Theory of Coulomb localization of electrons in disordered systems

N. M. Storonskiĭ and B. I. Fuks

(Submitted 10 April 1989)
Zh. Eksp. Teor. Fiz. **96**, 1880–1895 (November 1989)

It is shown that, in the field of randomly distributed Coulomb centers, besides Gaussian and Poissonian localized states there also exist hybrid states whose binding energy and properties are determined jointly by the quantum localization of electrons on small-scale Poissonian clusters and by the classical shift of the quantum level in the field of large-scale Gaussian fluctuations. A method of calculating the density of the hybrid states is proposed. It is established that, for all realistic values of the binding energy ε, the optimal Poissonian fluctuations are not quasi-point nuclei, small in comparison with the radius of the first Bohr orbit, but, on the contrary, are large in comparison with the latter, by virtue of which the large-ε asymptotic form of the density of Poissonian states in doped semiconductors significantly underestimates its value. For the example of a strongly doped semiconductor it is demonstrated that the spectrum of the density of localized states contains not only a Gaussian and a Poissonian part but also a broad energy interval in which hybrid states dominate. It is shown that the relatively rare repulsive hybrid states are distinguished by extremely small electron-capture coefficients and can have a substantial effect on nonequilibrium phenomena in doped semiconductors.

1. INTRODUCTION

A distinguishing feature of strong localization of electrons in a random Coulomb field is the important role of fluctuations of substantially different scales in the concentration of charged centers. Large-scale Gaussian fluctuations of a size of the order of the range r_{scr} of the Coulomb potential in the medium lead to the formation of states with a large binding energy determined by the classical localization of the electron$^{1)}$ in deep wells of the potential relief. Strongly bound states in a random Coulomb field can also be realized in another, essentially quantum manner. We are speaking of the localization of electrons on Poissonian (substantially non-Gaussian) clusters of attractive centers of extremely small, quantum size. As has been shown in a whole series of papers devoted to the study of deep tails of the density of states in various systems (see, e.g., Refs. 1–3), it is principally in these two limiting ways that localization of charge carriers is realized.

It is obvious that, besides states of these two types, there also exist states that are, in essence, hybrids of them, and arise in the localization of electrons on small-scale clusters that have fallen inside large-scale fluctuations. Such localization has not been considered previously, not because these states are extremely rare and the fluctuations corresponding to them are not optimal, but because, in the methods used to calculate the density of states, a restriction on the range of scales to be considered has been implicitly assumed. But the optimal fluctuations that realize the hybrid states are characterized by at least two radically different (a classical and a quantum) length scales.

The method proposed here for calculating the density of states, which makes it possible to find not only the densities of the classical and quantum localized states but also the density of the hybrid states, is based on the following physical considerations. Because of the large difference between the classical scale and the quantum scale, with good accuracy we can regard the optimal hybrid fluctuation as a superposition of two independent fluctuations: a large-scale, Gaussian fluctuation, and a small-scale Poissonian cluster of centers. For this reason, the binding energy of a hybrid state is equal to the sum of the binding energies of the electron at each of these fluctuations separately, and the product of the probabilities of formation of these fluctuations gives the probability of formation of the hybrid state.

These considerations can be confirmed without difficulty, starting from the expression for the density of states with binding energy$^{2)}$ ε (see, e.g., Ref. 2):

$$N(\varepsilon)=\frac{1}{\Omega}\left\langle\sum_{l}\delta(\varepsilon-\varepsilon_l)\right\rangle, \tag{1}$$

where ε_l is an eigenvalue of the one-particle Schrödinger equation for a localized particle of mass m:

$$-\frac{\hbar^2}{2m}\Delta\psi_l(\mathbf{r})+\sum_{j}u(\mathbf{r}-\mathbf{r}_j)\psi_l(\mathbf{r})=-\varepsilon_l\psi_l(\mathbf{r}). \tag{2}$$

Here, $u(\mathbf{r}-\mathbf{r}_j)$ is the potential energy of the particle in the field of a Coulomb center situated at the point $\mathbf{r}_j$, the symbol Σ denotes summation over all the centers, the symbol $\langle\ldots\rangle$ denotes averaging over the coordinates of these centers, Ω is the averaging volume, and l is the set of quantum numbers of a state. It is clear that the wave function of a particle localized near a certain point $\mathbf{R}_l$ is substantially influenced only by very close charges that fall within a region of radius r_l of the same order of magnitude as the characteristic quantum size. Therefore, with good accuracy the wave function is determined by the equation

$$-\frac{\hbar^2}{2m}\Delta\psi_{0l}(\mathbf{r})+\sum_{j}^{int}u(\mathbf{r}-\mathbf{r}_j)\psi_{0l}(\mathbf{r})=-\varepsilon_{0l}\psi_{0l}(\mathbf{r}), \tag{3}$$

where Σ^{int} denotes summation over the internal charges of the region under consideration. Taking the effect of the external charges on the magnitude of ε_l into account in first-order perturbation theory, we have

$$\varepsilon_l\approx\varepsilon_{0l}+\varepsilon_{1l}, \tag{4a}$$

$$\varepsilon_{1l}=-\int d\mathbf{r}\,|\psi_{0l}{}^2(\mathbf{r})|\sum_{j}^{ext}u(\mathbf{r}-\mathbf{r}_j), \tag{4b}$$

where $\Sigma^{\text{ext}}\ldots=\Sigma\ldots-\Sigma^{\text{int}}\ldots$. From formulas (1) and (4a), using the identity

$$\delta(\varepsilon-\varepsilon_{0l}-\varepsilon_{1l})=\int_{-\infty}^{\infty}d\varepsilon'\,\delta(\varepsilon'-\varepsilon_{0l})\delta(\varepsilon-\varepsilon'-\varepsilon_{1l}),$$

we obtain an expression for the density of states:

$$N(\varepsilon)\approx\frac{1}{\Omega}\int_{-\infty}^{\infty} d\varepsilon'\left\langle \sum_{l}\delta(\varepsilon'-\varepsilon_{0l})\langle\delta(\varepsilon-\varepsilon'-\varepsilon_{1l})\rangle^{ext}\right\rangle^{int}, \tag{5}$$

where the symbols $\langle...\rangle^{\text{int}}$ and $\langle...\rangle^{\text{ext}}$ denote averaging over the coordinates of only the internal and only the external charges, respectively. In deriving (5) we have assumed the distribution of charges to be uncorrelated and taken into account that ε_{0l} does not depend on the coordinates of the external centers.

The choice of r_l is made in the framework of the solution of a specific problem. Here it should be borne in mind that if r_l is significantly greater than the quantum size it is just as complicated to solve Eq. (3) as to solve Eq. (2). But if r_l is smaller than the quantum size, the corrections to the binding energy of the second (ε_{2l}) and higher orders become significant and formula (4a) becomes incorrect. Even if r_l is such that $\varepsilon_{2l} \ll \varepsilon_{0l}$, formula (5) is correct, generally speaking, only with logarithmic accuracy, since the density of strongly bound states depends exponentially on the energy. And only when the energy correction ε_{2l} changes the exponent of this exponential by less than unity does formula (5) have absolute accuracy.

Henceforth, we study exclusively the bulk properties of semiconductors. Since, in the three-dimensional case, the overwhelming contribution to the quantity $\langle\delta(\varepsilon-\varepsilon'-\varepsilon_{1l})\rangle^{\text{ext}}$ is made by the largest-scale fluctuations, the size of which is considerably greater than the quantum size, this quantity does not depend on the quantum numbers and is $P(\varepsilon-\varepsilon')$—the probability of the classical shift of the position of the allowed bands by an amount[3)] $\varepsilon-\varepsilon'$. Then formula (5) takes the form

$$N(\varepsilon)=\int_{-\infty}^{\infty} d\varepsilon'\rho_{\text{qu}}(\varepsilon')P(\varepsilon-\varepsilon')=\int_{-\infty}^{\infty} d\varepsilon' N(\varepsilon,\varepsilon'), \tag{6}$$

where

$$\rho_{\text{qu}}(\varepsilon)=\frac{1}{\Omega}\left\langle\sum_{l}\delta(\varepsilon-\varepsilon_{0l})\right\rangle^{int}. \tag{6a}$$

Here $N(\varepsilon,\varepsilon')$ is the density of states with total binding energy ε and quantum energy ε', and $\rho_{\text{qu}}(\varepsilon)$ is the density of quantum states.

Formula (6) is a generalization of expressions obtained earlier for the density of states. Thus, for example, neglecting the effect of the charges on the electron wavefunction, i.e., setting $\psi_{0l}\sim e^{i\mathbf{kr}}, \varepsilon_{0l} = -\hbar^2k^2/2m, \varepsilon'<0$, we find that

$$\rho_{\text{qu}}(\varepsilon)=\frac{2^{1/2}m^{3/2}}{\pi^2\hbar^3}\varepsilon^{1/2},$$

and formula (6) goes over into the well known quasiclassical expression that arises directly from the original ideas of Bonch-Bruevich, Kane, and Keldysh:

$$N(\varepsilon)=\frac{2^{1/2}m^{3/2}}{\pi^2\hbar^3}\int_{0}^{\infty} d\varepsilon'\varepsilon'^{1/2}\ P(\varepsilon+\varepsilon').$$

Considerable difficulties arise in the calculation of $\rho_{\text{qu}}(\varepsilon)$ for strongly localized Poissonian states in a random Coulomb field. Previously, in the solution of this problem given in Ref. 4, only the contribution made to the binding energy by the long-range part of $u(r)$ was taken correctly into account. Later, in Ref. 5, in which, in essence, the contribution of the singularity of $u(r)$ was assumed to be dominant, a more accurate expression for $\rho_{\text{qu}}(\varepsilon)$, asymptotically correct for large values of ε, was obtained. Below, in Sec. 2, it is shown that for all realistic values of ε it is important to take into account both singularities of the Coulomb potential. Thus, in a more exact (than in Ref. 5) calculation of the energy and wave function of the ground state of an electron on a Poissonian fluctuation, because of the long range of $u(r)$ the decrease of the binding energy with increase of the size of the fluctuation occurs much more weakly. As a result, the size of an optimal fluctuation is considerably greater than the radius of the first Bohr orbit of a point nucleus with the same charge, and not considerably smaller than it as shown in Ref. 5. As a consequence of the considerably greater probability of such fluctuations, the lower bound obtained in Sec. 3 for the quantity $\rho_{\text{qu}}(\varepsilon)$ is greater by many orders of magnitude than the values obtained in Refs. 4 and 5.

By replacing $P(\varepsilon-\varepsilon')$ in (6) by $\delta(\varepsilon-\varepsilon')$, we have another well known expression $N(\varepsilon)=\rho_{\text{qu}}(\varepsilon)$ (see Refs. 4 and 5) for the Poissonian part of the spectrum. However, since in the case of the Coulomb potential the characteristic energies of the functions $\rho_{\text{qu}}(\varepsilon)$ and $P(\varepsilon)$ are commensurate, generally speaking, and since these functions decrease exponentially with increase of their arguments, the principal contribution to the deep tail of the density of states can be made by hybrid states for which ε' and $\varepsilon-\varepsilon'$ are large positive quantities, i.e., in the spectrum $N(\varepsilon)$ one can distinguish not only a Gaussian and a Poissonian part but also a hybrid part, as is illustrated in Sec. 4 for the example of a strongly doped semiconductor (SDS).

Formula (6) introduces a classification of states by two independent parameters—the binding energy ε and the quantum energy ε', and this significantly extends the range of states that can be studied. These include not only those that make the principal contribution to $N(\varepsilon)$. The properties of states with the same binding energy but with different contributions from the classical and quantum energy can differ substantially. Also different will be their influence on the properties of the semiconductors. Of special interest are the relatively rare strongly localized states with a small or even negative binding energy that are formed by small-scale clusters of attractive centers that fall within large-scale repulsive fluctuations. Change of the charge state of such clusters (charge exchange) is an extremely lengthy process, since it is necessary for an electron to pass through a high and wide potential barrier. The barrier height, which, by virtue of the substantial difference in the scales of the attractive and the repulsive fluctuation, is close to $\varepsilon-\varepsilon'$, serves as the main factor governing the effective coefficient $\gamma(\varepsilon,\varepsilon')$ for capture into such states, which are similar to repulsive capture centers. As shown in Sec. 4, $\gamma(\varepsilon,\varepsilon')$ decreases steeply with increase of the barrier height, as a consequence of which it is precisely the relatively rare states with high barriers that can have the decisive influence on nonequilibrium phenomena in semiconductors.

2. THE OPTIMAL POISSONIAN FLUCTUATIONS

As the first step, we shall consider charge fluctuations in the approximation of a uniformly charged sphere (UCS). In this approach the problem is reduced to solving the Schrödinger equation with a potential produced by a UCS of radius R and with total charge Z and then calculating those optimal values R_ε and Z_ε for which the probability of formation of fluctuations with the ground-state energy ε is a maximum. Deep in the forbidden band, where the density of states is exponentially small, it is the optimal fluctuations that determine the leading term of the logarithmic quantity $\rho_{\text{qu}}(\varepsilon)$ (Ref. 1), and

$$\ln(\rho_{\text{qu}}(\varepsilon)/\rho_{\text{qu}}(0)) = \ln P(Z_\varepsilon, R_\varepsilon), \tag{7}$$

where $P(Z_\varepsilon, R_\varepsilon)$ is the probability of an optimal cluster.

The potential energy of an electron in the field of a UCS at a distance r from its center is equal to

$$V_R(r) = \begin{cases} -3/R + r^2/R^3 & 0 \leqslant r \leqslant R \\ -2/r, & r > R \end{cases} \tag{8}$$

In solving this problem we measure all energies in units of the ground-state energy of a point nucleus with charge $Z - Z^2\varepsilon_0$ ($\varepsilon_0 = me^4/2\hbar^2\varkappa^2$), and lengths in units of the Bohr radius $a_Z = a_{\text{B}}/Z$ of such a center ($a_{\text{B}} = \hbar^2\varkappa/e^2m$). The Schrödinger equation with the potential (8) can be solved exactly. It has been considered earlier by a number of authors (e.g., in Ref. 6). Its wave function $\varphi_\varepsilon(r,R)$ in the S-state has the form (see, e.g., Ref. 7)

$$\varphi_\varepsilon(r,R) = \begin{cases} C_1 e^{-r^2/2R^3} F\left(\beta, \dfrac{3}{2}, \dfrac{r^2}{R^{3/2}}\right), & 0 \leqslant r \leqslant R \\ C_2 e^{-y/2}\Big[F(\alpha,2,y)\ln y \\ \quad + \displaystyle\sum_{t=0}^{\infty} \frac{\Gamma(\alpha+t)}{\Gamma(\alpha)} \frac{\psi(\alpha+t) - \psi(t+2) - \psi(t+1)}{(t+1)!\,t!} y^t, \\ \quad + \dfrac{1}{y(\alpha-1)}\Big], & r > R \end{cases} \tag{9}$$

where W is the dimensionless binding energy, $\alpha = 1 - W^{-1/2}$, $\beta = \frac{1}{4}(3 - 3R^{1/2} + WR^{1/2})$, $y = 2W^{1/2}r$, $F(\alpha,\gamma,y)$ is the confluent hypergeometric function, $\Gamma(x)$ is the gamma function, and $\psi(x) = d\ln\Gamma(x)/dx$. From the conditions for the continuity of the wavefunction and its derivative at $r = R$ there follows a relation connecting the constants C_1 and C_2, and an equation for the dependence $W(R)$:

$$\begin{aligned} &\ln(2RW^{1/2})F(\alpha+1,3,2RW^{1/2})\frac{\alpha}{2} + \frac{F(\alpha,2.\,2RW^{1/2})}{2RW^{1/2}} \\ &+ \sum_{t=1}^{\infty} \frac{\Gamma(\alpha+t)}{\Gamma(\alpha)} \frac{\psi(\alpha+t)-\psi(t+2)-\psi(t+1)}{(t-1)!\,(t+1)!}(2RW^{1/2})^{t-1} \\ &+ \frac{1}{1-\alpha}(2RW^{1/2})^{-2} = \Big(\ln(2RW^{1/2})F(\alpha,2,2RW^{1/2}) \\ &+ \sum_{t=0}^{\infty} \frac{\Gamma(\alpha+t)}{\Gamma(\alpha)} \frac{\psi(\alpha+t)-\psi(t+2)-\psi(t+1)}{(t+1)!\,t!} \\ &\times (2RW^{1/2})^t - \frac{1}{1-\alpha}(2RW^{1/2})^{-1}\Big) \\ &\times \left(\frac{1}{2} + (2RW^{1/2})^{-1}\Big[-1 + \Big(1 - R^{1/2}\right. \\ &\left. + \frac{1}{3}WR^{3/2}\Big) + F\left(\beta+1, \frac{5}{2}, R^{1/2}\right)F^{-1}\left(\beta, \frac{3}{2}, R^{1/2}\right)\Big]\right) \end{aligned} \tag{10}$$

The solution of this transcendental equation for the ground state is given in Fig. 1 (curve 1). Its asymptotic forms are

$$W(R) = 1 - {}^4/_5R^2 + {}^{64}/_{63}R^3, \quad R \ll 1. \tag{11}$$

$$W(R) = 3(1 - R^{-1/3})/R, \quad R \gg 1. \tag{12}$$

We now find Z_ε and R_ε. If the concentration of charged centers (for definiteness, donors) in the semiconductor is equal to N_d, the probability that Z centers are found in a sphere of radius Ra_Z is determined by the Poisson formula and (for $Z \gg 1$, $\bar{n}$) can be written in the form

$$\ln P(Z, R) = -Z\ln(Z^4/e\bar{N}R^3), \tag{13}$$

where $\bar{n} = \bar{N}R^3/Z^3$ and $\bar{N} = 4\pi N_d a_{\text{B}}^3/3$. At the points of the extrema of the right-hand side of (13) for a given binding energy, by virtue of the condition

$$\varepsilon = Z^2 W(R) \tag{14}$$

(here and below, the energy is measured in units of ε_0), Z_ε and R_ε are related by the equation

$$\ln(Z_\varepsilon^4/\bar{N}R_\varepsilon^3) = 3(-2W(R_\varepsilon)/R_\varepsilon W_R'(R_\varepsilon) - 1). \tag{15}$$

Since the minimum of the right-hand side of (15) is approximately equal to 3, the above neglect of corrections $\bar{N}R_\varepsilon^3/Z_\varepsilon^4$ is always justified. From (14) and (15) follows an equation for the dependence $R_\varepsilon(\varepsilon)$:

$$\varepsilon\bar{N}^{-1/2} = R_\varepsilon^{3/2} W(R_\varepsilon)\exp[{}^3/_2(-2W(R_\varepsilon)/R_\varepsilon W_R'(R_\varepsilon) - 1)], \tag{16}$$

which is shown in Fig. 2. The right-hand side of (16) is a minimum at $R_1 = 5.8$, where it is equal to 18. For $\varepsilon > \varepsilon_{\min} = 18\bar{N}^{1/2}$, Eq. (16) has two solutions; one of them, with $R_\varepsilon > R_1$, corresponds to the minimum of the right-hand side of (13), while the other, with $R_\varepsilon > R_1$, corresponds to its maximum. It is the latter which determines the radius of the optimal UCS. The absence of roots of Eq. (16) with $\varepsilon < \varepsilon_{\min}$ is explained by the fact that, for small ε, in the UCS model only large-scale Gaussian fluctuations with $Z \approx \bar{n}$ and $R \gg R_1$ are optimal.

It can also be seen from Fig. 2 that the use of the approximation of a quasi-point nucleus ($R_\varepsilon \ll 1$) in the determination of the scale of the optimal fluctuations is possible only

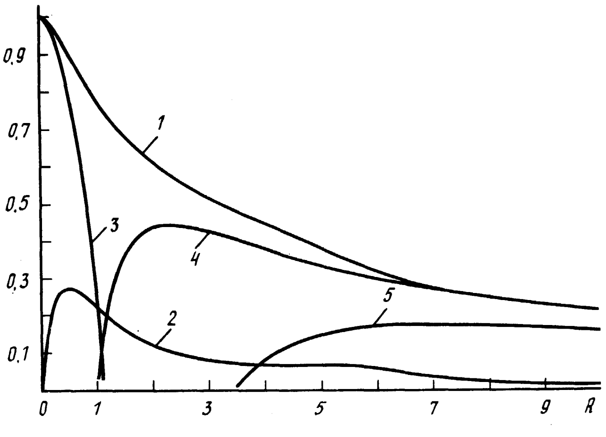

FIG. 1. 1—Dependence of the binding energy W of an electron in the field of a UCS on the radius R; 2—graph of the modulus $|W_R'(R)|$ of the derivative; 3—dependence $W(R)$ for a UCS in the model of Ref. 5; 4—graph of the function $W(R)$ calculated using formula (12); 5—dependence of the binding energy on the size of the fluctuation in Kane's model.

for unrealistically large values of ε. This result cannot be obtained if, in the determination of the binding energy, we take into account only the quadratic correction for the non-point nature of the nucleus (in the UCS approximation, curve *3* on Fig. 1 for the dependence $W(R)$ corresponds to this). However, the use of the small-R asymptotic form with allowance for the cubic correction [substitution of formula (11) into (16)] leads to the result that the argument of the exponential in the right-hand side of (16) is very large for all values of R_ε. Its minimum is reached at $R_\varepsilon \approx 1/3$ and is approximately equal to 45, i.e., it is possible to use (11) if $\ln(\varepsilon\bar{N}^{-1/2}) > 45$.

The graph given in Fig. 1 for the modulus $|W'_R(R)|$ of the derivative (curve *2*) shows that at $R \approx \frac{1}{3}$ the growth of $|W'_R(R)|$ slows appreciably, while at $R > 1/2$ the quantity $|W'_R(R)|$ even falls sharply and then decreases gently. The slow fall-off of $W(R)$ reflects the fact that upon dispersal of a cluster of Coulomb centers the potential energy $V(R)$ of an electron in the field of this cluster decreases appreciably more slowly than the field attracting the electron toward the center of the cluster, as a result of which the kinetic energy $T(R)$ of the electron decreases with increase of R just as rapidly as the potential energy, and their difference $W(R) = V(R) - T(R)$ decreases slowly. Therefore, it is because of the rapid increase of the probability of finding the Z charges in a sphere of larger radius that, for values of ε of practical interest, fluctuations with $R_\varepsilon \gg 1$ are optimal. From Fig. 2 it can be seen that, in a wide range of variation of $\bar{N}$, values of R_ε in the range $3.5 < R_\varepsilon < 5.5$ correspond to realistic values of ε. We note that the determination of $W(R)$ from the asymptotic formula (12), which is correct if the region of localization of the electron is small in comparison with the size of the fluctuation, also leads to considerable errors in R_ε and $\rho_{\text{qu}}(\varepsilon)$. This is connected with the fact that the given approximation (see curve 4 in Fig. 1) becomes highly accurate for $R > 9$, while for $R < 6$ it appreciably underestimates $W(R)$ and, especially, $|W'_R(R)|$. The binding energy in the Kane model[4] is an even stronger underestimate (curve 5 in Fig. 1).

From the formulas (7), (13), and (14) there follows an expression for $\rho_{\text{qu}}(\varepsilon)$:

$$\ln[\rho_{\text{qu}}(\varepsilon)/\rho_{\text{qu}}(0)]$$
$$= -\bar{N}^{1/4}(\varepsilon/W(R_\varepsilon)\bar{N}^{1/2})^{1/2}\ln[\varepsilon^2/e\bar{N}R_\varepsilon{}^3W^2(R_\varepsilon)], \tag{17}$$

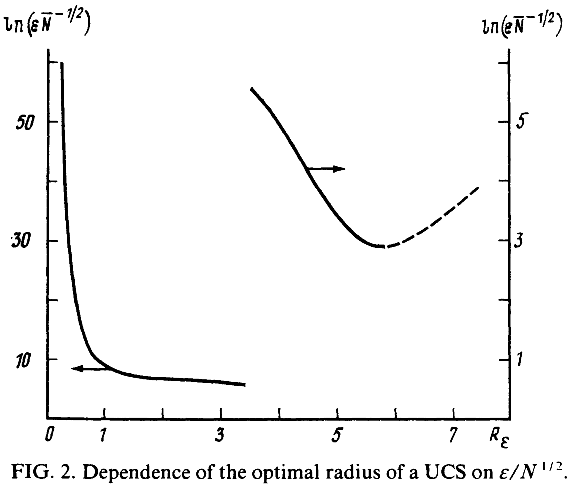

FIG. 2. Dependence of the optimal radius of a UCS on $\varepsilon/N^{1/2}$.

where R_ε is a function of $\varepsilon\bar{N}^{-1/2}$ [see formula (16)]. The universal curve 1 for the dependence of the quantity $\bar{N}^{-1/4}\ln[\rho_{\text{qu}}(\varepsilon)/\rho_{\text{qu}}(0)]$ on $\varepsilon\bar{N}^{-1/2}$ that follows from formulas (16) and (17) is given in Fig. 3. We recall that it is correct if $\varepsilon > 18\bar{N}^{-1/2}$ and $\varepsilon \gg 1$. For comparison, we give in the same figure the analogous dependences that follow from the results of Refs. 4 and 5 (curves 2 and 3). Although the ratio of the logarithms does not exceed 2, the estimate of $\rho_{\text{qu}}(\varepsilon)$ on the basis of curves 2 and 3 is an underestimate by several orders of magnitude.

Up to now, we have not taken screening into account, i.e., we have assumed that

$$a_B R_\varepsilon / Z_\varepsilon \ll r_{\text{scr}}. \tag{18}$$

It is clear that for $\bar{N} \ll 1$, and, in the case of strong compensation of impurities, for $\bar{N} \gg 1$ as well, when r_{scr} is substantially greater than a_B, the results of this section are applicable without restriction. In an SDS the screening length

$$r_0 = {}^1\!/_2 a_B (4\pi^2/9\bar{N})^{1/6}$$

can be much smaller than a_B. Then our results are correct only for very large values of ε and Z_ε, satisfying [as follows from (18)] the equivalent inequalities

$$Z_\varepsilon \gg 2R_\varepsilon(9\bar{N}/4\pi^2)^{1/6}, \quad \varepsilon^{1/2} \gg 2R_\varepsilon W^{1/2}(R_\varepsilon)(9\bar{N}/4\pi^2)^{1/6}. \tag{19}$$

For small ε, when the condition (19) is violated, i.e., when the characteristic length scales of the fluctuation and of the wavefunction are of the order of r_0, screening of the charge of distant centers accelerates the decrease of $W(R)$ with increase of R. This leads to a decrease of $\rho_{\text{qu}}(\varepsilon)$ at small values of ε in comparison with the values given by curve 1 in Fig. 3. In order that, for $\bar{N} \gg 1$, this curve be correct in the entire range in which it is determined, the condition (19) should also be fulfilled for the most weakly localized states with $R_\varepsilon = 5.8$ and $Z_\varepsilon^{\min} = 7.4\bar{N}^{1/4}$; this is possible if

$$\bar{N}^{1/12} \gg 1. \tag{20}$$

Thus, in reality, in SDS the characteristic scale of weakly localized Poissonian states cannot be assumed to be small in comparison with r_0. Since the wavefunctions of Gaussian states are even less localized, it may be expected that for $\bar{N} \gg 1$ the condition for applicability of the results of the calculation of the density of Gaussian states in the approximation of strong localization of the wavefunction relative to the screening length will be even more stringent than (20) (see Ref. 8).

If the condition (19) is not fulfilled, the separation of the charges into internal and external charges [see formulas (3)–(6)], the basis of which was a substantial difference in these scales, becomes inappropriate. The concept of hybrid states then also becomes meaningless.

3. THE DENSITY OF QUANTUM STATES

Although the quantity $\rho_{\text{qu}}(\varepsilon)$ that follows from (17) is substantially greater than the values obtained previously, it is not the case that it is even logarithmically close to $\rho_{\text{qu}}^{\text{true}}(\varepsilon)$—the true value of the density of quantum states. The point is that in the derivation of (17) we considered charge distributions of one class—uniform, or almost uniform inside a

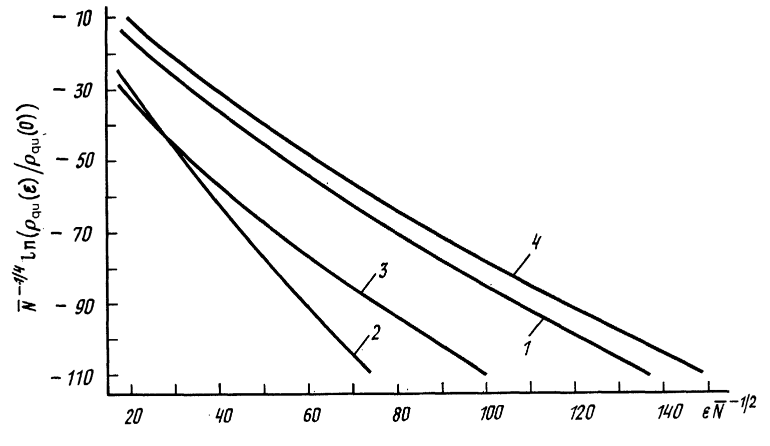

FIG. 3. Dependence of the density of quantum states on $\varepsilon/\bar N^{1/2}$.

certain sphere. When the contribution of all possible distributions and the point nature of the charge centers are taken into account, the quantity $\rho_{\rm qu}(\varepsilon)$ should increase significantly, as we shall see below.

We shall define $\rho_{\rm qu}(\varepsilon)$ by formula (6a). For a given distribution of charges we shall calculate the energy ε_{0l} in first-order perturbation theory, using as the zeroth approximation the solution $\varphi_\varepsilon(|\mathbf{r}-\mathbf{R}_l|, R_\varepsilon)$ [see formula (9)] of the Schrödinger equation for a UCS with charge Z_ε, radius R_ε, and center at the point $\mathbf{R}_l$. Writing all energies in units of ε_0, and lengths in units of $a_{Z_\varepsilon} = a_{\rm B}/Z_\varepsilon$, we have

$$\varepsilon_{0l}=\varepsilon+\sum_j^{int} E_1(|\mathbf{r}_j-\mathbf{R}_l|)-V_0(\varepsilon). \tag{21}$$

Here,

$$V_0(\varepsilon)=Z_\varepsilon^2\int d\mathbf{r}\,\varphi_\varepsilon^2(r,R_\varepsilon)\,V_{R_\varepsilon}(r)\equiv Z_\varepsilon^2\chi_\varepsilon,$$
$$E_1(|\mathbf{r}_j-\mathbf{R}_l|)=Z_\varepsilon\int d\mathbf{r}\,\varphi_\varepsilon^2(|\mathbf{r}-\mathbf{R}_l|,R_\varepsilon)\frac{2}{|\mathbf{r}-\mathbf{r}_j|}, \tag{22}$$

and $V_{R_\varepsilon}(r)$ is determined by formula (8). The position of the point $\mathbf{R}_l$ is determined from the condition for the maximum of ε_{0l}. Henceforth, to simplify the calculations we assume that the number of charged centers in the internal region is close to Z_ε, and find $\mathbf{R}_l$ from the condition

$$\sum_j^{int}(\mathbf{r}_j-\mathbf{R}_l)=0.$$

In a calculation of $\rho_{\rm qu}(\varepsilon)$ with logarithmic accuracy, this introduces only slight errors, by virtue of the spherical symmetry of the optimal fluctuation and the closeness of its charge to Z_ε, as is easily verified later.

Then, from (6a) we have

$$\rho_{\rm qu}(\varepsilon)=\frac{1}{\Omega}\left\langle\sum_l\delta\left(V_0(\varepsilon)-\sum_j^{int}E_1(|\mathbf{r}_j-\mathbf{R}_l|)\right)\right\rangle^{int}$$
$$=\frac{1}{\Omega}\prod_j\int\frac{d\mathbf{r}_j}{{}^4\!/_3\pi r_l^3}$$
$$\times\sum_l\delta\left(V_0(\varepsilon)-\sum_j^{int}E_1(|\mathbf{r}_j-\mathbf{R}_l|)\theta(r_l-|\mathbf{r}_j-\mathbf{R}_l|)\right)$$
$$=\frac{1}{\Omega}\prod_j\int\frac{d\mathbf{r}_j}{{}^4\!/_3\pi r_l^3}\int d\mathbf{R}_l\delta\left(\frac{1}{Z_\varepsilon}\sum_j(\mathbf{r}_j-\mathbf{R}_l)\theta(r_l-|\mathbf{r}_j-\mathbf{R}_l|)\right)$$
$$\times\delta\left(V_0(\varepsilon)-\sum_j E_1(|\mathbf{r}_j-\mathbf{R}_l|)\theta(r_l-|\mathbf{r}_j-\mathbf{R}_l|)\right), \tag{23}$$

where $\theta(x)=1$ for $x\geqslant 0$ and $\theta(x)=0$ for $x\leqslant 0$. Making the change of variables $\mathbf{r}_j=\mathbf{r}_j-\mathbf{R}_l$ and taking into account that $\int d\mathbf{R}_l=\Omega$, and then expanding the δ-functions in Fourier integrals, we have

$$\rho_{\rm qu}(\varepsilon)=\prod_j\int\frac{d\mathbf{r}_j}{{}^4\!/_3\pi r_l^3}\delta\left(\frac{1}{Z_\varepsilon}\sum_j\mathbf{r}_j\theta(r_l-r_j)\right)\delta$$
$$\times\left(V_0(\varepsilon)-\sum_j E_1(r_j)\theta(r_l-r_j)\right)$$
$$=\int_{-\infty}^{\infty}\frac{d\lambda}{2\pi}\int\frac{d\boldsymbol{\varkappa}}{(2\pi)^3}\exp\left\{i\lambda V_0(\varepsilon)\right.$$
$$\left.+\frac{\bar N}{Z_\varepsilon^3}\int_0^{\tilde r_l}drr^2\left[Z_\varepsilon^2\frac{\sin(\varkappa a_{\rm Б}r/Z_\varepsilon^2)}{\varkappa a_{\rm Б}r}\,e^{-i\lambda E_1(r)}-1\right]\right\}, \tag{24}$$

where $\tilde r_l=Z_\varepsilon r_l/a_{\rm B}$. Since the main contribution to this integral for $Z_\varepsilon\gg 1$ is made by relatively small values of $\varkappa$ such that $\varkappa r a_{\rm B}/Z_\varepsilon^2<1$, setting $\sin x=x-x^3/6$ and performing the integration over $\varkappa$ in (24), we have

$$\rho_{\rm qu}(\varepsilon)=\frac{1}{16\pi^{5/2}\bar E_{1\varepsilon}}$$
$$\times\int_{-\infty}^{\infty}dx\left[\frac{\bar N R_\varepsilon^5}{2Z_\varepsilon^7a_{\rm Б}^3}\int_0^{\tilde r_l/R_\varepsilon}dyy^4\exp\{-ix(g_\varepsilon(y)+1)\}\right]^{-3/2}$$
$$\times\exp\left\{ixZ_\varepsilon+3\bar N\frac{R_\varepsilon^3}{Z_\varepsilon^3}\right.$$
$$\left.\times\int_0^{\tilde r_l/R_\varepsilon}dyy^2[\exp\{-ix(g_\varepsilon(y)+1)\}-1]\right\}. \tag{25}$$

Here we have introduced the notation

$$\bar E_{1\varepsilon}=3\int_0^1 dy\,y^2E_1(yR_\varepsilon)$$

for the average value of $E_1(r)$ within a sphere of radius R_ε, and

$$V_0(\varepsilon)=Z_\varepsilon\bar E_{1\varepsilon},\quad g_\varepsilon(y)=E_1(yR_\varepsilon)/\bar E_{1\varepsilon}-1$$

and have made the change of variable $x=\lambda\bar E_{1\varepsilon}$. The integrand in (25) has a sharp maximum, which, as will be shown below, lies near the point

$$\overset{0}{x}_{max}=i\ln(Z_\varepsilon^4/\bar N R_\varepsilon^3).$$

By displacing the integration contour into the upper halfplane, so that it passes through the point of the maximum, and taking the integral in (25) by the method of steepest descent, we obtain

$$\rho_{qu}(\varepsilon)=\rho_0(\varepsilon)\exp\left\{ix_{max}Z_\varepsilon + \frac{3\overline{N}}{Z_\varepsilon^3}\int_0^{\tilde{r}_l/R_\varepsilon} dyy^2\left[\exp\{-ix_{max}(g_\varepsilon(y)+1)\}-1\right]\right\}, \quad (26)$$

where

$$\rho_0(\varepsilon)=\frac{5^{3/2}}{4\pi^2}\frac{Z_\varepsilon^3}{\varepsilon_0 a_B^3 R_\varepsilon^3 \chi_\varepsilon},$$

and x_{max} is the solution of the equation

$$Z_\varepsilon=\frac{3\overline{N}}{Z_\varepsilon^3}R_\varepsilon^3 e^{-ix_{max}}\int_0^{\tilde{r}_l/R_\varepsilon} dyy^2\exp\{-ix_{max}g_\varepsilon(y)\}(1+g_\varepsilon(y)). \quad (27)$$

In deriving (26) we replaced x by x_{max}^0 in the pre-exponential factor under the integral in (25), since, by virtue of the sharp change of the exponential near x_{max}, this introduces into $\rho_{qu}(\varepsilon)$ only relatively small corrections, allowance for which would constitute an excess of accuracy. [In deriving formula (23) we also neglected corrections of the same order of smallness.] In addition, in the pre-exponential factor we replaced

$$\int_0^{\tilde{r}_l/R_\varepsilon} dyy^4\exp\{-ix_{max}g_\varepsilon(y)\} \text{ by } \int_0^1 dyy^4=\frac{1}{5},$$

which also does not introduce substantial errors into $\rho_{qu}(\varepsilon)$. The reason for this, and for the fact that the quantity x_{max} from (27) differs little from x_{max}^0 (as a consequence of which the second derivative of the argument of the exponential at the saddle point is close to Z_ε) is the smallness of the quantity $g_\varepsilon(y)$ for $0\leqslant y\leqslant 1$, where it varies from a small positive value $g_\varepsilon(0)$ to a still smaller (in magnitude) negative value $g_\varepsilon(1)$, and the sharp decrease of the function $\exp\{-ix_{max}g_\varepsilon(y)\}$ for $y>1$. Typical examples of the behavior of the functions $g_\varepsilon(y)$ and $\exp\{-ix_{max}g_\varepsilon(y)\}$ are shown in Fig. 4. If in (26) we replace $\exp\{-ix_{max}g_\varepsilon(y)\}$ by unity for $y\leqslant 1$ and by zero for $y>1$, then x_{max} from (27) is equal to x_{max}^0, and, to within the pre-exponential factor, formula (26) coincides with (17). When the actual behavior of $g_\varepsilon(y)$ is taken into account, the integral in (27) is, to within principal-value corrections, equal to

$$I=\frac{1}{3}R_\varepsilon^3\left[1+\frac{3}{2}(-ix_{max})^2\int_0^1 dy\, y^2 g_\varepsilon^2(y) + \frac{3\exp\{-ix_{max}g_\varepsilon(1)\}}{ix_{max}\,\partial g_\varepsilon(y)/\partial y|_{y=1}}\right]. \quad (28)$$

In the square brackets in (28), the term 1 and the smaller second term, quadratic in x_{max}, are the result of expansion of the exponential under the integral in (27) in a power series on the segment $0\leqslant y\leqslant 1$. There is no linear term in (28), since it follows from the definition of $g_\varepsilon(y)$ that

$$\int_0^1 dy\, y^2 g_\varepsilon(y)=0.$$

The contribution of the remaining terms of the series is negligibly small; i.e., although $\exp\{-ix_{max}^0 g_\varepsilon(0)\}$ is considerably greater than unity, the principal contribution to the growth of $\rho_{qu}(\varepsilon)$ on account of fluctuations inside the sphere of radius R_ε is made by Gaussian fluctuations of the charge about its mean density. The third term is equal to unity for $\varepsilon=18\overline{N}^{1/2}$, and decreases with increase of ε. This term describes the increase of $\rho_{qu}(\varepsilon)$ on account of charges positioned at $r>R_\varepsilon$, and arises as a result of the integration over y from 1 to $\tilde{r}_1/R_\varepsilon$ with fulfillment of the conditions

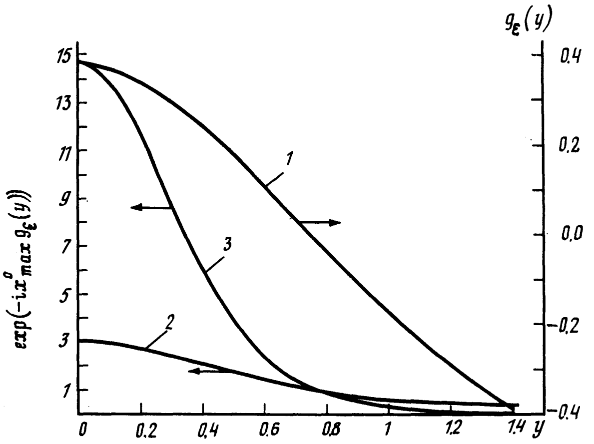

FIG. 4. *1*—Graph of the function $g_\varepsilon(y)$ for $\varepsilon=20\overline{N}^{1/2}$ ($R_\varepsilon=5.5$); *2*—graph of the function $\exp[-ix_{max}^0(\varepsilon)g_\varepsilon(y)]$ for $\varepsilon=20\overline{N}^{1/2}$ ($R_\varepsilon=5.5$); *3*—graph of the function $\exp[-ix_{max}^0(\varepsilon)g_\varepsilon(y)]$ for $\varepsilon=270\overline{N}^{1/2}$ ($R_\varepsilon=3.5$).

$$ix_{max}\frac{\partial g_\varepsilon(y)}{\partial y}\bigg|_{y=1}\gg 1$$

(which is the case) and

$$\frac{\tilde{r}_l-R_\varepsilon}{R_\varepsilon}>\left(ix_{max}\frac{\partial g_\varepsilon(y)}{\partial y}\bigg|_{y=1}\right)^{-1}.$$

Thus, the radius $\tilde{r}_1$ must be chosen to be slightly greater than R_ε. Using (28), from (27) we obtain

$$-ix_{max}\approx -ix_{max}^0-\ln\left(1+\frac{3}{2}(-ix_{max}^0)^2\int_0^1 dy\, y^2 g_\varepsilon(y) + \frac{3\exp\{-ix_{max}g_\varepsilon(1)\}}{ix_{max}^0\,\partial g_\varepsilon(y)/\partial y|_{y=1}}\right). \quad (29)$$

Although the corrections to ix_{max}^0 are always small, their contribution to $\rho_{qu}(\varepsilon)$ for $Z_{\varepsilon\gg 1}$ turns out to be important:

$$\ln\frac{\rho_{qu}(\varepsilon)}{\rho_0(\varepsilon)}=-Z_\varepsilon\left[\ln\frac{Z_\varepsilon^4}{e\overline{N}R_\varepsilon^3}-\ln\left(1+\frac{3}{2}\left(\ln\frac{Z_\varepsilon^4}{\overline{N}R_\varepsilon^3}\right)^2 \times\int_0^1 dy\, y^2 g_\varepsilon^2(y)-\frac{3[Z_\varepsilon^4/\overline{N}R_\varepsilon^3]^{g_\varepsilon(1)}}{\ln[Z_\varepsilon^4/\overline{N}R_\varepsilon^3]\,\partial g_\varepsilon(y)/\partial y|_{y=1}}\right)\right]. \quad (30)$$

The behavior of the right-hand side of formula (30) is illustrated by curve 4 in Fig. 3. The quantity $\rho_0(\varepsilon)$, measured in units of $\overline{N}^{3/4}/a_B^3\varepsilon_0$, varies from 4 at $\varepsilon=18\overline{N}^{1/2}$ to 34 at $\varepsilon=120\overline{N}^{1/2}$.

We note that Eq. (27) for the saddle point has not only the purely imaginary root, equal in the zeroth approximation to x_{max}^0, but also an infinite set of complex roots $x_{max}^{(n)}$. Therefore, $\rho_{qu}(\varepsilon)$ from (25) is equal to the sum of the contributions made by integrals taken in the neighborhoods of all the saddle points. For relatively small values of n, these roots, in the zeroth approximation, are equal to $x_{\max}^{(n)0} = x_{\max}^{0} + 2\pi n$, where $n = \pm 1, \pm 2, \ldots$, and, with allowance for the first corrections, are determined by formula (29) with $-i2\pi n$ added to the right-hand side and with $x_{\max}^{0}$ replaced by $x_{\max}^{(n)0}$. Using this expression for $x_{\max}^{(n)}$, it is not difficult to convince oneself that the factor $\exp\{ix_{\max}^{(n)} Z_\varepsilon\}$ in the formula for the density of states falls off rapidly with increase of n, and

$$\exp(ix_{max}Z_\varepsilon) \gg \exp(ix_{max}^{(n)} Z_\varepsilon),$$

i.e., the contribution to (26) from all the complex saddle points is negligibly small.

As regards the accuracy and the limits of applicability of formula (30), it is necessary to note the following: It can be shown that the density of quantum states that is described by this formula produces principally donor-concentration fluctuations of the form

$$\xi(r) = N_D\{\exp[-ix_{max}(\varepsilon)(1+g_\varepsilon(r/R_\varepsilon))]-1\}, \tag{31}$$

and that, in shape and magnitude, these fluctuations are close to the optimal fluctuation (determined in the framework of the optimal-fluctuation method proposed in Refs. 8–10) of the concentration of scattering centers. The density of states $\rho_{\mathrm{qu}}^{\mathrm{opt}}(\varepsilon)$ produced by the optimal concentration fluctuation exceeds the value of $\rho_{\mathrm{qu}}(\varepsilon)$ from formula (30) relatively weakly, when the two are compared using logarithmic accuracy. Allowance for the discreteness of the distribution of point charged centers shows that $\rho_{\mathrm{qu}}^{\mathrm{opt}}(\varepsilon)$ for large values of Z_ε is smaller than $\rho_{\mathrm{qu}}^{\mathrm{true}}(\varepsilon)$ only in proportion to the pre-exponential factor, and is significantly smaller than this quantity for a low concentration of centers in the optimal fluctuation. On the basis of the requirement that the spacing between centers be small in comparison with $a_{\mathrm{B}} - Z_\varepsilon \gg (R_\varepsilon/Z_\varepsilon)^3$, using the dependence $R_\varepsilon(\varepsilon)$ in Fig. 2 we find that the optimal-fluctuation method is applicable in real situations if $Z_\varepsilon \gg 3$–4. A detailed discussion of these questions goes beyond the scope of this article.

4. THE HYBRID STATES

The hybrid part of the spectrum. Below, with SDS as the example, we show that for Coulomb localization of electrons the spectrum of the density of states contains not only a Gaussian and a Poissonian part but also a part in which the main contribution to $N(\varepsilon)$ is made by hybrid states. For large ε, formula (6) can be written in the form

$$N(\varepsilon) = \int_0^\infty d\varepsilon' \rho_0(\varepsilon') \left[6\pi\left(\frac{2\pi}{3}\right)^{1/3} \overline{N}^{5/6}\right]^{-1/2} \times \exp\left[-\overline{N}^{1/4} f\left(\frac{\varepsilon}{\overline{N}^{1/2}}\right) - \frac{\overline{N}^{1/6}}{6(2\pi/3)^{1/3}} \frac{(\varepsilon-\varepsilon')^2}{\overline{N}}\right] \tag{32}$$

Formula (32) is true if the quantum-binding energy satisfies the condition (19). In this case $f(\varepsilon/\overline{N}^{1/2})$ is described by formula (30) (curve 4 on Fig. 3). The expression used in (32) for the Gaussian probability $P(\varepsilon - \varepsilon')$ of the classical shift (see, e.g., Ref. 1) is valid under conditions of linear screening, which are fulfilled for

$$(\varepsilon-\varepsilon')/\overline{N}^{1/2} \ll (9\pi/4)^{2/3} \overline{N}^{1/6}. \tag{33}$$

The growth of $f(x)$ with increase of its argument is slowed ($s(x) = \partial \ln f(x)/\partial \ln(x)$, $s(20) \approx 2$, $s(70) \approx 1$, $s(\infty) \to 1/2$) in comparison with the quadratic growth of the argument of the Gaussian exponential. Therefore, the integrand in (32) has a sharp maximum at the point $\varepsilon_{\max} = \eta\varepsilon$, where η is the solution of the equation

$$1 = \eta + \frac{A(x)}{2\eta} \frac{f(x\eta)}{f(x)} s(x\eta). \tag{34}$$

Here,

$$x = \frac{\varepsilon}{\overline{N}^{1/2}}, \quad A(x) = 6\left(\frac{2\pi}{3}\right)^{1/3} \overline{N}^{1/12} \frac{f(x)}{x^2},$$

$$B(x) = \left(\frac{3}{2\pi}\right)^{1/3} \overline{N}^{1/6} \frac{x^2}{6}.$$

Then,

$$N(\varepsilon) = \rho_0(x\eta)\left[1 + \frac{B(x)}{2} \frac{f''(x\eta)}{f(x)}\right]^{-1/2} \times \exp\left\{-B(x)\left[(1-\eta)^2 + A(x)\frac{f(x\eta)}{f(x)}\right]\right\}. \tag{35}$$

For the situation when $A(x)s(x)/2 \ll 1$ (which is always true for sufficiently large x), it is not difficult to find from Eq. (34) that

$$\eta = 1 - {}^1/_2 A(x)s(x), \tag{36}$$

and from (35) that

$$\ln\{N(\varepsilon)/\rho_0(\varepsilon)\} = -\overline{N}^{1/4} f(\varepsilon/\overline{N}^{1/2}) + {}^1/_4 B(\varepsilon/\overline{N}^{1/2}) \times [A(\varepsilon/\overline{N}^{1/2}) s(\varepsilon/\overline{N}^{1/2})]^2, \tag{37}$$

i.e., here the main part of the binding energy in an optimal hybrid fluctuation is due to quantum localization, and only a small fraction $[\frac{1}{2}A(x)s(x)]$ is due to the classical shift. However, the energy $\frac{1}{2}\varepsilon A(\varepsilon/\overline{N}^{1/2})s(\varepsilon/\overline{N}^{1/2})$ of this small fraction is large. And so long as it is much greater than the root-mean-square Gaussian deviation we have $\frac{1}{4}B(x)[A(x)s(x)]^2 \gg 1$, since for large x, when $\frac{1}{2}A(x)s(x) \ll 1$, we have $B(x) \gg 1$. Therefore, up to exceptionally large $\varepsilon < \varepsilon_{\mathrm{ls}}$, where $\varepsilon_{\mathrm{ls}}$ is the solution of the equation

$$\varepsilon_{\mathrm{ls}}/\overline{N}^{1/2} = (9\pi\overline{N}/4)^{1/6} f(\varepsilon_{\mathrm{ls}}/\overline{N}^{1/2}) s(\varepsilon_{\mathrm{ls}}/\overline{N}^{1/2}) \tag{38}$$

(for $\overline{N} = 10$ we have $\varepsilon_{\mathrm{ls}}/N^{1/2} \approx 300$), the density of states that is produced by hybrid fluctuations incorporating a small-scale Poissonian and a large-scale (ls) Gaussian fluctuation is considerably greater than the density of Poissonian states.

With decrease of ε the classical-shift fraction in the binding energy increases. In principle, it can become the main contribution. However, in an SDS this is possible for unrealistically large values of $\overline{N}$, even for the smallest admissible ε. Thus, from (34) and curve *4* in Fig. 3 it is not difficult to find that $\eta = 1/2$ for $\varepsilon = 40\overline{N}^{1/2}$ (in this case, $\varepsilon'_{\max} = 20\overline{N}^{1/2}$, i.e., lies near the lower boundary of the region in which curve *4* in Fig. 3 is determined), if $\overline{N}^{1/12} = 4.3$. Incidentally, as follows from (19), only for such values of $\overline{N}$ is formula (30) suitable for the calculation of the density of the most weakly localized quantum states, and only for such values of $\overline{N}$ in an SDS does there exist a Gaussian part of the spectrum on which $\ln(N(\varepsilon)/N(0)) \propto -\varepsilon^2$. We note also that for $\varepsilon' = \varepsilon'_{\max}$ the condition (33) for linear screening takes the form $x^{-1}f(x)s(x) \ll \overline{N}^{1/12}$, and, for not too large x, is fulfilled only for large $\overline{N}$.

Repulsive states. The effect of the relatively rare repulsive hybrid states with a large potential-barrier height $\varepsilon' - \varepsilon$ on nonequilibrium phenomena can be decisive only if the effective capture coefficient $\gamma(\varepsilon, \varepsilon')$ for capture in these states decreases with increase of the barrier (increase of ε') much more rapidly, up to large values of ε', than the two-parameter density $N(\varepsilon,\varepsilon')$. The point is that, when factors violating the equilibrium occupation of localized states by electrons are included, the smallest deviations $\delta f(\varepsilon,\varepsilon')$ of the degree of occupation, as follows from the equations of the charge-exchange kinetics, will be associated with the fastest states, to which correspond the largest values of $\gamma(\varepsilon,\varepsilon')$: $\delta f(\varepsilon,\varepsilon') \sim \gamma^{-1}(\varepsilon,\varepsilon')$. The density of the charge that arises in these states is

$$\delta\rho(\varepsilon, \varepsilon') \propto N(\varepsilon, \varepsilon')\delta f(\varepsilon, \varepsilon') \propto N(\varepsilon, \varepsilon')\gamma^{-1}(\varepsilon, \varepsilon').$$

If the maximum of this function lies at large values of ε', the principal contribution to the formation of nonequilibrium charge in localized states is made by the slow states, and it is their parameters that will determine the magnitude of this charge and the rate of its changes in nonstationary processes.

First we shall estimate the value of the capture coefficient for capture by repulsive states and convince ourselves that $\gamma(\varepsilon, \varepsilon')$ falls sharply with increase of ε'. If the charging of the repulsive states occurs in a thermally activated way, it is implemented only by free carriers with energy greater than the barrier height. The fraction of these carriers at large values of $\varepsilon' - \varepsilon$ is very small and is determined primarily by the factor $\exp[\varepsilon_0(\varepsilon - \varepsilon')/T]$. Therefore, the effective coefficient for thermal-activational capture $\gamma^{ia}(\varepsilon,\varepsilon')$ in the zeroth approximation is equal to

$$\ln\{\gamma^{ta}(\varepsilon, \varepsilon')/\gamma_0\} = -\varepsilon_0(\varepsilon' - \varepsilon)/T, \tag{39}$$

where γ_0 is the capture coefficient at an attractive center. In view of the logarithmic accuracy of the formula (39) the dependence of γ_0 on ε and ε' (i.e., on the distribution of the potential near the attractive nucleus) is unimportant here.

In the tunneling of carriers the capture coefficient $\gamma^t(\varepsilon,\varepsilon')$ depends in an essential way not only on the height of the barrier but also on its width and shape. Below, the quantity $\gamma^t(\varepsilon,\varepsilon')$ is calculated for a nondegenerate compensated semiconductor—the only object for which the characteristics of potential barriers of large amplitude are known. As shown in Ref. 1, if in the semiconductor there are not only donors but also acceptors, the concentration of which is such that $0 < K = (N_d - N_a)/N_a \ll 1$, the probability of raising the bottom of the conduction band through a height $u \gg \overline{N}^{1/3}K^{-1/3}$ (u is measured in units of ε_0) is, with logarithmic accuracy,

$$\ln\{P(u)/P(0)\} = -3^{-3/2}u^{3/2}K^{1/2}\overline{N}^{-1/2}, \tag{40}$$

and the barrier shape in an optimal fluctuation of this amplitude has the form $u(r) = u(1 - r/r_u)^2$. Here, r and $r_u = (u/3K\overline{N})^{1/2}$ are measured in units of a_B. The tunneling transmissivity of such a barrier for low-energy electrons is equal to

$$D = \exp\left(-2\int_0^{r_u} dr\, u^{1/2}(r)\right) = \exp(-u/(3K\overline{N})^{1/2}).$$

Therefore, for repulsive states with a positive or small negative binding energy, $\gamma^t(\varepsilon,\varepsilon')$ is described by the expression

$$\ln\{\gamma^t(\varepsilon, \varepsilon')/\gamma_1\} = -(\varepsilon' - \varepsilon)/(3K\overline{N})^{1/2}, \tag{41}$$

i.e., the quantity $\gamma^t(\varepsilon,\varepsilon')$, like $\gamma^{ta}(\varepsilon,\varepsilon')$, is determined primarily by the height of the potential barrier. It can be seen from formulas (39) and (41) that at high temperatures $T > T_1 = \varepsilon_0(3K\overline{N})^{1/2}$ the principal capture mechanism at repulsive states is thermally activated, while for $T < T_1$ it is a tunneling mechanism. Also, the fact that γ_0 is evidently appreciably greater than γ_1 can have a slight effect on the value of T_1. Thus, in doped semiconductors, near the allowed band or even inside it there exist localized states for which the exchange times with delocalized states [proportional to $\gamma^{-1}(\varepsilon,\varepsilon')$] are spread over an exceptionally wide range of values and can be very large.

We now elucidate the conditions under which repulsive states can have a substantial influence on nonequilibrium phenomena in weakly doped compensated semiconductors. For the case of low temperatures ($T < T_1$), using formulas (6), (30), (40), and (41), we have

$$N(\varepsilon, \varepsilon')/\gamma^t(\varepsilon, \varepsilon') \propto \exp[(\varepsilon' - \varepsilon)/(3K\overline{N})^{1/2} - (\varepsilon' - \varepsilon)K^{1/2}/3^{3/2}\overline{N}^{1/2} - \overline{N}^{1/4}f(\varepsilon'/\overline{N}^{1/2})]. \tag{42}$$

Here we are using the expression obtained earlier for $\rho_{qu}(\varepsilon)$ for a noncompensated semiconductor, since for $\overline{N} \ll 1$ we need not take the compensation into account. The maximum of (42) is reached at a value ε^{1t} satisfying the equation

$$1 = \frac{1}{2}K(\varepsilon^{1t} - \varepsilon)^{1/2} + (3K\overline{N}^{1/2})^{1/2}s(x)\frac{f(x)}{x}\bigg|_{x=\varepsilon^{1t}/\overline{N}^{1/2}}, \tag{43}$$

i.e., for small K and $\overline{N}$, by virtue of the previously noted distinctive features of the behavior of $f(x)$ and its logarithmic derivative $s(x)$, the quantity $\varepsilon^{1t} - \varepsilon \gg 1$ for all ε. In accordance with (41), such values of ε^{1t} correspond to exceptionally small capture coefficients. Therefore, the influence of the slow states on the nonequilibrium phenomena in compensated semiconductors should be extremely important.

For $T > T_1$ the condition (43) takes the form

$$\frac{T_1}{T} = \frac{1}{2}K(\varepsilon^{1t} - \varepsilon)^{1/2} + (3K\overline{N}^{1/2})^{1/2}s(x)\frac{f(x)}{x}\bigg|_{x=\varepsilon^{1t}/\overline{N}^{1/2}}, \tag{44}$$

i.e., the quantity $\varepsilon^{1t} - \varepsilon$ decreases with increase of the temperature, and, by virtue of (39), there is a sharp decrease in the characteristic times of the slow states. Finally, for those values of T, N, and ε for which

$$s(x)f(x)/x\big|_{x=\varepsilon/\overline{N}^{1/2}} \gg \overline{N}^{1/4}\varepsilon_0/T$$

the role of the repulsive states is unimportant.

It is necessary to note that an important role in the fact that the slow states can have a substantial influence on the nonequilibrium properties of semiconductors is played not only by the large magnitude of the density of quantum states but also by the relatively large probability of potential barriers as a consequence of their weak electron screening. In addition, with increase of the amplitude of the barriers their characteristic spatial scale increases. For these reasons, the probability of high barriers decreases comparatively slowly, and this makes it much easier for the equalities (43) and (44) to be fulfilled.

---

[1] If the quantity r_{scr} is large in comparison with the characteristic scale of the electron wavefunction.

[2] Here and below, the energy is measured downward from the unperturbed position of the bottom of the conduction band.

[3)]If fluctuations of all scales smaller than r_{scr} make equal contributions to the classical shift of the bands, as occurs in the two-dimensional case (see Ref. 3), it is not possible to go from (5) to (6) in this way.

---

[1]B. I. Shklovskiĭ and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, New York, 1984).
[2]I. M. Lifshitz, S. A. Gredeskul, and L. A. Pastur, *Introduction to the Theory of Disordered Systems* (Wiley, New York, 1988).
[3]V. A. Gergel' and R. A. Suris, Zh. Eksp. Teor. Fiz. **84**, 719 (1983) [Sov. Phys. JETP **57**, 415 (1983)].
[4]E. O. Kane, Phys. Rev. **131**, 79 (1963).
[5]B. I. Shklovskiĭ and A. L. Éfros, Zh. Eksp. Teor. Fiz. **58**, 657 (1970) [Sov. Phys. JETP **31**, 351 (1970].
[6]A. M. Sokolov and D. V. Ivanenko, *Quantum Field Theory* [in Russian] (Gostekhizdat, Moscow, Leningrad, 1952).
[7]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory, 3rd ed.* (Pergamon Press, Oxford, 1977).
[8]B. I. Halperin and M. Lax, Phys. Rev. **148**, 722 (1966).
[9]J. Zittartz and J. S. Langer, Phys. Rev. **148**, 741 (1966).
[10]I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **53**, 743 (1967) [Sov. Phys. JETP **26**, 462 (1968)].

Translated by P. J. Shepherd