Quantum Theory of Metallic Reflection

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In the classical (Drude) theory of the reflection and transmission of light at a metal surface, the component of electric intensity perpendicular to the surface is discontinuous there, the remaining components of the field vectors being continuous. In a more detailed description the interaction of the light with the metal is expressed as scattering by the conduction electrons according to quantum theory. Those components of the field vectors which were continuous in the classical theory retain very approximately their values in that theory. The electric intensity perpendicular to the surface, though given approximately elsewhere by the classical theory, fluctuates widely within a few electron wavelengths of the surface.

If this fluctuating field is used to calculate the surface photoelectric effect by Mitchell's method, the agreement of his result for a clean potassium surface with observation is improved. To a first approximation, the new theory predicts that the frequency at the peak of the spectral distribution curve for a clean surface of a metal depends only on the number N of free electrons per unit volume, and for different metals varies approximately as $N^{5/9}$; although the experimental results are uncertain, this is roughly the case. No calculations have been made for sensitized surfaces, but arguments based on the use of the Drude form seem to be precarious.

1. INTRODUCTION

THE classical phenomenological theory of the optical properties of metals assumes a discontinuous change in the optical constants at the surface of the metal. This implies a discontinuity in the normal component of the electric vector of the light at the surface, and hence a periodically varying surface charge density there. On the other hand, we should expect a quantum-mechanical treatment to give us a continuous electric field at the surface, and a transition layer near the surface in which the optical constants may be regarded as varying continuously from the values outside the metal to the values some distance within the metal, the latter being given by either the Drude or the Kronig theory.

In order to be able to write down the wave functions of the electrons within the metal, we must first make some simplifying assumptions about its internal structure. Kronig's[1] theory assumes that each electron moves effectively in a triply periodic potential field due to the positive ions of the lattice and the remaining electrons. It follows as a consequence of this theory that if the frequency is sufficiently greater than the reciprocal of the "relaxation time"[2] of a current set up in the lattice, the effects of the lattice are negligible, and the electrons may be treated as effectively free; for the alkali metals this seems to hold in the visible and ultraviolet regions. Zener[3] has shown indeed that the limits of transparency to ultraviolet light of the alkali metals as calculated from a free electron theory are in fair agreement with experiment. Under these circumstances, then, the electrons inside the metal may be treated as a Fermi gas. In such a treatment, we assume that apart from external disturbances, a particular electron moves in a field free space, the field of the rest of the electrons and that of the positive ions just cancelling each other. Darwin[4] has shown that in this case, the force acting on each electron is the "tube-force" or molar electric field, and not the Lorentz force.

2. THEORY FOR A GENERAL SURFACE BARRIER

We take for the wave equation representing an electron moving in a vector potential $\mathbf{A}$ and a scalar potential V (when the charge on an electron is $-e$):

$$-\frac{h^2}{8\pi^2 m}\nabla^2 u + \frac{eh}{2\pi i m c}(\mathbf{A}\cdot\nabla)u - eVu - \frac{ih}{2\pi}\frac{\partial u}{\partial t} = 0 \tag{1}$$

[1] R. de L. Kronig, Proc. Roy. Soc. **A124**, 409 (1929); **A133**, 255 (1931).
[2] Reference 1, p. 415 of the 1929 paper.
[3] C. Zener, Nature **132**, 968 (1933).
[4] C. G. Darwin, Proc. Roy. Soc. **A146**, 17 (1934).

for the light wave:

$$\mathbf{A} = \mathbf{B}(x)e^{-2\pi i\nu(t-(z\sin\theta)/c)} + \mathbf{B}^*(x)e^{2\pi i\nu(t-(z\sin\theta)/c)}, \qquad V = 0 \tag{2}$$

($V=0$ being provided by a change of gauge[5]), and for the surface barrier:

$$V = V(x), \qquad V(-\infty) = V_1, \qquad V(+\infty) = V_0. \tag{3}$$

The metal is taken to fill the half-space on the negative side of the yz plane. $V(x)$ is an arbitrary known function representing the effect of the surface, that has the limiting values at $\pm\infty$, and $\mathbf{B}(x)$ is an unknown, but definite vector function. We first find the solutions w of the unperturbed equation ($\mathbf{A}=0$):

$$-(h^2/8\pi^2 m)\boldsymbol{\nabla}^2 w - eVw - (ih/2\pi)(\partial w/\partial t) = 0, \tag{4}$$

which, for energy $E < -eV_0$ and coefficients k_y and k_z of y and z in the exponent take the form:

$$w = \{A_1\psi_1(x) + A_2\psi_2(x)\}e^{i(k_y y + k_z z)}e^{-2\pi i Et/h}, \tag{5}$$

where[6]

$$\psi_1(-\infty) \approx e^{-ik_x x}, \qquad \psi_2(-\infty) \approx e^{ik_x x}, \qquad A_1\psi_1(+\infty) + A_2\psi_2(+\infty) \approx A_3 e^{-px},$$

$$k_x^2 = (8\pi^2 m/h^2)(E+eV_1) - k_y^2 - k_z^2, \qquad p^2 = -(8\pi^2 m/h^2)(E+eV_0) + k_y^2 + k_z^2$$

(k_x and p are positive). Then putting $u = v + w$, v is given to a first approximation as a solution of:

$$-(h^2/8\pi^2 m)\boldsymbol{\nabla}^2 v - eVv - (ih/2\pi)(\partial v/\partial t) = -(eh/2\pi imc)(\mathbf{A}\cdot\boldsymbol{\nabla})w. \tag{6}$$

After putting in the values of $\mathbf{A}$ and w, this may be solved by writing v in the form:

$$v = \phi_1(x)e^{i(k_y y + k_z z)}e^{-(2\pi i/h)(E+h\nu)t}e^{2\pi i\nu(z\sin\theta)/c} + \phi_2(x)e^{i(k_y y + k_z z)}e^{-(2\pi i/h)(E-h\nu)t}e^{-2\pi i\nu(z\sin\theta)/c}, \tag{7}$$

where

$$\phi_1(x) = a_1(x)\psi_1^{(1)}(x) + a_2(x)\psi_2^{(1)}(x), \qquad \phi_2(x) = b_1(x)\psi_1^{(2)}(x) + b_2(x)\psi_2^{(2)}(x). \tag{8}$$

Neglecting ν/c in comparison with k_z (for the greater part of the electrons, the latter is about a thousand times the former) we obtain:

$$a_1(x) = c_1 + (2\pi e/chq)\int_0^x \psi_2^{(1)}\{i\mathbf{B}_x(s)(A_1\psi_1' + A_2\psi_2') - (k_y\mathbf{B}_y(s) + k_z\mathbf{B}_z(s))(A_1\psi_1 + A_2\psi_2)\}ds,$$

$$a_2(x) = c_2 - (2\pi e/chq)\int_0^x \psi_1^{(1)}\{i\mathbf{B}_x(s)(A_1\psi_1' + A_2\psi_2') - (k_y\mathbf{B}_y(s) + k_z\mathbf{B}_z(s))(A_1\psi_1 + A_2\psi_2)\}ds. \tag{9.1}$$

Here, $\psi_1^{(1)}$ and $\psi_2^{(1)}$ are the unperturbed solutions for $E^{(1)} = E + h\nu$, k_y, k_z; $\psi_1^{(2)}$ and $\psi_2^{(2)}$ are the unperturbed solutions for $E^{(2)} = E - h\nu$, k_y, k_z; also:

$$q^2 = (8\pi^2 m/h^2)(E^{(1)} + eV_1) - k_y^2 - k_z^2 = \mu\nu + k_x^2, \qquad \mu = 8\pi^2 m/h \tag{10.1}$$

(q is positive). Since $E^{(2)}$ is generally negative (for potassium this is so for $\lambda < 6000A$), we have for $b_1(x)$ and $b_2(x)$:

$$b_1(x) = d_1 - (2\pi i e/ch\rho)\int_0^x \psi_2^{(2)}\{i\mathbf{B}_x(s)(A_1\psi_1' + A_2\psi_2') - (k_y\mathbf{B}_y(s) + k_z\mathbf{B}_z(s))(A_1\psi_1 + A_2\psi_2)\}ds,$$

$$b_2(x) = d_2 + (2\pi i e/ch\rho)\int_0^x \psi_1^{(2)}\{i\mathbf{B}_x(s)(A_1\psi_1' + A_2\psi_2') - (k_y\mathbf{B}_y(s) + k_z\mathbf{B}_z(s))(A_1\psi_1 + A_2\psi_2)\}ds, \tag{9.2}$$

where

$$\rho^2 = -(8\pi^2 m/h^2)(E^{(2)} + eV_1) + k_y^2 + k_z^2 = \mu\nu - k_x^2 \tag{10.2}$$

(ρ is positive). The primes (not to be confused with the superscripts) as in (9.1) and (9.2) will always denote differentiation with respect to x. The constants of integration in the above expressions must be adjusted so that outside the metal, v falls off exponentially, and inside, v represents (at large distances in) either waves moving away from the surface or an exponentially decreasing solution. In calculating

[5] J. Frenkel, *Wave Mechanics—Advanced General Theory*, 1934, p. 368.
[6] If $E < -eV_1$, we get exponential forms for the unperturbed solutions:

$$\psi_1(-\infty) \approx e^{\rho x}, \qquad \psi_2(-\infty) \approx e^{-\rho x}, \qquad \rho^2 = -(8\pi^2 m/h^2)(E+eV_1) + k_y^2 + k_z^2; \qquad (\rho \text{ is positive.})$$

photoelectric emission, we are concerned only with the ϕ_1 term, as that involving $E-h\nu$ corresponds to stimulated emission; for the coherent scattering, however, both terms must be considered.

The current coherent with the incident light is given in terms of the vector potential by means of the well-known formula:

$$\mathbf{j} = -e\{(h/4\pi im)(u^*\nabla u - u\nabla u^*) + (e/mc)\mathbf{A}uu^*\}. \tag{11}$$

To obtain the total current $\mathbf{J}$, we must integrate $\mathbf{j}$ over all the states of the conduction electrons according to Fermi statistics. This $\mathbf{J}$, which combines the polarization and conduction currents, is then the same as that which appears in Maxwell's equations:

$$[\nabla \times \mathbf{H}] - (1/c)\dot{\mathbf{E}} = (4\pi/c)\mathbf{J}, \qquad \mathbf{H} = [\nabla \times \mathbf{A}], \qquad \mathbf{E} = -(1/c)\dot{\mathbf{A}}, \tag{12}$$

from which we obtain the relation:

$$[\nabla \times [\nabla \times \mathbf{A}]] + (1/c^2)\ddot{\mathbf{A}} = (4\pi/c)\mathbf{J} \tag{13}$$

between $\mathbf{A}$ and $\mathbf{J}$. Eliminating $\mathbf{J}$ between (13) and the integrated form of (11), we obtain an integral equation in the vector potential $\mathbf{A}$. In the above theory, we have neglected effects due to photoelectric emission and incoherent scattering. These two are of the same order of magnitude, and the former is known experimentally to be negligibly small for calculations of this type (there is generally about one photoelectron produced per 200 incident quanta).

We simplify the integral equation in the vector potential as much as possible before approximating to its solution. Outside the metal, $\mathbf{J} = 0$, and well inside the metal (where the electrons are not under the influence of the surface barrier), we have from classical theory that $\mathbf{J} = f_0\mathbf{A}$, where:

$$f_0 = -e^2N/mc, \quad N = \text{number of electrons per cc} \tag{14.1}$$

$$\epsilon = 1 + cf_0/\pi\nu^2, \tag{14.2}$$

the latter relating f_0 with the dielectric constant ϵ of the phenomenological theory; thus at large distances within the metal, $\mathbf{A}$ has the form:

$$\mathbf{A} = \mathbf{C}e^{\gamma x}e^{-2\pi i\nu(t-(z\sin\theta)/c)} + \mathbf{C}^*e^{\gamma x}e^{2\pi i\nu(t-(z\sin\theta)/c)}, \tag{15}$$

where $\mathbf{C}$ is a constant vector. Since we have assumed that the electrons are effectively free (except for the surface barrier), we expect the Drude results to apply everywhere except near the surface. The same argument that shows in the Drude theory that $\mathbf{B}_y(x)$, $\mathbf{B}_z(x)$, and $((4\pi/c)\mathbf{J}_x + (4\pi^2\nu^2/c^2)\mathbf{A}_x)$, (the tangential components of $\mathbf{A}$ and the normal component of $[\nabla \times \mathbf{H}]$) are continuous at the surface, now shows that these expressions vary only slowly, and to a first approximation may be taken to have everywhere the values given by the Drude theory. Thus we may put:

$$\mathbf{B}_y(x) = \mathbf{C}_ye^{\gamma x}, \qquad \mathbf{B}_z(x) = \mathbf{C}_ze^{\gamma x},$$

$$((4\pi/c)\mathbf{J}_x + (4\pi^2\nu^2/c^2)\mathbf{A}_x) = \{\chi e^{-2\pi i\nu(t-(z\sin\theta)/c)} + \chi^*e^{2\pi i\nu(t-(z\sin\theta)/c)}\}e^{\gamma x}. \tag{16}$$

We must now find $\mathbf{C}_y$, $\mathbf{C}_z$, χ, and γ from the Drude[7] theory in terms of the amplitude of the vector potential of the incident light wave. Using (15) for the light wave within the metal, we put:

$$\mathbf{A} = \{\mathbf{A}^{(0)}e^{-2\pi i\nu(t+(x\cos\theta/c)-(z\sin\theta)/c)} + \mathbf{A}^{(1)}e^{-2\pi i\nu(t-(x\cos\theta)/c-(z\sin\theta)/c)}\} + \text{conjugate},$$

for the wave outside, where $\mathbf{A}^{(0)} = (I_p\sin\theta, I_s, I_p\cos\theta)$ is the amplitude of the incident wave, and $\mathbf{A}^{(1)} = (R_p\sin\theta, R_s, -R_p\cos\theta)$ is the amplitude of the reflected wave. I_p and I_s are the components of the incident light vector parallel and perpendicular to the plane of incidence (xz-plane) respectively, θ being the angle of incidence, and R_p and R_s are similar quantities for the reflected beam. We find $\mathbf{E}$ and $\mathbf{H}$ from Maxwell's Eq. (12), and apply the boundary conditions (continuity of the tangential components of $\mathbf{E}$ and $\mathbf{H}$) at $x = 0$. We also require the relation:

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[7] P. Drude, *Theory of Optics* (English translation, 1907), part 2, section 2, chapter 4.

$$f_0 \mathbf{A} = \mathbf{J} = (c/4\pi)[\nabla \times \mathbf{H}] - (1/4\pi)\dot{\mathbf{E}}. \tag{12.1}$$

The y-component of this vector equation gives us the value of γ:

$$\gamma^2 = -(4\pi/c)(f_0 + (\pi \nu^2 \cos^2 \theta)/c) \tag{17.1}$$

(γ is real and positive). The x- and z-components of (12.1) are equivalent, and with the boundary conditions may be made to give:

$$\mathbf{C}_x = \frac{2I_p}{\sin \theta - (1/\cos \theta - c\gamma/2\pi i\nu)(c\gamma/2\pi i\nu \sin \theta)}, \tag{17.2}$$

$$\mathbf{C}_y = \frac{2I_s}{1 - c\gamma/2\pi i\nu \cos \theta}, \tag{17.3}$$

$$\mathbf{C}_z = \frac{2I_p}{1/\cos \theta - c\gamma/2\pi i\nu - (2\pi i\nu \sin^2 \theta)/c\gamma}, \tag{17.4}$$

$$\chi = (4\pi f_0/c + 4\pi^2 \nu^2/c^2)\mathbf{C}_x, \tag{17.5}$$

in terms of the amplitude of the incident light.

3. Theory for an Infinite Barrier

The form of the potential function $V(x)$ that is easiest to treat from a mathematical standpoint is that which gives a square barrier:

$$V(x) = 0, \quad x < 0; \qquad V(x) = V_0, \quad x > 0. \tag{3.1}$$

We shall consider in detail here the case of an infinite barrier ($V_0 = \infty$). The changes in the results necessary when a finite barrier is used will be discussed later. We retain the form of $\mathbf{A}$ given by (2) for $x < 0$ (the form outside the metal is unimportant). Then (5) becomes:

$$w = A_0(e^{-ik_x x} - e^{ik_x x})e^{i(k_y y + k_z z)}e^{-2\pi i E t/h}, \tag{5.1}$$

which satisfies the boundary condition at $x = 0$ for an infinite barrier (w vanishes); A_0 is a normalizing constant [which equals $(1/4\pi^3)^{\frac{1}{2}}$, for two electrons per h^3 of phase space]. Replacing $\mathbf{B}_y(x)$ and $\mathbf{B}_z(x)$ by their Drude values as in (16), and neglecting the slowly decreasing exponential term $e^{\gamma x}$ (which is important only for producing convergence at $-\infty$, and is practically unity near the surface), we find that the terms involving $\mathbf{B}_y$ and $\mathbf{B}_z$ cancel out of the current expression (11), and can therefore be left out of the coefficients (9.1) and (9.2) of the perturbed wave function (7). After evaluating the constants of integration in $a_1(x)$, $a_2(x)$, $b_1(x)$ and $b_2(x)$, we obtain:

$$a_1(x) = -a_2(0) + (2\pi e A_0/chq)\int_0^x e^{iqs}k_x \mathbf{B}_x(s)(e^{-ik_x s} + e^{ik_x s})ds,$$

$$a_2(x) = -(2\pi e A_0/chq)\int_{-\infty}^x e^{-iqs}k_x \mathbf{B}_x(s)(e^{-ik_x s} + e^{ik_x s})ds, \tag{9.3}$$

$$b_1(x) = -b_2(0) - (2\pi i e A_0/chp)\int_0^x e^{-ps}k_x \mathbf{B}_x(s)(e^{-ik_x s} + e^{ik_x s})ds,$$

$$b_2(x) = (2\pi i e A_0/chp)\int_{-\infty}^x e^{ps}k_x \mathbf{B}_x(s)(e^{-ik_x s} + e^{ik_x s})ds. \tag{9.4}$$

The part of the current given by (11) depending linearly on $\mathbf{A}$ is:

$$\mathbf{j} = -e\{(h/4\pi im)(w^*\nabla v - v\nabla w^* + v^*\nabla w - w\nabla v^*) + (e/mc)\mathbf{A}ww^*\}. \tag{11.1}$$

The current $\mathbf{J}$ is obtained from this by the integration:

$$\mathbf{J} = \int_0^k \pi(k^2 - k_x^2)\mathbf{j}dk_x \tag{18}$$

over the sphere of radius k in $k_x k_y k_z$-space; here $k = (3\pi^2 N)^{\frac{1}{3}}$, for N electrons per cc of metal, and two electrons per h^3 of phase space.

To obtain the integral equation in $\mathbf{B}_x(x)$, we first find the current $\mathbf{j}$, by substituting (5.1) for w, and (7) for v, with coefficients given by (9.3) and (9.4), into the current expression (11.1). Since the exponentials cancel out, except for $e^{\pm 2\pi i\nu[t-(z\sin\theta)/c]}$, and $\mathbf{B}_x$ comes out as a factor, it is convenient to express ϕ_1 and ϕ_2 as integrals of the form:

$$\phi_1 = \int_{-\infty}^0 g_1(x,s)\mathbf{B}_x(s)ds ; \qquad \phi_2 = \int_{-\infty}^0 g_2(x,s)\mathbf{B}_x(s)ds. \tag{19}$$

Doing this, we find directly that $g_1(x,s)$ and $g_2(x,s)$ are given by:

$$g_1(x,s) = -(2\pi eA_0/chq)4ik_x \sin qxe^{-iqs}\cos k_x s ; \qquad -\infty < s < x. \tag{20.1}$$

$$g_1(x,s) = -(2\pi eA_0/chq)4ik_x \sin qse^{-iqx}\cos k_x s ; \qquad x < s < 0. \tag{20.2}$$

$$g_2(x,s) = -(2\pi eA_0/ch\rho)4ik_x \sinh \rho xe^{\rho s}\cos k_x s ; \qquad -\infty < s < x. \tag{20.3}$$

$$g_2(x,s) = -(2\pi eA_0/ch\rho)4ik_x \sinh \rho se^{\rho x}\cos k_x s ; \qquad x < s < 0. \tag{20.4}$$

Then, with (11.1), these give for $\mathbf{j}_x$:

$$\mathbf{j}_x = \left[\int_{-\infty}^0 (eh/4\pi im)\{(e^{-ik_x x}-e^{ik_x x})(A_0 g_2^{*\prime}+A_0 g_1^{\prime})+ik_x(e^{-ik_x x}+e^{ik_x x})(A_0 g_2^*+A_0 g_1)\}\mathbf{B}_x(s)ds\right.$$
$$\left. -(e^2/mc)A_0^2 4\sin^2 k_x x\mathbf{B}_x(x)\right]e^{-2\pi i\nu(t-(z\sin\theta)/c)}+\text{conjugate}. \tag{21}$$

(The primes denote differentiation with respect to x, as before.) Substituting the value of $\mathbf{J}_x$ obtained from (18) and (21) into the last of (16), and equating coefficients of $e^{-2\pi i\nu[t-(z\sin\theta)/c]}$, we obtain finally the integral equation in $\mathbf{B}_x(x)$:

$$\chi = h(x)\mathbf{B}_x(x)+\int_{-\infty}^0 K(x,s)\mathbf{B}_x(s)ds \tag{22}$$

(neglecting the factor $e^{\gamma x}$ in χ), where

$$h(x) = \frac{4\pi^2\nu^2}{c^2}-\frac{4\pi e^2 A_0^2}{mc^2}\int_0^k 4\sin^2 k_x x(k^2-k_x^2)\pi dk_x$$

$$= \frac{4\pi^2\nu^2}{c^2}-\frac{4e^2}{\pi mc^2}\left\{\frac{k^3}{3}+\frac{k\cos 2kx}{4 x^2}-\frac{\sin 2kx}{8x^3}\right\}, \tag{23.1}$$

$$K(x,s) = \frac{2\pi ehA_0}{mc}\int_0^k \{-\sin k_x x[g_1'(x,s)+g_2^{*\prime}(x,s)]$$

$$+k_x\cos k_x x[g_1(x,s)+g_2^*(x,s)]\}(k^2-k_x^2)dk_x. \tag{23.2}$$

This equation cannot be solved by the usual method for treating integral equations, because the (real) function $h(x)$ has a zero on the negative real axis. However, we may rewrite (22) in the form:

$$\mathbf{B}_x(x) = \chi/[h(x)+\int_{-\infty}^0 \{K(x,s)\mathbf{B}_x(s)/\mathbf{B}_x(x)\}ds] \tag{24}$$

and obtain a first approximation to the solution by taking $\mathbf{B}_x$ constant (the Drude value, except for the exponential term) under the integral sign. This gives us:

$$\mathbf{B}_x(x) = \chi/[h(x)+\int_{-\infty}^0 K(x,s)ds]. \tag{25}$$

4. Application to the Theory of the Surface Photoelectric Effect

We have obtained explicitly in (16) and (25) approximate expressions for the vector potential existing inside a metal when we assume an infinite potential barrier at the surface. Before examining these in more detail, we shall consider what changes are necessary in the existing theory of the photoelectric effect to accommodate our new expressions for the vector potential, as the photoelectric

effect gives us a good opportunity to apply the present theory. A very complete treatment of the surface photoelectric effect has been given by Mitchell.[8] He assumes a finite square barrier at the surface (representing a clean surface), the vector potential inside the metal given by classical theory, and has calculated the perturbed wave functions by both the stationary and nonstationary methods. We wish to recalculate his Eq. (26), which gives the whole wave function of electrons outside the metal, by the stationary method, but using our value for the vector potential instead of that given by classical theory, and then to obtain the photoelectric current from this.

The calculation of the unperturbed function will be the same (except that we have used throughout the opposite sign for i). It should be noted that Mitchell calls the potential energy of the electron (not the scalar potential) V, and assigns to it the value $-h\nu_a$ inside the metal, and zero outside; this change of notation does not, of course, affect the final results. We shall use Mitchell's Eq. (13) for the light wave outside the metal, but our form (2) for the potential inside.[9] Since we have assumed that the amplitudes of the y and z components of the vector potential are essentially constant within the metal, we are led (as he was) to the conclusion that his functions ϕ_y and ϕ_z do not contribute appreciably to the current, as they are continuous across the boundary to a first approximation. The calculation of ϕ_x, however, will now be different, since we must replace his $\mathbf{a}_x$, which was constant, by our function $\mathbf{B}_x(x)$ inside the metal. It is necessary then to solve the differential equation in the perturbed function [Mitchell's Eq. (15)] by the method of the variation of parameters, and then to put in the condition that at large positive and large negative distances, ϕ_x is to represent a wave moving away from the surface. Doing this, we obtain instead of Mitchell's Eqs. (22) and (23):

$$\phi_x = (k_x/2q\mathbf{a}_x)\{c_x e^{-iqx} + \int^x_{-\infty} e^{-iq(x-s)}(e^{-ik_x s} - a_k e^{ik_x s})\mathbf{B}_x(s)ds$$

$$- \int^x_{-\infty} e^{iq(x-s)}(e^{-ik_x s} - a_k e^{ik_x s})\mathbf{B}_x(s)ds\}e^{i(k_y y + k_z z)}; \qquad x<0. \quad (26.1)$$

$$\phi_x = \{b_x e^{irx} - (pb_k/\mu\nu)e^{-px}\}e^{i(k_y y + k_z z)}; \qquad x>0. \quad (26.2)$$

(It will be noted that the sign of i is changed here.) We evaluate the constants b_x and c_x by means of the continuity conditions on ϕ_x and $\partial\phi_x/\partial x$ at $x=0$, and obtain for b_x:

$$b_x = -\frac{k_x}{\mathbf{a}_x(q+r)}\int^0_{-\infty} e^{-iqx}(e^{-ik_x x} - a_k e^{ik_x x})\mathbf{B}_x(x)dx + \frac{pb_k(q+ip)}{\mu\nu(q+r)} \quad (27)$$

instead of his expression (25). It is easy to show that these two expressions are equivalent when $\mathbf{B}_x(x)$ is taken constant (except for an exponential term that produces convergence at $-\infty$) and equal to $\mathbf{a}_x$. Then, finally, we obtain, corresponding to Mitchell's (26), the complete wave function outside the metal:

$$u = \{\alpha_k b_k e^{-px}e^{-(2\pi i/h)E_k t} + \lambda_x[b_x e^{irx} - (pb_k/\mu\nu)e^{-px}]e^{-(2\pi i/h)(E_k+h\nu)t}\}e^{i(k_y y + k_z z)}, \quad (28)$$

which is formally the same (except for the change in sign of i), but which has the value of b_x from our Eq. (27) instead of from his Eq. (25). The quantities α_k, b_k, a_k, p, q, r, k_x, λ_x, and μ have the same significance as in Mitchell's paper, and are tabulated here for convenience:

$$|\alpha_k|^2 = \tfrac{1}{2} \text{ (mean electron density inside metal)};$$

$$b_k = 2ik_x/(ik_x+p); \qquad a_k = (ik_x-p)/(ik_x+p);$$

$$p = (\mu\nu_a - k_x^2)^{\frac{1}{2}}; \qquad q = (k_x^2+\mu\nu)^{\frac{1}{2}}; \qquad r = [k_x^2+\mu(\nu-\nu_a)]^{\frac{1}{2}}; \quad (29)$$

$$k_x^2 = (8\pi^2 m/h^2)(E_k+h\nu_a) - k_y^2 - k_z^2;$$

$$\lambda_x = -(4\pi ie/ch)a_k\alpha_k; \qquad \mu = 8\pi^2 m/h.$$

[8] K. Mitchell, Proc. Roy. Soc. A146, 442 (1934).
[9] We shall use only the first term of (2) since the stimulated emission does not contribute to the photoelectric current, as Mitchell points out (reference 8, p. 448).

(k_x, k_y, k_z, q and μ have the same meaning as we assigned to them earlier in this paper.) That part of the normal component of the current density outside the metal which contains neither exponentially decreasing terms nor oscillating time factors (the photoelectric current) may then be obtained from our Eq. (11), or from Mitchell's (27) (which gives the correct result even though he omits the term involving Auu^*). This gives us:

$$\mathbf{j}_x = - (ehr/2\pi m) |\lambda_x b_x|^2 ; \qquad k_x^2 + \mu\nu > \mu\nu_a$$
$$\mathbf{j}_x = 0 ; \qquad k_x^2 + \mu\nu \leqq \mu\nu_a. \tag{30}$$

This current must, of course, be integrated over the conduction electrons before it gives the whole photoelectric current. However, because of the difficulties involved in effecting this integration even with the simpler value of the vector potential that Mitchell considers, we shall not attempt to do this here. But we can obtain a rough comparison with Mitchell's photoelectric yield curve by considering the ratio between our value and his value for b_x, and the manner in which it varies with the frequency of the incident light. In doing this, we use his Eqs. (73) and (74) for b_x and λ_x, where he has taken account of reflection and refraction at the surface of the metal according to classical theory (and change the sign of i). If we put:

$$I_0 = \int_{-\infty}^0 e^{-iqx}(e^{-ik_x x} - a_k e^{ik_x x})\mathbf{B}_x(x)dx \tag{31}$$

we have for the ratio R of our value of b_x to Mitchell's value of b_x:

$$R = \frac{-k_x\mu\nu I_0 + pb_k(q+ip)\mathbf{a}_{0x}}{(ik_x^2 - pq)b_k\mathbf{a}_{tx} + pb_k(q+ip)\mathbf{a}_{0x}}, \tag{32}$$

where $\mathbf{a}_{0x} = I_p \sin\theta + R_p \sin\theta$ is the total (incident and reflected) x component of the amplitude of the vector potential outside the metal, and $\mathbf{a}_{tx} = \mathbf{C}_x$ is the x component of the classically calculated transmitted amplitude. We wish, then, to find roughly the value of R and its dependence on the frequency ν. First, however, we must evaluate I_0, using the value of $\mathbf{B}_x$ from (25).

Consider the relative magnitudes of the terms in the denominator of (25). The first term $h(x)$ is real. Put for the second term:

$$\Lambda = \int_{-\infty}^0 K(x, s)ds. \tag{33}$$

The s-integration of Λ may be carried out simply and exactly and gives:

$$\Lambda = \frac{4ie^2}{\pi mc^2} \int_0^k \left\{ e^{-iqx}\left[\frac{1}{\mu\nu}\left(\sin k_x x \cos qx - \frac{k_x}{q}\cos k_x x \sin qx\right) \cdot (iq \cos k_x x - k_x \sin k_x x)\right.\right.$$
$$\left. + \left(i \sin k_x x + \frac{k_x}{q}\cos k_x x\right)\left(\frac{q}{\mu\nu} - \frac{\cos(q+k_x)x}{2(q+k_x)} - \frac{\cos(q-k_x)x}{2(q-k_x)}\right)\right]$$
$$- \frac{e^{px}}{\mu\nu}\left[\left(\sin k_x x \cosh px - \frac{k_x}{\rho}\cos k_x x \sinh px\right)(\rho \cos k_x x + k_x \sin k_x x)\right.$$
$$\left.\left. + (\rho - \rho \cosh px \cos k_x x - k_x \sinh px \sin k_x x)\left(\sin k_x x - \frac{k_x}{\rho}\cos k_x x\right)\right]\right\}(k^2 - k_x^2)k_x dk_x. \tag{34}$$

The k_x integration, on the other hand, is exceedingly complicated, as both q and ρ contain k_x under a radical. However, we can get an idea of the order of magnitude by assuming for purposes of integration that $k \ll (\mu\nu)^{\frac{1}{2}}$, when we can put approximately:

$$\sin k_x x \approx k_x x ; \qquad \cos k_x x \approx 1 ; \qquad q \approx (\mu\nu)^{\frac{1}{2}} ; \qquad \rho \approx (\mu\nu)^{\frac{1}{2}}.$$

We then obtain for the real and imaginary parts of Λ:

$$\mathfrak{R}[\Lambda] = \frac{4e^2}{\pi mc^2} \frac{2k^5}{15} \frac{1}{\mu\nu} \{\sin \xi - \xi \cos \xi\}, \tag{35.1}$$

$$\mathfrak{J}[\Lambda] = \frac{4e^2}{\pi mc^2} \frac{2k^5}{15} \frac{1}{\mu\nu} \{\cos \xi + \xi \sin \xi + e^\xi(1-\xi) - 2\}, \tag{35.2}$$

where
$$\xi = (\mu\nu)^{\frac{1}{2}}x. \tag{35.3}$$

Several points now present themselves. First, $h(x)$ is an even oscillating function that has one zero on the negative real axis, and an infinite number of complex zeros a considerable distance from the real axis. Second, $h(x)$ approaches a definite limit $(\chi/\mathbf{C}_x)$ as x becomes negatively infinite. Third, $\mathfrak{R}[\Lambda]$ is small compared to $h(x)$, except of course where the latter is zero. Fourth, $\mathfrak{J}[\Lambda]$ is also small compared to $h(x)$, and is positive for $0 > \xi > -1.78$, after which it is negative for some distance.

The zero point[10] of $h(x)$ may be calculated approximately from the equation:

$$\frac{\pi \nu^2 m}{3e^2 N} = \frac{1}{3} + \frac{\cos \eta}{\eta^2} - \frac{\sin \eta}{\eta^3} \approx \frac{\eta^2}{30} - \frac{\eta^4}{840} + \cdots, \tag{36}$$

where $\eta = 2kx$. We take the value $5 \cdot 10^{14}$ for ν, and $1.35 \cdot 10^{22}$ for N (for potassium). These give:

$$\eta_0 = -1.90; \qquad x_0 = -1.29 \cdot 10^{-8} \text{ cm}; \qquad \xi_0 = -0.95; \qquad (\partial h/\partial x)_0 = (4e^2 k^3/\pi mc^2)(0.094) > 0.$$

Thus $\mathbf{B}_x(x)$, which is of the form:

$$\chi / \{ (\partial h/\partial x)_0 (x - x_0) + \mathfrak{R}[\Lambda] + i\mathfrak{J}[\Lambda] \}$$

near x_0, has a pole approximately at:

$$x = x_0 - \{ [\mathfrak{R}\Lambda] + i\mathfrak{J}[\Lambda] \} / (\partial h/\partial x)_0.$$

If $\mathfrak{J}[\Lambda]$ is positive (ν is such that $0 > \xi > -1.78$), this is just below the negative real axis, and I_0 consists of its principal value (neglecting Λ) minus πi times the residue of the integrand at the pole. Again, if $\mathfrak{J}[\Lambda]$ is negative (ν such that $\xi < -1.78$), the pole lies just above the negative real axis, and I_0 consists of its principal value plus πi times the residue at the pole. Thus I_0 changes its value abruptly near that frequency for which $\xi = -1.78$. We can find this critical frequency approximately by putting:

$$\eta \approx -\nu (30\pi m/3e^2 N)^{\frac{1}{2}}$$

from (36), and substituting for x in ξ in terms of η. We then have (in the case of potassium):[11]

$$\nu_c^{\frac{1}{2}} \approx 2k \cdot 1.78/(\mu \cdot 10\pi m/e^2 N)^{\frac{1}{2}}; \qquad \nu_c \approx 8.45 \cdot 10^{14}.$$

We break up the integral I_0 into two parts of the same form:

$$I_1 = \int_{-\infty}^0 \mathbf{B}_x(x)e^{-i\delta_1 x}dx; \qquad \delta_1 = q + k_x > 0$$

$$I_2 = \int_{-\infty}^0 \mathbf{B}_x(x)e^{-i\delta_2 x}dx; \qquad \delta_2 = q - k_x > 0$$

such that: $I_0 = I_1 - a_k I_2$. We must remember that χ in reality has a small exponential term $e^{\gamma x}$ multiplying it, which is negligible except for producing convergence at $-\infty$. We thus have to evaluate an integral of the form:

$$I = \int_{-\infty}^0 (e^{-i\delta x}/h(x))dx; \qquad \delta > 0. \tag{37}$$

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[10] This is approximately the point where the dielectric constant ϵ vanishes.
[11] For different metals, $\nu_c \propto N^{5/9}$, since $k \propto N^{1/3}$.
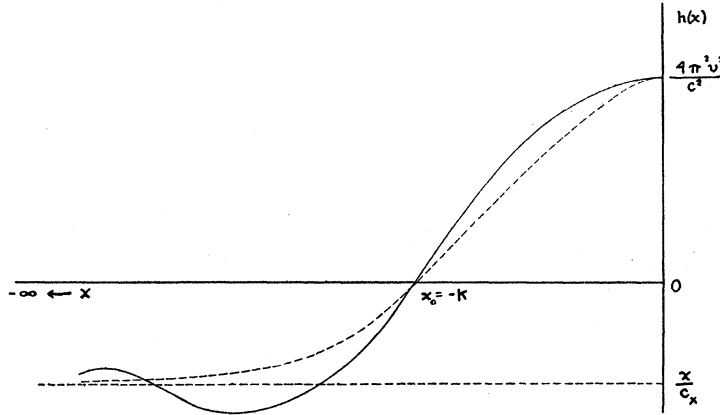
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FIG. 1. The function $h(x)$.

After inserting the form (23.1) for $h(x)$ into (37), this is quite a formidable integral to evaluate, especially with the pole at x_0. However, the important features of $h(x)$ as seen in Fig. 1 (solid line) are its values at zero and $-\infty$, and the point at which it vanishes. Therefore we should expect to get a good approximation to the integral by putting instead:

$$h(x) = 1/(\tau + \sigma x^2) - 1/\zeta, \tag{38}$$

where $\quad h(0) = \dfrac{1}{\tau} - \dfrac{1}{\zeta} = \dfrac{4\pi^2 \nu^2}{c^2}; \quad h(-\infty) = -\dfrac{1}{\zeta} = \dfrac{4\pi^2 \nu^2}{c^2} + \dfrac{4\pi f_0}{c}; \quad h(x_0) = 0; \quad x_0 = -((\zeta - \tau)/\sigma)^{\frac{1}{2}} = -K$

represented by the dotted line in the figure.

The integral (37) can then be expressed in terms of sine and cosine integrals:[12]

$$I = -(i\zeta/\delta) + (i\zeta^2/\sigma K)\{Ci(\delta K) \sin \delta K - si(\delta K) \cos \delta K - \theta\pi e^{i\delta K}\}, \tag{39}$$

where $\quad \theta = 1$, if the pole is below the negative real axis $(\nu < \nu_c)$;
$\quad\quad\quad\ \ \theta = 0$, if the pole is above the negative real axis $(\nu > \nu_c)$.

Putting (39) into the expression for I_0, we obtain:

$$I_0 = \chi\{-i\zeta/\delta_1 + (i\zeta^2/\sigma K)[Ci(\delta_1 K) \sin \delta_1 K - si(\delta_1 K) \cos \delta_1 K - \theta\pi e^{i\delta_1 K}]$$

$$+ a_k i\zeta/\delta_2 - a_k(i\zeta^2/\sigma K)[Ci(\delta_2 K) \sin \delta_2 K - si(\delta_2 K) \cos \delta_2 K - \theta\pi e^{i\delta_2 K}]\}. \tag{40}$$

Then, by inserting (40) into the ratio R given by (32), the latter reduces to

$$R = 1 + \frac{-k_x\mu\nu\chi\zeta^2 i}{\{(ik_x^2 - pq)a_{tx} + (q+ip)pa_{0x}\}\sigma Kb_k} \cdot \{[Ci(\delta_1 K) \sin \delta_1 K - si(\delta_1 K) \cos \delta_1 K - \theta\pi e^{i\delta_1 K}]$$

$$- a_k[Ci(\delta_2 K) \sin \delta_2 K - si(\delta_2 K) \cos \delta_2 K - \theta\pi e^{i\delta_2 K}]\}. \tag{41}$$

From (41) it is impossible to obtain a simple form for the variation with ν of $|R|^2$, this being the ratio of the new photoelectric current to that of Mitchell (for a given k_x). However, we can roughly estimate R by assigning numerical values to the quantities involved. The function $Ci(z) \sin z - si(z) \cos z$ falls off monotonically from $\pi/2$ at 0 (0.62 at 1, 0.40 at 2) approaching zero like $1/z$ as $z \to \infty$, and is therefore never large. Using a value of the frequency near ν_c, we find that $|R| \approx 6$, when $\theta = 1$, and $|R| \approx 1$, when $\theta = 0$. Although these results will be smoothed out somewhat when the k_x integration is

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[12] See Jahnke-Emde, *Tables of Functions* (2nd ed.), p. 79, for the notation used here.

performed, it will still be true that the resulting photoelectric current will decrease rather suddenly as ν passes through the critical value, and θ changes from one to zero.

This last point is quite important, as it brings Mitchell's theoretical curve (his Fig. 2) into better agreement with experiment. On the abscissa of this curve, $(\nu - \nu_g)/\nu_g$, our critical frequency ($8.45 \cdot 10^{14}$) lies at about 0.7. This means that our correction will raise his curve to the left of this point, and lower it towards the right. This will make a rather sharp peak on the low frequency side of ν_c, the position of which will nearly coincide with that of the experimental curve.[13] Detailed calculations of $|R|^2$ would be necessary before the exact forms of the experimental curve and this new theoretical curve could be compared.

This seems to indicate that the peak of the spectral selectivity curve is due principally to the effect of the pole of the vector potential function. This conclusion is confirmed by a comparison of the values of ν_c obtained by this rather rough theoretical approximation ($\nu_c \propto N^{5/9}$) with the rather uncertain experimental values for the peak of the spectral distribution curve, which in fact varies approximately as $N^{\frac{1}{3}}$ for the metals in the first three columns of the periodic table.[14]

5. Changes for a Finite Barrier

The vector potential used in the above calculations was that obtained by assuming an infinite barrier at the surface. The principal effect of making the barrier of finite height is that then the wave functions do not vanish identically at the surface, but have a small value there. This extends the transition layer slightly beyond the surface, and moves the singularity closer to the surface. Such changes would be unimportant in the theory as developed here, and the additional complications involved hardly warrant more detailed investigation at this time.

For the more complex forms of surface barriers, the theory becomes exceedingly complicated; for example, we need no longer have only one point at which the dielectric constant becomes zero. In particular, Zener's[15] argument in favor of Suhrmann's[16] theory of the selective photoelectric effect for sensitized surfaces as against that of Fowler[17] may now require reconsideration.

6. General Conclusions

We thus arrive at the conclusion that the Drude theory of the reflection of light at a metal surface, modified where necessary by Kronig's results, gives the electromagnetic field correctly except within a transition layer extending a few electron wavelengths from the surface. In this transition layer, the continuously varying electric intensity perpendicular to the surface, discontinuous in the Drude theory, does not have values near those given by that theory, but fluctuates considerably.[18] These fluctuations depend on the nature of the surface potential barrier in a complicated way, but their calculation seems to be required in the theory of the surface photoelectric effect.[19]

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[13] This curve in Mitchell's paper was taken from a paper of R. Suhrmann and H. Theissing, Zeits. f. Physik 52, 453 (1928).

[14] Hughes and DuBridge, *Photoelectric Phenomena*, 1932, table on p. 162; the values given there may not be, and certainly are not in the case of potassium, for really clean surfaces.

[15] C. Zener, Phys. Rev. 47, 15 (1935).

[16] R. Suhrmann, Ergebnisse der Exakten Naturwissenschaften 13, 148 (1934).

[17] R. H. Fowler, Proc. Roy. Soc. A128, 123 (1930).

[18] cp. the Gibbs phenomenon in Fourier series.

[19] Even in the simple case of a square barrier, it would hardly improve the results of that theory merely to average over the position of the surface, as suggested by Mitchell (reference 8, p. 461).