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#### Energy Distributions of Photoelectrons from Metals due to a Surface Effect\*

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Expressions are derived for the distribution in total energy of photoelectrons from a metal on the basis of the alternative assumptions concerning the photon absorption process made by DuBridge and by Fowler. The calculations are exact, avoiding the usual approximation that the frequency of the incident light must be near the threshold frequency. Expressions are given not only for the distribution in energy of electrons emitted in all directions but also for the energy distribution as a function of emission angle.

# I. INTRODUCTION

ARIOUS mechanisms have been proposed to describe the distribution in total energy of the photoelectrons emitted from a metal. The common characteristic of nearly all of the theoretical treatments is the assumption of the validity of the Sommerfeld model of a metal in which the energy states available to the free or conduction electrons are uniformly distributed in momentum space and in which the probability of occupation of a state is given by the Fermi function.

Differences among these theoretical approaches lie in the assumption about the way in which the probability of absorption of a photon depends upon the electron's initial and final states and in the assumption about the probability that the excited electron will escape the metal over the potential energy step at the surface.

In calculating the total energy distribution, Du-Bridge<sup>1,2</sup> assumed (1) that the probability of absorption of a photon was independent of the initial state of the electron, (2) that in absorbing the photon energy,  $h\nu$ , the direction of the electron velocity did not change, and (3) that an electron would escape from the metal if its "normal energy" (kinetic energy associated with that component of velocity normal to the surface) is sufficient to overcome the surface potential energy barrier  $W_a$ ; that is, the escape probability is 1 if the normal kinetic energy after the absorption of the photon is greater than  $W_a$ , and is 0 if the normal energy is less than  $W_a$ . By making approximations valid if  $\nu$ , the frequency of the incident light, is not much greater than  $\nu_0$ , the threshold frequency at absolute zero, DuBridge was able to show that the total energy distribution was proportional to the product of E, the kinetic energy outside the metal, and the Fermi factor  $= 1/\{1+\exp[(E-E_{\max})/kT]\}$ , where  $E_{\max}$  is the maximum kinetic energy of emission at 0°K.

In deriving an expression for the spectral distribution of photoelectrons near the threshold frequency, Fowler<sup>3</sup> made assumptions (1) and (3) above, but assumed in place of (2) that all of the absorbed photon energy  $h\nu$  went to increasing the electron's normal kinetic energy and that the velocity components parallel to the surface were unchanged. (This distinction between the DuBridge assumption and the Fowler assumption is clearly stated by Darrow<sup>4</sup> and by Rudberg.<sup>5</sup> DuBridge himself used<sup>1,2</sup> Fowler's assumption in his calculation of the energy distribution of *normal* energies. That there is still confusion on this point is shown by Maurer's<sup>6</sup> statement that in calculating the distribution in energy of photoelectrons from a metal the assumptions used by DuBridge "were those adopted by Fowler in his treatment of the spectral distribution function . . . the absorption of a quantum was assumed not to alter the direction of motion of the electron." Maurer's subsequent development is then based on Fowler's assumption that the absorption of a quan-

<sup>\*</sup> Work supported by the National Science Foundation. <sup>1</sup> L. A. DuBridge, Phys. Rev. 43, 727 (1933). <sup>2</sup> L. A. DuBridge, New Theories of the Photoelectric Effect (Hermann & Cie, Paris, 1935).

<sup>&</sup>lt;sup>3</sup> R. H. Fowler, Phys. Rev. 38, 45 (1931).
<sup>4</sup> K. K. Darrow, Rev. Sci. Instr. 4, 467 (1933).
<sup>5</sup> E. Rudberg, Phys. Rev. 48, 811 (1935).
<sup>6</sup> R. J. Maurer, *Handbook of Physics* (McGraw-Hill Book Company, Inc., New York, 1958), pp. 8–66.

tum does change the direction of the electron.) Rudberg<sup>5</sup> calls this assumption "Fowler 2" and has used it to calculate the total energy distribution function. He shows that in the approximation,  $\nu$  near  $\nu_0$ , it reduces to the same as that calculated by DuBridge, namely, the first power of the energy times the Fermi factor.

A more complicated assumption by Fowler,<sup>3</sup> in which the probability of absorption of a quantum does depend upon the initial state of the electron, leads to an approximate energy distribution function involving  $E^{\frac{1}{2},5}$ The development of Mitchell<sup>7</sup> leads to an approximate energy distribution function involving  $E^{\frac{3}{2},5,8}$  Hill<sup>9</sup> considered various types of surface barriers and the corresponding functions to describe the probability that an electron will absorb a quantum and then escape through the surface. If he makes the assumption that this probability depends only on the rate at which the electrons appear at the surface, his approach essentially reduces to that based on the "Fowler 2" assumptions and his energy distribution function has the same linear dependence on E. Buckingham's<sup>10</sup> study of the dependence of the effective surface barrier on the momentum of the impinging electrons leads to no essential change in the form of the energy distribution.

The common feature of the distribution functions described above is the Fermi factor. This factor dominates the shape of the distribution function in the vicinity of maximum energy. That it is correct was shown convincingly by Roehr<sup>1,11,2</sup> who analyzed his experimental current-voltage curves according to the method invented by DuBridge.<sup>1,2</sup> DuBridge's method involves the plotting of current-voltage data in a way analogous to that devised by Fowler<sup>3</sup> for the analysis of spectral distribution data.

In the low-energy region the shape of the experimental energy distribution curves of Roehr<sup>11</sup> for molybdenum and Brady<sup>12</sup> for potassium showed an upward curvature which gives strength to Mitchell's theory predicting an  $E^{\frac{3}{2}}$  dependence. However, Liben's<sup>13</sup> measurements on calcium, made by deflecting electrons in a magnetic field, would tend to show a linear dependence



- <sup>7</sup> K. Mitchell, Proc. Roy. Soc. (London) A146, 442 (1934).
  <sup>8</sup> K. Mitchell, Proc. Roy. Soc. (London) A153, 513 (1936).
  <sup>9</sup> A. G. Hill, Phys. Rev. 53, 184 (1938).
  <sup>10</sup> M. J. Buckingham, Phys. Rev. 80, 704 (1950).
  <sup>11</sup> W. W. Roehr, Phys. Rev. 44, 866 (1933).
  <sup>12</sup> J. J. Brady, Phys. Rev. 46, 768 (1934).
  <sup>13</sup> L. Libar, Phys. Rev. Bar, 51 (42 (1927)).

- <sup>13</sup> I. Liben, Phys. Rev. 51, 642 (1937).

on energy were it not for the peculiar failure of the distribution curves to go through the origin. The energy distribution curves obtained by Hill<sup>9</sup> for sodium change shape so drastically with the frequency of the incident light that they cannot be taken as evidence for or against the validity of any of the competing theories.

The difficulties involved in making meaningful energy distribution measurements have been described by Apker, Taft, and Dickey.<sup>14</sup> By carefully avoiding contact potentials between a tungsten emitter and its supports they have shown that, except for the high-energy tail, the current-voltage characteristic is truly parabolic. From this it follows that the energy distribution curve, obtained by differentiation of the current-voltage characteristic, is truly linear in the low energy region.

Thus it appears that the best experimental data for tungsten, at least, agree with the form of the energy distribution function derivable from the simplest mechanism, that of DuBridge or that of Fowler.

It is the function of this paper to develop in detail the distribution functions which follow from these two sets of assumptions and to do this in an exact way whose validity is not restricted to values of  $\nu$  near  $\nu_0$ . A comparison with the development of DuBridge's assumptions by DuBridge himself and of Fowler's assumptions by others reveals the features which have forced these earlier arguments into approximations. A novel feature of the present development is that it gives not only expressions for the distribution in energy of electrons emitted in all directions but also simple expressions for the energy distribution of photoelectrons as a function of emission angle.

This paper is restricted to a discussion of the surface photoelectric effect in which absorption of a photon by an electron is possible because of the potential energy step at the surface of a metal. Because the potential in the interior of a Sommerfeld metal is uniform, the electrons in the conduction band are completely free, unable to absorb photons because of the impossibility of the simultaneous conservation of momentum and energy. In a more realistic model of a metal which recognizes the periodic nature of the potential, the electrons in the conduction band are only quasi-free and are able to interact wih the lattice. Such electrons can absorb photons and then escape the metal, giving rise to a volume photoelectric effect.15,16

#### II. GENERAL

## a. Nomenclature

The problem will be discussed in terms of spherical coordinates  $r, \theta, \phi$ , where  $\theta$  is the angle between the r

<sup>14</sup> L. Apker, E. Taft, and J. Dickey, Phys. Rev. 73, 46 (1948). <sup>15</sup> Experimental evidence for a volume effect is given by meas-urements of the distribution in energy of electrons from low work function alkali metals illuminated by high-energy photons. Such measurements, which show a preponderance of low-energy elec-trons, have been described by J. Dickey, Phys. Rev. 81, 612 (1951) and by S. Methfessel, Z. Physik 147, 442 (1957).

<sup>16</sup> For a recent discussion of the volume photoelectric effect in metals see A. Meesen, J. phys. radium **22**, 308 (1961).

vector and the z axis. The z direction is chosen normal to the surface of the metal.  $\phi$  is the angle between the projection of the r vector on the plane of the surface and the x axis. In such spherical coordinates a small increment of solid angle  $\equiv d\Omega = \sin\theta d\theta d\phi$ .

The relation between spherical and Cartesian coordinates in *velocity space* is shown in Fig. 1. The component of a velocity normal to the surface is  $v_z = v \cos\theta$ . An incremental volume of velocity space  $\equiv d\tau = v^2 dv$  $\times \sin\theta d\theta d\phi$  which, expressed in terms of solid angle, is  $v^2 dv d\Omega$ .

The energy symbols used are those defined in Fig. 2 which shows the energy diagram traditional in discussions based on the Sommerfeld theory of a metal. The zero of energy is chosen as the potential energy inside the metal.  $W_a$  is the height of the potential energy barrier at the surface of the metal.  $\mu$  is the Fermi level which equals the energy of the most energetic electrons at absolute zero of temperature.  $\psi$  is the work function  $=W_a-\mu=h\nu_0$ , where  $\nu_0$  is the threshold frequency at absolute zero.  $E_1$  is the energy of a particular electron before it has absorbed a quantum.  $E_2 = E_1 + h\nu$  is the energy of that electron after it has absorbed a quantum. Because of the choice of the zero of energy,  $E_1$  and  $E_2$ equal the kinetic energies, before and after quantum absorption, of the electron inside the metal. After the electron has escaped from the metal, its kinetic energy is

$$E = E_2 - W_a = E_1 + h\nu - W_a. \tag{1}$$

The subscript 1, whether applied to an energy, velocity, or angle refers to the electron before it absorbs the quantum, subscript 2 refers to the electron after it has been excited, and no subscript refers to the electron after it has escaped the metal.

# b. Energy Distribution Inside the Metal

The velocity distribution function of the electrons before excitation is defined as  $N(\tau_1) = dN/d\tau_1$  = the number of electrons per unit volume of the metal per unit volume of velocity space. That is,  $dN = N(\tau_1)$  $\times d\tau_1$  = the number of electrons per unit volume of the metal which have velocities in the velocity space interval  $d\tau_1$ . Expressed in terms of spherical coordinates,  $dN = N(\tau_1)v_1^2 dv_1 \sin\theta_1 d\theta_1 d\phi_1$ ; and in terms of the solid angle in which the velocity vectors lie,  $dN = N(\tau_1)$  $\times v_1^2 dv_1 d\Omega$ . By using the relation between kinetic energy and velocity,  $E_1 = mv_1^2/2$ , dN can be expressed as

$$dN = (2/m^3)^{\frac{1}{2}} N(\tau_1) E_1^{\frac{1}{2}} dE_1 d\Omega_1.$$
<sup>(2)</sup>

dN is now thought of as the number of electrons per unit volume of the metal whose directions of motion lie in the solid angle  $d\Omega_1$  and whose kinetic energy is  $E_1$ within the range  $dE_1$ .

According to the Sommerfeld theory of metals the states available to the free conduction electrons are uniformly distributed in velocity space. That is, the number of states per unit volume of the metal per



FIG. 2. Energy diagram for Sommerfeld metal.

unit volume of velocity space equals a constant, c. The probability that a particular state is occupied is given by the Fermi-Dirac distribution function=1/ $(1+e^{(E_1-\mu)/kT})$ , which behaves in the well-known way, being approximately 1 for values of  $E_1$  below the Fermi level  $\mu$ , and approximately 0 for values of  $E_1$  greater than  $\mu$ , the suddenness of the drop from 1 to 0 being less at higher temperatures. Thus  $N(\tau_1)=c/(1+e^{(E_1-\mu)/kT})$ . This can also be written in terms of the kinetic energy of the escaped electrons by writing  $E_1$  as  $E-h\nu+W_a$ . In this event  $E_1-\mu=E-h\nu+W_a-\mu$  $=E-h\nu+\psi=E-(h\nu-\psi)=E-E_{\rm max}$ , where  $E_{\rm max}=h\nu$  $-\psi$  has the physical meaning of the maximum energy of the emitted photoelectrons from the surface of a metal at 0°K. Thus

$$N(\tau_1) = c/(1 + e^{(E - E_{\max})/kT}).$$
(3)

In the development which follows, however, some of the conclusions do not depend upon a knowledge of the proper form of  $N(\tau_1)$ . Interesting results follow from the mild assumption that the initial electron distribution is isotropic, that is, that  $N(\tau_1)$  is not a function of direction.

# c. Rate of Electron Excitation

The rate at which electrons of the type being considered come to unit area of the surface is simply the product of the normal component of velocity and the number of electrons per unit volume, i.e.,  $dN_s' = v_{z_1} dN$  $= v_1 \cos\theta_1 N(\tau_1) d\tau_1$ . This rate can be written in terms of velocity as  $dN_s' = N(\tau_1) v_1^3 dv_1 \cos\theta_1 \sin\theta_1 d\theta_1 d\phi_1 = N(\tau_1)$  $\times v_1^3 dv_1 \cos\theta_1 d\Omega_1$  or, in terms of energy, as

$$dN_s' = (2/m^2)N(\tau_1)E_1dE_1\cos\theta_1\sin\theta_1d\theta_1d\phi_1 \quad (4a)$$

$$= (2/m^2)N(\tau_1)E_1dE_1\cos\theta_1d\Omega_1.$$
(4b)

These electrons will absorb photons at a rate,  $dN_a'$  which is some fraction, a, of the rate at which they come to the surface,  $dN_s'$ . That is,  $dN_a' = adN_s'$  where a, the probability that an electron will absorb a photon, is a linear function of the light intensity. For the moment, a may be considered a function also of photon energy, electron energy, and electron direction.

## d. Coordinate Transformation for Going Over a Potential Barrier

When an electron escapes from a metal it goes over a potential energy barrier,  $W_a$ . This has the effect of reducing the component of the electron's velocity normal to the surface but the components of velocity parallel to the surface remain constant. This means, in terms of symbols introduced earlier, that  $\phi$  remains constant ( $\phi_2 = \phi$ ) and that  $v_2 \sin\theta_2 = v \sin\theta$ . This latter result, written in terms of energy, is  $E_2 \sin^2\theta_2 = E \sin^2\theta$ , which leads by differentiation to

$$E_2 \sin\theta_2 \cos\theta_2 d\theta_2 = E \sin\theta \cos\theta d\theta. \tag{5}$$

The rate,  $dN_e'$ , at which electrons escape from the metal will be in general some fraction, t, of the rate,  $dN_a'$ , at which they have come to the surface and absorb photons. That is,

$$dN_{e}' = tdN_{a}' = atdN_{s}', \tag{6}$$

where  $dN_s'$  is given by Eq. (4). For the moment t may be considered a function of electron energy and electron direction although both the DuBridge assumptions and the Fowler assumptions include t=1.



FIG. 3. Normalized energy distribution functions. (a) DuBridge  $(v_{z_1})$ ; (b) DuBridge  $(v_{z_2})$ ; (c) Fowler  $(v_{z_1})$ ; (d) Fowler  $(v_{z_2}, \theta=90^\circ)$ ; (e) Fowler  $(v_{z_2}, \theta=0^\circ)$ .

#### **III. DUBRIDGE ASSUMPTION**

#### a. Exact Results

In calculating the total energy distribution function DuBridge assumed that the absorption of a quantum did not change the direction of motion of the electron. (This is assumption 2 in the Introduction.) In terms of the symbols used here this means that  $\phi_1 = \phi_2$  and  $\theta_1 = \theta_2$ . When these substitutions are made and  $E_1$  written in terms of  $E_2$  [Eq. (1)], Eq. (4) converts to  $dN_s' = (2/m^2)$  $\times N(\tau_1)(E_2 - h\nu)dE_2 \cos\theta_2 \sin\theta_2 d\theta_2 d\phi_2$ . Equation (5) and the fact that  $\phi_2 = \phi$  allows this to be written as  $dN_s'$  $= (2/m^2)N(\tau_1)(E_2 - h\nu)dE_2(E/E_2) \cos\theta \sin\theta d\theta d\phi$ . By writing  $E_2$  in terms of E [Eq. (1)], this becomes

$$dN_{s}' = (2/m^{2})N(\tau_{1})\frac{E+W_{a}-h\nu}{E+W_{a}}EdE\cos\theta\sin\theta d\theta d\phi \quad (7a)$$

$$= (2/m^2)N(\tau_1) \frac{E + W_a - h\nu}{E + W_a} E dE \cos\theta d\Omega.$$
(7b)

The rate at which electrons escape from unit area of the surface is given by Eq. (6) as

$$dN_{s}' = atdN_{s}' = at(2/m^{2})N(\tau_{1})$$

$$\times \frac{E + W_{a} - h\nu}{E + W_{a}} EdE \cos\theta \sin\theta d\theta d\phi \quad (8a)$$

$$=at(2/m^2)N(\tau_1)\frac{E+W_a-h\nu}{E+W_a}EdE\cos\theta d\Omega.$$
 (8b)

Thus, in a given direction  $\theta$ , the photoelectric current per unit surface area, per unit solid angle per unit energy of the emitted electrons is

$$\frac{dN_{e}'}{d\Omega dE} = at(2/m^2)N(\tau_1)\frac{E+W_a-h\nu}{E+W_a}E\cos\theta.$$
 (9)

Notice the implication of this equation if a (the absorption factor), t (the escape factor), and  $N(\tau_1)$  (the initial distribution factor) are all functions of energy alone. It is that the energy distribution of the emitted electrons is also isotropic except for the Lambert's law factor,  $\cos\theta$ . With these assumptions Eq. (8a) can be integrated over all directions of emission to give the total energy distribution function:

$$\int \int dN_{e}' = at(2/m^{2})N(\tau_{1})\frac{E+W_{a}-h\nu}{E+W_{a}}EdE$$

$$\times \int_{0}^{\pi/2}\cos\theta\sin\theta d\theta \int_{0}^{2\pi}d\phi$$

$$= at(2\pi/m^{2})N(\tau_{1})\frac{E+W_{a}-h\nu}{E+W_{a}}EdE.$$
(10)

As described in the Introduction, DuBridge's other assumptions were: (1) a = constant at a fixed frequency, (3) t=1, and also that  $N(\tau_1)=c/(1+e^{(E-E_{\max})/kT})$ . Under these assumptions the exact shape of the energy distribution function is

$$\int \int dN_{e'} \propto \frac{E + W_a - h\nu}{E + W_a} \times \frac{EdE}{1 + e^{(E - E_{\max})/kT}}.$$
 (11)

This function is shown as solid curve (a) in Fig. 3. The curves of Fig. 3 have been drawn for the special case of tungsten, at a temperature of absolute zero, illuminated by light of wavlength approximately 1000 A  $(h\nu = 12.0 \text{ ev})$ .

Experimentally determined values for tungsten are: the work function  $\psi = 4.5 \text{ ev}$ ,<sup>14</sup> the potential energy step at the surface  $W_a = 12.5 \text{ ev}$ .<sup>17</sup>

#### b. Comparison with the DuBridge Development

By making approximations valid if  $\nu$  is near  $\nu_0$ , DuBridge derived an energy distribution function of the form  $EdE/(1+e^{(E-E_{\max})/kT})$ . That Eq. (11) also reduces to this form in the same approximation can be shown by writing the ratio  $(E+W_a-h\nu)/(E+W_a)$  as  $1-h\nu/(E+W_a)$ . This is almost constant if the range of E (from 0 to  $E_{\max}$ ) is small compared with  $W_a$ , that is, if  $\nu$  is near  $\nu_0$ .

However, the fact that the development by Du-Bridge and the development in this paper lead to the same approximate answer is not a sign that the two approaches are equivalent.

In arriving at his<sup>2</sup> Eq. (44), "in which no approximations have been made," DuBridge uses a concept which has meaning only if the later approximations *are* made. Thus Eq. (44) cannot give an exact answer. The questionable concept is in the following sentence.<sup>2</sup> "If we multiply the number of electrons per unit volume having the velocity  $u_1$ " ( $u_1=v_2$  in our notation) "by the value of the velocity component  $\xi_1$  normal to the surface" ( $\xi_1=v_{z_2}=v_2\cos\theta_2$  in our notation) "we obtain the number arriving at unit area of the surface in unit time." The trouble here is that those electrons having velocity  $v_2$  have many different directions so that one ought not to talk of *the* velocity component normal to the surface.

A second point which seems questionable in the DuBridge argument is the use of  $v_{z_2}$  instead of  $v_{z_1}$  ( $\xi_1$  instead of  $\xi$ ) to obtain the rate at which the electrons arrive at the surface. It is true that after electrons of a particular velocity and direction are excited they have a normal velocity component  $= v_{z_2}$  but nevertheless, the rate at which these electrons come up to the surface is determined by  $v_{z_1}$ .

For sake of comparison an exact energy distribution function has been calculated using the factor  $v_{z_2}$  instead of the correct factor  $v_{z_1}$ . It turns out to be

$$\int \int dN_{e}' \propto \left(\frac{E+W_{a}-h\nu}{E+W_{a}}\right)^{\frac{1}{2}} \times \frac{EdE}{1+e^{(E-E_{\max})/kT}}.$$
 (12)

This function is shown in Fig. 3 as the dotted curve (b). It has been normalized so that its maximum ordinate equals the maximum ordinate of curve (a).

#### **IV. FOWLER ASSUMPTION**

#### a. Exact Result

In calculating the spectral distribution function Fowler assumed that all of the absorbed photon energy,  $h\nu$ , went to increasing the electron's *normal* kinetic energy and that the velocity components parallel to the surface were unchanged. In terms of the symbols used here this means that  $\phi_1 = \phi_2$  and  $v_1 \sin\theta_1 = v_2 \sin\theta_2$ . This latter result, written in terms of energy is  $E_1 \sin^2\theta_1$  $= E_2 \sin^2\theta_2$  which leads by differentiation to  $E_1 \sin\theta_1$  $\times \cos\theta_1 d\theta_1 = E_2 \sin\theta_2 \cos\theta_2 d\theta_2$ . By making this last substitution and using also the facts that  $dE_1 = dE_2$  and  $\phi_1 = \phi_2$ , Eq. (4a) converts to  $dN_s' = (2/m^2)N(\tau_1)$  $\times E_2 dE_2 \cos\theta_2 \sin\theta_2 d\theta_2 d\phi_2.$ 

In going over the potential barrier Eq. (5) holds as well as the relations  $dE_2 = dE$  and  $\phi_2 = \phi$ . Thus  $dN_s'$  becomes

$$dN_s' = (2/m^2)N(\tau_1)EdE\cos\theta\sin\theta d\theta d\phi$$
 (13a)

$$= (2/m^2)N(\tau_1)EdE\cos\theta d\Omega.$$
(13b)

(The above two-step process can be viewed more directly as a one-step process in which the electron surmounts a potential energy step  $=W_a-h\nu$ , i.e., its kinetic energy changes directly from  $E_1$  to  $E_2$ )

From here on the argument is identical to that given in Sec. III (a). The equations analogous to Eq. (8) to Eq. (11) are:

$$dN_{e}' = atdN_{s}' = at(2/m^{2})N(\tau_{1})EdE\cos\theta\sin\theta d\theta d\phi \quad (14a)$$

$$= at(2/m^2)N(\tau_1)EdE\cos\theta d\Omega, \qquad (14b)$$

$$dN_{e}'/d\Omega dE = at(2/m^2)N(\tau_1)E\cos\theta,$$
(15)

$$\int \int dN_e' = at(2\pi/m^2)N(\tau_1)E\cos\theta,$$
(16)

$$\int \int dN_{e'} \propto \frac{EdE}{1 + e^{(E - E_{\max})/kT}}.$$
(17)

The total energy distribution function at T=0 given by Eq. (17) is shown as the solid curve (c) in Fig. 3.

#### b. Comparison with the Usual Derivation Based on Fowler's Assumptions

Most derivations of the energy distribution function based on Fowler's assumptions (for example, references

<sup>&</sup>lt;sup>17</sup> Data by Rupp analyzed by R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, New York, 1936), Table 42.

5 and 6) make use of approximations in arriving at the same expression, Eq. (17), which has been shown above to be exact. Maurer's<sup>6</sup> derivation is forced into an approximation by the same trouble appearing in the DuBridge development, namely the use of a single value of the velocity component normal to the surface to describe the many values of this component belonging to electrons moving in different directions. Combined with the simple assumption that the probability of an electron absorbing a quantum is proportional to the number of times per second that the electron appears at the surface, Hill's<sup>9</sup> approach can lead, without approximations, to Eq. (17), but says nothing about the energy distribution as a function of emission angle as does Eq. (15).

Again for the sake of comparison, an exact energy distribution function can be calculated on the basis of Fowler's assumptions except that the factor  $v_{z_2}$  is used instead of the correct factor  $v_{z_1}$  to determine the rate at which electrons come to the surface. The result analogous to Eq. (14a) is

$$dN_{e}' = at(2/m^{2})N(\tau_{1}) \left(\frac{E+W_{a}}{E+W_{a}-h\nu}\right)^{\frac{1}{2}} EdE\cos\theta\sin\theta d\phi$$
$$\times \left[\frac{1-(E\sin\theta)^{2}/(E+W_{a})^{2}}{1-(E\sin\theta)^{2}/(E+W_{a})(E+W_{a}-h\nu)}\right]^{\frac{1}{2}}.$$
 (18)

This is too complicated to integrate over all directions to give the total energy distribution. However the function has a simple form for emission parallel to the surface ( $\theta = 90^\circ$ ) and for emission normal to the surface ( $\theta = 0^\circ$ ). These extremes are plotted as curves (d) and (e) in Fig. 3.

#### V. SUMMARY AND CONCLUSIONS

The distribution in energy of photoelectrons from a metal has been calculated on the basis of alternative assumptions due to DuBridge and to Fowler as to the mechanism of the photon-absorption process. The derivations are exact, avoiding the approximations usually made. With the approximation of small maximum energy of the emitted electrons, both results give an energy distribution function showing a linear dependence on energy. At larger energies of the emitted electrons the Fowler assumptions lead exactly to the same first power dependence on energy. However, the DuBridge assumptions lead exactly to a function involving a first power dependence modified by a factor which is a slowly varying function of energy.

The calculations have been carried out in terms of energy distributions written as a function of the direction of motion of the electrons, both inside the metal and outside. Thus expressions have been derived for the energy distribution of photoelectrons in terms of the emission angle. The general conclusion is reached that if the factors entering into the photoelectric mechanism are isotropic the energy distribution of the emitted electrons will also be isotropic except for a Lambert's law factor. This conclusion also holds if one makes Fowler's assumption that only the normal component of electron momentum is affected during the photon absorption process.

The validity of the Fowler-DuBridge assumptions, even for a pure surface effect for a real metal, is very much an open question. Indeed, the agreement between the Fowler-DuBridge conclusions and the experimental results for tungsten may be only accidental. It is believed, however, that, given these assumptions, their consequences have been accurately described here.

Although the simple assumptions due to Fowler and to DuBridge have been emphasized, the approach used here is not necessarily restricted to these assumptions. In particular, Eqs. (10) and (16) are valid for any isotropic form of the absorption factor and the escape factor, and Eqs. (9) and (15) are valid for any form whatever of these factors.

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