Two-Photon Photoelectric Effect

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(Received March 2, 1962; revised manuscript received September 6, 1962)

The surface photoelectric current from a pure metal surface is calculated when the frequency of the incident radiation is less than the threshold frequency but greater than one-half the threshold frequency. To do this, second-order stationary perturbation theory is used. The current thus found is normally small. However at great intensities, such as those produced by optical masers, the current might be measurable.

THE photoelectric effect for metals may be subdivided into the volume photoelectric effect and the surface photoelectric effect.[1] The volume photoelectric effect is due to the emission of the bound electrons in the solid. This effect is of little importance near threshold but should not be neglected in general.[2] The surface photoelectric effect is due to the emission of the "free" electrons in the conduction band while they are interacting with the surface barrier. The theory of the surface photoelectric effect from metals has been thoroughly treated by Mitchell.[3] He assumed the electrons moved in a Sommerfeld type of potential and that the energy distribution of the electrons was given by Fermi-Dirac statistics. He also assumed the wavelength of the incident monochromatic wave is large compared to the wavelength of the electrons in the conduction band. Then by using first-order perturbation theory, he found the current from the metal surface. He showed that in the limit for long time, the time-dependent perturbation theory gave the same result as that given by stationary perturbation theory. This paper will draw heavily upon his stationary perturbation calculation.

The inclusion of reflection and refraction in the theoretical treatment of the photoelectric effect in a reasonable manner is difficult. Mitchell[3] used the measured optical constants in a purely classical treatment which implies a discontinuous change in the optical constants at the surface. Since the surface photoelectric effect occurs in a depth of about 10^{-7} cm,[4] this method is subject to a serious objection. Schiff and Thomas[5] developed a quantum-mechanical theory of metallic reflection in an attempt to resolve this difficulty. However their results proved to be too unwieldy to be of much use. Makinson,[6] in a compromise between the pure classical treatment and the quantum-mechanical treatment, tried a semiclassical treatment which added little to the agreement between experimental results and theory. Buckingham[7] has refined Makinson's treatment to include the dependency of the surface barrier for an electron upon the electron's momentum.

To an important extent, the lack of agreement which exists between theory and experiment can be accredited to the great difficulty in producing a pure metal surface for experimental purposes. Minute quantities of dissolved gases may greatly change the photoelectric characteristics of a metal surface.[8]

The treatment used in this paper which neglects reflection, refraction, and surface roughness seems to yield a quantum efficiency much lower, for the first-order perturbation calculations, than the observed values. For sodium it is as much as several hundred times lower. One would hope that this type of favorable disagreement might continue on over to the second-order case also.

The advent of the maser has made available a very intense monochromatic source of electromagnetic radiation in the infrared and visible region.[9–11] The great intensity and narrow linewidth of masers have made possible the performance of several interesting experiments and have encouraged the theoretical development relating to nonlinear effects. Franken[12] has produced the optical second harmonic by using an optical ruby maser. Kaiser and Garrett[13] have reported the observation of a two-photon transition. Bloembergen *et al.*[14,15] have generalized the laws of optics to include the nonlinear effects produced at maser intensities. Kleinman[16] and Braunstein[17] have discussed two-photon processes in crystals and nonlinear optical effects.

As previously mentioned, Mitchell[3] used only first-order perturbation theory in his theoretical treatment of the surface photoelectric effect. For this approximation no photoelectric current can be produced at frequencies

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less than the threshold frequency when the metal is at absolute zero. What is attempted in this paper is the calculation of the surface photoelectric current from a pure metal, using the model which Mitchell developed so successfully, but assuming that the frequency of the incident radiation is less than the threshold frequency but greater than one-half the threshold frequency. To do this, we must use second-order perturbation theory. Realizing the difficulty in achieving agreement between photoelectric theory and experiment, we do not expect to have our results compare in absolute size to experimental results. However, it is hoped that our results will indicate the lower bound for the current. The actual current should be larger, possibly several orders of magnitude larger as this seems to be the case with previous first-order results.

The model which Mitchell[3] used, and which we will use, assumes that the electron moves in a constant potential inside and outside of the metal with a step discontinuity at the metal surface. This model inherently neglects the volume photoelectric effect. We shall assume that monochromatic radiation is incident upon the metal surface. We shall use second-order perturbation theory to calculate the probability flux in the outward normal direction from the metal. This will yield the current density due to a single electron. To find the total current, we shall integrate our result for a single electron over the total number of electrons which can be excited to the free state. In our calculation we shall neglect reflection and refraction of the incident radiation. There exists little promise that the inclusion of any of the previous treatments of reflection would improve significantly the comparison of our results with experimental results.

We shall find that we get a current from the surface when we are at maser's intensities. Furthermore, the escaping electrons, for which we have neglected any type of collisions, will be associated with an energy level $2h\nu$ above their initial energy level. Thus, the Einstein photoelectric equation, which holds at absolute zero, must be modified to state that the maximum kinetic energy of a photoelectron is equal to the sum of the energies of the photons absorbed less the work function of the metal. For our case this becomes

$$KE_{\max}=2h\nu-\phi.$$

We will first calculate the needed wave functions to second order and then the photoelectric current for the specified frequency interval.

CALCULATION OF THE WAVE FUNCTIONS

Let the potential energy of the electron, excluding its interaction with the radiation field, be given by $V(x',y',z')$. Let the radiation field be described by the vector potential $\mathbf{A}$ and the scaler potential Φ, which we set equal to zero. Then from the Lorentz relation, we have that

$$\nabla\cdot\mathbf{A}=0. \tag{1}$$

The wave equation for such a nonrelativistic electron is given by

$$\left[-\frac{\hbar^2}{2m}\nabla'^2+\frac{i\hbar e}{mc}\mathbf{A}\cdot\nabla'+\frac{e^2A^2}{2mc^2}+V\right]\psi=i\hbar\frac{\partial\psi}{\partial t'}. \tag{2}$$

To place this equation in dimensionless form, we make the following substitutions:

$$\begin{aligned}&\boldsymbol{\nabla}=\lambda_0\nabla'/\sqrt{2},\quad \lambda_0=\hbar/mc,\quad t'=\lambda_0 t/c,\\ &W=V/mc^2,\quad \mathbf{G}=e\mathbf{A}/mc^2\sqrt{2}.\end{aligned} \tag{3}$$

We then have that

$$\nabla^2\psi-W\psi+i\frac{\partial\psi}{\partial t}=2i\mathbf{G}\cdot\nabla\psi+G^2\psi. \tag{4}$$

We express ψ in terms of a series expansion as follows:

$$\psi=\sum\psi(n)e^{i(\alpha+n\omega)t}, \tag{5}$$

where n is the summation index which assumes the integer values from $-\infty$ to ∞, where α is a constant which corresponds to $-\lambda_0/\hbar c$ times the energy of the electron when $\mathbf{A}=0$, and ω is $2\pi\lambda_0/c$ times the frequency of the radiation field. Let the vector potential term be given by

$$\mathbf{G}=\mathbf{K}e^{i\omega t}+\mathbf{M}e^{-i\omega t}, \tag{6}$$

where

$$\mathbf{K}=\mathbf{M}^*. \tag{7}$$

Substituting this expression for $\mathbf{G}$ and the expansion for ψ into Eq. (4), we obtain

$$\begin{aligned}\sum\{&[\nabla^2-W-(\alpha+n\omega)-2\mathbf{K}\cdot\mathbf{M}]\psi(n)e^{i(\alpha+n\omega)t}\\ &-2i\mathbf{K}\cdot\nabla\psi(n)e^{i(\alpha+n\omega+\omega)t}-2i\mathbf{M}\cdot\nabla\psi(n)e^{i(\alpha+n\omega-\omega)t}\\ &-K^2\psi(n)e^{i(\alpha+n\omega+2\omega)t}-M^2\psi(n)e^{i(\alpha+n\omega-2\omega)t}\}=0.\end{aligned} \tag{8}$$

The coefficient of each term such as $e^{i(\alpha+k\omega)t}$ must be equal to zero for the above equation to be satisfied. Therefore, we may write

$$\begin{aligned}&[\nabla^2-W-(\alpha+k\omega)-2\mathbf{K}\cdot\mathbf{M}]\psi(k)-2i\mathbf{K}\cdot\nabla\psi(k-1)\\ &-2i\mathbf{M}\cdot\nabla\psi(k+1)-M^2\psi(k+2)-K^2\psi(k-2)=0.\end{aligned} \tag{9}$$

For presently obtainable electromagnetic fields, the number $|\mathbf{G}|$ is much less than one. We assume that $\psi(n)$ is of the order of $|\mathbf{G}|^{|n|}$. Then from Eq. (9) we have, by neglecting all terms of second and higher order in $|\mathbf{G}|$, that

$$[\nabla^2-W-(\alpha-\omega)]\psi(-1)-2i\mathbf{M}\cdot\nabla\psi(0)=0, \tag{10}$$

$$[\nabla^2-W-\alpha]\psi(0)=0, \tag{11}$$

$$[\nabla^2-W-(\alpha+\omega)]\psi(1)-2i\mathbf{K}\cdot\nabla\psi(0)=0. \tag{12}$$

We note that $\psi(1)$ corresponds to an energy level $h\nu$ below the initial state while $\psi(-1)$ corresponds to an energy level $h\nu$ above the initial state, and $\psi(0)$ corre-

sponds to the wave function when there is no electromagnetic field present.

The metal surface will correspond to the yz plane and the metal will extend to $-\infty$ in the x direction. We shall take the xy plane to be the plane of incidence of the radiation, the angle of incidence to be θ. We assume that the electron sees a constant potential inside the metal which is less than the constant potential it sees outside the metal.

Solution for $\psi(0)$

If the potential V has the form

$$V=-h\nu_a, \quad x<0$$
$$=0, \quad x>0$$

then we have

$$W=-W_a=-2\pi\nu_a\lambda_0/c, \quad x<0$$
$$=0, \quad x>0 \tag{13}$$

and we may write Eq. (11) as

$$(\nabla^2+W_a-\alpha)\psi(0)=0, \quad x<0 \tag{14}$$

$$(\nabla^2-\alpha)\psi(0)=0, \quad x>0. \tag{15}$$

The solutions for these equations are well known. If we let

$$(W_a-\alpha)^{1/2}=\beta, \quad \beta^2=\beta_x^2+\beta_y^2+\beta_z^2,$$
$$(-\alpha)^{1/2}=\gamma, \quad \gamma^2=\gamma_x^2+\beta_y^2+\beta_z^2, \tag{16}$$

and

$$Y\equiv e^{i\beta_y y}+e^{-i\beta_y y}, \tag{17}$$

$$Z\equiv e^{i\beta_z z}+e^{-i\beta_z z}, \tag{18}$$

then the solutions are:

For $x<0$,

$$\psi(0)=a(e^{i\beta_x x}+be^{-i\beta_x x})YZ; \tag{19}$$

for $x>0$,

$$\psi(0)=de^{i\gamma_x x}YZ. \tag{20}$$

We see that γ_x will be real and positive if the electron has a positive energy (free for $x>0$) or it is a pure positive imaginary number if the electron has a negative energy. We are free to choose $\beta_x>0$.

Since $\psi(0)$ and $\partial\psi(0)/\partial x$ must be continuous at $x=0$, we have

$$d=a(1+b), \tag{21}$$

$$d\gamma_x=a(1-b)\beta_x. \tag{22}$$

Solution for $\psi(-1)$

The vector potential may be written as

$$\mathbf{A}=2\mathbf{A}_0\cos\{2\pi\nu[t'+(x'\cos\theta+y'\sin\theta)/c]\}. \tag{23}$$

Then from Eq. (6) we see that

$$\mathbf{K}=\mathbf{G}(0)e^{i(x\cos\theta+y\sin\theta)\omega/\sqrt{2}}, \tag{24}$$

where

$$\mathbf{G}(0)=e\mathbf{A}_0/mc^2\sqrt{2}. \tag{25}$$

We shall assume that the wavelength of the radiation is large compared to the wavelength of the electron so we may neglect the spatial variation in $\mathbf{G}$. This is equivalent to assuming that $\omega/\sqrt{2}\ll\beta_x, \beta_y, \beta_z$. With this assumption and Eqs. (13), (7), and (24), our equation for $\psi(-1)$ becomes:

For $x<0$,

$$[\nabla^2+W_a-(\alpha-\omega)]\psi(-1)-2i\mathbf{G}(0)\cdot\nabla\psi(0)=0; \tag{26}$$

for $x>0$,

$$[\nabla^2-(\alpha-\omega)]\psi(-1)-2i\mathbf{G}(0)\cdot\nabla\psi(0)=0. \tag{27}$$

Let us define the quantities β_1 and γ_1 such that

$$\beta_1=[W_a-(\alpha-\omega)]^{1/2}, \quad \beta_1^2=\beta_{1x}^2+\beta_y^2+\beta_z^2, \tag{28}$$

$$\gamma_1=[-(\alpha-\omega)]^{1/2}, \quad \gamma_1^2=\gamma_{1x}^2+\beta_y^2+\beta_z^2. \tag{29}$$

For $x<0$ and $\beta_{1x}>0$ we let

$$\psi(-1, H)=fe^{i\beta_{1x}x}YZ. \tag{30}$$

For $x>0$, we have

$$\psi(-1, H)=ge^{i\gamma_{1x}x}YZ. \tag{31}$$

We note that γ_{1x} may be real or imaginary. It is real if the electron has energy above the vacuum level. As Mitchell has pointed out, the solutions must correspond to waves leaving the surface both inside and outside of the metal. Equations (30) and (31) are consistent with this.

For the particular solution let us use

$$\psi(-1, P)=(2i/\omega)\mathbf{G}(0)\cdot\nabla\psi(0). \tag{32}$$

The general solution for $\psi(-1)$ will be the sum of the homogeneous solution and the particular solution. The general solution for $\psi(-1)$ is:

For $x<0$,

$$\psi(-1)=fe^{i\beta_{1x}x}YZ+\psi(-1, P); \tag{33}$$

for $x>0$,

$$\psi(-1)=ge^{i\gamma_{1x}x}YZ+\psi(-1, P). \tag{34}$$

Since $\mathbf{G}(0)\cdot\nabla\psi(0)$ is continuous at $x=0$, we have

$$f=g. \tag{35}$$

We also have the condition that $\partial\psi(-1)/\partial x$ must be continuous at $x=0$. Therefore we have

$$f=[2G_x(0)W_a d]/\omega(\beta_{1x}-\gamma_{1x}). \tag{36}$$

Second-Order Equation

From Eq. (9) we see that the equation for $\psi(-2)$ to second order is given by

$$[\nabla^2-W-(\alpha-2\omega)]\psi(-2)$$
$$=2i\mathbf{G}(0)\cdot\nabla\psi(-1)+\mathbf{G}^2(0)\psi(0). \tag{37}$$

The homogeneous solution for Eq. (37) is:

For $x<0$, $\beta_{2x}>0$,

$$\psi(-2, H)=re^{-i\beta_{2x}x}YZ; \tag{38}$$

for $x>0$,

$$\psi(-2, H)=se^{i\gamma_{2x}x}YZ, \tag{39}$$

where

$$\beta_2=[W_a-(\alpha-2\omega)]^{1/2} \quad \text{and} \quad \gamma_2=[-(\alpha-2\omega)]^{1/2}. \tag{40}$$

To obtain Eqs. (38) and (39) we have again used the condition that the wave function must correspond to waves leaving the surface as Mitchell[3] has pointed out.

For the particular solution let us use

$$\psi(-2, P)=[G^2(0)\psi(0)/2\omega] + (2i/\omega)G(0)\cdot\nabla[\psi(-1, H)+\tfrac{1}{2}\psi(-1, P)]. \tag{41}$$

From the boundary condition that $\psi(-2)$ must be continuous at $x=0$, we have

$$r=s+2G_x^2(0)W_ad/\omega^2. \tag{42}$$

We also will make use of the boundary condition that $\partial\psi(-2)/\partial x$ must be continuous at $x=0$. Therefore we have

$$s=(2/\omega^2)G_x^2(0)W_ad[-\beta_{2x}-2\beta_{1x}-2\gamma_{1x}+\gamma_x]/(\gamma_{2x}+\beta_{2x}). \tag{43}$$

PHOTOELECTRIC CURRENT

To compute the photoelectric current, we will calculate the current density due to a single electron and then integrate over the conduction electrons which can escape. The current density vector for a single electron is given by

$$\mathbf{j}'=\mathbf{j}+\mathbf{J}, \tag{44}$$

where

$$\mathbf{j}=-(\zeta 2/i\lambda_0^4)(\psi^*\nabla\psi-\psi\nabla\psi^*), \tag{45}$$

$$\mathbf{J}=-(4ec/\lambda_0^3)\mathbf{G}\psi\psi^*, \tag{46}$$

where $\zeta=e\hbar/m$. Equation (45) corresponds to a flow of electrons from one region to another while Eq. (46) corresponds to the current due to the electron oscillating in the radiation field. Since $\mathbf{J}$ does not imply a net flow of electrons we shall neglect this term. We shall be interested in the x component of $\mathbf{j}$ for $x>0$. We have for the x component then that

$$j(x)=-(2\zeta/i\lambda_0^4)(\psi^*\partial\psi/\partial x-\psi\partial\psi^*/\partial x). \tag{47}$$

For the case where $\nu_0>\nu>\nu_0/2$, where ν_0 is the threshold frequency, the only part of the wave function which does not decay exponentially for $x>0$ is given by

$$\psi''(-2)=se^{i\gamma_{2x}x}YZ. \tag{48}$$

If we average over the y and z variables, we have that

$$j(x)=-8\zeta\gamma_{2x}ss^*/\lambda_0^4. \tag{49}$$

We note that γ_x and γ_{1x} are pure imaginary numbers, while γ_{2x} is real.

We have then that

$$j(x)=-128\,\mu|a|^2R(\beta_x), \tag{50}$$

where $R(\beta_x)$ is given by

$$R(\beta_x)=\frac{\beta_x^2(\beta_x^2+2\omega-W_a)^{1/2}\{3W_a+\omega-\beta_x^2+2[(\omega+\beta_x^2)(2\omega+\beta_x^2)]^{1/2}+2[(W_a-\beta_x^2)(W_a-\omega-\beta_x^2)]^{1/2}\}}{4\omega-W_a+2\beta_x^2+2[(2\omega+\beta_x^2)(2\omega-W_a+\beta_x^2)]^{1/2}}, \tag{51}$$

and μ is given by

$$\mu=(\zeta G_x^4(0)W_a)/(\lambda_0^4\omega^4). \tag{52}$$

We may now relate $|a|^2$ to the mean density of electrons in the metal and thereby to the Fermi-Dirac distribution. We have that

$$\langle\psi\psi^*\rangle=8|a|^2. \tag{53}$$

Therefore, where W_f is the Fermi energy, we have that

$$8|a|^2=\frac{2d\beta_xd\beta_yd\beta_z}{8\pi^3\{1+\exp[(\beta^2-W_f)c^2/8\pi^2T]\}}. \tag{54}$$

The second-order current term is given by

$$j_t(x)=-\frac{4\mu}{\pi^3}\int\frac{R(\beta_x)d\beta_xd\beta_yd\beta_z}{1+\exp[(\beta^2-W_f)c^2/8\pi^2T]}. \tag{55}$$

We assume that we may set $T=0°\text{K}$ and still have a reasonable approximation. We have then for $\beta_x^2+\beta_y^2+\beta_z^2-W_f<0$ that

$$j_t(x)=-\frac{4\mu}{\pi^3}\int R(\beta_x)d\beta_xd\beta_yd\beta_z, \tag{56}$$

and for $\beta_x^2+\beta_y^2+\beta_z^2-W_f>0$ we have that

$$j_t(x)=0. \tag{57}$$

We may set $d\beta_yd\beta_z=\rho d\rho d\theta$ and $\beta_y^2+\beta_z^2=\rho^2$. The limits of integration for θ are 0 and 2π and for ρ, 0 and $(W_f-\beta_x^2)^{1/2}$. Integrating over θ and ρ, we have

$$j_t(x)=-\frac{4\mu}{\pi^2}\int_{0\text{ or }(W_a-2\omega)^{1/2}}^{W_f^{1/2}}(W_f-\beta_x^2)R(\beta_x)d\beta_x. \tag{58}$$

If $W_a-2\omega<0$, then the lower limit is zero, otherwise it is $(W_a-2\omega)^{1/2}$.

We may write Eq. (58) in the following form:

$$j_t(x)=-\left(\frac{e^5c}{4^5\pi^7m^2\hbar^2}\right)\left[\frac{4\pi m\nu_0}{\hbar}+(3\pi^2n)^{2/3}\right]\times I\frac{\nu_0^3}{\nu^3}E^4(0)\sin^4\theta, \tag{59}$$

where n is the number of conducting electrons per unit volume. The number I is given by

$$I=\int_{0 \text{ or } (\mu-2\eta)^{1/2}}^{(\mu-1)^{1/2}} d\lambda \frac{(\mu-1-\lambda^2)\lambda^2(\lambda^2+2\eta-\mu)^{1/2}\{3\mu+\eta-\lambda^2+2[(\eta+\lambda^2)(2\eta+\lambda^2)]^{1/2}+2[(\mu-\lambda^2)(\mu-\eta-\lambda^2)]^{1/2}\}}{4\eta-\mu+2\lambda^2+2[(2\eta+\lambda^2)(2\eta-\mu+\lambda^2)]^{1/2}}, \quad (60)$$

where

$$\lambda=\beta_x/\omega_0^{1/2}, \quad \eta=\omega/\omega_0, \quad \mu=W_a/\omega_0. \quad (61)$$

A comment should be made on the θ dependency of the current. Equation (59) implies the current is a maximum for $\theta=90°$. As Mitchell pointed out in his first paper, this is due to the neglection of reflection and refraction. Normally the maximum for the first-order photoelectric effect occurs when the angle of incidence is about 60°.

The integral of Eq. (60) is reasonably easy to integrate numerically for a particular metal and for a given incident frequency. For sodium we have

$$I=0.11, \quad (62)$$

where we have used the value of[18] 2.28 eV for the work function[19] 3.12 eV for the Fermi energy. Also, we set the wavelength of the incident radiation equal to 7000 Å. After using the relationship that $A_x(0)=E_x(0)\lambda/4\pi$ and substituting numerical values for the constants, we have for the current

$$j_t(x)=7.8\times10^{-31}E_x^4(0) \text{ A/cm}^2, \quad (63)$$

where $E_x(0)$ is the x component of the amplitude of the incident radiation expressed in volts per meter.

Equation (63) seems to imply an extremely small current. However, it is not as small as one might initially think. Franken[12] has estimated that an electric field of the order of 10^7 V/m was produced by focusing the output of an optical ruby maser in his experiment on the generation of optical harmonic. Then Eq. (63) would imply that, even for a very small spot size, this field intensity would yield a current which would be of a measurable size. Peak power of 10^7 W/cm^2 for an unfocused optical maser has been reported.[15] This corresponds to an electric field of 6×10^8 V/m. The spot size is probably the order of 0.5 sq cm and the time duration is probably of the order of 10^{-8} sec. This gives a total energy content of only about 0.05 J. A field of 6×10^8 V/m yields a very large current according to Eq. (63). One would expect that other factors might begin to enter which would limit this to a smaller value. In particular the metal surface may be unduly heated.

For optical frequencies, field intensities of the order of 10^8 V/m will not produce field emission. The reason is rather simple. The field does not act in one direction long enough to free the electron from the metal.

It is of interest to note that $E_x^4(0)$ varies as the reciprocal of the spot area squared for a maser which has a constant energy output. However, the total current produced varies as the reciprocal of the area since the current is the product of the current density times the area. Therefore, one may greatly reduce the thermal effects of the incident radiation by increasing the spot size of the optical maser.

There are many techniques which may have to be used and/or developed to observe this phenomena but it is not the purpose of this paper to design such an experiment.

We have not proven that the second-order effect is observable but we have shown that it might be. The question as to whether there is any metal surface which yield a measurable current of this type before the surface undergoes serious heating is yet to be resolved.

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