Boundary condition for the distribution function of conduction electrons scattered by a metal surface

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It is shown that, under certain assumptions, the quantum collision integral for conduction electrons scattered by perturbations of the surface potential barrier can be replaced, in the quasiclassical region, by a boundary condition for the distribution function. The general boundary condiiton and its explicit form in a semi-infinite metal are obtained for the cases of scattering by small-amplitude roughnesses, by large but smooth roughnesses, and by point defects distributed within the surface layer. A correction to the current density due to scattering by small roughnesses under conditions of the anomalous skin effect is obtained without making use of the boundary condition.

1. INTRODUCTION

In kinetic theory, the surface scattering of conduction electrons is usually taken into account by means of a boundary condition that relates the distribution functions of the electrons incident on and reflected from the surface. The simplest such condition, first introduced by Fuchs[1], is a linear relationship which includes a phenomenological parameter that has the meaning of a coefficient of reflection of electrons by the surface. The general form of the boundary condition is that of a linear relation, integrated over the momenta, whose basic properties can be analyzed within the framework of the phenomenological approach[2-4]. Some authors (see the review in[4]) have used semi-intuitive considerations to set the kernel of this relation in correspondence with the probability of electron scattering by the surface, which is then calculated in simplified models. The subsequent derivations of the boundary conditions for the two simplest types of surface scattering are presented in[5, 6]. Baskin and Éntin[5] have considered the scattering by localized defects randomly placed on the surface, and have shown that at small concentrations the amplitude of volume scattering by a single defect enters into the boundary condition. Fal'kovskiĭ[6] has taken into account the effect of surface roughnesses with small amplitude; the corresponding boundary condition contains the correlation function of the roughness amplitudes at different points.

An essential assumption in the above derivations of the boundary condition is that the electron wave function vanishes at the metal boundary, which corresponds to the approximation of the surface potential by a rectangular barrier of infinite height. A similar assumption has been used to solve other problems (see, e.g.,[7, 8]) in which surface perturbations must be taken into account. The actual finiteness of the height and region of variation of the surface barrier affects the probability of electron scattering, leading to a smooth decay of the wave function within some layer near the surface. To account for the related effects, and to generalize the results of[5, 6] to more complex types of surface scattering, we must introduce explicitly the surface potential of an "ideal" boundary, the perturbations of which will lead to electron scattering by the surface. The problem then arises of the proof of the boundary condition for the distribution functions and of its relation to the scattering potential. The solution of this problem is the aim of the present work.

We shall discuss a generalized electron collision integral that describes the contribution of surface scattering to the quantum kinetic equation for the density matrix, in the representation of the electron wave functions in the field of the ideal boundary. Under certain assumptions it is possible to replace the collision integral in the quasiclassical region with a boundary condition for the distribution functions. This condition is in the nature of an integral over the momenta, and its kernel is related either to the matrix elements of the scattering operator or to the transition probability between stationary states of the electron near the boundary. We shall show that in the proper approximations the boundary condition reduces to the results of[5, 6], and we shall obtain its explicit form for other simple cases, when scattering occurs from smooth roughnesses or from point defects distributed within the surface layer.

In conclusion, to illustrate the possibility of taking surface scattering into account without the use of boundary conditions, we shall present the results of a quantum-mechanical calculation of the current density under conditions of the anomalous skin effect in scattering by roughnesses of small amplitude. These results apply to the quasiclassical region, for which the corresponding analysis based on the boundary condition was given by Fal'kovskiĭ[9], and include the quantum corrections of Van Gelder[10].

2. THE KINETIC EQUATION

The starting point for our discussion is the quantum kinetic equation for conduction electrons scattered by a static potential. An equation of this type, as applied to the calculation of impurity conductivity, was studied in detail by Kohn and Luttinger[11], whose results have subsequently been developed further and generalized (see, e.g.,[12-14]). We have to analyze situations in which the density matrix in the momentum representation has significant nondiagonal elements that describe the reaction of electrons in a bounded metal to a spatially inhomogeneous electromagnetic field. Since no generally-accepted treatment of such situations is given in the literature, we shall describe briefly the derivation of the

kinetic equation that we use here, so that we can formulate the assumptions to be used and show the possibility of including the specific features of the surface scattering.

It is convenient to begin with the Liouville equation for the Laplace transform of the single-particle density matrix $\rho(t)$:

$$\rho(z)=\int_0^\infty dt\exp(izt)\rho(t), \tag{2.1}$$

which is of the form

$$z\rho(z)-\hbar^{-1}[H,\ \rho(z)]-\hbar^{-1}[H_\omega',\ \rho(z-\omega)]=i\rho^{in}, \tag{2.2}$$

where H is the electron Hamiltonian including the scattering potential, H'_ω is the amplitude of the Hamiltonian of the interaction with an electromagnetic field varying like $\exp(-i\omega t)$, and ρ^{in} is the initial value of the density matrix. In the approximation linear in the field interaction, the density matrix consists of an unperturbed part ρ_0 and a correction ρ_1 that is proportional to the field potential. To obtain the kinetic equation we must average the operators ρ_0 and ρ_1 over configurations of the scattering potential that are equivalent from the macroscopic point of view. In our case this averaging (for which we use the symbol $\langle\ldots\rangle$) corresponds to the average over the shapes of the roughnesses of the metal boundary and over the positions of the point defects.

By separating the part of the Hamiltonian that describes scattering,

$$V=H-\langle H\rangle\equiv H-H_0, \tag{2.3}$$

and solving formally the equation for the difference $\rho_0(z)-\langle\rho_0(z)\rangle$ and $\rho_1(z)-\langle\rho_1(z)\rangle$, we can write for $\langle\rho_0(z)\rangle$ and $\langle\rho_1(z)\rangle$ a system of equations that includes the initial value ρ^{in}. The stationary value of the density matrix $\bar\rho=\bar\rho_0+\bar\rho_1$ is obtained with the help of the limiting transition

$$\bar\rho_0=\lim_{s\to0}\{is\langle\rho_0(is)\rangle\},\qquad \bar\rho_1=\lim_{s\to0}\{is\langle\rho_1(\omega+is)\rangle\}. \tag{2.4}$$

in which the parameter s can be assumed to be real. By performing this limiting transition in the equations for $\langle\rho_0(z)\rangle$ and $\langle\rho_1(z)\rangle$ we can verify that when the condition

$$\lim_{s\to0}\left\{is\left\langle\left[V,\int_{-\infty}^{\infty}d\varepsilon R\left(\varepsilon+\frac{\hbar\omega+is}{2}\right)(\rho^{in}-\langle\rho^{in}\rangle)R\left(\varepsilon-\frac{\hbar\omega+is}{2}\right)\right]\right\rangle\right\}=0 \tag{2.5}$$

is satisfied for any ω ($R(E)$ is the resolvent of the operator H), the initial value ρ^{in} drops out of the equations. Thus, when Eq. (2.5) holds for any ρ^{in}, the kinetic equations for the stationary values $\bar\rho_0$ and $\bar\rho_1$ must be independent of the initial conditions. In the cases considered here of scattering by point defects and by surface roughnesses, Eq. (2.5) is satisfied because the difference $\rho^{in}-\langle\rho^{in}\rangle$ is nondiagonal in the momentum representation.

The equilibrium density matrix f is determined from the condition that the collision integral I_0 in the equation for $\bar\rho_0$ vanish:

$$-\hbar^{-1}[H_0,\ \bar\rho_0]=I_0, \tag{2.6}$$

which gives

$$\lim_{s\to0}\langle[V,F_0(s)]\rangle=0, \tag{2.7}$$

$$F_0(s)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}d\varepsilon R\left(\varepsilon+\frac{is}{2}\right)[V,f]R\left(\varepsilon-\frac{is}{2}\right). \tag{2.8}$$

Neglecting the change in the electron energy due to scattering, we shall assume that f is a Fermi function of the Hamiltonian H_0, and make use of this assumption to write an equation for the part of the density matrix that is linear in the interaction with the field. Using the explicit form of the operator H'_ω, it is convenient to replace $\bar\rho_1$ with the difference $g=\bar\rho_1-\rho_L$, where ρ_L satisfies

$$[\rho_L,H_0]=[H_\omega^A,f],\qquad H_\omega^A=-\frac{e}{c}\int d\mathbf{r}\mathbf{v}(\mathbf{r})\mathbf{A}_\omega(\mathbf{r}), \tag{2.9}$$

$\mathbf{v}(\mathbf{r})$ is the current density operator, and $\mathbf{A}_\omega$ is the amplitude of the vector potential. The kinetic equation for g is of the form

$$-i\omega g+i\hbar^{-1}[H_0,\ g]+C=I, \tag{2.10}$$

where the field part C and the operator I are specified by the following formulas:

$$[C,H_0]=[H_\omega^E,f],\qquad H_\omega^E=e\int d\mathbf{r}\mathbf{v}(\mathbf{r})\mathbf{E}_\omega(\mathbf{r}), \tag{2.11}$$

$$I=-\lim_{s\to0}\langle\hbar^{-1}[V,F_1(s)]\rangle, \tag{2.12}$$

$$F_1(s)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}d\varepsilon R\left(\varepsilon+\frac{\hbar\omega+is}{2}\right)\hbar\{\Phi(s)+i\hbar^{-1}[V,g]+I\}R\left(\varepsilon-\frac{\hbar\omega+is}{2}\right), \tag{2.13}$$

$$\Phi(s)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}d\varepsilon R\left(\varepsilon+\frac{is}{2}\right)\{[H_\omega^E,F_0(s)]+[V,C]\}R\left(\varepsilon-\frac{is}{2}\right). \tag{2.14}$$

Equation (2.10) contains the electromagnetic field amplitude $\mathbf{E}_\omega(\mathbf{r})$ (rather than the potential amplitudes). This equation is the quantum analog of the Boltzmann equation; in the absence of a magnetic field, the role of the term ρ_L in the calculation of average values is to compensate for the increments due to the change in momentum in the electromagnetic field. In the derivation above (in contrast to that given in[13]) there is no need to introduce unwarranted assumptions about the form of the initial value of the density matrix in order to guarantee gauge invariance of the kinetic equation; we have made use only of the fully justified condition (2.7). It is also important to note the definition (2.3) of the operators H_0 and V; in the case of surface scattering there is a significant difference between $H_0=\langle H\rangle$ and the Hamiltonian of a free electron.

We now consider the form of the collision integral I in our problem. We shall discuss surface scattering in an isotropic semiinfinite metal with a quadratic electron-dispersion law. The influence of an ideal boundary will be represented by a one-dimensional potential barrier of height U. Aligning the xy plane with the metal surface, the eigenfunctions of H_0 can be written in the form

$$\psi_p(\mathbf{r})\equiv\psi_{\kappa k}(\boldsymbol{\rho},z)=S^{-1/2}e^{i\kappa\rho}\chi_k(z), \tag{2.15}$$

where $\boldsymbol{\rho}$ and $\hbar\boldsymbol{\kappa}$ are the projections of the electron radius-vector and momentum on the xy plane, for the variables x and y we take periodic boundary conditions with a normalization to a surface area S, and $\hbar k=(2m\epsilon_p-\hbar^2\kappa^2)^{1/2}$, where ϵ_p is the electron energy. Inside the metal ($z<0$, $\epsilon<U$) we have the following asymptotic expression for the function $\chi_k(z)$:

$$\chi_k(z)\to(2/\pi)^{1/2}\sin(kz-\alpha(k)),\qquad z\to-\infty, \tag{2.16}$$

in which the phase $\alpha(k)$ depends on the shape of the barrier; for a rectangular barrier we have $\tan\alpha(k)=k/\sqrt{k_0^2-k^2}$, where $\hbar k_0=\sqrt{2mU}$.

To write the collision integral I in the H_0 representation, we introduce from [11, 14] the scattering operator T(E), which satisfies the equation

$$T(E)=V+VR_0(E)T(E), \tag{2.17}$$

where $R_0(E)$ is the resolvent of H_0. Then Eq. (2.12) for the matrix elements $I_{pp'}$ can be put in the following form:

$$I_{pp'}=\lim_{s\to 0}\Big\{\Big\langle\sum_{p_1}[R_{0p}(\varepsilon_{p_1}+\hbar\omega+is)D_{pp_1}L^{-}_{p_1p'}(\varepsilon_{p_1},\varepsilon_{p'})-L^{+}_{pp_1}(\varepsilon_p,\varepsilon_{p'})\cdot$$

$$\cdot R_{0p_1}(\varepsilon_{p'}+\hbar\omega+is)D_{p_1p'}]+\sum_{p_1p_2}\Big[Q^{pp'}_{p_1p_2}\Big(\varepsilon_{p_1}-\frac{\hbar\omega+is}{2}\Big)R_{0p_1}(\varepsilon_{p_2}+\hbar\omega+is)D_{p_1p_2}$$

$$-Q^{pp'}_{p_1p_2}\Big(\varepsilon_{p_1}+\frac{\hbar\omega+is}{2}\Big)R_{0p_2}(\varepsilon_{p_1}+\hbar\omega+is)D_{p_2p_1}\Big]\Big\rangle\Big\}; \tag{2.18}$$

$$D_{pp'}=\hbar^{-1}(\hbar\omega+is+\varepsilon_{p'}-\varepsilon_p)g_{pp'}-iI_{pp'}-i\Phi_{pp'}(s), \tag{2.19}$$

$$L^{\pm}_{pp'}(E,E')=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\varepsilon T_{pp'}\Big(\varepsilon\pm\frac{\hbar\omega+is}{2}\Big)\Big[\Big(\varepsilon-\frac{\hbar\omega+is}{2}-E\Big)^{-1}$$

$$-\Big(\varepsilon+\frac{\hbar\omega+is}{2}-E'\Big)^{-1}\Big], \tag{2.20}$$

$$Q^{pp'}_{p_1p_2}(E)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\varepsilon\frac{1}{\varepsilon-E}T_{pp_1}\Big(\varepsilon+\frac{\hbar\omega+is}{2}\Big)T_{p_2p'}\Big(\varepsilon-\frac{\hbar\omega+is}{2}\Big)$$

$$\cdot\Big[R_{0p'}\Big(\varepsilon-\frac{\hbar\omega+is}{2}\Big)-R_{0p}\Big(\varepsilon+\frac{\hbar\omega+is}{2}\Big)\Big]. \tag{2.21}$$

The summation over p in Eq. (2.18) includes the summation over κ and the integration over k from 0 to ∞, taking into account the degeneracy of states with $\hbar k > \sqrt{2mU}$. When the matrix elements of the scattering operator are averaged over the configurations of the scattering potential, a diagonal singularity appears in the momentum representation. In the surface-scattering case a diagonal singularity appears only in the momentum components lying in the plane of the metal boundary; we then have

$$\langle T_{pp'}\rangle=\delta_{\varkappa\varkappa'}\langle T_{p\varkappa k'}\rangle,\quad \langle T_{pp_1}T_{p_1p'}\rangle=\delta_{\varkappa_1\varkappa_2}\langle T_{p\varkappa_1k_1}T_{\varkappa_1k_1p'}\rangle. \tag{2.22}$$

Since the scattering potential is concentrated in a narrow layer near the boundary, the dependence on the normal component of the momentum in Eq. (2.22) is smooth. It is this fact which determines the principal difference between the electron collision integrals for the cases of surface and volume scattering.

3. THE BOUNDARY CONDITION

If the scale of the field inhomogeneity is large in comparison with the de Broglie wavelength of the electron, the matrix elements $g_{pp'}$ are nonzero only for values of the difference $p-p'$ that are small compared to the sum $p+p'$. In this case, which corresponds to the validity of the quasiclassical approximation, the form of the collision integral can be simplified significantly.

In Eq. (2.18) we neglect frequency dispersion and the influence of the electromagnetic field (the term $\Phi_{pp'}(s)$ in Eq. (2.19)), which describe purely quantum effects. In addition, using (2.22), the first term on the right side of Eq. (2.18) can be transformed as follows:

$$\int_0^{\infty}dk_1g_{\varkappa kk_1}\langle L^{-}_{\varkappa k_1\varkappa k}\rangle\approx\langle L^{-}_{\varkappa k\varkappa k}\rangle\int_0^{\infty}dk_1g_{\varkappa kk_1}\equiv\langle L^{-}_{p}\rangle G_p. \tag{3.1}$$

We have assumed that the characteristic scale of variation of the matrix elements $T_{pp'}$ as functions of the difference $k-k'$ (which is of the order of the reciprocal of the effective radius of the surface potential) is large compared with the scale of variation of $g_{pp'}$. Similarly, we have

$$\int_0^{\infty}dk_2\langle Q^{pp}_{\varkappa_1k_1\varkappa_1k_2}\rangle g_{\varkappa_1k_1\varkappa_1k_2}\approx\langle Q^{pp}_{p_1p_1}\rangle G_{p_1}. \tag{3.2}$$

We can also carry out a transformation similar to (3.1) and (3.2) in the terms on the right side of Eq. (2.18) that contain the matrix elements of I, but the role of the quantity $g_{pp'}$ will be played by the resolvents $R_{0p}(\epsilon_{p'}+is)$. In these approximations the collision integral I is diagonal, and after the optical theorem is used for the scattering operator, Eq. (2.18) for $I_{pp}\equiv I_p$ takes the form

$$I_p=-\sum_{p'}J_{pp'}\Big(G_p-\frac{\pi m}{\hbar k}I_p-G_{p'}+\frac{\pi m}{\hbar k'}I_{p'}\Big), \tag{3.3}$$

$$J_{pp'}=\lim_{s\to 0}\Big\{\frac{2}{\pi\hbar}\int_{-\infty}^{\infty}d\varepsilon\langle T_{pp'}(\varepsilon+is)T_{p'p}(\varepsilon-is)\rangle$$

$$\cdot\frac{s^2}{[(\varepsilon-\varepsilon_p)^2+s^2][(\varepsilon-\varepsilon_{p'})^2+s^2]}\Big\}. \tag{3.4}$$

To clarify the meaning of the quantity G_p, consider the relation between the density matrix (or more accurately, its nonequilibrium part) $g_{pp'}$ and the quasiclassical distribution function. For simplicity, we shall not write out explicitly the variables (ρ, κ) that correspond to motion in the boundary plane, which can be taken into account with no particular difficulty. The quantity $g_{kk'}$ is related to the density matrix in the coordinate representation, g(z, z') by

$$g_{kk'}=\int dz\int dz'\chi_k(z)g(z,z')\chi_{k'}(z')\approx\frac{1}{2\pi}\int dz[\varphi(z,Q)e^{iqz}+\varphi(z,-Q)e^{-iqz}$$

$$-\varphi(z,q)e^{2i(Qz-\alpha(k))}-\varphi(z,-q)e^{-2i(Qz-\alpha(k))}]. \tag{3.5}$$

In writing the second part of this equation we have neglected the contribution to the integral from the narrow surface region, within which g(z, z') is comparatively small; this allows us to use the asymptotic expression (2.16) for the wave functions. In addition, we have set $\alpha(k)\approx\alpha(k')$. The function $\varphi(z, Q)$ is the density matrix in a mixed representation (quantum distribution function), $Q=(k+k')/2$, and $q=k-k'$; in the quasiclassical case, when $Q\gg q$ and $\varphi(z, Q)$ is a smooth function of z, we can neglect the last two terms in Eq. (3.5) and set $Q=k$. Then, taking the definition (3.1) into account, we obtain

$$g_{kk'}\approx\varphi_q(k)+\varphi_{-q}(-k), \tag{3.6}$$

$$G_k=\int_0^{\infty}dk'g_{kk'}\approx\int_{-\infty}^{\infty}dqg_{kk'}=\varphi(0,k)+\varphi(0,-k), \tag{3.7}$$

where $\varphi_q(k)$ is the Fourier transform of $\varphi(z, k)$, while $\varphi(0, k)$ and $\varphi(0, -k)$ have the meaning of boundary values of the distribution functions of the incident and reflected electrons. Thus, in the given approximations, G_p is simply related to the distribution function on the metal boundary.

In the well-known approach first suggested by Fuchs[1], the presence of surface scattering is described by a boundary condition in the form $\varphi(0,-k)=(1-P)\varphi(0,k)$, where P is the coefficient of diffusivity of electron reflection from the surface[1)]. It is easy to show that this boundary condition is equivalent to the introduction, into the Boltzmann equation for the sum $\varphi_q(k)+\varphi_{-q}(-k)$, of a term I_k that plays the part of an electron-surface collision integral and satisfies the equation

$$I_k=-\frac{\hbar k}{2\pi m}P\Big(G_k-\frac{\pi m}{\hbar k}I_k\Big). \tag{3.8}$$

A comparison of this equation with Eq. (3.3) establishes the relationship between our collision integral and the Fuchs boundary condition, and permits us to connect the diffusivity coefficient (when it can properly be said to exist) with the operator for the scattering of the electron by the perturbations of an ideal metal surface.

Equation (3.3) is equivalent to a boundary condition in integral form. This sort of boundary condition was discussed in[2-4], but the existing microscopic justifications[5,6] in the particular models are limited by the assumption that the potential barrier is of infinite height that the surface scattering is weak. Our result, which is free of these limitations, can be written in the form

$$\varphi(0;-k,\varkappa)=\varphi(0;k,\varkappa)-\frac{2\pi m}{\hbar k}\sum_{p'}J_{pp'}[\varphi(0;k,\varkappa)-\varphi(0;k',\varkappa')]. \quad (3.9)$$

This condition possesses all the general properties that were postulated in the phenomenological approach; in particular, it guarantees the absence of a particle flux through the surface.

In addition, the analysis above gives an indication of the limits of applicability of the boundary conditions for the distribution functions in the solution of the kinetic equation. They are specified by the requirement that the effective radius of the surface potential and the decay range of the electron wave function near the boundary be small compared with the characteristic scale of variation of the distribution function.

In the investigation of essentially quantum phenomena we must use the collision integral (2.18) in its general form, noting that the specific details of the quantum numbers p were not taken into account when we wrote it down. Quantum effects can be important not only in special conditions, when the quantization of the electron orbital motion is significant (the quantum size effect, magnetic surface levels, etc.), but also in the comparatively simpler case of the anomalous skin effect[10].

We obtained Eq. (3.3) for a semi-infinite metal. However, the derivation can be carried out in an entirely similar fashion under the conditions of the classical size effect, where, although the meaning of the quantity G_p changes slightly because of the inclusion of a second boundary, Eq. (3.3) remains practically unchanged.

4. SURFACE SCATTERING

In this section we discuss the boundary conditions for the simplest typical cases of surface electron scattering. In all these cases we can immediately take the energy integral in the general formula (3.4), taking the limit as $s \to 0$. We then obtain

$$J_{pp'}=\frac{2\pi}{\hbar}\langle|T^{+}_{pp'}(\varepsilon_p)|^2\rangle\delta(\varepsilon_p-\varepsilon_{p'}),\qquad T^{+}(\varepsilon)=\lim_{s\to 0}T(\varepsilon+is). \quad (4.1)$$

The combination $(2\pi m/\hbar k)J_{p'p}$ in the boundary condition (3.9) can be interpreted as the probability of a single scattering of an electron from state p to state p', per unit interval of the wave numbers k; its summation over $p' \neq p$ gives the total scattering probability w_p of an electron with momentum p in all directions except that corresponding to specular reflection. By the use of the optical theorem we can express w_p in terms of the diagonal element of the scattering operator:

$$w_p=1-\left|1-i\frac{2\pi m}{\hbar k}\langle T_{pp}{}^{+}(\varepsilon_p)\rangle\right|^2. \quad (4.2)$$

In some cases the integral operator acting on $\varphi(0; k, \varkappa)$ in Eq. (3.9) can be reduced to multiplication by a function of p, which has the meaning of an effective diffusivity coefficient. If there is an electric field, nonuniform along the z axis, acting parallel to the surface in an isotropic semi-infinite metal, the distribution function of the electrons incident on the boundary can be written in the form

$$\varphi(0;\ k,\ \varkappa)=\varkappa\mathbf{D}(k,\ \varepsilon_p), \quad (4.3)$$

where the vector $\mathbf{D}(\mathbf{k}, \epsilon_p)$ is parallel to the field and does not depend explicitly on $\varkappa$. The boundary condition (3.9) reduces to the Fuchs condition in two cases. First, if $J_{pp'}$ does not depend on the direction of $\varkappa'$, then the integral term in Eq. (3.9) vanishes and the part of a diffusivity coefficient is played by the total scattering probability w_p. Second, if the $\mathbf{D}(\mathbf{k}')$ is a smooth function compared with $J_{pp'}$, then we can set $\mathbf{D}(\mathbf{k}') \approx \mathbf{D}(\mathbf{k})$ in the integral term of Eq. (3.9), and the quantity that plays the part of P is

$$P=\frac{2\pi m}{\hbar k}\sum_{p'}J_{pp'}\left(1-\frac{\varkappa\varkappa'}{\varkappa^2}\right). \quad (4.4)$$

This situation occurs under conditions close to the normal skin effect, when $\mathbf{D}(\mathbf{k})$ depends weakly on k.

The specific form of scattering typical of a surface is due to statistically distributed geometric irregularities (roughnesses) of the boundary. The usual treatment of electron scattering by roughnesses is based on an analogy with the problems of scattering of acoustic and electromagnetic waves by a statistically irregular surface (see[15]), and in effect assumes a surface potential barrier of rectangular form and infinite height. In a more general approach, the finiteness of the barrier height and of the region of decay must be taken into account. For a rectangular barrier of height U, the scattering potential of a rough surface can be written in the form

$$V(\rho,z)=U\Theta(z-h(\rho))-V_0(z),\quad \Theta(z>0)=1,\quad \Theta(z<0)=0, \quad (4.5)$$

where $h(\rho)$ is a random function that describes the shape of the roughnesses, and $V_0(z)$ is the potential of an ideal boundary, specified according to Eq. (2.3) by the condition $\langle V\rangle = 0$. The averages must now be taken over the different shapes of $h(\rho)$, and we assume that $\langle h(\rho)\rangle = 0$.

When the amplitude h of the roughnesses is sufficiently small, the scattering by potential (4.5) can be analyzed by perturbation theory. In this case it should be kept in mind that the simple expansion of the scattering operator T in powers of V implies the assumption that the characteristic value h is small compared to the damping scale of the wave function $\chi_k(z)$ near the surface, i.e., compared to $h/\sqrt{2mU}$. Strictly speaking, therefore, this expansion becomes inapplicable in the limit of large U. However, by expanding the matrix elements of V in terms of h, we can use Eq. (2.17) to construct a series for T in powers of h, the terms of which will in general stem from different powers of V. It can be shown that each term of this series tends to a finite limit as $U \to \infty$, and that the expansion of the matrix elements $T_{pp'}$ in powers of h will be correct only if $k, k' \ll h^{-1}$.

The formal result corresponds to a direct "expansion" of the potential V in powers of $h(\rho)$. In the approximation linear in h we obtain for a potential of arbitrary shape

$$V(\rho,z)=\int d\rho' u(\rho-\rho',z)h(\rho'), \quad (4.6)$$

where the kernel $u(\rho, z)$ describes the effective interaction between the electron and the surface. Then the scattering probability takes the form

$$J_{pp'}=(2\pi)^3\hbar^{-1}S\xi(\varkappa-\varkappa')|u_{pp'}|^2\delta(\varepsilon_p-\varepsilon_{p'}), \quad (4.7)$$

$$\xi(\varkappa)=(2\pi)^{-2}\int d\rho\exp(-i\varkappa\rho)\langle h(0)h(\rho)\rangle, \quad (4.8)$$

where $u_{pp'}$ is the matrix element of the function $u(\rho, z)$.

For a rectangular potential barrier of arbitrary height, the quantity $h^2kk'/\pi mS$ occurs in place of $u_{pp'}$. Then by substituting the expression (4.7) in the boundary condition (3.9) we can easily show that it becomes equivalent to the Fal'kovskiĭ condition[6]. Thus, in the first approximation of perturbation theory this boundary condition is correct for a boundary potential barrier of any height. Note, however, that $J_{pp'}$ begins to depend weakly on U as early as the second order of perturbation theory.

For an arbitrary barrier, when the correlation function $\langle h(0)h(\rho)\rangle$ varies slowly by comparison with $u(\rho, z)$, we can set $\kappa' \approx \kappa$ in the matrix element $u_{pp'}$, and from the applicability conditions of perturbation theory, we can expand the square $|u_{pp'}|^2$ in powers of k and k' only when k is small; in this case we again arrive at the Fal'kovskiĭ boundary condition.

The problem of scattering by roughnesses of relatively large amplitude, when $hk \gg 1$, is also greatly simplified when the variation of the function $h(\rho)$ is slow. If the distance over which $h(\rho)$ varies is large compared to the characteristic amplitude h and the decay range of the potential barrier, the scattering potential of the roughnesses can be put in the following form:

$$V(\rho, z)=W(z-h(\rho))-V_0(z). \quad (4.9)$$

This expression is a generalization of Eq. (4.5) to the case of a surface barrier $W(z)$ of arbitrary shape. We can now write the matrix element of the scattering operator in the form

$$T^+_{pp'}(\varepsilon_{p'})=S^{-1}\int d\rho\int dz\exp\{-i(\varkappa-\varkappa')\rho\}\chi_k(z)V(\rho, z)\eta^+_{\varkappa'k'}(\rho, z); \quad (4.10)$$

then from the Lippman-Schwinger equation we obtain

$$\eta^+_{\varkappa k}(\rho, z)=\chi_k(z)+\int d\rho'\int dz'R_0^+(\rho-\rho', z, z'; \varepsilon_{\varkappa k})\cdot\exp\{i\varkappa(\rho'-\rho)\}\times V(\rho', z')\eta^+_{\varkappa k}(\rho', z'). \quad (4.11)$$

The assumption that the variation of $h(\rho)$ is smooth allows us to remove the functions $V(\rho', z')$ and $\eta^+_p(\rho', z')$ from under the integral over ρ' in Eq. (4.11), setting $\rho' \approx \rho$; then the integral over ρ' is taken over the resolvent R_0^+ only, and the problem becomes one-dimensional. We can conveniently estimate the omitted terms by writing down the Schrödinger equation for $\eta^+_p(\rho, z)$; they can be considered negligible only if the characteristic gradients of $h(\rho)$ are small compared to unity and to the ratio k/κ, and the radius of curvature of the surface $z = h(\rho)$ is large compared to k^{-1}. These assumptions correspond to the validity of the Kirchhoff method in the theory of wave scattering by an uneven surface (see[15], Chap. VII), which is applied to the phenomenological treatment of electron scattering in, for instance,[2, 7, 16]. Note that, in the existing literature, the Kirchhoff method is actually used only to analyze the differential and integral scattering probabilities. Our approach, based on Eq. (4.11), allows us first to formulate the boundary condition for the distribution function and then simply to state the applicability limits of the results.

In the approximations cited above the function $\eta^+_p(\rho, z)$ does not depend on κ, and the dependence on ρ enters parametrically through $h(\rho)$. Thus Eq. (4.1) can be written in the form

$$J_{pp'}=\frac{2\pi}{\hbar}S^{-1}\int d\rho e^{-i(\varkappa-\varkappa')\rho}\langle\tau^+_{k'k}(\varepsilon_k, 0)\,\tau^-_{kk'}(\varepsilon_{k'}, \rho)\rangle\cdot\delta(\varepsilon_k-\varepsilon_{k'}+\varepsilon_\varkappa-\varepsilon_{\varkappa'}), \quad (4.12)$$

where $\tau(\epsilon, \rho)$ is the scattering operator in the one-dimensional problem, and $\epsilon_k = \epsilon_p - \epsilon_\kappa$. By assumption, the correlation function $\langle\tau^+(0)\tau^-(\rho)\rangle$ decays so slowly that $|\kappa-\kappa'| \ll k, k'$ for the characteristic scattering events in Eq. (4.12). The conservation of energy is then guaranteed by the smallness of the difference $k-k'$ compared to the sum $k+k'$. With sufficient accuracy, we can neglect the square of $k-k'$ compared to $(k+k')^2$, so that, because the integral over ρ in Eq. (4.12) is symmetric under the interchange of k and k', we can replace both k and k' with $(k+k')/2$ in evaluating the integral. Thus, to specify the expression (4.12) it is enough to find the diagonal element $\tau_{kk}(\epsilon_k, \rho) \equiv \tau_k(\rho)$.

We note that the function $\eta^+_k(z)$ satisfies the one-dimensional Schrödinger equation with the potential $W(z-h)$. Therefore $\eta^+_k(z+h)$ can differ only by a phase factor from the function $\bar\chi_k(z)$ that describes stationary states with the barrier $W(z)$ and has an asymptotic expression of the form (2.16) with the phase $\alpha(k)$ replaced by $\bar\alpha(k)$. On the other hand, the asymptotic formula for $\eta^+_k(z)$ from Eq. (4.10) can be expressed in terms of τ_k. Thus we have

$$\eta_k(z)\to\sqrt{\frac{2}{\pi}}\frac{1}{2i}[e^{ikz-i\bar\alpha(k)-ikh}-e^{-ikz+i\bar\alpha(k)+ikh}]e^{i\beta(k)}, \quad z\to-\infty, \quad (4.13)$$

$$\eta_k(z)\to\sqrt{\frac{2}{\pi}}\frac{1}{2i}\left[e^{ikz-i\alpha(k)}-e^{-ikz+i\alpha(k)}\left(1-i\frac{2\pi m}{\hbar^2k}\tau_k\right)\right], \quad z\to-\infty. \quad (4.14)$$

The phase $\beta(k)$ is specified by the requirement that the first terms in Eqs. (4.13) and (4.14) be identical, each describing a wave incident on the surface; from this we can easily find τ_k:

$$\tau_k=-i\frac{\hbar^2k}{2\pi m}[1-\exp 2i(kh+\bar\alpha(k)-\alpha(k))] \quad (4.15)$$

and after we exchange $k \to (k+k')/2$ and substitute this into Eq. (4.12) we obtain

$$J_{pp'}=\frac{2\pi}{\hbar}\left(\frac{\hbar^2}{2m}\right)^2S^{-1}K\left(\frac{\varkappa-\varkappa'}{k+k'}\right)\delta(\varepsilon_p-\varepsilon_{p'}), \quad (4.16)$$

$$K(\gamma)=(2\pi)^{-2}(k+k')^2\int d\rho\exp\{-i(k+k')\gamma\rho\}\langle\exp\{i(k+k')[h(0)-h(\rho)]\}\rangle\approx(2\pi)^{-2}\int d\mu\exp(-i\gamma\mu)\left\langle\exp\left(i\mu\frac{dh}{d\rho}\right)\right\rangle. \quad (4.17)$$

The transition to the final expression in Eq. (4.17) corresponds to the determination of the short-wave ($hk \gg 1$) asymptotic form of $K(\gamma)$.

The function $K(\gamma)$ has the meaning of a distribution function of the gradients of $h(\rho)$ and drops off rapidly for values of γ larger than the characteristic values of $\nabla_\rho h(\rho)$, which are small compared to unity and to k/κ. For this reason we can expand all the smoothly varying functions under the integral in Eq. (3.9) in powers of $\kappa-\kappa'$ to arrive at the following expression:

$$\varphi(0; k, \varkappa)-\varphi(0; -k, \varkappa)\approx$$
$$\approx 2\Gamma\left\{1+2k\frac{\partial}{\partial k}-\frac{1}{2}\varkappa^2\left(\frac{1}{k}\frac{\partial}{\partial k}+\frac{\partial^2}{\partial k^2}\right)\right\}\varphi(0; k, \varkappa), \quad (4.18)$$

$$\Gamma=\langle(\nabla_\rho h(\rho))^2\rangle\equiv\int d\gamma\gamma^2K(\gamma).$$

The derivative of the function $\varphi(0; k, \kappa) = \kappa D(k, \epsilon_p)$ with respect to k is taken at constant energy ϵ_p. If the skin effect is nearly normal, then $D(k, \epsilon_p)$ depends weakly on k and only the first term on the right side of Eq. (4.18) is significant, which corresponds to the Fuchs boundary condition with the diffusivity coefficient $P = 2\Gamma$. The value of this coefficient is small, while the integral scattering probability, calculated from Eqs. (4.2) and (4.15), is $w_p = 1 - \langle \exp 2ikh(\rho) \rangle^2$, and is close to unity at $kh \gg 1$.

In the region of the anomalous skin effect Eq. (4.18) is valid as long as the ratio of the depth of the skin layer to the length of the mean free path is large compared to the gradients of $h(\rho)$. Then the most important terms on the right side of Eq. (4.18) are those proportional to κ^2, and the boundary condition for the distribution function does not have the form of the Fuchs condition, but contains derivatives with respect to k.

An analysis of the scattering by roughnesses shows that the scattering is strong (diffusivity coefficient of order unity) when the amplitudes of the functions $h(\rho)$ and their gradients are sufficiently large. A detailed solution of the problem under these conditions encounters essential difficulties similar to those that occur in the theory of wave scattering.

We note that the boundary conditions (3.9) that we have obtained serve to open certain paths for a subsequent phenomenological approach.

Another type of surface scattering of conduction electrons is due to point defects of the crystal surface. If we neglect interference effects in the scattering from different defects, it is sufficient to find the scattering operator from a single defect. By multiplying the transition probability for scattering at a single center times the surface concentration of defects, we obtain the desired transition probability. In the case when the effective radius of the defect potential is large compared to the decay range of the wave function near the surface, in solving the problem of scattering for characteristic momenta much smaller than $\sqrt{2mU}$ we can use the stationary wave functions for a rectangular potential barrier of infinite height. Then the matrix element $T^+_{pp'}$ is proportional to the difference $F(\kappa, k; \kappa', k') - F(\kappa, -k; \kappa', k')$, where $F(p, p')$ is the amplitude of bulk scattering by the potential of the given defect. A similar result was obtained in[5], where the scattering by defects of different types was analyzed.

We have considered another limiting case, when the scattering is from defects whose effective radius is small compared to the electron wavelength. In this case, generally speaking, the behavior of the wave function near the surface plays an essential role. We must keep in mind, however, that in a real situation the small-radius defects are not localized exactly on the surface, but are distributed with probability density w(z) within some surface layer. If the layer thickness d is large compared to the effective radius of the surface potential, the deviation of the barrier from a rectangular shape can be neglected, and by assuming the exponential form $w(z) = d^{-1}\exp(z/d)$ we can find the diffusivity coefficient:

$$P = 32\pi n f_0 d \frac{f_0 p_0}{1 + (f_0 p_0)^2} \frac{kd}{1 + (2kd)^3}, \qquad (4.19)$$

where n is the surface concentration of defects, f_0 is the length for scattering length from the defect potential, and $p_0 = \sqrt{\kappa^2 + k^2}$. To obtain the result (4.19) we made use of the theory of low-energy scattering and computed the matrix element $T^+_{pp'}$ in a manner similar to that used in, for instance,[14]. The integral term in Eq. (4.3) vanishes, so that $T^+_{pp'}$ does not depend on the direction of κ'.

According to Eq. (4.19), at $p_0 d \gg 1$ the diffusivity coefficient is a nonmonotonic function of the electron grazing angle. At $kd \gg 1$, the increase of P is inversely proportional to the sine of the grazing angle as the direction of incidence deviates from the normal to the surface; this may be explained by the increased distance traveled by the electron in passing through the layer of scattering defects. At $kd \ll 1$ this behavior is superseded by a quantum effect related to the smallness of the absolute square of the electron wave function in the region occupied by defects, and P becomes proportional to the sine of the grazing angle. Note that the indicated asymptotic behavior of P is practically independent of the form of the defect distribution function w(z).

5. CURRENT DENSITY IN THE CASE OF WEAK SURFACE SCATTERING

In Sec. 3 we showed that the use of a boundary condition to take account of surface scattering effects is related to the neglect of quantum effects due to the decay of the electron wave functions near the surface. The role played by these effects can be analyzed simply in the case of weak surface scattering, when the collision integral can be treated as a small correction in the kinetic equation, and the scattering can be considered in the Born approximation. We must then begin from the complete expression for I (see Eqs. (2.12)–(2.14)). We give here the result of the calculation of the Fourier amplitude of the current density $j_{q\omega}$ (here q is the z-component of the wave vector) for scattering under the conditions of the anomalous skin effect, when bulk scattering also plays a part that is small and can be described by a relaxation time τ.

The quantity $j^x_{q\omega}$ consists of three terms:

$$j_{q\omega}{}^x = \sigma(q, \omega) E_{q\omega}{}^x + j_{q\omega}{}^{qu} + j_{q\omega}{}^h, \qquad (5.1)$$

where $\sigma(q, \omega)$ is the transverse bulk conductivity; $j^{qu}_{q\omega}$ is a quantum correction due to the influence of the ideal surface, which was studied in detail by van Gelder[10]; and $j^h_{q\omega}$ is the contribution from scattering by roughnesses. Assuming that the surface barrier has a rectangular shape and infinite height, we have

$$j_{q\omega}{}^h = \int_{-\infty}^{\infty} dq' \sigma^h(q, q', \omega) E_{q'\omega}, \qquad (5.2)$$

$$\sigma^h(q, q', \omega) = \frac{2e^2\hbar^6}{(2\pi)^4 m^4 \omega} \int d\varkappa \int d\varkappa' \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dk' \cdot$$

$$\cdot \xi(\varkappa - \varkappa')(f_p - f_{p'}) M^*_{pp'}(q) M_{pp'}(q') \delta(\varepsilon_p - \varepsilon_{p'} + \hbar\omega), \qquad (5.3)$$

$$M_{pp'}(q) = \varkappa k'(k+q)(\varepsilon_{\varkappa' k+q} - \varepsilon_{\varkappa k} - \hbar\omega - i\hbar/\tau)^{-1} + \varkappa' k(k'+q)(\varepsilon_{\varkappa' k'+q} - \varepsilon_{\varkappa' k'} + \hbar\omega + i\hbar/\tau)^{-1}, \qquad (5.4)$$

where the function $\xi(\kappa)$ is as specified by Eq. (4.8). To obtain Eq. (5.3), we substituted in the total collision integral (2.12) the value of $g_{pp'}$ obtained without taking account of surface scattering, then replaced $R(\epsilon)$ everywhere with $R_0(\epsilon)$ and, after passing to the limit $s \to 0$, kept only the most significant delta-function parts of the resolvents.

The quasiclassical limit of Eq. (5.3) is obtained if we neglect q by comparison with k, and $\hbar\omega$ by comparison with ϵ_p; then, in particular, the difference $f_p - f_{p'}$, is replaced by $-\hbar\omega\partial f_p/\partial\epsilon_p$. It is easily apparent that in this limit $\sigma^h(q, q', \omega)$ coincides with the corresponding Fal'kovskiĭ expression[9]. An estimate of the quantum corrections shows that they are of the same order of magnitude as the contribution of $j_{q\omega}^{qu}$ in Eq. (5.1) relative to the bulk part. Thus, for the case of weak surface scattering a quantum mechanical calculation, which does not use the boundary condition, leads to a result that includes the van Gelder corrections.

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[1)]More commonly, a specularity coefficient equal to 1−P is introduced. The use of the quantity P in our analysis leads to some reduction in the length of the formulas.

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