Comment on "Field emission as a probe of the surface density of states"

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It is shown that the primary contribution to the field-emission current comes from electrons with *total* momentum equal to zero in a direction parallel to the metal surface and that the field-emission current measures the density of states at a point several angstroms from the metal surface. An explicit expression is derived for the error made in using the transfer-Hamiltonian technique to calculate the tunneling probability of an electron through a one-dimensional barrier, and it is pointed out that the error is small in the case of field emission.

In this comment we amplify and clarify some of the conclusions of "Field emission as a probe of the surface density of states" by Penn and Plummer (PP).[1] More explicitly, we make the following points. (a) PP concluded that electrons with reduced momentum nearly equal to zero in a direction parallel to the metal surface make the primary contribution to the field-emission current. We show here that it is actually electrons with total momentum nearly equal to zero in a direction parallel to the surface which are mainly responsible for the observed field-emission current. (b) PP stated that field emission measures the metal density of states at the classical turning point (roughly 2 Å outside the metal surface). We note that rather than measuring the density of states at the turning point the field-emission current measures the density of states at a location in the tunneling barrier where the total potential is essentially one dimensional (about 4 Å from the surface). (c) The work of PP was based on the transfer-Hamiltonian method. We derive an explicit expression for the error involved in using that method which is valid for arbitrary barrier, shapes, and we point out that the error is small in the case of the field-emission barrier.

(a) PP showed that field-emission measurements of the total energy distribution from a clean metal surface provide information about the density of states near the surface. The field-emitted current per unit energy at energy ω was shown to be given by Eq. (23) of PP:

$$j(\omega) \simeq (2\hbar/m)\, S f(\omega) \sum_m D_0^2 [E_m - (\hbar^2/2m)(k_{\parallel}^m)^2] \times N_m^2\, \delta(\omega - E_m)\ , \qquad (1)$$

where S is the surface area of the metal, $f(\omega)$ is the Fermi function, $\sum_m$ denotes a sum over metal eigenstates, D_0^2 is the usual barrier penetration probability with image potential corrections, E_m is the metal eigenvalue, $\vec{k}_{\parallel}^m$ is the electron momentum parallel to the metal surface, and N_m is a factor which matches the amplitude of the WKB wave function in the barrier to the metal wave function. The physical basis for Eq. (1) is that throughout the major portion of the barrier through which electrons tunnel the potential is very nearly a function of x only (the coordinate in the direction normal to the surface) and is nearly independent of y and z. Thus the major part of the tunneling process can be handled one dimensionally by the WKB method even though the wave function within and at the surface of the metal depends on y and z as well as x and is not at all free-electron-like; the WKB-type wave function that obtains in the barrier must be given the proper amplitude so as to match it to the three-dimensional wave function of the metal. This matching factor is N_m of Eq. (1). The factor N_m takes into account the non-free-electron characteristics of the metal as well as the symmetry properties so that N_m can, for example, vanish by reason of symmetry for a d-band electron traveling along a symmetry axis. Thus, Eq. (1) is entirely consistent with the work of Politzer and Cutler.[2]

Equation (1) can be rewritten in a way which makes physical interpretation more transparent. The metal wave function can be expanded as

$$\psi_m(\vec{r}) = \sum_{\vec{G}_{\parallel}} \alpha_{\vec{G}_{\parallel}}^{(m)}(x)\, e^{i(\vec{k}_{\parallel}^m - \vec{G}_{\parallel})\cdot\vec{\rho}}\ , \qquad (2)$$

where the set $\{\vec{G}_{\parallel}\}$ comprises the parallel components of $\{\vec{G}\}$, $\vec{\rho}$ is parallel to the surface and the reciprocal-lattice vectors that are chosen to represent the Bloch waves. The requirement that $\psi_m(\vec{r})$ satisfy the Schrödinger equation yields

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{\hbar^2}{2m}(\vec{k}_{\parallel}^m - \vec{G}_{\parallel})^2 - E + V_0(x)\right)\alpha_{\vec{G}_{\parallel}}^{(m)}(x) = -\sum_{\vec{G}'_{\parallel}\neq\vec{G}_{\parallel}} V_{\vec{G}_{\parallel}-\vec{G}'_{\parallel}}(x)\, \alpha_{\vec{G}'_{\parallel}}^{(m)}(x)\ , \qquad (3)$$

where $V_{\vec{G}_{\parallel}}(x)$ is the $\vec{G}_{\parallel}$th Fourier component of the potential $V(\vec{r})$. In the region of the barrier where the potential depends only on x, $V_{\vec{G}_{\parallel}}(x) = 0$ for $\vec{G}_{\parallel} \neq 0$.

In this region the right-hand side of Eq. (3) is zero and each component $\alpha^{(m)}_{\vec{G}_\parallel}$ of the wave function satisfies a one-dimensional Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V_0(x)\right)\alpha^{(m)}_{\vec{G}_\parallel}(x) = \left(E-\frac{\hbar^2}{2m}(\vec{k}^m_\parallel-\vec{G}_\parallel)^2\right)\alpha^{(m)}_{\vec{G}_\parallel}(x)\ . \tag{4}$$

At the point x_0 defined in PP to be an arbitrary point far into the barrier region, the potential is one-dimensional and the solutions of Eq. (4) for $\alpha^{(m)}_{\vec{G}_\parallel}(x_0)$ are decaying exponentials. The dominant term in Eq. (2) is consequently $\alpha^{(m)}_0(x_0)$, which is given by the WKB approximation

$$\psi_m(x_0)\simeq\alpha^{(m)}_0(x_0)\,e^{i\vec{k}^m_\parallel\cdot\vec{\rho}} = N_m\kappa_m^{-1/2}(x_0)\exp\left(-\int_{x_m}^{x_0}\kappa_m\,dx+i\vec{k}^m_\parallel\cdot\vec{\rho}\right), \tag{5a}$$

$$\kappa_m=(2m/\hbar^2)^{1/2}[V_m-E_m+(\hbar^2/2m)(k^m_\parallel)^2]^{1/2}\ , \tag{5b}$$

where N_m is the amplitude of the WKB wave function and x_m is the turning point as explained in PP. Let $\lambda_m(x)$ be that $\vec{G}_\parallel=0$ solution of Eq. (4) which becomes $\kappa_m^{-1/2}\exp(-\int_{x_m}^{x}\kappa_m\,dx)$ for large x. Then by the definition of $\lambda_m(x)$

$$\alpha^{(m)}_0(x)=N_m\lambda_m(x). \tag{6}$$

Evaluating (6) at $x=x_m$ gives

$$N_m=\alpha^{(m)}_0(x_m)/\lambda_m\ , \tag{7a}$$

where

$$\lambda_m=\lambda_m(x_m). \tag{7b}$$

Expression (7a) for N_m is similar to (30a) of PP but is more accurate. It reduces to (30a) of PP only if the $\vec{G}_\parallel\neq0$ components $\alpha^{(m)}_{\vec{G}_\parallel}(x)$ of $\Psi_m(\vec{r})$ are negligible at $x=x_m$. From Eq. (2) we note that (7a) can be written

$$N_m=\alpha^{(m)}_0(x)/\lambda_m = \int_{x=x_m}dS\,e^{-i\vec{k}^m_\parallel\cdot\vec{\rho}}\ \psi_m(\vec{r})/\lambda_m\ , \tag{8}$$

where the integral is taken over the surface $x=x_m$. Consequently Eq. (31) of PP is valid if $\Psi_m(x_m)$ in (31) is replaced by

$$\alpha^{(m)}_0(x)=\int_{x=x_m}dS\,e^{-i\vec{k}^m_\parallel\cdot\vec{\rho}}\,\psi_m(\vec{r}) \tag{9}$$

to give

$$j(\omega)\simeq(2\hbar/m)Sf(\omega)\,\lambda^{-2}(\omega)\times\sum_m D_0^2[E_m-(\hbar^2/2m)(\vec{k}^m_\parallel)^2]\times|\alpha^{(m)}_0(x_m)|^2\,\delta(\omega-E_m)\ . \tag{10}$$

The earlier comments pertaining to the validity of Eq. (1) apply to Eq. (10) as well. The interpretation of Eq. (10) is not quite as simple as that of Eq. (31) in PP which it replaces because of the area average of $\Psi_m(\vec{r})$ involved in $\alpha^{(m)}_0(x_m)$. From Eq. (2), $|\alpha^{(m)}_0(x_m)|^2$ is the probability that an electron at the distance x_m from the surface has a *total* momentum $\vec{k}^m_\parallel$ parallel to the surface. The tunneling probability D_0 is appreciable only if $k^m_\parallel\simeq0$; hence $j(\omega)$ measures the density of state at energy ω and position x_m of those electrons having zero *total* momentum parallel to the metal surface. This is in contrast to Eq. (31) of PP which implies that $j(\omega)$ measures the density of states of electrons having zero *crystal* momentum parallel to the surface.

(b) In deriving Eq. (10) it was assumed that the potential is a function of x only for $x>x_m$ where x_m is the turning point. This approximation is rather poor as discussed in PP. We now eliminate that approximation. Let x_c be a point sufficiently far from the metal that the potential is essentially one dimensional. From a calculation by Appelbaum and Hamann[3] it appears that $x_c\sim3$–4 Å. It is easily shown that for $x\geq x_c$ the WKB approximation is valid. Equation (5a) can be replaced by

$$\psi_m(x_0)\simeq\alpha^{(m)}_0(x_0)\,e^{i\vec{k}^m_\parallel\cdot\vec{\rho}}=N'_m\kappa_m^{-1/2}(x_0)\exp\left(-\int_{x_c}^{x_0}\kappa_m\,dx+i\vec{k}^m_\parallel\cdot\vec{\rho}\right)\ . \tag{11}$$

Note that the lower limit of the integral in (11) is x_c. Because the WKB approximation is valid at $x=x_c$ one has

$$N'_m=\alpha^{(m)}_0(x_c)\,\kappa_m^{1/2}(x_c). \tag{12}$$

Proceeding as in PP leads to

$$j(\omega)=(2\hbar/m)Sf(\omega)\kappa_m(x_c)\sum_m D_0^2[E_m-(\hbar^2/2m)(k^m_\parallel)^2]\ |\alpha^{(m)}_0(x_c)|^2\varphi_m^2\delta(\omega-E_m), \tag{13a}$$

where

$$\alpha_0^{(m)}(x_c) = \int_{x=x_c} ds\, e^{-i\vec{k}_{\parallel}^{m}\cdot\vec{\rho}}\,\psi(\vec{r}) \tag{13b}$$

and

$$\varphi_m^2 = \exp\left[2\int_{x_m}^{x_c} dx\left(\frac{2m}{\hbar^2}\right)^{1/2}\{V_m - eFx - [E_m - (\hbar^2/2m)(k_{\parallel}^{m})^2]\}^{1/2}\right] . \tag{13c}$$

In (13c) x_m is the turning point defined by

$$V_m(x_m) - eFx_m = E_m - (\hbar^2/2m)(k_{\parallel}^{m})^2 \tag{14}$$

and $V_m(x)$ is the image potential. The factor φ_m appears in (13a) because $\alpha_0^{(m)}$ is evaluated at x_c rather than at x_m as in the less accurate Eq. (10). The interpretation of (13a) is essentially the same as that of Eq. (10) except that the current measures the density of states at x_c rather than x_m and the density of states is weighted by the factor φ_m.

Again following PP and using Eq. (13) we conclude that $R = j(\omega)/j_0(\omega)$ measures the density of metal states with total momentum normal to the metal surface at a distance x_c from the surface where $j_0(\omega)$ is the usual free-electron expression for the field-emission current.

(c) We now derive an expression that relates the exact one-dimensional tunneling current for a barrier of arbitrary shape to the tunneling current as determined by the Bardeen version of the transfer-Hamiltonian theory. This provides a direct justification for the use of the transfer-Hamiltonian method in the case of the field-emission barrier and should be useful for estimating the error made by the transfer-Hamiltonian method for other types of barriers as well.

For the sake of simplicity we will consider tunneling through a rectangular barrier; however, our considerations are equally valid for any barrier. Figure 1(a) shows the barrier. Let Ψ_l be an eigenfunction of the Hamiltonian that is outgoing away from the barrier at $x = -\infty$ and Ψ_r is an eigenfunction that is outgoing at $x = +\infty$. The probability that an electron tunnels from the left side of the barrier to the right side is calculated by assuming that the eigenfunction on the left consists of an incoming part Ψ_l^* and an outgoing reflected part $R\Psi_l$, while the eigenfunction on the right consists only of a transmitted part $T\Psi_r$. Let x_0 be an arbitrary point in the barrier region. Then $\Psi_l(x_0)$ is the wave function which is outgoing at $x = +\infty$. The boundary conditions at x_0 are then

$$\psi_l^* + R\,\psi_l = T\psi_r , \tag{15a}$$

$$\psi_l'^* + R\,\psi_l' = T\,\psi_r' , \tag{15b}$$

where it is understood that all wave functions are evaluated at $x = x_0$. The barrier penetration probability D is given by the ratio of the transmitted to incident currents

$$D = \langle T\psi_r | j_{op} | T\psi_r\rangle / \langle \psi_l^* | j_{op} | \psi_l^*\rangle , \tag{16a}$$

where

$$j_{op} = \frac{i\hbar}{2m}\left(\frac{\overleftarrow{\partial}}{\partial x} - \frac{\overrightarrow{\partial}}{\partial x}\right)_{x_0} . \tag{16b}$$

D is independent of the value of x at which j_{op} is evaluated. We have chosen the point $x = x_0$. Solving Eq. (15) for T and using the result in Eq. (16) yields

$$D = 4\,\mathrm{Im}\,\alpha_l\,\mathrm{Im}\,\alpha_r / |\alpha_l - \alpha_r|^2 , \tag{17a}$$

where

$$\alpha_l = \psi_l'(x_0)/\psi_l(x_0) \tag{17b}$$

and

$$\alpha_r = \psi_r'(x_0)/\psi_r(x_0) . \tag{17c}$$

The current is given by[4]

$$j = e\rho D , \tag{18}$$

where ρ is the density of states and $v = \partial\epsilon/\partial k$ is the group velocity of an electron approaching the

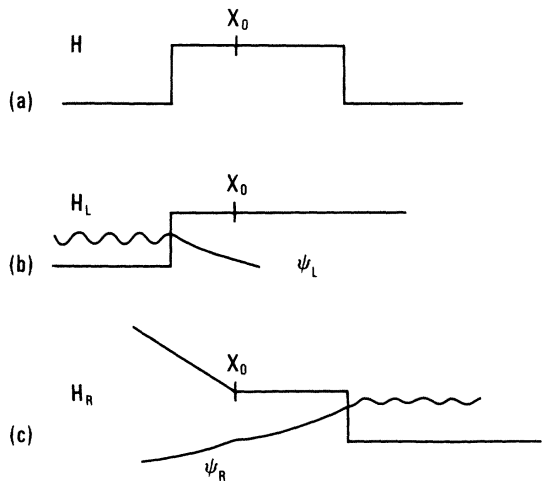

FIG. 1. (a) Square-well barrier potential through which the tunneling probability is to be calculated. x_0 is an arbitrary point in the barrier. (b) Left potential associated with H_L. ψ_L denotes an eigenfunction of H_L. (c) Right potential associated with H_R. ψ_R denotes an eigenfunction of H_R.

barrier. The density of states is proportional to $(\partial\epsilon/\partial k)^{-1}$ and consequently

$$j=(2e/\pi\hbar)D\ . \tag{19}$$

The expression for the current obtained by the use of Eq. (17) in Eq. (19) has been derived by Caroli *et al.*[5] in a less direct manner.

The tunneling current in the transfer-Hamiltonian approximation is given by[4]

$$j_T=(2\pi e/\hbar)\,|\langle\psi_L|H-H_L|\psi_R\rangle|^2\,\rho_L\,\rho_R\ , \tag{20}$$

where H_L, Ψ_L, and ρ_L denote a left-system Hamiltonian, its eigenfunction, and density of states, respectively. In the Bardeen version of the transfer-Hamiltonian method the left- and right-system Hamiltonians must satisfy

$$H_L=H,\quad x\le x_0 \tag{21a}$$

$$H_R=H,\quad x\ge x_0 \tag{21b}$$

where x_0 is an arbitrary point in the barrier and H is the true Hamiltonian denoted in Fig. 1(a). If H_L and H_R satisfy the conditions of Eq. (21) then Eq. (20) becomes[4]

$$\begin{aligned} j_T&=2\pi e\hbar\,|\langle\psi_L|j_{op}|\psi_R\rangle|^2\,\rho_L\,\rho_R\\ &=\tfrac{1}{2}\pi e\hbar^3m^{-2}\,|\psi_R'\psi_L-\psi_R\psi_L'|^2\,\rho_L\,\rho_R\\ &=\tfrac{1}{2}\pi e\hbar^3m^{-2}\,\rho_L(x_0)\,\rho_R(x_0)\,|\alpha_L-\alpha_R|^2\ , \end{aligned} \tag{22a}$$

where

$$\alpha_L=\psi_L'(x_0)/\psi_L(x_0)\ , \tag{22b}$$

$$\alpha_R=\psi_R'(x_0)/\psi_R(x_0)\ , \tag{22c}$$

and ρ_L is the left-system density of states at x_0,

$$\rho_L(x_0)=|\psi_L(x_0)|^2\,\rho_L \tag{22d}$$

and

$$\rho_R(x_0)=|\psi_R(x_0)|^2\,\rho_R\ . \tag{22e}$$

A particular choice for the left-system Hamiltonian is shown in Fig. 1(b) and the right-system Hamiltonian is chosen to be that of Fig. 1(c).

In order to relate the expression for the true current given by Eq. (19) to the transfer-Hamiltonian result j_T of Eq. (22a) we form

$$W_L=(\psi_l'\,\psi_L-\psi_L'\,\psi_l)_{x_0} \tag{23}$$

from which it follows that

$$\mathrm{Im}\,\alpha_l=\frac{\pi\hbar^2}{2m}\left|\frac{W_L}{\psi_l\,\psi_L}\right|^2\rho_L(x_0)\ , \tag{24}$$

where we have used $\mathrm{Im}(\Psi_L'/\Psi_L)_{x_0}=0$ which holds because Ψ_L carries no current and we have used the relation

$$\rho_L(x_0)=\frac{2m}{\pi\hbar^2}\,\mathrm{Im}\,\frac{\psi_l\psi_L}{W_L} \tag{25}$$

which follows from the fact that in the region $x\le x_0$ we have $H_L=H$ so that Ψ_l and Ψ_L are two independent eigenfunctions of H_L. An equation equivalent to Eq. (24) holds for $\mathrm{Im}\,\alpha_R$. Using Eq. (24) in Eq. (19) to give j and comparing with j_T from Eq. (22) yields

$$j_T=j\left|1-\frac{(\alpha_L-\alpha_r)(\alpha_R-\alpha_l)}{(\alpha_L-\alpha_l)(\alpha_R-\alpha_r)}\right|^2\ . \tag{26}$$

Thus the current j_T calculated from the transfer Hamiltonian differs from the true current j by a correction term which is very small if $\alpha_L\simeq\alpha_r$ *or* $\alpha_R\simeq\alpha_l$. In the case of the square barrier $\Psi_L\propto\exp(-\kappa x)$ and $\alpha_L=-\kappa$ while $\alpha_r\propto[\exp(-\kappa x)+e^{-2\kappa L}e^{\kappa x}]$ for x in the barrier region, where k is wave vector of an electron in the barrier and L is the width of the barrier. For large L it then follows that

$$\alpha_r-\alpha_L\simeq 2\kappa\exp[-2\kappa(L-x_0)] \tag{27}$$

and j_T differs from j by an exponentially small term. For a wide barrier of a simple shape such as encountered in field emission it is clear from Eq. (26) that $j_T\simeq j$ as long as a sensible choice for H_L or H_R is made. Generally speaking one should choose $H_L=H$ or $H_R=H$ throughout the barrier region if such a choice is convenient.

In conclusion, field emission measures the density of states with total momentum parallel to the metal surface at a distance several angstroms from the surface (the point at which the barrier potential becomes essentially one dimensional). Furthermore, an explicit formula for the error made in applying the transfer-Hamiltonian method to an arbitrary one-dimensional barrier has been derived and used to justify the transfer-Hamiltonian approach to the field-emission problem.

We wish to thank P. Soven and E. W. Plummer for a number of useful conversations.

Note added in proof: Obviously, the conclusion that the primary contribution to the field emission current is due to electrons with $k_{\|}\simeq 0$ is based on the assumption that the factor N_m in Eq. (1) is not zero for electrons with $k_{\|}\simeq 0$. It has been shown for $W(100)$ by Politzer and Cutler[2] as well as Modinos and Nicolau[6] and more recently stressed by Feuchtwang, Cutler, and Gadzuk[7] that for symmetry reasons $N_m\simeq 0$ for states with $k_{\|}\simeq 0$ (at least for those states that lie near the Fermi energy). Consequently, for $W(100)$ field emission does not measure the one-dimensional density of states near the surface. However, Eqs. (10) and (13) remain valid and so the current is still related to the density of states near the surface but in a more complicated way.

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