Electron Tunneling with Diffuse Boundary Conditions

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The tunneling of electrons through potential barriers with plane boundaries involves the conservation of tangential quasimomentum (specular transmission). The boundaries between metals and insulators (e.g., oxides) in thin-film tunneling structures can be very irregular or rough, so that the specular transmission condition must be replaced by a "diffuse" transmission condition which allows nonconservation of tangential momentum. The tunnel current for diffuse boundary conditions and for arbitrary band structures and potential-barrier shapes has been calculated. Compared to the result for specular boundary conditions, the integrand in the expression for the tunnel current contains a factor $U(E,\mathbf{p}_t)=\sum\rho(\mathbf{p}_t')\pi(\mathbf{p}_t',\mathbf{p}_t)/\rho(\mathbf{p}_t)$ for each metal [$\rho(\mathbf{p}_t)$ = linear density of states for fixed tangential momentum $\mathbf{p}_t$, $\pi(\mathbf{p}_t',\mathbf{p}_t)$ is proportional to the probability that the diffuse boundaries change $\mathbf{p}_t'$ to $\mathbf{p}_t$, and the sum is over the "shadow" of the energy surface $E(\mathbf{p})$]. Under reasonable assumptions for $\pi(\mathbf{p}_t',\mathbf{p}_t)$, no appreciable effect of the densities of state on U or on the tunnel current should occur. The effects of diffuse transmission conditions on field emission from many-valley semiconductors and on tunneling between superconductors are briefly discussed.

1. INTRODUCTION

ALL the existing treatments of electron tunneling through thin insulating films or surface potential barriers (field emission) involve conservation of the electron quasimomentum component ($\mathbf{p}_t$) parallel (or tangential) to the boundary. This results from the assumption of a one-dimensional barrier region and is referred to as specular transmission by analogy with the similar case of reflection. However, as pointed out by Harrison,[1] many sheet resistance measurements for thin metal films indicate predominantly diffuse reflection at metallic surfaces.[2] Thus it seems likely that corresponding diffuse boundary conditions will apply for the tunneling of electrons through thin oxide films between metals. Clearly, the type of boundary condition applicable will depend on the irregular deviation of the boundaries from a plane (roughness) and thus must depend on the process of fabrication. Indeed, careful annealing of thin gold films can lead to the absence of a thickness effect on resistivity,[3] thus indicating specular reflection (assuming a mainly isotropic Fermi surface). Also, the observed size dependences for resistivity and galvanomagnetic effects in thin electropolished single crystals of bismuth[4] are consistent with the theory involving the highly anisotropic Fermi surface and assuming specular reflection.[5]

To estimate the effect of nonspecular boundary conditions, wave functions have been constructed for the electrons on either side of the barrier, which imply that an electron incident on the barrier with a given value of $\mathbf{p}_t$ is incoherently scattered into all the possible states of the same energy inside the barrier region without conservation of $\mathbf{p}_t$.

The case of partial specular and diffuse transmission has also been considered with different proportions of each for the two boundaries. Field emission from fine points might be a case where the boundary at the surface of the emitter is nonspecular while the other boundary (in vacuum) is specular. Although here again it will depend on how smooth the emitter is.

The effects of diffuse boundary conditions on field emission from many-valley semiconductors and tunneling between superconductors separated by a thin oxide film are discussed in the final section.

2. CALCULATION

Since there appears to be "no unique way of introducing a diffuse transmission [boundary] condition" (cf. Ref. 1), the following simple artifice has been adopted. Assume that the barrier region extends from x_a to x_b with metals to the left of x_a and right of x_b. Following Bardeen's[6] method, applied to a one-electron model, let the wave function $\psi_a(E_a,\mathbf{p}_{at})$ represent an electron of energy E_a in metal a when a specular transmission condition applies. It corresponds to a reflected plane wave in the region $x<x_a$ and an exponentially decaying wave in the region $x>x_a$. It will now be *assumed* that if the transmission is not specular (i.e., the boundary is not plane) an electron of energy E in metal a can be represented by the wave function

$$\Phi_a(E,\mathbf{p}_{at}')=\sum_{\mathbf{p}_{at}} A_0(\mathbf{p}_{at}',\mathbf{p}_{at})\psi_a(E_a,\mathbf{p}_{at})\,,\quad x<x_a \qquad \text{(1a)}$$

$$=\sum_{\mathbf{p}_{at}} A_i(\mathbf{p}_{at}',\mathbf{p}_{at})\psi_a(E_a,\mathbf{p}_{at})\,,\quad x>x_a\,, \qquad \text{(1b)}$$

where the sum over $\mathbf{p}_{at}$ extends over the projection of the energy surface $E_a(\mathbf{p})$, in metal a, on a plane parallel to the boundary region. (This projection has been referred to as the "shadow" region in Ref. 1.) For a specular boundary, $\Phi_a(E,\mathbf{p}_{at})$ would still be a solution of Schrödinger's equation, in the region $x<x_b$, if each coefficient $A_i(\mathbf{p}_{at}',\mathbf{p}_{at})$ were equal to the corresponding

[1] W. A. Harrison, Phys. Rev. **123**, 85 (1961).
[2] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, 1954), p. 248.
[3] M. S. P. Lucas, Appl. Phys. Letters **4**, 73 (1964).
[4] A. N. Friedman and S. H. Koenig, IBM J. Res. Develop. **4**, 158 (1960).
[5] F. S. Ham and D. Mattis, IBM J. Res. Develop. **4**, 143 (1960). P. J. Price, *ibid.* **4**, 152 (1960).

coefficient $A_0(\mathbf{p}_{at}',\mathbf{p}_{at})$. It will be assumed that for a nonspecular boundary $A_i(\mathbf{p}_{at}',\mathbf{p}_{at})$ and $A_0(\mathbf{p}_{at}',\mathbf{p}_{at})$ are not necessarily equal. The values of the A_0 and A_i coefficients will depend on the nature of the boundary layer. Specific assumptions are introduced later in the section.

In a similar fashion the wave function $\Phi_b(E_b,\mathbf{p}_{bt}')$ for an electron of energy E_b in metal b can be written

$$\Phi_b(E_b,\mathbf{p}_{bt}')=\sum_{\mathbf{p}_{bt}} B_0(\mathbf{p}_{bt}',\mathbf{p}_{bt})\psi_b(E_b,\mathbf{p}_{bt}), \quad x>x_b \tag{2a}$$

$$=\sum_{\mathbf{p}_{bt}} B_i(\mathbf{p}_{bt}',\mathbf{p}_{bt})\psi_b(E_b,\mathbf{p}_{bt}), \quad x<x_b, \tag{2b}$$

where the sum over $\mathbf{p}_{bt}$ extends over the shadow of the energy surface in metal b. Following Bardeen[6] we then consider the tunneling of an electron from metal a to metal b as a transition between the states Φ_a and Φ_b. The probability per unit time of the transition is given by

$$\tau_{ab}=(2\pi/\hbar)|\mathfrak{M}_{ab}|^2\rho_b f_a(1-f_b), \tag{3}$$

where ρ_b is the density of states in metal b for fixed tangential momentum $\mathbf{p}_{bt}'$, f_a and f_b are the occupation probabilities of the states and the matrix element is given by[7]

$$\mathfrak{M}_{ab}=\int \Phi_b^*(H-E_a)\Phi_a d\tau. \tag{4}$$

Thus the transmitted current density j is given by

$$j=(2q/\Delta)\sum_{\mathbf{p}_{at}',\mathbf{p}_{bt}'}\int \tau_{ab}\rho_a dE \tag{5}$$

$$=(4\pi q/\Delta\hbar)\sum_{\mathbf{p}_{at}',\mathbf{p}_{bt}'}\int |\mathfrak{M}_{ab}|^2\rho_a\rho_b(f_a-f_b)dE, \tag{6}$$

where Δ is the area of the barrier region. For specular transmission of both boundaries this reduces to the expression[1]

$$j_S=(4\pi q/\Delta\hbar)\sum_{\mathbf{p}_t}\int |M_{ab}|^2\rho_a\rho_b(f_a-f_b)dE \tag{7a}$$

$$=(8\pi^2 q/h^3)\int (f_a-f_b)dE\left[\int |M_{ab}|^2\rho_a\rho_b d^2p_t\right], \tag{7b}$$

where the matrix element M_{ab} is only nonvanishing if $\mathbf{p}_{a\perp}=\mathbf{p}_{b\perp}=\mathbf{p}_\perp$, say. For completely diffuse boundaries, $\mathfrak{M}_{ab}$ will be independent of the initial and final value of the tangential momentum so that

$$j_D=(4\pi q/\Delta\hbar)\int |\mathfrak{M}_{ab}|^2\hat{\rho}_a\hat{\rho}_b(f_a-f_b)dE, \tag{8}$$

where

$$\hat{\rho}_a=\sum_{\mathbf{p}_t}\rho_a=(\Delta/h^2)\int \rho_a d^2p_t \tag{9}$$

is the usual three-dimensional density of states. [NB since $\hat{\rho}_a\hat{\rho}_b$ is proportional to Δ^2, $|\mathfrak{M}_{ab}|^2$ must be proportional to Δ^{-1}, cf. Eq. (17b) below.]

Turning now to the evaluation of the matrix element $\mathfrak{M}_{ab}$ by substituting into Eq. (4) from Eqs. (1) and (2), we have

$$\mathfrak{M}_{ab}=\sum_{\mathbf{p}_b} A_i^*(\mathbf{p}_{at}',\mathbf{p}_t)B_0(\mathbf{p}_{bt}',\mathbf{p}_{bt})M_{ab}(\mathbf{p}_t), \tag{10}$$

where the "specular" matrix element is given by

$$M_{ab}(\mathbf{p}_{at})\delta_{\mathbf{p}at,\mathbf{p}bt}=\int \psi_b^*(E_b,\mathbf{p}_{bt})(H-E_a)\psi_a(E_a,\mathbf{p}_{ab})d\tau \tag{11}$$

so that the sum over $\mathbf{p}_\perp$ is over the overlap region of the two shadows. [Here we have used the fact that the integrands in Eqs. (4) and (11) are nonvanishing only when $x>x_b$.]

Before evaluating $\mathfrak{M}_{ab}$ for nonspecular boundaries, we will test the form of the wave functions by considering that the Φ functions are produced from the ψ functions by a *unitary* transformation. Thus, if $A_i\equiv A_0$ and $B_i\equiv B_0$, the current density derived from Eq. (6) should equal that derived from Eq. (7) for specular boundaries or the equation

$$\sum_{\mathbf{p}_{at}',\mathbf{p}_{bt}'}|\mathfrak{M}_{ab}|^2\rho_a(\mathbf{p}_{at}')\rho_b(\mathbf{p}_{bt}')=\sum_{\mathbf{p}_t}|M_{ab}|^2\rho_a(\mathbf{p}_t)\rho_b(\mathbf{p}_t) \tag{12}$$

must hold. That this is the case can easily be verified using Eq. (10) and the relation

$$\sum_{\mathbf{p}_{at}'}\rho(\mathbf{p}_{at}')A^*(\mathbf{p}_{at}',\mathbf{p}_{at})A(\mathbf{p}_{at}',\mathbf{p}_{at}'')=\rho(\mathbf{p}_{at})\delta_{\mathbf{p}at,\mathbf{p}at''}, \tag{13}$$

which can be shown to lead to the closure property for the complete set of $\Phi_a(E_a,\mathbf{p}_{at}')$ functions.

For the case of nonspecular boundaries

$$|\mathfrak{M}_{ab}|^2=\sum_{\mathbf{p}_t}|A_i|^2|B_0|^2|M_{ab}|^2, \tag{14}$$

where we have neglected cross terms by *assuming* an arbitrary phase dependence of the A_i and B_0 coefficients. (This is physically equivalent to the assumption of incoherent scattering at the boundary regions.) Inserting

[6] J. Bardeen, Phys. Rev. Letters **6**, 57 (1961).

[7] This differs slightly from the corresponding expression given in Ref. 6. Carrying out the perturbation calculation indicated in Ref. 6, we find that Bardeen's matrix element M_{mn} should equal $\int\psi_{mn}^*(H-W_0)\psi_0 d\tau$, where the integrand is nonzero only for $x>x_b$. However, if $W_{mn}=W_0$, out expression for M_{mn} is equal to the complex conjugate of the expression given in Ref. 6, thus leaving the tunneling probability unaltered.

this value for $\mathfrak{M}_{ab}$ into Eq. (6) then gives

$$j=\frac{8\pi^2 q}{\Delta h}\int (f_a-f_b)dE\sum_{\mathbf{p}_t}|M_{ab}|^2 \times\sum_{\mathbf{p}_{at}'}|A_i|^2\rho_a\sum_{\mathbf{p}_{bt}'}|B_0|^2\rho_b. \quad (15)$$

Harrison[1] has derived the value of M_{ab} for gradual transition regions. Using the WKB approximation, he finds

$$|M_{ab}|^2=(4\pi^2\rho_a\rho_b)^{-1}e^{-\eta}, \quad (16)$$

where

$$\eta=(2/\hbar)\int_a^{x_b}|p_x|dx. \quad (17)$$

Thus j_s is completely independent of the densities of state while, more generally, using Eq. (6)

$$j=\frac{2q}{h\Delta}\int (f_a-f_b)dE\sum_{\mathbf{p}_t}\frac{e^{-\eta}}{\rho_a\rho_b}\sum_{\mathbf{p}_{at}'}|A_i|^2\rho_a\sum_{\mathbf{p}_{bt}'}|B_0|^2\rho_b \quad (18)$$

with

$$\sum_{\mathbf{p}_t}|A_i|^2=\sum_{\mathbf{p}_t}|B_0|^2=1 \quad (19)$$

from the normalization conditions. Let

$$U_a(E,\mathbf{p}_t)\equiv\frac{\sum_{\mathbf{p}_{at}'}|A_i(\mathbf{p}_{at}',\mathbf{p}_t)|^2\rho_a(\mathbf{p}_{at}')}{\rho_a(\mathbf{p}_t)}. \quad (20)$$

Then Eq. (18) can be written more compactly as

$$j=(2q/h^3)\int (f_a-f_b)dE\int e^{-\eta}U_aU_bd^2p_t \quad (21)$$

and, using Eq. (19),

$$\sum_{\mathbf{p}_t}U_a(E,\mathbf{p}_t)\rho_a(\mathbf{p}_t)=\sum_{\mathbf{p}_{at}'}\rho_a(\mathbf{p}_{at}')=\hat{\rho}_a. \quad (22)$$

We now consider the values of the coefficients A_i and B_0. For the specular case

$$|A_i|^2=(h^2/\Delta)\delta_{\mathbf{p}at',\mathbf{p}t},\qquad |B_0|^2=(h^2/\Delta)\delta_{\mathbf{p}bt',\mathbf{p}t}, \quad (23)$$

so that $U_a=U_b=1$, and the usual result [cf. Eqs. (7b) and (16)] is recovered.

From Eq. (1), $|A_i(\mathbf{p}_{at}',\mathbf{p}_t|^2$ can be interpreted as the probability that the vector $\mathbf{p}_t$ is in the element of area $d\mathbf{p}_t$. In the Appendix it is shown that if *reflection* from a perfectly diffuse surface leads to a reflected vector $\mathbf{p}$ which is uniformly distributed over the energy surface $E(\mathbf{p})$,then the probability that $\mathbf{p}_t$ is in the element of area $d\mathbf{p}_t$ is proportional to $\rho(\mathbf{p}_t)d\mathbf{p}_t$. If we now *assume* a similar result for completely diffuse transmission, then

$$|A_i|^2=\rho_a(\mathbf{p}_t)/\hat{\rho}_a,\qquad |B_0|^2=\rho_b(\mathbf{p}_t)/\hat{\rho}_b, \quad (24)$$

and $U_a=U_b=1$ again. The result is reasonable since the incident electrons already have their $\mathbf{p}$ values uniformly distributed over the energy surface $E(\mathbf{p})$. Thus, under the present assumption, diffuse scattering prior to tunneling does not alter the distribution of $\mathbf{p}_t$ values. It is however, not clear that other assumptions concerning the distribution of $\mathbf{p}_t$ values are not possible.

It will now be assumed as a simple example that the probability for the vector $\mathbf{p}_t$ to be in the element of area $d\mathbf{p}_t$ is proportional to $d\mathbf{p}_t$. Then

$$|A_i|^2=h^2/\Delta S_a(E),\qquad |B_0|^2=h^2/\Delta S_b(E), \quad (25)$$

where $S(E)$ is the area of the shadow of the energy surface E, and

$$U=(h^2/\Delta)(\hat{\rho}/\rho S). \quad (26)$$

For spherical energy surfaces it can be shown that

$$U=2[1-(p_t^2/p^2)]^{1/2}, \quad (27)$$

so that

$$j_D=4\left(\frac{2q}{h^3}\right)\int (f_a-f_b)\times\left[\int e^{-\eta}\left(1-\frac{p_t^2}{p_a^2}\right)^{1/2}\left(1-\frac{p_t^2}{p_b^2}\right)^{1/2}d^2p_t\right]dE. \quad (28)$$

This is equal to four times the value of j_S if the two factors involving square roots are replaced by one. The latter is a reasonable approximation for sufficiently large shadows, i.e., when

$$(d\eta/dp_t)_0 p\gg 1,$$

since the tunneling factor $e^{-\eta}$ usually decreases rapidly as p_t increases from zero.

More generally, the factor

$$U=\int \rho d^2p_t/\rho S \quad (29a)$$

$$=\frac{\partial E/\partial p_x}{S}\int\frac{dp_ydp_z}{(\partial E/\partial p_x)} \quad (29b)$$

can differ appreciably from the value 2 and be anisotropic for energy surfaces in the conductors that are appreciably nonspherical. {E.g., for a cylindrical energy surface whose height is K times its base diameter, $U=2+K$ if p_x is the cylinder axis and $U=(3\pi/2K)\times[1-\{p_y^2/(p_y^2+p_x^2)\}]^{1/2}$ if p_z is the cylinder axis.} This is apart from any anisotropy that could arise in the tunneling probability $e^{-\eta}$, due to nonisotropic energy surfaces in the barrier region, which would also affect j_S. Of course, in practice, an anisotropic tunnel current can only arise if at least one of the outer metals or the insulating layer are single-crystalline. For mixed specular and diffuse transmission

$$|A_i|^2=(h^2/\Delta)[(1-P_a)S_a^{-1}+P_a\delta_{\mathbf{p}at',\mathbf{p}at}], \quad (30)$$
$$|B_0|^2=(h^2/\Delta)[(1-P_b)S_b^{-1}+P_b\delta_{\mathbf{p}bt',\mathbf{p}bt}],$$

where $P_{a,b}$ (the "polish") measures the relative amount of specular transmission on either boundary. (The quantity P is similar to the parameter introduced to measure the amount of specular reflection in the theory of thin-film sheet resistance.[8]) Then it can be shown that

$$\begin{aligned} j=&(1-P_a)(1-P_b)j_D+P_aP_bj_S \\ &+P_b(1-P_a)\frac{2q}{h^3}\int(f_a-f_b)\left[\int e^{-\eta}\left(\frac{h^2}{\Delta}\frac{\hat{\rho}_a}{\rho_aS_a}\right)d^2p_t\right]dE \\ &+P_a(1-P_b)\frac{2q}{h^3}\int(f_a-f_b)\left[\int e^{-\eta}\left(\frac{h^2}{\Delta}\frac{\hat{\rho}_b}{\rho_bS_b}\right)d^2p_t\right]dE, \end{aligned} \quad (31)$$

where j_D is given by Eq. (28). For spherical energy surfaces and with the various factors $(1-p_t^2/p^2)^{1/2}$ taken as unity,

$$j\approx(2-P_a)(2-P_b)j_S. \quad (32)$$

The case of field emission from a point (surface a) through a potential barrier in vacuum (surface b) can be treated by setting $P_b=1$ and $f_b=0$.

From the structure of Eqs. (20) and (21) it seems unlikely that any surface conditions would lead to a strong dependence of the tunnel current j on the density of states ρ.

3. DISCUSSION

The basic assumption underlying our technique for treating tunneling through a barrier with diffuse boundaries is that the tangential momentum of an electron passing through the boundary is not conserved [cf. Eqs. (1) and (2)]. Rather, an electron with any tangential momentum $\mathbf{p}_{at}$ outside boundary a can be transmitted into a state of the same energy with any other tangential momentum $\mathbf{p}_{at}'$ inside the barrier provided $\mathbf{p}_{at}'$ is inside the shadow of the energy surface E_a. The latter condition can be shown to be plausible by considering the corresponding case of diffuse internal reflection from the surface of a conductor. Ham and Mattis[5] have argued that $\mathbf{p}_t$ must be conserved during specular reflection in agreement with the result for specular transmission. Now if diffuse reflection from a surface is caused by its roughness, we can consider the reflection of an electron from a portion of surface inclined to the (y,z) plane which gives the mean position of the surface. Then the component of $\mathbf{p}$ in the inclined surface will be conserved, thus leading to a change in $\mathbf{p}_t$. the component in the (y,z) plane. However, the final value of $\mathbf{p}_t$ must still be inside the shadow region since the final value of $\mathbf{p}$ is still on the constant energy surface E. It seems reasonable that if all the reflected electrons have $\mathbf{p}_t$ values which lie inside the shadow region, the same will be true for the transmitted electrons.

On the basis of experimental observations of field emission from various low-index crystal planes forming an n-type Si tip, Busch and Fischer[9] have argued that the tangential component of electron momentum is not conserved. This is because if $\mathbf{p}_t$ were conserved, very little emission would be observed for a {111} plane as compared with a {100} plane, due to the large initial value of $\mathbf{p}_t$ in the former case leading to a relatively very low tunnel probability. However, experimentally the two emission currents are comparable in magnitude. The authors suggest three reasons for a possible nonconservation of $\mathbf{p}_t$: (1) diffuse boundaries, (2) change in crystal periodicity parallel to the surface, (3) phonon absorption or emission. If our description for diffuse transmission is accepted item (1) cannot be the explanation since $\mathbf{p}_t$ must remain inside the shadow region which consists of six elipses in the {111} plane, far removed from the origin. Also item (2), together with the assumption of specular transmission, would probably not lead to nonconservation of $\mathbf{p}_t$ since changes in the band structure, along the direction normal to the boundaries of the barrier, are in fact assumed by Harrison[1] in his calculation for specular tunneling. Possibly the combination of items (1) and (2) could lead to the required change in $\mathbf{p}_t$ if the correct electron energy surfaces for Si, near the {111} surface planes, actually had shadows with portions close to the origin of momentum space. [Incidentally, it is also difficult to accept item (3) since the ratio of the probability of indirect (phonon assisted) tunneling to the probability of direct tunneling (for the same effective barrier height) is usually a small number, e.g., about 10^{-3} for the similar case of $p-n$ junction tunneling in Ge.[10]]

The calculations have shown that the expression for the tunnel current [cf. Eq. (21)] for nonspecular transmission differs from that for specular transmission by a pair of additional factors $U_a(E,\mathbf{p}_t)$ $U_b(E,\mathbf{p}_t)$ [cf. Eqs. (20) and (21)] where, for example,

$$U_a=\sum_{\mathbf{p}_t'}\rho(\mathbf{p}_t')\pi(\mathbf{p}_t',\mathbf{p}_t)/\rho(\mathbf{p}_t) \quad (33)$$

and $\pi(\mathbf{p}_t',\mathbf{p}_t)=|A_i(\mathbf{p}_t',\mathbf{p}_t)|^2$ is proportional to the probability that diffuse scattering changes the tangential momentum from $\mathbf{p}_t'$ to $\mathbf{p}_t$. Although we have not been able to derive $\pi(\mathbf{p}_t',\mathbf{p}_t)$ from first principles, the discussion in the previous section indicates that U_a and thus (j) are unlikely to depend strongly on the density of states.

Cohen, Falicov, and Phillips[11] have shown that if metals a and b are superconducting, Eq. (6) for the

[8] K. Fuchs, Proc. Cambridge Phil. Soc. 34, 100 (1938).

[9] G. Busch and T. Fischer, Physik Kondensierten Materie 1, 367 (1963).

[10] E. O. Kane, J. Appl. Phys. 32, 83 (1961).

[11] M. H. Cohen, L. M. Falicov, and J. C. Phillips, Phys. Rev. Letters 8, 316 (1962).

tunnel current holds provided the matrix element $\mathfrak{M}_{ab}$ is that appropriate to an electron transfer between *normal electron states* on either side of the barrier while the state densities in Eq. (6) refer to the *superconducting state*. Thus Eq. (21) for j will apply with U_a replaced by

$$U_a{}^S(E,\mathbf{p}_{at})=\sum_{\mathbf{p}_{at}'}|A_i{}^2(\mathbf{p}_{at}',\mathbf{p}_{at})|^2\rho_a{}^S(\mathbf{p}_{at}')/\rho_a{}^N(\mathbf{p}_{at}), \quad (34)$$

where the superscripts S and N refer to "normal" and "superconducting," respectively, and U_b is similarly replaced by $U_b{}^S$. Hence

$$\left(\frac{j^S}{j^N}\right)\approx\frac{1}{qV}\int(f_a-f_b)\left[\frac{U_a{}^SU_b{}^S}{U_a{}^NO_b{}^N}\right]_{\mathbf{p}_t=0}dE, \quad (35)$$

where we have assumed that $\int e^{-\eta}d\mathbf{p}_t$ is constant for the small voltage (V) and energy range involved and that $e^{-\eta}$ decreases very rapidly as p_t increases from zero. For specular boundary conditions, or when $|A_i|^2$ is given by Eq. (24), the factor in square brackets reduces to $[\rho_a{}^S\rho_b{}^S/\rho_a{}^N\rho_b{}^N]_{p_t}=0$ in essential agreement with the result of Giaver and Megerle.[12] If $|A_i|^2$ is independent of $\mathbf{p}_t$ [cf. Eq. (25)], then the factor in square brackets reduces to $[\hat{\rho}_a{}^S\hat{\rho}_b{}^S/\hat{\rho}_a{}^N\hat{\rho}_b{}^N]$, neglecting the very small change in the areas of the shadows. For spherical energy surfaces,the last two expressions are essentially the same [cf. Eq. (27)] since ρ is approximately proportional to $\hat{\rho}$, the factor $(1-p_t{}^2/p^2)^{1/2}$ being incorporated in the integral over $\mathbf{p}_t$. In fact, the experimental tunneling-current results in Ref. 12 have been analyzed on the basis of three-dimensional, rather than one-dimensional, densities of state because of the approximate proportionality of ρ and $\hat{\rho}$.

[12] I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961).

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APPENDIX. REFLECTION FROM A PERFECTLY DIFFUSE SURFACE

It will be assumed that after internal reflection of an electron from the diffuse surface of a metal, its quasi-momentum vector $\mathbf{p}$ is distributed randomly over the energy surface $E(\mathbf{p})$ (provided the normal component of velocity points into the metal). Then the probability that the vector $\mathbf{p}$ is in an element of area $d\sigma$ on the energy surface is proportional to the volume element

$$dv=d\sigma dE/|\nabla_{\mathbf{p}}E(\mathbf{p})|. \quad (A1)$$

Let $d\sigma_t$ be the projection of $d\sigma$ on the reflecting surface. Then

$$d\sigma_t/d\sigma=\nabla_{\mathbf{p}}E\cdot\mathbf{p}_x/(|\nabla_{\mathbf{p}}E|p_x) \quad (A2)$$

so that

$$dv=d\sigma_t dEp_x/\mathbf{p}_x\cdot\nabla_{\mathbf{p}}E. \quad (A3)$$

But, if L is the thickness of the metal layer,

$$\rho(\mathbf{p}_t)=\frac{2L/h}{\partial E/\partial p_x}=\frac{2L/h}{\mathbf{p}_x\cdot\nabla_{\mathbf{p}}E}p_x, \quad (A4)$$

thus

$$dv=(h/2L)dE\rho(\mathbf{p}_t)d\sigma_t \quad (A5)$$

from which it follows that the probability that $\mathbf{p}_t$ is in the surface element $d\sigma_t$ is proportional to $\rho(\mathbf{p}_t)d\sigma_t$.