

THEORY OF EXTERNAL PHOTOEFFECT FROM THE SURFACE OF A METAL

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The surface photoeffect from a metal in a dielectric or in a solution is considered by applying the so-called threshold theory of production of slow particles, without making any assumptions regarding the concrete shape of the potential barrier at the boundary. In one limiting case the relations derived go over into the well-known Fowler formula for photoemission in vacuum. However in the case of photoemission in a medium in which Debye screening occurs (electrolyte) or in a dielectric with a sufficiently high dielectric constant, qualitatively different results are obtained. In particular, the quadratic law for the quantum yield predicted by the Fowler theory is replaced by a $\frac{3}{2}$ law. The explicit dependence of the quantum yield on frequency of the incident light is considered in a general form. The theory yields a quantitative explanation of a number of experimental data and predicts some new effects.

1. FORMULATION OF PROBLEM

INTEREST has recently been renewed in the study of the surface external photoeffect¹⁾ (photoemission) from metals^[1-10]. The renewed interest in the surface photoeffect is connected primarily with the appearance of new interesting light sources, which make it possible to investigate surface multiphoton processes^[2,3]. In recent years, a number of new detailed experiments were also performed on the interface between a metal and a dielectric or a metal and a semiconductor^[4-8], for the purpose of investigating the potential barrier. In addition, experiments were started on the interface between a metal and an electrolyte solution^[8-10]. In the latter case, the features of the construction of the interface between the metal and the electrolyte^[12] make it possible, by applying a relatively small potential difference, to vary quite noticeably the properties of the surface and its photoemission characteristics. This uncovers wide prospects for using the external surface photoeffect to obtain important experimental information on the properties of interfaces and adsorption layers.

The theoretical analysis of the photoeffect produced under the influence of monochromatic radiation of frequency ω has been the subject of a large number of papers^[13-18]. The basis of the calculations is usually chosen to be the general expression for the density of the photoemission current I from the metal, in the form

$$I = \int j(E, p_{\parallel}, A) \left[1 + \exp\left(\frac{E - \mu}{kT}\right) \right]^{-1} \rho(E, p_{\parallel}) \theta(p^2) dE dp_{\parallel}. \quad (1)$$

¹⁾The surface external photoeffect is the result of the possible interaction between the electrons and protons as a result of a change of the potential on the boundary of the metal^[11]. The surface photoeffect predominates at light frequencies lower than the so-called threshold of the ultraviolet transparency of the metals ω^* (the photon energy corresponding to ω^* is of the order of 8-10 eV). At frequencies higher than ω^* , the volume photoeffect comes into play, which is weakly dependent on the properties of the surface and which arises essentially because either phonons or impurities take part as third bodies in the interaction between the photons and the electrons of the metal.

Here $j(E, p_{\parallel}, A)$ denotes the asymptotic value of the z component of the density of the partial current of electrons as $z \rightarrow \infty$, averaged over the surface of the metal (the z axis is normal to the surface); p is the value of the z component of the momentum of the emitted electron p_z far from the surface; E and $p_{\parallel} = \{p_x, p_y\}$ are respectively the alternating energy and momentum components of the initial electrons in the metal and lie in the plane (xy) ; $A = \{A, A_0\}$ is the potential of the incident electromagnetic wave; μ is the chemical potential of the electrons in the metal, T is the absolute temperature, k is Boltzmann's constant, and $\rho(E, p_{\parallel})$ is the distribution density function. The θ -function $\theta(p^2)$ in (1) is the result of the energy and the momentum conservation laws.

As seen from (1), the main task is to calculate the quantity $j(E, p_{\parallel}, A)$. So far, two different approaches were used. The first, employed for the first time in Fowler's phenomenological theory of the single-photon photoeffect^[15] reduces essentially to a simple replacement of the quantity j in (1) by a certain constant; in many other less successful phenomenological theories, a more complicated form of j is postulated. In the second approach, different variants of which for single- and multiphoton processes are being developed to this very day^[17-18], the quantity j is obtained from a solution of the quantum-mechanical problem, in which the motion of the electrons in the metal is described by a model of "boxes" with different, frequently quite complicated "wall" shapes. The non-equivalence of the two indicated approaches - the phenomenological one^[15] and the apparently more accurate model one - is seen already from the fact that when $T = 0$ they yield essentially different dependences of I on the light frequency ω as ω approaches the threshold frequency ω_0 of the single-photon photoeffect.²⁾ Experiments on the photoemission of electrons in vacuum, however, confirm precisely the Fowler theory, according to which the photocurrent $I \sim (\omega - \omega_0)^2$ when $T = 0$, and at the present time this theory can be regarded as uni-

²⁾The concept of the threshold frequency ω_0 is discussed in greater detail below.

versally accepted^[19-20] in spite of the understanding that it is based on a number of insufficiently justified assumptions.

In the present paper we determine j by a new approach connected with the use of the methods of calculating the so-called threshold production phenomena in quantum mechanics^[21-22]. The possibility of using such methods here is based on the fact that the electrons emitted in the surface photoeffect possess essentially a kinetic energy not exceeding 1-3 eV, and their "well depth" in the metal is smaller (in absolute magnitude). The analysis can therefore be performed essentially without reference to a concrete model of the metal. In such an approach it is possible, first, to justify Fowler's theory and to establish the limits of its applicability. Second, the general threshold analysis makes it possible to describe a number of phenomena where the indicated theory is not valid. Included among such phenomena, in particular, is the surface photoeffect on the interface between a metal and an electrolyte solution.

In the case of surface photoemission from a metal into a dielectric with a sufficiently large dielectric constant, it is also possible to predict a distinct dependence of the photocurrent on ω , which enters in Fowler's law only in the limit of very low energies. A number of theoretical conclusions can be compared in this case with the already available experimental data.

2. INITIAL EXPRESSIONS

In the case of the surface photoeffect, it is essentially sufficient to employ the one-dimensional analysis for the calculation of j . We shall assume that the metal occupies the space $-\infty \leq z \leq 0$. By virtue of the symmetry, the effect is due only to the z -component of the electric field of the light wave³⁾; the effect of the magnetic component on the electrons, and relativistic effects in general can obviously be neglected (we shall henceforth use "electrons" for brevity to denote in general all quasiparticles fermions and carriers with charge $-e$). In view of the averaging over the surface, the effective potential in which the electrons move can be regarded as dependent on z only. For the same reason, the current is derived from wave functions whose dependence on $\mathbf{r}_{\parallel} = \{x, y\}$ can be specified, both before and after the absorption of the photons, by means of the factor $\exp(i\mathbf{p}_{\parallel} \cdot \mathbf{r}_{\parallel})$, which is best separated from the very beginning. In accordance with the foregoing, the asymptotic value of the current $j(\mathbf{E}, \mathbf{p}_{\parallel}, A)$ is derived from final-state wave functions, of the form $\psi_f(\mathbf{s}, z) \exp(i\mathbf{p}_{\parallel} \cdot \mathbf{r}_{\parallel})$, which depend in a nontrivial manner only on the coordinate z (we have introduced here the composite parameter $\mathbf{s} = \{\mathbf{E}, \mathbf{p}, \mathbf{p}_{\parallel}, A\}$), and in the asymptotic limit as $z \rightarrow \infty$ the function $\psi_f(\mathbf{s}, z)$ should be proportional to $\exp(ipz)$. If we confine ourselves for simplicity to the single-photon approxima-

tion, then the equation for $\psi_f^{(1)}(\mathbf{s}, z)$ can be written in the form (we put $e = \hbar = c = 1$ throughout)

$$\left\{ -\frac{\partial^2}{\partial z^2} + 2m(z)U(z) - [2m(z)(E + \omega) - \mathbf{p}_{\parallel}^2] \right\} \psi_f^{(1)}(z) = U_A \psi_0(z). \quad (2)$$

Here U_A is an operator describing the electromagnetic interaction in the first order and does not contain the time. For the case of nonrelativistic electrons, its form is

$$U_A(z) = i \left(\frac{\partial}{\partial z} A_z(z) + A_z(z) \frac{\partial}{\partial z} \right) + 2m(z)A_0(z). \quad (3)$$

Here $m(z)$ is the effective mass of the electron, which generally speaking has different constant values deep in the metal ($m(z) = m_0, z \rightarrow -\infty$), and outside the metal ($m(z) = m, z \rightarrow \infty$) and does not coincide with the usual value of m_e .

The functions $A(z)$ and $A_0(z)$ are connected with the time-dependent components of the potential in the following manner:

$$\begin{aligned} A(z, t) &= [A(z)e^{-i\omega t} + A^*(z)e^{i\omega t}]e^{vt}, \quad v \rightarrow 0. \\ A_0(z, t) &= [A_0(z)e^{-i\omega t} + A_0^*(z)e^{i\omega t}]e^{vt}, \quad v \rightarrow 0. \end{aligned} \quad (4)$$

The dependence of $A(z)$ on the coordinates (x, y) at incidence angles not very close to $\pi/2$ can be neglected, since all the characteristic dimensions that enter in the problem are much smaller than the wavelength of the light.

The function $\psi_0(\mathbf{E}, \mathbf{p}_{\parallel}, z)$ which enters in (2) describes the initial state of the electron in the metal, and is by definition a regular function that attenuates at $z \rightarrow \infty$. The equation satisfied by the function $\psi_0(\mathbf{E}, \mathbf{p}_{\parallel}, z)$ is

$$\left\{ -\frac{\partial^2}{\partial z^2} + \mathbf{p}_{\parallel}^2 + 2m(z)[U(z) - E] \right\} \psi_0(z) = 0. \quad (5)$$

The term containing $U(z)$ describes all the interactions of the electron inside and outside the metal, except the interaction with the electromagnetic wave. At the frequencies under consideration, it can be regarded as independent of the time.

We must emphasize especially that the following conclusions are practically independent of the type of interaction inside the metal, provided this interaction can be regarded as "sufficiently strong,"⁴⁾ and therefore there is no need to specify in detail the type of the function $U(z)$ when $z \leq 0$.

To describe the motion of the electrons outside the metal, we note that the main part of the emitted electrons has an energy much higher than kT , and therefore the deceleration processes for them become significant only at distances larger than their de Broglie wavelength. The motion of such electrons far from the surface can be described, without taking into account the deceleration, as the motion of particles with mass m in an effective potential well, the depth V of which depends on the properties of the medium into which the electrons are emitted^[23] (in the case of emission into vacuum $V = 0$ and $m = m_e$). Thus, at a certain distance δ from the surface of the metal, the function $U(z)$ can be written in the form

³⁾Besides symmetry consideration, it is also necessary to bear in mind that in the frequency region under consideration, when almost total reflection from the surface of the metal takes place, the tangential components of the electric component of the field are much smaller than the normal components.

⁴⁾The corresponding mathematical condition will be given below (see (14)).

$$U(z) = -V - \alpha/z, \quad z \geq \delta. \quad (6)$$

The second term in (6) takes into account the image forces, with $\alpha = 0$ in the case of emission into a medium with Debye screening (electrolyte), and $\alpha = e^2/4\epsilon$ for emission into a dielectric or vacuum (here ϵ is the dielectric constant of the medium relative to the image forces). The distance δ is equal in order of magnitude to the region where the surface forces decrease and image forces are formed. In the case of emission into an electrolyte solution, δ coincides with the dimension of the dense part of the double layer and amounts to several Angstroms^[12]. The detailed character of the variation of the potential in the interval $[0, \delta]$ turns out to be insignificant in many respects for the consideration of the threshold effects.

After determining $\psi_f^{(1)}$ from (2), we can obtain the current density $j^{(1)}$ with the aid of the relation

$$j = \frac{i}{2m} \left(\psi_f \frac{\partial \psi_f^*}{\partial z} - \psi_f^* \frac{\partial \psi_f}{\partial z} \right) = \frac{p}{m} |\psi_f|^2, \quad z \rightarrow \infty \quad (7)$$

(from now on the index (1) will be omitted for brevity).

3. THRESHOLD ANALYSIS OF PHOTOEMISSION

For the case of a monochromatic wave, the density of the photocurrent j can be written in the form of a function of p and ω , (i.e., $j = j(p, \omega)$). We shall now show under what conditions the dependence of $j(p, \omega)$ on its arguments can be determined in general form, and we shall find this dependence.

Recognizing that the function $\psi_0(z)$ attenuates rapidly, when $z > 0$ and using (6), we can rewrite (2) in the region $z \leq \delta$, with exponential accuracy, in the form

$$\left[\frac{\partial^2}{\partial z^2} + p^2 + \frac{2m\alpha}{z} \right] \psi_f(z) = 0, \quad (8)$$

$$p = \sqrt{2m(E + V + \omega) - p_{||}^2}. \quad (9)$$

Equation (8) coincides with the equation that describes the motion in a Coulomb field with zero orbital angular momentum^[21-22]. From the asymptotic form of ψ_f it follows that when $p^2 > 0$ the function ψ_f in should be in the general case proportional the region $z \geq \delta$ to the well-known^[21] Coulomb function $\chi_{p,0}^+(pz, m\alpha z)$, which has the limiting form^[21]

$$\chi_{p,0}^+(pz, m\alpha z) = \exp \{i(pz + \delta_0 + \eta \ln 2pz)\}, \quad z \rightarrow \infty, \quad (10a)$$

$$\chi_{p,0}^+(pz, m\alpha z) = C_0^{-1} \{1 + pz(2\eta O(m\alpha z) + iC_0^2)\}, \quad pz \rightarrow 0, \quad (10b)$$

where

$$\delta_0 \equiv \arg \Gamma(1 - i\eta), \quad C_0 \equiv \left[\frac{2\pi\eta}{1 - e^{-2\pi\eta}} \right]^{1/2}, \quad \eta \equiv \frac{m\alpha}{p}.$$

$O(m\alpha z)$ in (10b) is a certain function that does not depend on p and whose order of magnitude is unity ($m\alpha z$ is not assumed small in this case).

Thus, accurate to an inessential phase factor, we have

$$\psi_f = \frac{1}{2ip} \chi_{p,0}^+(pz, m\alpha z) \theta(p^2) M^{(1)}(p, \omega), \quad z > \delta, \quad (11)$$

where $M^{(1)}(p, \omega)$ is a certain function that does not depend on the coordinate z and represents, as can be readily verified, the suitably normalized matrix element of the transition. The general form of $M^{(1)}(p, \omega)$ is discussed in Sec. 4.

We note further that inasmuch as the quantity $pz\eta = \alpha mz$ does not depend on p , the entire expression in the curly brackets of (10b) is a function of z only (the dependence of the last term of (10b) on p arises, as can be readily seen, only in that region of values of p where this term can be neglected compared with the first). By virtue of the foregoing, if the condition

$$p\delta < 1 \quad (12)$$

is satisfied, we get from (10b) and (11) an expression for ψ_f near the surface of the metal:

$$\psi_f|_{z=\delta} = \frac{M^{(1)}(p, \omega)}{2ipC_0} R(\delta), \quad (13)$$

where $R(\delta)$ (the expression in the curly brackets of (10b) when $z = \delta$) is a certain dimensionless quantity that no longer depends on p or ω .

In the "internal" region $z < 0$, as seen from (2), the energy enters in the equation of motion only in the form of a sum with a large interaction inside the metal. Therefore, if the function ψ_f has no singularities when $z < 0$, it should vary little in the case of a relatively small change of the final energy. Namely, when the conditions $|E + \omega + V| < |U + V|$ and $|E + \omega + V| < |U + V + \omega|$, together with the condition that follows from them with allowance for (9),

$$p^2 < 2m|U(z) + V + \omega|, \quad (14)$$

are satisfied, it is possible, when $z < 0$, to replace $E - p_{||}^2/2m$ by $-(V + \omega)$ both in the left side of (12) and in the argument of $(E, p_{||}, z)$. Accordingly, provided there are no resonant energy levels near the threshold, it follows from (2) in (6) that if the condition (4) is satisfied then $\psi_f|_{z=0}$ is a function that is finite in accordance with the definition of the problem and does not depend in our approximation explicitly on p^5 . Since the modulus of the wave function cannot change noticeably over the distance δ when the condition (12) is satisfied in the case of nonsingular potentials, the value of the function $|\psi_f|_{z=\delta}^2$ can be approximately equated to $|\psi_f|_{z=0}^2$. Hence, using (13), we get

$$|M^{(1)}(p, \omega)|^2 = 4p^2 C_0^2 \zeta(\delta, \omega), \quad (15)$$

where for brevity we introduced the notation

$$\zeta(\delta, \omega) = |\psi_f|_{z=0}^2 / |R(\delta)|^2.$$

Using now (7), we obtain with the aid of (10), (11), and (15) the following expression for the density of the partial photoemission current

$$j(p, \omega) = \frac{1}{4m\eta} |M^{(1)}(p, \omega)|^2 = \zeta \frac{p\alpha}{m} \left[1 - \exp\left(-\frac{p\alpha}{p}\right) \right]^{-1}, \quad (16)$$

where $p\alpha \equiv 2\pi m\alpha$ (in dimensional units, $p\alpha = \pi e^2 m/2\epsilon\hbar$). Expression (16) has been obtained in the so called threshold approximation, that is, under the assumption that the conditions (12) and (14) are satisfied, as is always the case for sufficiently small final momenta p or at frequencies sufficiently close to threshold.

Expression (16) simplifies in two limiting cases;

⁵⁾We emphasize that this conclusion, as well as all the following ones, can be obtained also without considering in explicit form the equation for the electronic function inside the metal.

$$j(p, \omega) = \begin{cases} \frac{p_\alpha}{m} \xi(\delta, \omega), & p \ll p_\alpha, \\ \frac{p}{m} \xi(\delta, \omega), & p \gg p_\alpha. \end{cases} \quad (17a)$$

$$(17b)$$

The critical value $p = p_\alpha$ corresponds to a final kinetic energy of the photoelectrons $E_\alpha = p_\alpha^2/2m$ equal to

$$E_\alpha = \frac{m}{m_0} \frac{33.54}{e^2} \text{ eV.}$$

In the case of emission into vacuum or into a dielectric with not too large a value of ϵ , the value $p = p_\alpha$ is reached only after condition (12) is violated, corresponding to a final kinetic energy of the electron on the order of $3m_e/m$ eV, that is, certainly far from threshold. This justifies by the same token, according to (17a), Fowler's approach in which $j = \text{const}$ is assumed. To the contrary, in the case of emission of electrons into a medium in which the long-range Coulomb forces are rapidly screened, say an electrolyte solution, corresponding to $\alpha = 0$, the equality (17b) holds. In the case of emission into a dielectric with high electron polarizability, the following situation may be realized: the photocurrent has a "Coulomb" form (17a) in the immediate vicinity of the threshold, but with increasing ω the Coulomb interaction becomes negligibly small, and even inside the threshold region, in accordance with (16) a transition to (17b) characteristic of the short-range forces takes place.

Expressions having a similar dependence on p can be written also for the multiphoton component of the photocurrent density.

4. FREQUENCY DEPENDENCE OF THE THRESHOLD PHOTOCURRENT

In the preceding section we obtained in general form the threshold dependence of the photocurrent density $j(p, \omega)$ on p . We now find also the character of the explicit dependence of $j(p, \omega)$ on ω . To this end we consider in great detail the previously introduced matrix element $M^{(1)}(p, \omega)$, which can be written in the form⁶⁾

$$M^{(1)}(p, \omega) = \int_{-\infty}^{\infty} \psi^- U_A \psi_0 dz \\ = \int_{-\infty}^{\infty} \psi^- \left[i \frac{\partial}{\partial z} A_z + i A_z \frac{\partial}{\partial z} + 2m(z) A_0(z) \right] \psi_0 dz. \quad (18)$$

Here $\psi^-(z)$ is a solution of (5) in which the initial energy E is replaced by the final energy $E + \omega$; when $z \rightarrow \infty$ this solution is a traveling plane wave propagating in the direction of negative z , and its normalization is chosen such that the coefficient in front of $\exp(-ipz)$ is equal to unity in the asymptotic expression when $z \rightarrow \infty$ (when any solution of the equation under consideration is a linear combination of the solutions $\exp(ipz)$ and $\exp(-ipz)$, see p. 604 of [22]).

We note that all of the foregoing results can be ob-

tained in principle from an analysis of (18); we have preferred to follow, however, a different path in Sec. 3, since the physical meaning of the main premises is clearer there.

Expression (18) for $M^{(1)}(p, \omega)$ is best transformed with the aid of double integration by parts into

$$M^{(1)}(p, \omega) = \int_{-\infty}^{\infty} \left\{ A_z(z) i \left(-\frac{\partial \psi^-}{\partial z} \psi_0 + \psi^- \frac{\partial \psi_0}{\partial z} \right) + 2m(z) A_0(z) \psi^- \psi_0 \right\} dz \\ = \int_{-\infty}^{\infty} \left\{ \left(\int_{-\infty}^z A_z(z') dz' \right) i \left[\frac{\partial^2 \psi^-}{\partial z^2} \psi_0 - \psi^- \frac{\partial^2 \psi_0}{\partial z^2} \right] \right. \\ \left. + \left(\int_{-\infty}^z \frac{\partial A_0}{\partial z'} dz' \right) 2m(z) \psi^- \psi_0 \right\} dz. \quad (19)$$

As can readily be obtained from the expressions for ψ^- and ψ_0 , the expression in the square brackets of (19) is equal to $-2m(z) \omega \psi^- \psi_0$, whence we get finally

$$M^{(1)}(p, \omega) = -2 \int_{-\infty}^{\infty} \xi(z) m(z) \psi^- \psi_0 dz, \quad (20)$$

where

$$\xi(z) \equiv \int \left(i \omega A_z(z') - \frac{\partial A_0(z')}{\partial z'} \right) dz' = \int \mathcal{E}_z(z') dz' \quad (20')$$

($\mathcal{E}_z(z)$ is the z -component of the electric field of the wave)⁷⁾.

The choice of the limit in the integral (20'), which determines $\xi(z)$, is based on considerations of convenience in calculation, since it follows from the equations satisfied by the functions ψ^- and ψ_0 that

$$\int_{-\infty}^{\infty} [m(z) \psi^-(z) \psi_0(z)] dz = 0.$$

It is also useful to use a somewhat different form of (20). Namely, bearing in mind that ψ^- satisfies the same equation as ψ_0 except that E is replaced by $E + \omega$, and writing the equation for ψ^- in the form $\hat{S} \psi^- = 0$, we readily get from (5)

$$\psi_0 = -\frac{1}{2m(z)\omega} \hat{S} \psi_0. \quad (21)$$

Using now in (20) this substitution as well as the Hermitian character of the operator \hat{S} , we can rewrite (20) in the form

$$M^{(1)} = \frac{1}{\omega} \int_{-\infty}^{\infty} \left(2\mathcal{E}_z \psi_0 \frac{\partial \psi^-}{\partial z} + \frac{\partial \mathcal{E}_z}{\partial z} \psi^- \psi_0 \right) dz. \quad (22)$$

Attention is called to the evident gauge invariance of the expressions (20) and (22).

If we assume, as is customarily done^[13,17,18], that $\mathcal{E}(z)$ is described in all of space by a plane wave and

$$\mathcal{E}_z(z) = \mathcal{E}_0 \sin \theta \sin \Phi e^{i\omega z \cos \theta},$$

where \mathcal{E}_0 is the amplitude of the incident wave, θ is the angle of incidence, and Φ is the angle between the plane of polarization and plane of incidence) then the second term of (22) can be omitted at the wavelengths under consideration, and in the first term $\mathcal{E}_z(z)$ can

⁶⁾The corresponding expression can be obtained rigorously by solving the nonstationary problem with adiabatic application of the interaction at $t = -\infty$ [24]. In this case it is most convenient to use the formalism that employs a retarded Green's function.

⁷⁾When we write $\xi(z)$ in the form of an integral of $\mathcal{E}_z(z)$, we make use of the fact that a nonvanishing contribution to the probability of the transition under consideration can be made only by the first terms in the expressions for the potentials (4).

be replaced by $\mathcal{E}_0 \sin \theta \sin \Phi$ (dipole approximation). Transforming (22) once more by means of the substitution (21) with allowance for (14), we obtain

$$|M^{(1)}(p, \omega)|^2 = \frac{\mathcal{E}_0^2 \sin^2 \theta \sin^2 \Phi}{\omega^4} \times \left| \int_{-\infty}^{\infty} \left[\frac{dU}{dz} - (U+V) \frac{1}{m(z)} \frac{dm(z)}{dz} \right] \Psi^{-1} \Psi_0 dz \right|^2. \quad (23)$$

As seen from (23), the integrand differs from zero only in a narrow region $\sim \delta$ near the surface and does not depend explicitly on ω .

Bearing in mind that the energy flux in the incident wave is $J \sim \mathcal{E}_0^2 \cos \theta$, we obtain for the quantum yield Y , i.e., the number of photoelectrons per incident photon,

$$Y \sim \omega^{-3} \text{tg } \theta \sin \theta \sin^2 \Phi. \quad (24)$$

This result (under the additional assumption $\Phi = \pi/2$) was obtained in the model of an ideal electron gas in a square box^[17]. As seen from the foregoing, however, it is not at all connected with the choice of the form of the potential barrier, and it follows only from the assumption that the z -component of the electromagnetic wave does not attenuate in the metal over distances that are significant for the surface photoeffect.

It is more reasonable, however, to use for \mathcal{E}_2 the expression obtained by considering the reflection of an electromagnetic wave in a medium having a real dielectric constant that varies continuously to negative values^[25], since real negative values of the dielectric constant are characteristic of metals in the frequency region under consideration^[26]. This case is to a certain degree the reverse of that considered earlier, since the wave field attenuates here very rapidly inside the metal.

Since the effective dielectric constant ϵ_ω is larger than zero outside the metal and is negative inside the metal, it goes through zero at a certain point z_0 within a region δ near the surface. In accordance with^[25], the electric field in the vicinity of z_0 is determined by the expression

$$\mathcal{E}_z(z) = -\frac{2\mathcal{E}_0 \sin \theta \sin \Phi}{a(z-z_0) + i\kappa}, \quad (25)$$

where $a(\omega) > 0$ is the coefficient of expansion of the function $\epsilon_\omega(z) = a(\omega)(z-z_0) + \dots$. The appearance of an imaginary increment κ ($\kappa > 0$) is connected with the presence in the general case of a small positive imaginary component of the quantity ϵ_ω ^[25].

Integrating (20) once by parts and using (25) we get⁸⁾ $j \sim J |a(\omega)|^{-2}$. Since $a(\omega)$ usually depends weakly on ω for metals at frequencies that are sufficiently close to the threshold frequency ω_0 ⁹⁾, we get for the quantum yield

⁸⁾The possible below-threshold Coulomb "beats" are of no significance here in view of the further averaging over the continuous spectrum of the electrons in the metal.

⁹⁾In the "free" electron approximation, when $\epsilon_\omega(z) = 1 - [\omega^*(z)/\omega]^2$ (here $\epsilon_\omega(z) = 4\pi c^2 N(z) m_0$, where $N(z)$ is the electron density), bearing in mind that $\omega^*(z_0) = \omega$, we get

$$a(\omega) = \frac{\partial \epsilon_\omega}{\partial z} \Big|_{z=z_0} = -2 \frac{d}{dz} (\ln \omega^*(z))_{z=z_0},$$

where $a(\omega)$ does not depend on ω when $N(z)/m_0 \sim \exp(-kz)$.

$$Y \sim \omega \text{tg } \theta \sin \theta \sin^2 \Phi. \quad (26)$$

In the general case the explicit dependence of Y on ω can lie between (24) and (26), and can be determined only by solving the separate problem of the damping of the normal component of the electric field of the light wave on the boundary.

5. EXPRESSION FOR THE INTEGRAL DENSITY OF THE PHOTOCURRENT

Substituting (16) in (1) we obtain for the integral density of the photocurrent I , in the single-photon approximation,¹⁰⁾

$$I = \int_{-\omega-V}^{\infty} \frac{dE}{1 + \exp\{(E-\mu)/kT\}} \int_0^{\sqrt{2m(E+V+\omega)}} \zeta \frac{p_\alpha}{m} [1 - \exp(-p_\alpha/p)]^{-1} \times \rho(E, p_\parallel) 2\pi |p_\parallel| d|p_\parallel|. \quad (27)$$

The quantity μ in (27) is expressed in terms of the threshold frequency of the single-photon photoeffect (red boundary), defined by the condition $\omega_0 = W$, where W is the work function of the electron from the Fermi surface. The quantity μ in (27) is expressed in terms of the threshold frequency of the single-photon photoeffect (red boundary), defined by the condition $\omega_0 = W$, where W is the work function of the electron from the Fermi surface of the metal into the surrounding medium. In the case under consideration $W = -(\mu + V)$ and therefore

$$\omega_0 = -(\mu + V). \quad (28)$$

Substitution of the threshold expression (16) in (27) is obviously justified if the conditions

$$|\omega - \omega_0| < E_F, \quad |\omega - \omega_0| < 1/2m\delta^2 \quad (29)$$

which follow from (12) and (14), are satisfied, in view of the presence in the distribution factor of a cutoff factor. The quantity E_F in (29), $E_F = |U + V + \omega_0|$, is the Fermi energy in the metal, reckoned from the bottom of the conduction band.

The factor $\rho(E, p_\parallel)$ in (27) varies little in the integration region if the conditions (29) are satisfied, and can be taken outside the integral sign at a certain average point. Then, integrating with respect to $|p_\parallel|$, we obtain for the two limiting cases (17a) and (17b), after simple transformations,

$$I = \mathcal{A}_0 \chi_\alpha T^2 \int_0^\infty \frac{x}{e^{x-\beta} + 1} dx, \quad (30a)$$

$$I = \mathcal{A}_0 \chi T^2 \int_0^\infty \frac{x^{3/2}}{e^{x-\beta} + 1} dx. \quad (30b)$$

Here \mathcal{A}_0 is the Sommerfeld constant, given in dimensional units by $\mathcal{A}_0 = 4\pi e k^2 m_e / (2\pi \hbar)^3 = 120 \text{ A/cm}^2 \text{-deg}^2$; χ_α and χ are certain functions determined by the properties of the metal and of the interface, and do not depend explicitly on T ; $\beta \equiv (\omega - \omega_0)/kT$.

Thus the main laws governing the surface photoeffect in the near-threshold region of frequencies are

¹⁰⁾It is assumed that the projections of the Fermi surface $E = \mu$ and of the equal-energy surfaces $E + \omega$ on the plane $(p_x p_y)$ includes a sufficient vicinity of the origin (see also the remarks concerning surface resonant levels at the end of the article).

determined respectively by the behavior of the functions that depend only on $\beta = (\omega - \omega_0)/kT$

$$B_1(\beta) = \int_0^{\infty} \frac{x}{e^{x-\beta} + 1} dx,$$

$$B_{3/2}(\beta) = \int_0^{\infty} \frac{x^{3/2}}{e^{x-\beta} + 1} dx. \quad (31)$$

Expression (30a) coincides with the final formula for the photocurrent density in Fowler's theory^{[15], 11)} Expression (30b), which is obtained if the long-range Coulomb forces are insignificant, has an entirely different character¹²⁾. In particular, when $(\omega - \omega_0) \gg kT$, when the Fermi distribution can be replaced by the θ -function $\theta(\beta - x)$, we get from (30)

$$I = A_0 \chi_\alpha \frac{(\omega - \omega_0)^2}{2k^2}, \quad \beta \gg 1, \quad (32a)$$

$$I = A_0 \chi_\alpha \frac{4}{15} \frac{\sqrt{2m}}{p_\alpha k^2} (\omega - \omega_0)^{5/2}, \quad \beta \gg 1. \quad (32b)$$

Thus, in the case of photoemission into vacuum or into a dielectric with ϵ close to unity, the "parabolic" Fowler's law $I \sim (\omega - \omega_0)^2$ holds in the region $\beta \gg 1$. To the contrary, in the case of photoemission into a medium in which "screening" of the surface takes place (say into an electrolyte solution), the laws (30b)–(32b) should hold directly in the threshold region, for in this case $p_\alpha = 0$; when $\beta \gg 1$ we get "5/2 law" $I \sim (\omega - \omega_0)^{5/2}$.

In the reduction of the experimental results with the aid of the theory of^[15] it is customary to use the function $f(\beta) \equiv \log B_1(\beta)$, called the universal Fowler function^{[19, 20] 13)}, obviously, when comparing (30b) with experiment it may be convenient to use the universal function

$$b(\beta) \equiv \lg \left(\int_0^{\infty} \frac{x^{3/2}}{e^{x-\beta} + 1} dx \right), \quad (33)$$

a plot of which is shown in Fig. 1. For comparison, we also show there a plot of the function

$$f(\beta) \equiv \lg \left(\int_0^{\infty} \frac{x}{e^{x-\beta} + 1} dx \right). \quad (33')$$

Let us see how the transition from the parabolic Fowler's law to the "5/2 law" is effected. A transition of this kind can be observed experimentally in photoemission into a dielectric with sufficiently large values of ϵ ¹⁴⁾. In the case when $\beta \gg 1$ the Fermi distribution

¹¹⁾The well known function $\int_{-\infty}^{\beta} \ln(1 + e^t) dt$ (from the final formula of the theory of^[15]) is obtained from $B_1(\beta)$ by a single integration by parts and subsequent changes of variable $\beta - x = t$.

¹²⁾We note that the function $B_{3/2}(\beta)$ was investigated earlier in connection with a different problem, that of calculating the average energy of an ideal electron gas, and was tabulated in^[27].

¹³⁾For example, in the so-called "isothermal method" the experimental plot of $\log(Y/T^2)$ is made to coincide with the theoretical $f(\beta)$ curve, and χ_α and ω_0 are determined from the shift relative to the origin.

¹⁴⁾We note that in all the foregoing relations it is necessary to substitute not the static value of ϵ , but that corresponding to the spectrum of the photoelectron velocities.

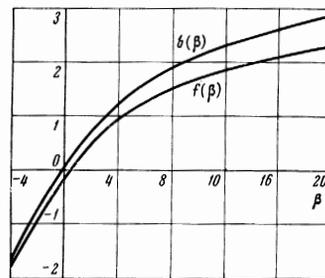


FIG. 1. Plots of the functions $b(\beta)$ and $f(\beta)$, given by formulas (33) and (33') and describing the photocurrents in a medium with Debye screening electrolyte) and in vacuum, respectively.

in (27) can be replaced by a θ -function. Going over to new variables, we obtain after integrating once

$$I = A_0 \chi_\alpha \frac{(\omega - \omega_0)^2}{2k^2} \int_0^1 \frac{2(1-x) dx}{1 - \exp[-(\gamma x)^{-1/2}]}$$

$$= A_0 \chi_\alpha \frac{(\omega - \omega_0)^2}{2k^2} \begin{cases} 1 + 8\gamma e^{-1/\sqrt{\gamma}} + \dots & \gamma \ll 1 \\ \frac{8}{15} \sqrt{\gamma} + \frac{1}{2} + \frac{2}{9} \frac{1}{\sqrt{\gamma}} + \dots & \gamma \gg 1. \end{cases} \quad (34)$$

Here $\gamma = (\omega - \omega_0)/E_\alpha$. It is easy to see that formulas (32a) and (32b) are obtained from (34) when $\gamma \ll 1$ and $\gamma \gg 1$ respectively. A plot of the function

$$g(\gamma) \equiv \lg \left(\int_0^1 \frac{2(1-x) dx}{1 - \exp[-(\gamma x)^{-1/2}]} \right) \quad (35)$$

is shown in Fig. 2. We call attention to the fact that $g(\gamma)$ has an inflection point.

As follows from (34), an experimentally observable deviation from Fowler's formula (on the order of several percent) should occur already when

$$(\omega - \omega_0) \sim 10m / m_e e^2 \text{ (eV)}.$$

The energy distribution of the photoemission electrons differs in the general threshold case from that obtained when Fowler's formula is used, and is determined by integrating (17) with respect to $|p_{\parallel}|$. In the two limiting cases under consideration we obtain for the probability of the distribution of the final kinetic energy of the electrons $p^2/2m$, in units of kT ,

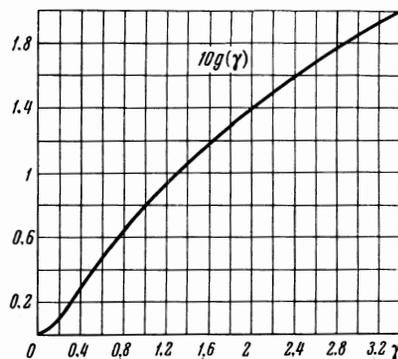


FIG. 2. Plot of the function $g(\gamma)$, given by formula (35) and showing, in a logarithmic scale, the transition from Fowler's law to the "5/2 law."

$$dw(u) = \frac{2}{\beta^2} \frac{u}{e^{u-\beta} + 1} du \quad (\beta \gg 1, \gamma \ll 1), \quad (36a)$$

$$dw(u) = \frac{5}{2\beta^{5/2}} \frac{u^{3/2}}{e^{u-\beta} + 1} du \quad (\beta \gg 1, \gamma \gg 1). \quad (36b)$$

Here $u \equiv p^2/2mkT$. We call attention to the fact that in the second case the most probable final energy is larger than in the first, and consequently the number of slow electrons is smaller.

We emphasize once more that all the foregoing results were obtained without any specific assumptions concerning the form of the potential barrier or the properties of the Fermi surface of the metal (unlike in [13-18]).

We note also the singularities of the external photoeffect on the interface between the metal and the electrolyte solution. The external potential difference applied between the metal and the solution falls off essentially within very short distances from the surface of the metal. Therefore, when a potential φ is applied (polarization of the electrode), a change takes place in the depth of the potential well by an amount $e\varphi$. Accordingly, in agreement with (28), the red edge of the photoeffect should also shift,

$$\omega_0(\varphi) = \omega_0(0) + e\varphi, \quad (37)$$

where $\omega_0(0)$ is its value in the absence of polarization (the potential φ is best reckoned from the so-called zero-charge potential [12]).

The relations obtained for I determine, with allowance for (37), the current-voltage characteristic of the metal-electrolyte system under the conditions of the external photoeffect.

If (29) is violated and the photon energy is already much above the threshold, the photocurrent should start decreasing. This is seen, for example, from (18), if at relatively large energies we replace in it the function ψ^- by a plane wave; in this case, in accordance with the known properties of the Fourier transformation, the quantity ψ_f , and with it also j , will decrease with increasing p (with $j \rightarrow 0$ as $p \rightarrow \infty$). This means that if ω increases and (29) is violated, the deviations from (32a) and (32b) should be in the direction of decreasing current I. It also follows from the latter considerations that the point of deviation can be used to determine experimentally a very important characteristic of the metal, namely the quantity δ .

With further increase of the frequency, however, the decrease of the surface photoemission current can be masked by the incipient volume photoeffect.

6. COMPARISON WITH EXPERIMENT. CONCLUSION

Greatest interest attaches to a verification of the “ $5/2$ law” predicted by the theory developed here. This can be done by directly measuring the dependence of the photocurrent on the interface between a metal and an electrolyte solution as a function of the applied potential difference when illuminated with monochromatic light. A number of such investigations were performed recently [8-10]. Barker, Gardner and Sammon [8] obtained data on the surface photoeffect on the boundary between liquid mercury and aqueous solutions of electrolytes of different compositions. They attempted to interpret the results with the aid of a quadratic depend-

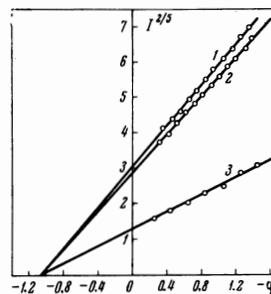


FIG. 3. Reduction of the experimental results of [8] with the aid of formulas (32b) and (37). The ordinates represent the photocurrent raised to the $2/5$ power (in relative units) as a function of the electrode potential with the sign reversed (in volts); zero corresponds to the potential of a standard calomel electrode. 1—0.2M solution of KCl, saturated N_2O ; 2—0.2M solution of NaF, saturated N_2O ; 3—0.2M solution of KCl + 3.3×10^{-3} M solution of N_2O . Wavelength of light 2537 Å.

ence of the photocurrent on the applied potential difference, in accordance with Fowler's law [(32a) with (37) taken into account]. However, the experimental points did not fit on straight lines, making it necessary to construct graphs consisting of two straight lines.

The same experimental data were reduced by us with the aid of formulas (32b) and (37). As seen from Fig. 3, we obtained, in good agreement with the theory, for a fixed light frequency and for solutions of different compositions, a family of straight lines emerging from a single point. Knowing the potential at the point of intersection and the energy of the radiation quantum, it is possible to determine with the aid of (37) the work function of a fast electron from mercury into water at the zero-charge potential. This quantity turns out to be $W_{H_2O} = 3.3$ eV.¹⁵⁾ The difference between this value and the work function in vacuum ($W_V = 4.5$ eV) characterizes the energy of interaction between the epithermal electron and the water.

An agreement with the “ $5/2$ law” in the case of the photocurrent on the interface between mercury and an electrolyte solution is obtained also when other data are used [9].

We emphasize that the above-described use of relations (32b) and (37) to determine the work function is essentially a new method of experimentally measuring this quantity, differing from the hitherto employed isothermal and isochoric methods [19], in which one varies the radiation frequency and the temperature of the metal respectively.

In the proposed “method of varying the electrode potential” the measurements can be performed at a fixed electrode temperature and using only one emission frequency. It is very important that besides the potential of the electrode, it is possible also to vary the concentration and the composition of the solution, the structure of the solvent, etc.¹⁶⁾

¹⁵⁾The obtained value agrees with general thermodynamic estimates [28], according to which W_{H_2O} should be “somewhat larger than 3 eV.”

¹⁶⁾We note that the $\chi_\alpha(\omega)$ dependence cannot distort the results of measurements by the method of varying the potential, unlike the results of the isothermal method, where it is tacitly assumed that $\chi_\alpha = \text{const}$.

Experiments on photoemission into vacuum, as already indicated, confirm well Fowler's theory, and by the same token formula (32a). We emphasize here that the agreement with experiment was obtained under the assumption that χ_α depends weakly on the frequency. This may prove, in accordance with the results of Sec. 4, that the z-component of the light wave practically does not penetrate into the metal. In this connection, it is of particular interest to determine experimentally with greater accuracy the explicit dependence of the photocurrent on the frequency.

Let us stop to discuss further the results of the experiments on the photoeffect on a metal-dielectric interface in which are included such secondary effects as the influence of the field of the resultant electron cloud. Goodman^[6] investigated the photoemission from gold into the conduction band of silicon oxide. He observed deviations from Fowler's law in that the photocurrent started to increase at $(\omega - \omega_0) \sim 0.5$ eV, in agreement with formula (34) at a reasonable value of the dielectric constant ϵ .

We emphasize that, in accordance with the statements at the end of Sec. 5, the deviations from Fowler's law due to the violation of (29) should lead, to the contrary, to a decrease of the photocurrent with increasing ω . The inadequacy of Fowler's theory in describing photoemission into dielectrics was noted also by other workers^[4,5], but owing to the limited amount of presented data it is impossible to perform a full quantitative comparison with the theory.

Special notice should be taken of one particular cause of the possible deviation from the foregoing laws at low values of $\omega - \omega_0$ inside the threshold region. Besides the incipient influence of the structure of the liquid or the dielectric, as well as of thermal fluctuations which assume an important role when $|\omega - \omega_0| \sim kT$, the deviation may be due to the appearance of resonant surface electron levels, which lead to a strong dependence of the wave function on the energy when the quantity $\omega - \omega_0$ is close to the resonant value (usually on the order of several tenths of an electron volt). The formation of such levels can be for example, the consequence of the existence of complexes with charge transport or other forms of chemical bonds on the surface of the metal^[10]. An important method of verifying the foregoing considerations may be also the analysis of the energy distribution of the photoelectrons.

In conclusion, it should be noted that the general approach used in this paper can be used also in many other cases, particularly in an analysis of the different forms of secondary emission in the region of low energies, the internal photoeffect, thermal desorption, etc.

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