ll r_C^{-2}$ which overlaps with the first region the level density is determined by a standard function of the parameter $(E - E_0)/(\mu a^2)^2$. In the "diffusion" region $|E - E_0| \sim (\mu a^2)^2$ the wave functions are not even approximately plane waves, because on its boundary the damping becomes of the same order of magnitude as the energy. The density of states in this region is equal in order of magnitude to μ/α^2 . Below the diffusion region the level density decreases exponentially (according to the law $\exp\{-\text{const}(-x)^{1/2}\}$). The states in this region are obtained as a result of density fluctuations which lead to effective potential wells for the electron. We have considered throughout the absolute value of the electron energy to be considerably smaller than the energy of the bound level.

The relaxation time of a plane wave τ is determined for $E \gg (\langle v \rangle^2 n^{-1/3})^{2/5}$ from the formula of the kinetic theory of gases. For smaller values of E the relaxation takes place mainly on density fluctuations.

The region of large densities $n/\alpha^3 \gg 1$ is only characteristic for resonance scattering. In this region there are no bound levels or plane waves. The wave functions have a characteristic dimension $n^{-1/3}$. In the case of a Poisson distribution the density of states is given by a standard function $\varphi(k/n^{1/3})$ [see (20)]. The energy smearing of the boundary of the spectrum is proportional to $n^{2/3}$. The concept of a shift of the boundary is therefore in this case meaningless.

For $k^2 \gg n^{2/3}$ the particle is practically free. The region of negative energies that are large in absolute value is determined by the random approach of two scatterers to distances less than $n^{-1/3}$. The level density in this region decreases as $|E|^{-5/2}$.

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