THE SPATIAL DISTRIBUTION OF PHOTOELECTRONS

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(Received December 6, 1929)

Abstract

The perturbation of a hydrogen-like atom by a plane polarized electromagnetic wave is considered on the basis of Dirac's equation, and perturbed wave functions are obtained. These functions lead by a method similar to that used by Sommerfeld in his "Wellenmechanisches Ergänzungsband" to a formula for the spatial distribution of the photoelectrons. To the first approximation this formula differs from that given by a factor 5/9 in the second term. The angle between the average direction of the emission of the photoelectrons and the electric vector of the incident wave appears therefore to be equal to $h\nu/cmv$ instead of the value $(9/5)(h\nu/cmv)$ given. The factor 5/9 follows from the consideration of the normalizing factors for the spherical harmonics, which were not introduced by Sommerfeld. A second approximation has also been obtained showing the influence of electron spin. This approximation differs from that obtained by Carrelli in that the spin and some other terms not considered by Carrelli and also the factor 5/9 appear.

THE photoelectric effect has been treated theoretically on the basis of the wave mechanics by G. Wentzel,[1] G. Beck[2] and by A. Sommerfeld,[3] who gave a better approximation than the first two authors. However, all these authors have started either from the ordinary form of the Schrödinger equation (Wentzel, Beck) or from the form which takes into account the magnetic field but does not consider the relativity and spin effects. It is therefore of some interest to make the corresponding calculations on the basis of the wave equation given by Dirac. By means of this equation the relativity corrections and the spin influence can be found.

The computations in the present paper will proceed in a manner closely similar to the one used by Sommerfield in his book.

I. Perturbation of a Hydrogen-Like Atom by an Electromagnetic Wave

Dirac has shown[4] that the Hamiltonian expression for one electron can be written in the form

$$H=(p_0+eA_0/c)+\rho_1(\sigma,p+eA/c)+\rho_3 mc. \tag{1}$$

In this expression ρ_1, ρ_3 are four-row matrices, σ is a vector four-row matrix, whose components σ_1, σ_2, σ_3 are ordinary four-row matrices which satisfy the following relations

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[1] G. Wentzel, Zeits. f. Physik **40**, 574 (1926); **41**, 828 (1926).

[2] G. Beck, Zeits. f. Physik **41**, 443 (1927).

[3] A. Sommerfeld, Atombau und Spektrallinien, Wellenmechanisches Ergänzungsband, p. 207.

[4] P. A. M. Dirac, Proc. Roy. Soc. **A117**, 610 (1928); **118**, 351 (1928).

$$\begin{aligned}\sigma_1\sigma_2 &= i\sigma_3 = -\sigma_2\sigma_1\\ \sigma_2\sigma_3 &= i\sigma_1 = -\sigma_3\sigma_2 \\ \sigma_3\sigma_1 &= i\sigma_2 = -\sigma_1\sigma_3\end{aligned} \tag{2}$$

$$\sigma_1{}^2=1\ ;\quad \sigma_2{}^2=1\ ;\quad \sigma_3{}^2=1. \tag{3}$$

Similar relations are valid for ρ_1, ρ_3; moreover all σ's are commutable with all ρ's.

The parenthesis $(\sigma,\ p+eA/c)$ stands for a scalar product of the two vectors σ and $p+eA/c$. A is the vector potential, A_0 the scalar potential.

To the Hamiltonian (1) correspond two mutually adjoint functions, ψ and ϕ, each of which has four components.

To obtain Dirac's equations it is to be assumed that

$$p_0=\frac{ih}{2\pi c}\frac{\partial}{\partial t} \tag{4}$$

and p is to be interpreted as a vector operator, whose components are given by the relations

$$p_x=-\frac{ih}{2\pi}\frac{\partial}{\partial x}\ ;\qquad p_y=-\frac{ih}{2\pi}\frac{\partial}{\partial y}\ ;\qquad p_z=-\frac{ih}{2\pi}\frac{\partial}{\partial z}\,. \tag{5}$$

Then simultaneously

$$(p_0+eA_0/c)\psi+\rho_1(\sigma,p+eA/c)\psi+\rho_3mc\psi=0 \tag{6}$$

$$\phi(-p_0+eA_0/c)+\phi\rho_1(\sigma,-p+eA/c)+\phi\rho_3mc=0. \tag{7}$$

In the Eqs. (6) and (7) the following notation has been used. If μ is a four rowed matrix, then

$$\mu\psi=\sum_{k=1}^{4}\mu_{ik}\psi_k \qquad (i=1,2,3,4) \tag{8}$$

$$\phi\mu=\sum_{k=1}^{4}\phi_k\mu_{ki} \qquad (i=1,2,3,4) \tag{9}$$

If the matrices ρ and σ are hermitian, as, for instance, those given by Dirac,[4] ϕ is the conjugate complex function to ψ. This will be the case in the present paper. The operators p_0 and p in Eq. (7) operate backwards.

Dirac has shown, also, that the electric charge and current densities are given by

$$\rho=-e\varphi\psi \tag{10}$$

and

$$J=ec\phi\rho_1\sigma\psi. \tag{11}$$

In these expressions $\phi\psi$ stands for $\sum_{k=1}^{4}\phi_k\psi_k$ and $\phi\mu\psi$ for $\sum_{i,k=1}^{4}\phi_i\mu_{ik}\psi_k$.

It will be convenient to use the equations of second order, which correspond to the Eqs. (6) and (7) and in the present case will be equivalent to them. These equations were also derived by Dirac and can be written in the form

$$\left\{-\left(\frac{ih}{2\pi c}\frac{\partial}{\partial t}+\frac{eV}{c}\right)^2+\left(-\frac{ih}{2\pi}\nabla+\frac{eA}{c}\right)^2+m^2c^2\right\}\psi + \frac{eh}{2\pi c}(\sigma,H)\psi+\frac{ieh}{2\pi c}\rho_1(\sigma,E)\psi=0 \quad (12)$$

$$\left\{-\left(-\frac{ih}{2\pi c}\frac{\partial}{\partial t}+\frac{eV}{c}\right)^2+\left(\frac{ih}{2\pi}\nabla+\frac{eA}{c}\right)^2+m^2c^2\right\}\phi + \frac{eh\phi}{2\pi c}(\sigma,H)-\frac{ieh}{2\pi c}\phi\rho_1(\sigma,E)=0 \quad (13)$$

In these equations ∇ stands for a vector operator with components $\partial/\partial x$, $\partial/\partial y$, $\partial/\partial z$; H and E are the magnetic and electric field intensities which correspond to the scalar potential $V=A_0$ and the vector potential A, whereas (σ, H) and (σ, E) are scalar products of vectors σ and H or σ and E respectively.

The point of departure for the following considerations will be an undisturbed hydrogen-like atom in the k-th quantum state, consequently V will be equal to Ze/r, where Ze is the charge of the nucleus. The corresponding initial proper functions will be denoted by ψ_k and ϕ_k. As in the present case ϕ_k is always the conjugate complex function to ψ_k it will be sufficient to consider only the functions ψ.

Accordingly the initial conditions are described by the equations

$$\left\{-\left(\frac{ih}{2\pi c}\frac{\partial}{\partial t}+\frac{eV}{c}\right)^2+\left(-\frac{ih}{2\pi}\nabla\right)^2+m^2c^2\right\}\psi_k+\frac{ieh}{2\pi c}\rho_1(\sigma,E_0)\psi_k=0 \quad (14)$$

where E_0 designates the intensity of the electrostatic field of the nucleus.

Eq. (14) can be written in the form

$$\frac{1}{c^2}\frac{\partial^2\psi_k}{\partial t^2}-\Delta\psi_k-\frac{4\pi ieV}{hc^2}\frac{\partial\psi_k}{\partial t}-\frac{4\pi^2e^2V^2}{h^2c^2}\psi_k+\frac{4\pi^2m^2c^2}{h^2}\psi_k+\frac{2\pi ie}{hc}\rho_1(\sigma,E_0)\psi_k=0 \quad (15)$$

It will be now supposed that the atom is disturbed by a plane polarized electromagnetic wave, whose field can be derived from the vector potential

$$A=A_x=a\cos 2\pi\nu\left(t-\frac{z}{c}\right)$$

It is known that

$$H=\operatorname{curl} A\ ;\quad E=-\operatorname{grad} A_0-\dot{A}/c \quad (16)$$

and therefore

$$\begin{aligned} H_x=H_z=0\ ;\quad H_y&=a\cdot(2\pi\nu/c)\sin 2\pi\nu(t-z/c) \\ E_y=E_z=0\ ;\quad E_x&=a\cdot(2\pi\nu/c)\sin 2\pi\nu(t-z/c)\,. \end{aligned} \quad (17)$$

Eqs. (17) correpond to an electromagnetic wave, which proceeds in the direction of the z axis and is polarized in the yz plane.

If the values (17) are applied to Eq. (12) it assumes the form

$$\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}-\frac{4\pi^2e^2V^2}{h^2c^2}\psi-\frac{4\pi ieV}{hc^2}\frac{\partial\psi}{\partial t}-\Delta\psi-\frac{4\pi iea}{hc}\cos 2\pi\nu\left(t-\frac{z}{c}\right)\frac{\partial\psi}{\partial x}$$
$$+\frac{4\pi^2e^2a^2}{h^2c^2}\psi\cos^2 2\pi\nu\left(t-\frac{z}{c}\right)+\frac{4\pi^2m^2c^2}{h^2}\psi+\frac{4\pi^2\nu ea}{hc^2}\sin 2\pi\nu\left(t-\frac{z}{c}\right)\sigma_2\psi \tag{18}$$
$$+\frac{2\pi ie}{hc}\rho_1(\sigma,E_0)\psi+\frac{4\pi^2iea\nu}{hc^2}\rho_1\sigma_1\psi\sin 2\pi\nu\left(t-\frac{z}{c}\right)=0.$$

It is convenient to introduce exponentials instead of sines and cosines in Eq. (18). Moreover the term with a^2 as a factor can be neglected, since usually the amplitude a of the disturbing wave is very small. Then

$$\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}-\frac{4\pi^2e^2V^2}{h^2c^2}\psi-\frac{4\pi ieV}{hc^2}\frac{\partial\psi}{\partial t}-\Delta\psi+\frac{4\pi^2m^2c^2}{h^2}\psi+\frac{2\pi ie}{hc}\rho_1(\sigma,E_0)\psi$$
$$-\frac{2\pi iea}{hc}\frac{\partial\psi}{\partial x}\left[e^{2\pi i\nu(t-z/c)}+e^{-2\pi i\nu(t-z/c)}\right]-\frac{2\pi^2\nu iea}{hc^2}\left[e^{2\pi i\nu(t-z/c)}\right. \tag{19}$$
$$\left.-e^{-2\pi i\nu(t-z/c)}\right]\sigma_2\psi+\frac{2\pi^2eva}{hc^2}\left[e^{2\pi i\nu(t-z/c)}-e^{-2\pi i\nu(t-z/c)}\right]\rho_1\sigma_1\psi=0.$$

Eq. (19) can be simplified by the introduction of a perturbation parameter $\chi=-2\pi iea/hc$. On account of the factor a this parameter is a small quantity, so that all the terms, which have a power of a larger than unity as a factor can be neglected. Therefore it can be assumed that

$$\psi=\psi_k+\chi v+\cdots \tag{20}$$

In the expression above ψ_k denotes the proper function for the initial state of the atom and therefore

$$\psi_k=\bar{\psi}_k e^{-2\pi iE_kt/h} \tag{21}$$

where E_k is the proper energy of the atom in the initial state and $\bar{\psi}_k$ is a function of the spatial coordinates only. On account of Eq. (20) the substitution of (21) into Eq. (19) leads to

$$\frac{1}{c^2}\frac{\partial^2 v}{\partial t^2}-\frac{4\pi^2e^2V^2}{h^2c^2}v-\frac{4\pi ieV}{hc^2}\frac{\partial v}{\partial t}-\Delta v+\frac{4\pi^2m^2c^2}{h^2}v+\frac{2\pi ie}{hc}\rho_1(\sigma,E_0)v$$
$$+\frac{\partial\bar{\psi}_k}{\partial x}\left\{\exp\left[-\frac{2\pi i}{h}(E_k+h\nu)t+2\pi i\nu\frac{z}{c}\right]\right.$$
$$\left.+\exp\left[-\frac{2\pi i}{h}(E_k-h\nu)t-2\pi i\nu\frac{z}{c}\right]\right\} \tag{22}$$
$$+\frac{\pi\nu}{c}\left\{\exp\left[-\frac{2\pi i}{h}(E_k-h\nu)t-2\pi i\nu\frac{z}{c}\right]\right.$$

$$-\exp\left[-\frac{2\pi i}{h}(E_k+h\nu)t+2\pi i\nu\frac{z}{c}\right]\Big\}\sigma_2\psi$$

$$+\frac{i\pi\nu}{c}\Big\{\exp\left[-\frac{2\pi i}{h}(E_k-h\nu)t-2\pi i\nu\frac{z}{c}\right]$$

$$-\exp\left[-\frac{2\pi i}{h}(E_k+h\nu)t+2\pi i\nu\frac{z}{c}\right]\Big\}\rho_1\sigma_1\bar{\psi}=0$$

The terms with the squares of χ were omitted, according to the former assumption.

The form of Eq. (22) suggests that

$$v=v_+e^{-(2\pi i/h)(E_k+h\nu)t}+v_-e^{-(2\pi i/h)(E_k-h\nu)t}. \tag{23}$$

If z/λ is written instead of $\nu z/c$ then, on account of (23) Eq. (22) takes the form

$$\begin{aligned}&-\frac{4\pi^2}{h^2c^2}(E_k\pm h\nu)^2v_\pm-\frac{4\pi^2e^2V^2}{h^2c^2}v_\pm-\frac{8\pi^2eV}{h^2c^2}(E_k\pm h\nu)v_\pm-\Delta v_\pm\\&+\frac{4\pi^2m^2c^2}{h^2}v_\pm+\frac{2\pi ie}{hc}\rho_1(\sigma,E_0)v_\pm+\frac{\partial\bar{\psi}_k}{\partial x}e^{\pm 2\pi iz/\lambda}\\&\mp\frac{\pi\nu}{c}e^{\pm 2\pi iz/\lambda}\sigma_2\bar{\psi}_k\mp\frac{i\pi\nu}{c}e^{\pm 2\pi iz/\lambda}\rho_1\sigma_1\bar{\psi}_k=0.\end{aligned} \tag{24}$$

All upper signs in this equation belong together; the same applies to the lower signs.

Eq. (24) can be written in the form

$$\begin{aligned}\Delta v_\pm+\frac{4\pi^2}{h^2c^2}[(E_k\pm h\nu+eV)^2-m^2c^4]v_\pm-\frac{2\pi ie}{hc}\rho_1(\sigma,E_0)v_\pm\\=\frac{\partial\bar{\psi}_k}{\partial x}e^{\pm 2\pi iz/\lambda}\mp\frac{\pi}{\lambda}e^{\pm 2\pi iz/\lambda}\sigma_2\bar{\psi}_k\mp\frac{i\pi}{\lambda}e^{\pm 2\pi iz/\lambda}\rho_1\sigma_1\bar{\psi}_k.\end{aligned} \tag{25}$$

Since

$$(E_k\pm h\nu+eV)^2-m^2c^4=(E_k\pm h\nu+eV+mc^2)(E_k\mp h\nu+eV-mc^2) \tag{26}$$

and, except for very great values of ν, the expression $E_k\pm h\nu+eV$ is nearly equal to mc^2, it follows that the Eq. (25) differs from that given by Sommerfeld[5] only by the terms connected with the electron spin.

However, it is to be remembered that in Eq. (25) the functions v_+ and v_- stand for four components each. Furthermore in Sommerefeld's equations e is the electron charge, whereas in the present paper e denotes the absolute value of the electron charge. This explains the difference of signs, since eV stands for Sommerfeld's $-U$.

The solution of the Eq. (25) can be assumed in the form of an infinite series of the proper solutions of the undisturbed problem. However it is to

[5] A. Sommerfeld, reference 3, p. 195, Eq. (8).

be taken into account, that the hydrogen atom has a continuum of proper functions for electron energies greater than mc^2 in addition to a discrete set of proper functions for electron energies less than mc^2. Accordingly

$$v_{\pm} = \sum_j B_j^{\pm}\bar{\psi}_j + \int B^{\pm}(E')\bar{\psi}(E')dE'. \tag{27}$$

However, the expansion of the right side of the Eq. (25) into a corresponding series of proper functions meets a difficulty pointed out by Darwin.[6] Darwin has shown that the proper functions of the hydrogen atom form an incomplete set of orthogonal functions and that therefore it is not possible to develop an arbitrary four component function into a series of these proper functions. To do this the number of orthogonal solutions must be doubled. It means that in order to go through the calculations the existence of the solutions which correspond to the negative proper energies of the electron must be admitted. These solutions are obtained if the sign of the electron charge in Dirac's equation is changed from negative to positive and it is clear that they have no physical meaning. Therefore it is to be remembered that only those terms of the above mentioned series expansion which correspond to positive proper energies are to be taken into account in further considerations.

According to these considerations the series expansion can be written in the following form

$$\frac{\partial\bar{\psi}_k}{\partial x}e^{\pm 2\pi iz/\lambda} \mp \frac{\pi}{\lambda}e^{\pm 2\pi iz/\lambda}\sigma_2\bar{\psi}_k \mp \frac{i\pi}{\lambda}e^{\pm 2\pi iz/\lambda}\rho_1\sigma_1\bar{\psi}_k = \sum_j A_j^{\pm}\bar{\psi}_j + \int A^{\pm}(E')\bar{\psi}(E')dE'. \tag{28}$$

The integrals in the equation above are to be extended from $E' = mc^2$ to $E' \rightarrow \infty$ and from $E' = -mc^2$ to $E' \rightarrow -\infty$, but only the integrals within positive limits have a physical meaning.

The functions $\bar{\psi}_j$, $\bar{\psi}(E')$ are solutions of the undisturbed Eq. (14) and therefore

$$-\frac{4\pi^2}{h^2c^2}E_j^2\bar{\psi}_j - \Delta\bar{\psi}_j - \frac{8\pi^2}{h^2c^2}E_jeV\bar{\psi}_j - \frac{4\pi^2e^2V^2}{h^2c^2}\bar{\psi}_j + \frac{4\pi^2m^2c^2}{h^2}\bar{\psi}_j + \frac{2\pi ie}{hc}\rho_1(\sigma, E_0)\bar{\psi}_j = 0. \tag{29}$$

Similar equation is valid for $\bar{\psi}(E')$

The Eq. (29) leads to

$$\Delta\bar{\psi}_j - \frac{2\pi ie}{hc}\rho_1(\sigma, E_0)\bar{\psi}_j = -\frac{4\pi^2}{h^2c^2}[(E_j+eV)^2 - m^2c^4]\bar{\psi}_j. \tag{30}$$

[6] G. Darwin, Proc. Roy. Soc. **A118**, 654 (1928).

If Eqs. (27), (28) and (30) are substituted into (26), then it is found that

$$B_j^{\pm}=\frac{h^2c^2}{4\pi^2}\frac{A_j^{\pm}}{(E_k\pm h\nu+eV)^2-m^2c^4}$$
$$B^{\pm}(E')=\frac{h^2c^2}{4\pi^2}\frac{A^{\pm}(E')}{(E_k\pm h\nu+eV)^2-(E'+eV)^2}\,. \qquad (31)$$

On account of these relations Eqs. (20) leads to

$$\begin{aligned}\psi=\bar{\psi}_k e^{-2\pi i E_k t/h}-\frac{hciea}{2\pi}\Bigg\{&\Bigg[\sum_j\frac{A_j^{+}\bar{\psi}_j}{(E_k+h\nu+eV)^2-(E_j+eV)^2}\\&+\int\frac{A^{+}(E')\bar{\psi}(E')dE'}{(E_k+h\nu+eV)^2-(E'+eV)^2}\Bigg]e^{-2\pi i(E_k+h\nu)t/h}\\&+\Bigg[\sum_j\frac{A_j^{-}\bar{\psi}_j}{(E_k-h\nu+eV)^2-(E_j+eV)^2}\\&+\int\frac{A^{-}(E')\bar{\psi}(E')dE'}{(E_k-h\nu+eV)^2-(E'+eV)^2}\Bigg]e^{-2\pi i(E_k-h\nu)t/h}\Bigg\}\,.\end{aligned} \qquad (32)$$

From Eq. (10) the electric charge density is

$$\begin{aligned}\rho=-e\bar{\phi}_k\bar{\psi}_k+\frac{hciea}{2\pi}\Bigg\{&e^{2\pi i\nu t}\Bigg[\sum_j\frac{A_j^{+*}\bar{\phi}_j\bar{\psi}_k}{(E_k+h\nu+eV)^2-(E_j+eV)^2}\\&-\sum_j\frac{A_j^{-}\bar{\phi}_k\bar{\psi}_j}{(E_k-h\nu+eV)^2-(E_j+eV)^2}\Bigg]+e^{-2\pi i\nu t}\Bigg[\sum_j\frac{A^{-*}\bar{\phi}_j\bar{\psi}_k}{(E_k-h\nu+eV)^2-(E_j+eV)^2}\\&-\sum_j\frac{A_j^{+}\bar{\phi}_k\bar{\psi}_j}{(E_k+h\nu+eV)^2-(E_j+eV)^2}\Bigg]\Bigg\}\,.\end{aligned} \qquad (33)$$

According to the former assumptions the terms whose coefficients are proportional to a^2 were neglected, furthermore the integrals, which correspond to the continuous spectrum are not written out.

From Eq. (33), which is very similar to the one given by Sommerfeld[7] the dispersion formulas could be obtained in the usual way.

As long as $h\nu\ll mc^2$

$$(E_k\pm h\nu+eV)^2-(E_j+eV)^2\backsimeq 2mc^2(E_k-E_j\pm h\nu) \qquad (34)$$

because the energy values include the energy mc^2, so that on the one hand eV is negligibly small with regard to E_k or E_j (except for the K-levels of the heavy elements) and on the other hand each of these terms differs only negligibly (with the same exception) from mc^2 (the energy mc^2 in electron-volts is of the order of $5\cdot 10^5 v$.

With that simplification the Eq. (33) leads to the usual dispersion formula. Only when $h\nu$ begins to be comparable with mc^2 and especially for the

[7] A. Sommerfeld, reference 3, p. 197.

heaviest elements does Eq. (33) give results differing appreciably from the usual dispersion formula. As $h\nu$ is equal to mc^2 for $\lambda \leqq 24XU$ it follows that the difference begins to be appreciable for X-rays of the order of 0.1A.

According to Eq. (28) the value of $Aj^{\pm}$ is given by

$$A_j^{\pm}=\frac{1}{C_j}\left\{\int\bar{\phi}_j\frac{\partial\bar{\psi}_k}{\partial x}e^{\pm 2\pi iz/\lambda}d\tau\mp\frac{\pi}{\lambda}\int e^{\pm 2\pi iz/\lambda}\bar{\phi}_j\sigma_2\bar{\psi}_k d\tau\mp\frac{i\pi}{\lambda}\int e^{\pm 2\pi iz/\lambda}\bar{\phi}_j\rho_1\sigma_1\bar{\psi}_k d\tau\right\}. \tag{35}$$

Eq. (35) is obtained if Eq. (28) is multiplied by $\bar{\phi}_j$ on the left-hand side and integrated over the whole space. Furthermore the normalizing integrals

$$\int\bar{\phi}_j\bar{\psi}_j d\tau=C_j \tag{36}$$

are to be used. The integrations in the expressions (36) extend over the whole space.

II. The Photoelectric Current

The photoelectric current excited in a given direction by an electromagnetic wave incident on a hydrogen like atom can now be found on the basis of Eq. (32). Only the photoelectric emission from a single atom will be considered here. To calculate this emission, those excited states of the atom which belong to the continuous spectrum are to be considered. Therefore in the present case the sums in Eq. (32) can be omitted as irrelevant. The values of the coefficients $A^{\pm}(E')$ are given by the formulas

$$A^{\pm}(E')=\frac{1}{C(E')}\left\{\int\bar{\phi}(E')\frac{\partial\bar{\psi}_k}{\partial x}e^{\pm 2\pi iz/\lambda}d\tau\mp\frac{\pi}{\lambda}\int\bar{\phi}(E')\sigma_2\bar{\psi}_k e^{\pm 2\pi iz/\lambda}d\tau\mp\frac{i\pi}{\lambda}\int\bar{\phi}(E')\rho_1\sigma_1\bar{\psi}_k e^{\pm 2\pi iz/\lambda}d\tau\right\} \tag{37}$$

where

$$C(E')=\lim_{\Delta_n E'\to 0}\frac{\int\Delta_n\bar{\phi}(E')\Delta_n\bar{\psi}(E')d\tau}{\Delta_n E'} \tag{38}$$

(the integral extends over the whole space) and

$$\Delta_n\bar{\phi}(E')=\int_{\Delta_n E'}\bar{\phi}(E')dE'\ ;\quad \Delta_n\bar{\psi}(E')=\int_{\Delta_n E'}\bar{\psi}(E')dE' \tag{39}$$

(see Fuess[8]).

In Eq. (32) the term $\bar{\psi}_k e^{-2\pi iE_k t/h}$ can be also omitted. This term represents the initial k-th quantum state of the atom and therefore its radial part contains an exponential of the type $e^{-\mu r}$, where μ is a real positive number.

[8] E. Fuess, Ann. d. Physik **81**, 281 (1926).

Since $\mu \sim 10^9$ this exponential vanishes very rapidly with increasing r. (The same applies to the terms of the sums in Eq. (32)). On the other hand the radial parts of the functions $\bar{\varphi}(E')$ have as a factor an exponential $e^{\mu' r}$ where μ' is purely imaginary. They vanish therefore only slowly with growing r. It follows that for the values of r great compared with the atomic dimensions (and it is these values that are to be considered for the photoelectric effect) only the integrals in Eq. (32) are to be taken into account.

According to Sommerfeld[9] the integrands of these integrals can be separated into three factors

$$a)\ \frac{A^{\pm}(E')}{(E_k \pm h\nu + eV)^2 - (E' + eV)^2}\,; \qquad b)\ \bar{\psi}(E') \qquad \text{and} \qquad c)\ e^{-2\pi i (E_k \pm h\nu) t/h}$$

In the factor (a) only V depends upon the coordinates, but, as V is equal to $e\,Z/r$ it can be safely omitted in the computations. The factor (a) then becomes a constant, i.e. it depends only upon E'.

The factor (c) gives the dependence of $\bar{\psi}$ upon the time. The expression $E_k \pm h\nu$ in the exponent can be interpreted as the energy of the photoelectron. The kinetic energy of the photoelectron is

$$\epsilon = E_k \pm h\nu - mc^2.$$

If the $+$ sign is taken this can be written in the form $\epsilon = h\nu - J$ where $J = mc^2 - E_k$ is the ionization potential. The corresponding expression with the $-$ sign becomes negative. Hence there cannot be given a physical interpretation to the corresponding parts of ψ unless the possibility of existence of states with negative total energy is admitted. The existence of these states has already been admitted to obtain an expansion of the right side of the perturbed Eq. (25) into a series of the proper functions of the undisturbed problem. The factor $E_k - h\nu$ could then be written in the form $-(-E_k + h\nu)$ and the negative kinetic energy of the photoelectron, which evidently has no physical significance would be $\epsilon' = -(-E_k + h\nu) - (-mc^2)$ or $\epsilon' = -(h\nu - J)$. This forms an analogue to Einstein's photoelectric equation.

According to the above considerations these parts of ϕ which correspond to the $-$ sign in the expression $E_k \pm h\nu$ can be omitted, the more so, that the parts with the $+$ sign will be incomparably greater than the parts with the $-$ sign on account of the expression $(E_k + h\nu + eV)^2 - (E' + eV)^2$ in the denominator of the integrands, which tends to zero with E' tending to $E_k + h\nu$.

The factor (b) is the really interesting one for the determination of the spatial distribution of the photoelectrons. Moreover it must be added that only the radial parts of the functions ψ have the continuous spectra. The directional parts have only the discrete proper functions. Therefore on account of the foregoing considerations the following expressions are properly to be used in the subsequent calculations (because $A_j^{\pm}$ and $A(^{\pm}E')$ should be explicity written as $A_{jkm}^{\pm}$ and $A_{km}^{\pm}(E')$)

[9] A. Sommerfeld, reference 3, p. 209.

$$\psi \cong -\frac{hciea}{2\pi} e^{-2\pi i(E_{k_0}+h\nu)t/h} \left\{ \sum_k \sum_m \int \frac{\overset{+}{A}_{km}(E')\bar{\psi}_{km}(E')dE'}{(E_{k_0}+h\nu+eV)^2-(E'+eV)^2} \right\}. \quad (40)$$

To avoid the divergence of the integral in (40) the integration can be performed according to Wentzel[10] along a path which extends slightly around the pole $E'=E_{k_0}+h\nu$ into the positive part of the complex plane E'.

Darwin[11] has shown that the solutions of Dirac's equations for a central electrostatic field can be written in the form

$$\begin{aligned} \bar{\psi}_{km}^{(1)} &= -iF_k P_{k+1}^{m} & \bar{\psi}_{km}^{(3)} &= (k+m+1)G_k P_k^{m+1} \\ \bar{\psi}_{km}^{(2)} &= -iF_k P_{k+1}^{m-1} & \bar{\psi}_{km}^{(4)} &= (-k+m)G_k P_k^{m+1} \end{aligned} \quad (41)$$

and

$$\begin{aligned} \bar{\psi}_{km}^{(1)} &= -i(k+m)F_{-k-1}P_{k-1}^{m} & \bar{\psi}_{km}^{(3)} &= G_{-k-1}P_k^{m} \\ \bar{\psi}_{km}^{(2)} &= -i(-k+m+1)F_{-k-1}P_{k-1}^{m+1} & \bar{\psi}_{km}^{(4)} &= G_{-k-1}P_k^{m+1}. \end{aligned} \quad (42)$$

The functions P_k^m are spherical harmonics defined in the following way

$$P_k^m = (k-m)!\sin^m\theta \left(\frac{d}{d\cos\theta}\right)^{k+m} \left(\frac{\cos^2\theta-1}{2^k\cdot k!}\right)\cdot e^{im\phi}. \quad (43)$$

It can be shown that

$$P_k^{-m} = (-1)^m P_k^{m*} \quad (44)$$

so that only the values of P_k^m for positive m need to be known. Furthermore

$$\int_0^\pi \int_0^{2\pi} P_k^m P_k^{m*} \sin\theta d\theta d\phi = \frac{4\pi}{2k+1}(k+m)!(k-m)!. \quad (45)$$

The functions F_k and G_k depend upon the radius r only and satisfy the relations

$$\begin{aligned} &\frac{2\pi}{h}\left(\frac{E+eV}{c}+mc\right)F_k + \frac{dG_k}{dr} - \frac{k}{r}G_k = 0 \\ &-\frac{2\pi}{h}\left(\frac{E+eV}{c}-mc\right)G_k + \frac{dF_k}{dr} + \left(\frac{k+2}{r}\right)\cdot F_k = 0. \end{aligned} \quad (46)$$

For a hydrogen-like atom with the nuclear charge Ze the potential V is equal to eZ/r and so, if the following notation is used

$$\frac{2\pi}{h}\left(\frac{E}{c}+mc\right) = A^2; \quad \frac{2\pi}{h}\left(\frac{E}{c}-mc\right) = B^2 \quad \frac{2\pi e^2 Z}{hc} = \gamma = Z\alpha \quad (47)$$

where α is the Sommerfeld fine structure constant, then instead of (46)

$$\begin{aligned} &\left(A^2+\frac{\gamma}{r}\right)F_k + \frac{dG_k}{dr} - \frac{k}{r}G_k = 0 \\ &\left(B^2+\frac{\gamma}{r}\right)G_k - \frac{dF_k}{dr} - \frac{k+2}{r}F_k = 0. \end{aligned} \quad (48)$$

[10] G. Wentzel, Zeits. f. Physik **40**, 574 (1926).

[11] C. G. Darwin, reference 6.

The solutions (41) and (42) correspond to different values of the inner quantum number j. For the solution (41) $j=k+\frac{1}{2}$, for (42) $j=k-\frac{1}{2}$. Moreover, for the solution (41) $-k-1\leq m\leq k$ which leads to $2k+2$ different solutions, whereas for the type (42) one has $-k\leq m\leq k-1$ i.e. $2k$ different solutions. In each case there are $2j+1$ solutions as it should be.

In the subsequent calculations the normalizing integrals for the proper functions (41) and (42) are used. These integrals were given by Darwin[12] For the solution (41)

$$C'_{km}=\int\bar{\phi}_{km}\bar{\psi}_{km}d\tau=4\pi(k+m+1)!(k-m)!\int_0^\infty(F_k{}^2+G_k{}^2)r^2dr \qquad (49)$$

and for the solution (42)

$$C''_{km}=\int\bar{\phi}_{km}\bar{\psi}_{km}d\tau=4\pi(k+m)!(k-m-1)!\int_0^\infty(F^2_{-k-1}+G^2_{-k-1})r^2dr\,. \qquad (50)$$

It is also to be noted that the solutions (41) and (42) form an orthogonal set of functions, i. e.

$$\int\bar{\phi}_{kmj}(E)\bar{\psi}_{k'm'j'}(E')d\tau=0 \qquad (51)$$

except for $E=E'$, $k=k'$, $m=m'$ and $j=j'$ (j—inner quantum number).

Darwin has also shown that for $E<mc^2$ a hydrogen-like atom has a set of discrete proper values of E, which correspond to the solutions (41) and (42). For $E>mc^2$ there are solutions for each value of E. This last condition corresponds to the existence of a continuous spectrum. It can be shown that in this latter case F_k and G_k are complex functions, which to the first approximation correspond to spherical waves diverging from the nucleus (or converging towards the nucleus).

To find the approximate forms of F_k and G_k for $r\rightarrow\infty$ all terms in Eqs. (48) with r in the denominator can be omitted in the first approximation. This leads to

$$A^2F+dG/dr=0\ ; \qquad B^2G-dF/dr=0 \qquad (52)$$

with both A^2 and B^2 positive. Hence

$$A^2F+\frac{1}{B^2}\frac{d^2F}{dr^2}=0\ ; \qquad B^2G+\frac{1}{A^2}\frac{d^2G}{dr^2}=0 \qquad (53)$$

and

$$F=ae^{iABr}\ ; \quad G=be^{iABr}. \qquad (54)$$

These values of F and G substituted into Eqs. (52) give

$$a=-ibB/A=-ibp \qquad (55)$$

p is a small quantity and so $\bar{\psi}^{(1)}$ and $\psi^{(2)}$ are small compared with $\bar{\psi}^{(3)}$ and $\bar{\psi}^{(4)}$.

[12] C. G. Darwin, reference 6.

In the second approximation a and b can be considered as varying slowly with r and so all terms with a/r^2, a'/r and a'' and analogous terms for b are to be omitted. If the values (53) and (54) are substituted into Eqs. (48) the above assumption leads to

$$a'+\frac{a}{r}\left[1-\frac{i\gamma}{2}\left(\frac{A}{B}+\frac{B}{A}\right)\right]=0 \tag{56}$$

and the same equation for b

If one puts

$$\frac{\gamma}{2}\left(\frac{A}{B}+\frac{B}{A}\right)=\delta \tag{57}$$

then the Eq. (56) takes the form

$$a'+\frac{a}{r}(1-i\delta)=0 \tag{58}$$

whence

$$a=Ce^{i\delta \log r}/r. \tag{59}$$

Therefore finally

$$\begin{aligned} F &= -ipCe^{i(ABr+\delta \log r)}/r \\ G &= Ce^{i(ABr+\delta \log r)}/r. \end{aligned} \tag{60}$$

On the basis of the notations (47) it can easily be found that AB is usually of the order 10^9, whereas δ is, for high speed photoelectrons and low atomic numbers, small compared with unity. As the log r varies much more slowly than r it follows that δ log $r=\tau$ can be considered to this approximation as a constant.

All is now prepared for the actual calculation of the coefficient $A^{+}_{km}(E')$ in Eq. (40). These coefficients are given by Eq. (37), which, written in the developed form is

$$\begin{aligned} C_{km}(E')A_{km}(E') = &\int \bar{\phi}^{(1)}_{km}(E')\frac{\partial\bar{\psi}^{(1)}_{k_0}}{\partial x}e^{2\pi iz/\lambda}d\tau \\ &+\int \bar{\phi}^{(2)}_{km}(E')\frac{\partial\bar{\psi}^{(2)}_{k_0}}{\partial x}e^{2\pi iz/\lambda}d\tau \\ &+\int \bar{\phi}^{(3)}_{km}(E')\frac{\partial\bar{\psi}^{(3)}_{k_0}}{dx}e^{2\pi iz/\lambda}d\tau+\int \bar{\phi}^{(4)}_{km}(E')\frac{\partial\bar{\psi}^{(4)}_{k_0}}{\partial x}e^{2\pi iz/\lambda}d\tau \\ &-\frac{\pi}{\lambda}\Big[-i\int \bar{\phi}^{(1)}_{km}(E')\bar{\psi}^{(2)}_{k_0}e^{2\pi iz/\lambda}d\tau+i\int \bar{\phi}^{(2)}_{km}(E')\bar{\psi}^{(1)}_{k_0}e^{2\pi iz/\lambda}d\tau \\ &-i\int \bar{\phi}^{(3)}_{km}(E')\bar{\psi}^{(4)}_{k_0}e^{2\pi iz/\lambda}d\tau+i\int \bar{\phi}^{(4)}_{km}(E')\bar{\psi}^{(3)}_{k_0}e^{2\pi iz/\lambda}d\tau\Big] \end{aligned} \tag{61}$$

$$-\frac{i\pi}{\lambda}\left[\int \bar{\phi}^{(1)}_{km}(E')\bar{\psi}^{(4)}_{k_0}\, e^{2\pi iz/\lambda}d\tau + \int \bar{\phi}^{(2)}_{km}(E')\bar{\psi}^{(3)}_{k_0}\, e^{2\pi iz/\lambda}d\tau \right.$$

$$\left. + \int \bar{\phi}^{(3)}_{km}(E')\bar{\psi}^{(2)}_{k_0}\, e^{2\pi iz/\lambda}d\tau + \int \bar{\phi}^{(4)}_{km}(E')\bar{\psi}^{(1)}_{k_0}\, e^{2\pi iz/\lambda}d\tau\right].$$

The Eq. (61) follows from (37) if it is remembered that, according to Dirac[13]

$$\sigma_2 = \begin{vmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{vmatrix} \quad \text{and} \quad \rho_1\sigma_1 = \begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix}. \tag{62}$$

To simplify the calculations it will be supposed that the hydrogen-like atom considered is initially in the normal unexcited state. According to Darwin two possibilities are then to be considered[14].

Either

$$\begin{aligned} \bar{\psi}^{(1)}_{k_0} &= \frac{-i\gamma}{1+(1-\gamma^2)^{1/2}} P_1{}^0 r^\beta e^{-r/a_0} & \psi^{(3)}_{k_0} &= r^\beta e^{-r/a_0} \\ \bar{\psi}^{(2)}_{k_0} &= \frac{-i\gamma}{1+(1-\gamma^2)^{1/2}} P_1{}^1 r^\beta e^{-r/a_0} & \psi^{(4)}_{k_0} &= 0 \end{aligned} \tag{63}$$

or

$$\begin{aligned} \bar{\psi}^{(1)}_{k_0} &= \frac{-i\gamma}{1+(1-\gamma^2)^{1/2}} P_1{}^{-1} r^\beta e^{-r/a} & \bar{\psi}^{(3)}_{k_0} &= 0 \\ \bar{\psi}^{(2)}_{k_0} &= \frac{-i\gamma}{1+(1-\gamma^2)^{1/2}} P_1{}^0 r^\beta e^{-r/a_0} & \bar{\psi}^{(4)}_{k_0} &= -r^\beta e^{-r/a_0} \end{aligned} \tag{64}$$

In the equations above β denotes $(1-\gamma^2)^{1/2}-1$ and a_0 is equal to a/Z where a is the radius of the first Bohr orbit.

Accordingly either

$$\begin{aligned} \frac{\partial\bar{\psi}^{(1)}_{k_0}}{\partial x} &= \frac{-i\gamma}{1+(1-\gamma^2)^{1/2}}\frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})P_1{}^0 r \sin\theta\cos\phi \qquad (rP_1{}^0 = z) \\ \frac{\partial\bar{\psi}^{(2)}_{k_0}}{\partial x} &= \frac{-i\gamma}{1+(1-\gamma^2)^{1/2}}\frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})P_1{}^1 r \sin\theta\cos\phi - \frac{i\gamma}{1+(1-\gamma^2)^{1/2}} r^{\beta-1}e^{-r/a_0} \\ \frac{\partial\bar{\psi}^{(3)}_{k_0}}{\partial x} &= \frac{\partial}{\partial r}(r^\beta e^{-r/a_0}) \qquad (rP_1{}^1 = x+iy) \\ \frac{\partial\bar{\psi}^{(4)}_{k_0}}{\partial x} &= 0 \end{aligned} \tag{65}$$

[13] P. A. M. Dirac, Proc. Roy. Soc. **117,** 680 (1928).

[14] C. G. Darwin, l. c.

or

$$\frac{\partial\bar{\psi}_{k_0}^{(1)}}{\partial x}=-\frac{i\gamma}{1+(1-\gamma^2)^{1/2}}\frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})P_1^{-1}r\sin\theta\cos\phi+\frac{i\gamma}{1+(1-\gamma^2)^{1/2}}r^{\beta-1}e^{-r/a_0}$$

$$\frac{\partial\bar{\psi}_{k_0}^{(2)}}{\partial x}=-\frac{i\gamma}{1+(1-\gamma^2)^{1/2}}\frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})P_1^{0}r\sin\theta\cos\phi \qquad (-rP_1^{-1}=x-iy)$$

$$\frac{\partial\bar{\psi}_{k_0}^{(3)}}{\partial x}=0 \tag{66}$$

$$\frac{\partial\bar{\psi}_{k_0}^{(4)}}{\partial x}=-\frac{\partial}{\partial r}(r^{\beta}e^{-r/a_0}).$$

These two possibilities will be considered separately.

The integrals in Eq. (61) differ from zero only for certain definite values of k and m. The next step of the computations consists in determining these values.

On account of the appearance of the factor $e^{2\pi iz/\lambda}$ in the integrands there are two possible ways of performing the computations. Either as Sommerfeld has done, one can develop the function $e^{2\pi ir\cos\theta/\lambda}$ into a series of powers of $r\cos\theta/\lambda$ and then can calculate the possible values of the coefficients $A_{km}(E')$ on the basis of this expansion or one can start from the function $e^{2\pi ir\cos\theta/\lambda}$ itself. This last method was used recently by Carrelli.[15] Both these methods lead to the same results on account of the absolute and uniform convergence of the series

$$1+\frac{x}{1!}+\frac{x^2}{2!}+\frac{x^3}{3!}+\cdots \tag{67}$$

for all points of the x plane. The series (67) can be therefore integrated term by term, which gives the same result as the integration of the function e^x itself. The same applies to the products of the exponential by various spherical harmonics and the products of the expansion (67) by these harmonics.

Carrelli finds the coefficients $A_{km}(E')$ in the form of the functions of a quantity R equal to

$$\lambda/2\pi\ (1/a_0+iAB)$$

and then develops these functions into series of R. Sommerfeld's method leads immediately to the power series of R as the value for $A_{km}(E')$. It is obvious that both these power series are identical.

Carrelli has computed only the coefficients $A_{11}(E')$ and $A_{21}(E')$ on the basis of the Schrödinger equation and in his calculations took into account only the first two terms of the power series expansions for each of these coefficients. These terms were of the order of $1/R^2$ and $1/R^4$ for the coefficient $A_{11}(E')$ and of the orders of $1/R^3$ and $1/R^5$ for the coefficient $A_{21}(E')$.

[15] A. Carrelli, Zeits. f. Phys. **56**, 694 (1929).

To be consistent Carrelli should also find the first term of the expansion, which corresponds to the coefficient $A_{31}(E')$, whose order is $1/R^4$ and the first term of the expansion for $A_{41}(E')$ which is of the order of $1/R^5$. These last two terms were neglected by Carrelli and this invalidates his result. To appreciate the influence of the above mentioned terms one has to consider that in Carrelli's case the perturbed wave function can be written in the form

$$\psi=A_{11}Q_1^1 \cos\phi+A_{21}Q_2^1 \cos\phi+A_{31}Q_{31}^1 \cos\phi+A_{41}Q_4^1 \cos\phi \tag{68}$$

where $Q_k{}^m$ denote the spherical harmonics used by Carrelli. The values of the harmonics in (68) are

$$\begin{aligned} &Q_1^1=\sin\theta && Q_2^1=3\sin\theta\cos\theta \\ &Q_3^1=(3/2)\sin\theta(5\cos^2\theta-1) && Q_4^1=(5/2)\sin\theta\cos\theta(7\cos{}^2\theta-3) \end{aligned} \tag{69}$$

whence

$$\psi=\sin\theta\cos\phi\left\{A_{11}+3A_{21}\cos\theta+\frac{15}{2}A_{31}\cos^2\theta \right.$$
$$\left. -\frac{3}{2}A_{31}+\frac{35}{2}\cos^3\theta A_{41}-\frac{15}{2}A_{41}\cos\theta\right\}. \tag{70}$$

It follows, that the terms omitted by Carrelli were

$$-\frac{3}{2}A_{31} \quad \text{and} \quad -\frac{15}{2}A_{41}\cos\theta.$$

In the present paper Sommerfeld's method of computation will be used. To obtain the degree of approximation comparable with that of Carrelli the exponential $e^{2\pi i r\cos\theta/\lambda}$ will be developed into a power series, whose first four terms will be retained. Thus

$$e^{2\pi i\cos\theta/r}=1+\frac{2\pi ir}{\lambda}\cos\theta-\frac{2\pi^2r^2}{\lambda^2}\cos^2\theta-\frac{4\pi^3ir^3}{3\lambda^3}\cos^3\theta. \tag{71}$$

To find the values of k and m for which Eq. (61) differs from zero it is sufficient to take into account the orthogonality relations for the functions $P_k{}^m$, as Sommerfeld has done. Those relations are

$$\int_0^\pi\int_0^{2\pi} P_k{}^mP_l{}^{n*}\sin\theta d\theta d\phi=0\begin{pmatrix} k\neq l \\ m\neq n\end{pmatrix}. \tag{72}$$

Furthermore in Eqs. (65) and (66) $\frac{1}{2}(e^{i\phi}+e^{-i\phi})$ can be written instead of $\cos\phi$. The values of the functions $P_k{}^m$ for those values of k and m which enter into consideration in this paper are given below

$$\begin{aligned} &P_0{}^0=1 && P_1^1=\sin\theta e^{i\phi} \\ &P_1{}^0=\cos\theta && P_2^1=3\sin\theta\cos\theta e^{i\phi} \\ &P_2{}^0=3\cos^2\theta-1 && P_3^1=3\sin\theta(5\cos^2\theta-1)e^{i\phi} \end{aligned}$$

$$P_3{}^0=3(5\cos^3\theta-3\cos\theta) \qquad P_4^1=15\sin\theta(7\cos^3\theta-3\cos\theta)e^{i\phi}$$
$$P_4{}^0=3(35\cos^4\theta-30\cos^2\theta+3) \tag{73}$$
$$P_2{}^2=3\sin^2 e^{2i\phi}$$
$$P_3{}^2=15\sin^2\theta\cos\theta e^{2i\phi}$$
$$P_4^2=15\sin^2\theta(7\cos^2\theta-1)e^{2i\phi}.$$

It will be supposed now that the initial state of the atom is given by Eqs. (63) and (65). The two types of the solutions, given by the Eqs. (41) and (42) have to be considered separately. The reasoning quite similar to that of Sommerfeld shows that for the solution (41) the coefficients $A'_{km}(E')$ (the accent is used to denote the first type of the solution) are different from zero for

$$\begin{array}{llll} k=0 & m=-1 & k=3 & m=\pm 1 \\ k=1 & m=\pm 1 & k=4 & m=\pm 1 \\ k=2 & m=\pm 1 & & \end{array} \tag{74}$$

Similarly for the solution (42) the coefficients $A''_{km}(E')$ (two accents denote the second type of solution) are different from zero for

$$\begin{array}{llll} k=1 & m=-1 & k=4 & m=\pm 1 \\ k=2 & m=\pm 1 & k=5 & m=\pm 1 \\ k=3 & m=\pm 1 & & \end{array} \tag{75}$$

It is to be noted that for the term $-4\pi^3 ir^3\cos^3\theta/3\lambda^3$ in the expansion (71) only the integrals in Eq. (61) with the greatest absolute value were taken into account.

For the sake of brevity the following notations are used in the subsequent calculations (κ is equal to AB).

$$\int_0^\infty \frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})e^{-i\kappa r}r^2dr=Q_1 \tag{76}$$

$$\int_0^\infty \frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})e^{-i\kappa r}r^3dr=Q_2 \tag{77}$$

$$\int_0^\infty \frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})e^{-i\kappa r}r^4dr=Q_3 \tag{78}$$

$$\int_0^\infty r^\beta e^{-r/a_0}e^{-i\kappa r}dr=Q_4 \tag{79}$$

$$\int_0^\infty r^\beta e^{-r/a_0}e^{-i\kappa r}rdr=Q_5 \tag{80}$$

$$\int_0^\infty r^\beta e^{-r/a_0}e^{-i\kappa r}r^2dr=Q_6 \tag{81}$$

$$\int_0^\infty \frac{\partial}{\partial r}(r^\beta e^{-r/a_0})e^{-i\kappa r}rdr=Q_7 \tag{82}$$

$$\int_0^\infty \frac{\partial}{\partial r}(r^\beta e^{-r/a_0})e^{-i\kappa r}r^2dr=Q_8 \tag{83}$$

$$\int_0^\infty \frac{\partial}{\partial r}(r^\beta e^{-r/a_0})e^{-i\kappa r}r^3dr=Q_9 \tag{84}$$

$$\int_0^\infty \frac{\partial}{\partial r}(r^\beta e^{-r/a_0})e^{-i\kappa r}r^4dr=Q_{10}. \tag{85}$$

If the values (73) of the spherical harmonics and the normalizing integrals (49) and (50) are taken into account then with regard to Eq. 61 it follows after some easy calculations that

$$A'_{0,-1}(E')=\frac{\pi}{\lambda}Q_5\left(i+\frac{\gamma p}{6}\right)+\frac{\pi^2}{3\lambda^2}Q_6(2p+i\gamma) \tag{86}$$

$$A'_{1,1}(E')=-\frac{i\gamma p}{12}Q_1+\frac{\pi^2}{30\lambda^2}i\gamma pQ_3+\frac{Q_7}{6}-\frac{\pi^2}{15\lambda^2}Q_9+\frac{i\pi^2}{15\lambda^2}\gamma pQ_6-\frac{\pi\gamma}{6\lambda}Q_5 \tag{87}$$

$$A'_{1,-1}(E')=\frac{i\gamma p}{12}Q_1-\frac{\pi^2}{30\lambda^2}i\gamma pQ_3-\frac{Q_7}{6}+\frac{\pi^2}{15\lambda^2}Q_9-\frac{2\pi^2}{3\lambda^2}Q_6+\frac{\pi\gamma}{6\lambda}Q_5 \tag{88}$$

$$A'_{2,1}(E')=\frac{\pi\gamma p}{30\lambda}Q_2+\frac{i\pi}{\lambda}Q_8-\frac{\pi^2}{15\lambda^2}i\gamma Q_6-\frac{2i\pi^3}{105\lambda^3}Q_{10} \tag{89}$$

$$A'_{3,1}(E')=\frac{\pi^2}{210\lambda^2}i\gamma pQ_3-\frac{\pi^2}{105\lambda^2}Q_9 \tag{90}$$

$$A'_{2,-1}(E')=-\frac{\pi\gamma p}{30\lambda}Q_2-\frac{i\pi}{\lambda}Q_8+\frac{\pi^2}{15\lambda^2}i\gamma Q_6+\frac{2i\pi^3}{105\lambda^3}Q_{10} \tag{91}$$

$$A'_{3,-1}(E')=-\frac{\pi^2}{210\lambda^2}i\gamma pQ_3+\frac{\pi^2}{105\lambda^2}Q_9 \tag{92}$$

$$A'_{4,1}(E')=-\frac{2i\pi^3}{2835\lambda^3}Q_{10} \tag{93}$$

$$A'_{4,-1}(E')=\frac{2i\pi^3}{2835\lambda^3}Q_{10} \tag{94}$$

$$A''_{1,-1}(E')=\frac{i\gamma p}{6}Q_1-\frac{\pi^2}{15\lambda^2}i\gamma pQ_3+\frac{i\gamma p}{2}Q_4-\frac{Q_7}{3}+\frac{2\pi^2}{15\lambda^2}Q_9+\frac{2\pi^2}{3\lambda^2}Q_6 +\frac{\pi}{\lambda}Q_5\left(ip-\frac{\gamma}{6}\right) \tag{95}$$

$$A''_{2,1}(E')=\frac{\pi\gamma p}{30\lambda}Q_2+\frac{i\pi}{15\lambda}Q_8+\frac{\pi\gamma p}{6\lambda}Q_5-\frac{\pi^2}{15\lambda^2}i\gamma A_6-\frac{2i\pi^3}{105\lambda^3}Q_{10} \tag{96}$$

$$A''_{2,-1}(E')=-\frac{\pi\gamma p}{30\lambda}Q_2-\frac{\pi\gamma p}{6\lambda}Q_5-\frac{i\pi}{5\lambda}Q_8-\frac{2\pi^2}{3\lambda^2}Q_6(p+i\gamma)+\frac{2i\pi^3}{35\lambda^3}Q_{10} \tag{97}$$

$$A''_{3,1}(E')=\frac{\pi^2 i\gamma p}{105\lambda^2}Q_3-\frac{2\pi^2}{105\lambda^2}Q_9+\frac{\pi^2}{15\lambda^2}i\gamma pQ_6 \tag{98}$$

$$A''_{3,-1}(E')=-\frac{2\pi^2}{105\lambda^2}i\gamma pQ_3+\frac{4\pi^2}{105\lambda^2}Q_9 \tag{99}$$

$$A''_{4,1}(E')=-\frac{2i\pi^3}{945\lambda^3}Q_{10} \tag{100}$$

$$A''_{4,-1}(E')=\frac{2i\pi^3}{567\lambda^3}Q_{10} \tag{101}$$

$$\left.\begin{aligned}A''_{5,1}(E')&=0\\ A''_{5,-1}(E')&=0\end{aligned}\right\} \tag{102}$$

If it is taken into account that

$$\frac{\partial}{\partial r}(r^{\beta}e^{-r/a_0})=\left(\beta r^{\beta-1}-\frac{r^{\beta}}{a_0}\right)e^{-r/a_0} \tag{103}$$

and

$$\frac{\partial}{\partial r}(r^{\beta-1}e^{-r/a_0})=\left((\beta-1)r^{\beta-2}-\frac{r^{\beta-1}}{a_0}\right)e^{-r/a_0} \tag{104}$$

then with the notation $q=1/a_0+i\kappa$ and

$$S=\int_0^{\infty} r^{\beta}e^{-qr}dr \tag{105}$$

it can be shown by integration by parts that

$$Q_1=-\frac{S}{a_0q}(1+a_0q) \tag{106}$$

$$Q_2=-\frac{S}{a_0q^2}(2+a_0q) \tag{107}$$

$$Q_3=-\frac{2S}{a_0q^3}(3+a_0q) \tag{108}$$

$$Q_4=S \tag{109}$$

$$Q_5=\frac{S}{q} \tag{110}$$

$$Q_6=\frac{2S}{q^2} \tag{111}$$

$$Q_7=-\frac{S}{a_0q}\left(1+\gamma^2\frac{ia_0k}{2}\right) \tag{112}$$

$$Q_8=-\frac{2S}{a_0q^2}\left[1+\frac{i\gamma^2}{2}\left(i+\frac{a_0k}{2}\right)\right] \tag{113}$$

$$Q_9=-\frac{6S}{a_0q^3} \tag{114}$$

$$Q_{10}=-\frac{24S}{a_0q^4} \tag{115}$$

The expressions (106) (115) were simplified by taking into account the fact that β is equal to $(1-\gamma^2)^{1/2}-1$ or approximately to $-\gamma^2/2$ and is therefore very small. Accordingly it was put equal to zero in all the Q's with the exception of Q_7 and Q_8 whose values, on the evidence of the expressions (86)-(102) are the most important ones. Therefore in the expressions (112) and (113) β was put equal to $-\gamma^2/2$.

On the basis of Eqs. (41) and (42) together with (40) one can write if the radial parts of the functions $\psi_{km}(E')$ which are common to all terms on account of the expressions (60), are omitted

$$\begin{aligned}\bar{\psi}_3\sim &A'_{0,-1}(E')(0-1+1)P_0^{-1}+A'_{1,-1}(E')(1-1+1)P_1^{-1}\\ &+A'_{1,1}(E')(1+1+1)\cdot P_1^{1}+A_{2,1}(E')(2+1+1)P_2^{1}+A'_{2,-1}(E')(2-1+1)P_2^{-1}\\ &+A'_{3,1}(E')(3+1+1)P_3^{1}+A'_{3,-1}(E')(3-1+1)P_3^{-1}+A'_{4,1}(E')(4+1+1)\cdot P_4^{1}\\ &+A'_{4,-1}(E')(4-1+1)P_4^{-1}+A''_{1,-1}(E')P_1^{-1}+A''_{2,1}(E')P_2^{1}\\ &+A''_{2,-1}(E')P_2^{-1}+A''_{3,1}(E')P_3^{1}+A''_{3,-1}(E')P_3^{-1}+A''_{4,1}(E')P_4^{1}\\ &+A''_{4,-1}(E')P_4^{-1}=P_1^{1}\cdot 3A'_{1,1}(E')+P_1^{-1}[A'_{1,-1}(E')+A''_{1,-1}(E')]\\ &+P_2^{1}[4A'_{2,1}(E')+A''_{2,1}(E')]+P_2^{-1}[2A'_{2,-1}(E')+A''_{2,-1}(E')]\\ &+P_3^{1}[5A'_{3,1}(E')+A''_{3,1}(E')]+P_3^{-1}[3A'_{3,-1}(E')+A''_{3,-1}(E')]\\ &+P_4^{1}[6A'_{4,1}(E')+A''_{4,1}(E')]+P_4^{-1}[4A'_{4,-1}(E')+A''_{4,-1}(E')].\end{aligned} \tag{116}$$

and

$$\psi_4 \sim A'_{0,-1}(E')(0-1)P_0^0+A'_{1,1}(E')(-1+1)P_1^2+A'_{1,-1}(E')(-1-1)P_1^0$$
$$+A'_{2,1}(E')(-2+1)P_2^2+A'_{2,-1}(E')(-2-1)\cdot P_2^0+A'_{3,1}(E')(-3+1)P_3^2$$
$$+A'_{3,-1}(E')(-3-1)P_3^0+A'_{4,1}(E')(-4+1)P_4^2+A'_{4,-1}(E')(-4-1)P_4^0$$
$$+A''_{1,-1}(E')P_1^0+A''_{2,1}(E')P_2^2+A''_{2,-1}(E')P_2^0+A''_{3,1}(E')P_3^2+A''_{3,-1}(E')P_3^0$$
$$+A''_{4,1}(E')P_4^2+A''_{4,-1}(E')P_4^0=-P_0^0A'_{0,-1}(E')+P_1^0[A''_{1,-1}(E') \tag{117}$$
$$-2A'_{1,-1}(E')]+P_2^0[A''_{2,-1}(E')-3A'_{2,-1}(E')]+P_2^2[A''_{2,1}(E')-A'_{2,1}(E')]$$
$$+P_3^0[A''_{3,-1}(E')-4A'_{3,-1}(E')]+P_3^2[A''_{3,1}(E')-2A'_{3,1}(E')]$$
$$+P_4^0[A''_{4,-1}(E')-5A'_{4,-1}(E')]+P_4^2[A''_{4,1}(E')-3A'_{4,1}(E')].$$

With regard to $\bar{\psi}_1$ and $\bar{\psi}_2$ it is to be remembered that they are small, of the order of p, when compared with $\bar{\psi}_3$, $\bar{\psi}_4$. Therefore it is sufficient to compute for them only the terms with the greatest absolute values and hence only the terms with the coefficients $A'_{1,-1}(E')$, $A'_{1,1}(E')$ and $A''_{1,-1}(E')$ are considered. Thus

$$\begin{aligned}\bar{\psi}_1&=-p\{P_2^1A'_{1,1}(E')+P_2^{-1}A'_{1,-1}(E')+P_0^{-1}(1-1)A''_{1,-1}(E')\}\\&=-p\{P_2^1A'_{1,1}(E')+P_2^{-1}A'_{1,-1}(E')\}\end{aligned} \tag{118}$$

and

$$\begin{aligned}\bar{\psi}_2&=-p\{P_2^2A'_{1,1}(E')+P_2^0A'_{1,-1}(E')+P_0^0(-1-1+1)A''_{1,-1}(E')\}\\&=-p\{P_2^2A'_{1,1}(E')+P_2^0A'_{1,-1}(E')-P_0^0A''_{1,-1}(E')\}.\end{aligned} \tag{119}$$

If Eqs. (86) (102) and (106) (115) are taken into account and substituted into Eqs. (116) (119) then after some calculation

$$\bar{\psi}_1=-p\sin\theta\cos\theta\cos\phi \tag{120}$$

$$\bar{\psi}_2=-p\sin^2\theta\cos\phi e^{i\phi} \tag{121}$$

$$\begin{aligned}\bar{\psi}_3=&\left(1+\gamma^2\frac{ia_0\kappa}{2}\right)\sin\theta\cos\phi-\frac{i\gamma p}{2}(1+a_0q)\sin\theta\cos\phi+\frac{i\gamma pa_0q}{2}\sin\theta e^{-i\phi}\\&+\frac{4\pi i}{\lambda q}\sin\theta\cos\theta\cos\phi\left[1+\frac{i\gamma^2}{2}\left(i+\frac{a_0\kappa}{2}\right)\right]+\frac{\pi\gamma p}{\lambda q}(2+a_0q)\sin\theta\cos\theta\cos\phi\\&-\frac{\pi\gamma a_0}{\lambda}\sin\theta\cos\theta\cos\phi-\frac{12\pi^2}{\lambda^2q^2}\sin\theta\cos^2\theta\cos\phi\\&+\frac{2\pi^2}{\lambda^2q^2}(3+a_0q)i\gamma p\sin\theta\cos^2\theta\cos\phi-\frac{2\pi^2}{\lambda^2}\frac{a_0}{q}i\gamma p\sin\theta\cos^2\theta e^{i\phi}\\&+\frac{\pi a_0}{2\lambda}\sin\theta(\gamma e^{i\phi}+2ipe^{-i\phi})-\frac{2\pi^2}{\lambda^2}\frac{a_0}{q}\sin\theta\cos\theta(2pe^{-i\phi}-i\gamma e^{i\phi})\\&-\frac{32i\pi^3}{\lambda^3q^3}\sin\theta\cos^3\theta\cos\phi\end{aligned} \tag{122}$$

$$\psi_4=\frac{\pi i a_0}{\lambda}-\frac{i\gamma p a_0 q}{2}\cos\theta. \tag{123}$$

In the Eq. (123) only the terms with the greatest absolute values were taken into account, the rest can be safely omitted to the present approximation. Moreover in all the four Eqs. (120)-(123) the common factor $-S/a_0q$ was omitted.

The Eqs. (120), (121), (122) and (123) represent a spherical material wave diverging from the considered atom, whose amplitude depends upon the direction in space. This can be seen at once if one takes into account the neglected common radial factors. Therefore the spatial distribution of the photoelectrons (whose kinetic energy and velocity do not depend upon the direction of emission as can be seen from the foregoing discussion) is given by the intensity of these waves or by the density of electric charge emitted in a considered direction, which is equal to

$$-e\overline{\phi\psi}=-e(\bar{\phi}_1\bar{\psi}_1+\bar{\phi}_2\bar{\psi}_2+\bar{\phi}_3\bar{\psi}_3+\bar{\phi}_4\bar{\psi}_4). \tag{10}$$

It is to be remembered that ϕ is conjugate complex with regard to ψ. According to the relations (120)-(123)

$$\begin{aligned}
\phi\psi\sim\; & p^2\sin^2\theta\cos^2\phi+\frac{\pi^2a_0{}^2}{\lambda^2}+\frac{\gamma^2p^2}{4}a_0{}^2qq^*\cos^2\theta-\frac{\pi a_0{}^2}{2\lambda}\gamma p(q+q^*)\cos\theta \\
& +\sin^2\theta\cos^2\phi+\frac{16\pi^2}{\lambda^2qq^*}\sin^2\theta\cos^2\theta\cos^2\phi-\frac{4\pi i}{\lambda qq^*}(q-q^*)\sin^2\theta\cos\theta\cos^2\phi \\
& +\frac{2\pi a_0k\gamma^2}{\lambda qq^*}(q+q^*)\sin^2\theta\cos\theta\cos^2\phi+\left[\frac{2\pi i\gamma^2}{\lambda qq^*}(q-q^*)\right. \\
& \left.-\frac{\pi\gamma^2a_0\kappa}{\lambda qq^*}(q+q^*)\right]\sin^2\theta\cos\theta\cos^2\phi-\frac{12\pi^2}{\lambda^2q^2q^{*2}}(q^2+q^{*2})\sin^2\theta\cos^2\theta\cos^2\phi \\
& +\frac{a_0i\gamma p}{2}(q^*-q)\sin^2\theta\cos^2\phi+\frac{2\pi\gamma p}{\lambda}\left(a_0+\frac{q+q^*}{qq^*}\right)\sin^2\theta\cos\theta\cos^2\phi \\
& -\frac{2\pi a_0\gamma}{\lambda}\sin^2\theta\cos^2\theta\cos^2\phi+\frac{i\gamma p a_0}{2}(qe^{-i\phi}-q^*e^{i\phi})\sin^2\theta\cos\phi \\
& +\frac{\pi a_0}{\lambda}(\gamma\cos\phi+2p\sin\phi)\sin^2\theta\cos\phi+\frac{6\pi^2 i}{\lambda^2q^2q^{*2}}(q^{2*}-q^2)\gamma p\sin^2\theta\cos^2\theta\cos^2\phi \\
& -\frac{2\pi^2}{\lambda^2}\,\frac{a_0i\gamma p}{qq^*}(q-q^*)\sin^2\theta\cos^2\theta\cos^2\phi-\frac{4\pi^2}{\lambda^2}\,\frac{a_0p}{qq^*}\cdot(qe^{i\phi}+q^*e^{-i\phi})\sin^2\theta\cos^2\theta\cos\phi \\
& +\frac{2\pi^2}{\lambda^2}\,\frac{a_0i\gamma}{qq^*}(q^*e^{i\phi}-qe^{-i\phi})\sin^2\theta\cos^2\theta\cos\phi \\
& +\frac{32}{\lambda^3(qq^*)^3}i\pi^3(q^3-q^{*3})\sin^2\theta\cos^3\theta\cos^2\phi
\end{aligned} \tag{124}$$

$$-\frac{2\pi^2 a_0 i\gamma p}{\lambda^2}\sin^2\theta\cos^2\theta\cos\phi(e^{-i\phi}/q-e^{-i\phi}/q^*)$$

$$+\frac{48i\pi^3}{\lambda^3 qq^*}\left(\frac{1}{q}-\frac{1}{q^*}\right)\sin^2\theta\cos^3\theta\cos^2\phi\cdot$$

If on the other hand the initial state of the atom is described by Eqs. (64) and (66) then it is found that for the solutions of the type (41) the coefficients $A'_{km}(E')$ are different from zero for

$$\begin{array}{llll} k=0 & m=0 & k=3 & m=0,\ -2 \\ k=1 & m=0,\ -2 & k=4 & m=0,\ -2 \\ k=2 & m=0,\ -2 & & \end{array} \tag{125}$$

whereas for the type (42) $A''_{km}(E')$ differ from zero for

$$\begin{array}{llll} k=1 & m=0 & k=3 & m=0,\ -2 \\ k=2 & m=0,\ -2 & k=5 & m=0,\ -2 \\ k=3 & m=0,\ -2 & & \end{array} \tag{126}$$

After some calculations quite similar to the ones given previously for the foregoing possibility it follows that in this second case

$$\bar{\psi}_1=p\sin^2\theta\cos\phi e^{-i\phi}$$

$$\bar{\psi}_2=-p\sin\theta\cos\theta\cos\phi \tag{127}$$

$$\bar{\psi}_3=\frac{\pi i a_0}{\lambda}-\frac{i\gamma p a_0 q}{2}\cos\theta \tag{128}$$

$$\bar{\psi}_4=-\left\{\left(1+\frac{\gamma^2 i a_0\kappa}{2}\right)\sin\theta\cos\phi-\frac{i\gamma p}{2}(1+a_0q)\sin\theta\cos\phi+\frac{i\gamma p a_0 q}{2}\sin\theta e^{i\phi}\right. \tag{129}$$

$$+\frac{4\pi i}{\lambda q}\sin\theta\cos\theta\cos\phi\left[1+\frac{i\gamma^2}{2}\left(i+\frac{a_0\kappa}{2}\right)\right]+\frac{\pi\gamma p}{\lambda q}(2+a_0q)\sin\theta\cos\theta\cos\phi$$

$$-\frac{\pi\gamma a_0}{\lambda}\sin\theta\cos\theta\cos\phi-\frac{12\pi^2}{\lambda^2q^2}\sin\theta\cos^2\theta\cos\phi+\frac{2\pi^2}{\lambda^2q^2}(3+a_0q)i\gamma p\sin\theta\cos^2\theta\cos\phi$$

$$-\frac{2\pi^2}{\lambda^2}\frac{a_0}{q}i\gamma p\sin\theta\cos^2\theta e^{-i\phi}+\frac{\pi a_0}{2\lambda}\sin\theta(\gamma e^{-i\phi}+2pie^{i\phi}) \tag{130}$$

$$\left.-\frac{2\pi^2}{\lambda^2}\frac{a_0}{q}(2pe^{i\phi}-i\gamma e^{-i\phi})\sin\theta\cos\theta-\frac{32i\pi^3}{\lambda^3q^3}\sin\theta\cos^3\theta\cos\phi.\right\}$$

Therefore in this case

$$\phi\psi=p^2\sin^2\theta\cos^2\phi+\frac{\pi^2a_0^2}{\lambda^2}+\frac{\gamma^2p^2a_0^2qq^*}{4}\cos^2\theta-\frac{\pi a_0^2\gamma p}{2\lambda}(q+q^*)\cos\theta$$

$$+\sin^2\theta\cos^2\phi+\frac{16\pi^2}{\lambda^2 qq^*}\sin^2\theta\cos^2\theta\cos^2\phi-\frac{4\pi i}{\lambda qq^*}(q-q^*)\sin^2\theta\cos\theta\cos^2\phi$$
$$+\frac{2\pi a_0\kappa\gamma^2}{\lambda qq^*}(q+q^*)\sin^2\theta\cos\theta\cos^2\phi+\left[\frac{2\pi i\gamma^2}{\lambda qq^*}(q-q^*)\right.$$
$$\left.-\frac{\pi\gamma^2 a_0\kappa}{\lambda qq^*}(q+q^*)\right]\sin^2\theta\cos\theta\cos^2\phi-\frac{12\pi^2}{\lambda^2(qq^*)^2}(q^2+q^{*2})\sin^2\theta\cos^2\theta\cos^2\phi$$
$$+\frac{a_0 i\gamma p}{2}(q^*-q)\sin^2\theta\cos^2\phi+\frac{2\pi\gamma p}{\lambda}\left(a_0+\frac{q+q^*}{qq^*}\right)\sin^2\theta\cos\theta\cos^2\phi \tag{131}$$
$$-\frac{2\pi\gamma a_0}{\lambda}\sin^2\theta\cos\theta\cos^2\phi+\frac{i\gamma p a_0}{2}(qe^{i\phi}-q^*e^{-i\phi})\sin^2\theta\cos\phi$$
$$+\frac{\pi a_0}{\lambda}\sin^2\theta\cos\phi(\gamma\cos\phi-2p\sin\phi)+\frac{6\pi^2 i}{\lambda^2(qq^*)^2}(q^{*2}-q^2)\gamma p\sin^2\theta\cos^2\theta\cos^2\phi$$
$$+\frac{2\pi^2 a_0 i\gamma p}{\lambda^2 qq^*}(q^*-q)\sin^2\theta\cos^2\theta\cos^2\phi-\frac{4\pi^2}{\lambda^2}\frac{a_0 p}{qq^*}(qe^{-i\phi}+q^*e^{i\phi})\sin^2\theta\cos^2\theta\cos\phi$$
$$+\frac{2\pi^2}{\lambda^2}\frac{a_0 i\gamma}{qq^*}(q^*e^{-i\phi}-qe^{i\phi})\sin^2\theta\cos^2\theta\cos\phi$$
$$+\frac{32i\pi^3}{\lambda^3(qq^*)^3}(q^3-q^{*3})\sin^2\theta\cos^3\theta\cos^2\phi$$
$$-\frac{2\pi^2 a_0 i\gamma p}{\lambda^2}\sin^2\theta\cos^2\theta\cos\phi(e^{-i\phi}/q-e^{i\phi}/q^*)$$
$$+\frac{48i\pi^3}{\lambda^3 qq^*}\left(\frac{1}{q}-\frac{1}{q^*}\right)\sin^2\theta\cos^3\theta\cos^2\phi\cdot$$

According to G. Wentzel[16] the average of the expressions (124) and (131) is to be taken to find the real spatial distribution of the photoelectrons. Therefore this distribution is given by

$$\phi\psi\sim p^2\sin^2\theta\cos^2\phi+\frac{\pi^2 a_0^2}{\lambda^2}+\frac{\gamma^2 p^2 a_0^2 qq^*}{4}\cos^2\theta-\frac{\pi a_0^2\gamma p}{2\lambda}(q+q^*)\cos\theta$$
$$+\sin^2\theta\cos^2\phi+\frac{16\pi^2}{\lambda^2 qq^*}\sin^2\theta\cos^2\theta\cos^2\phi-\frac{4\pi i}{\lambda qq^*}(q-q^*)\sin^2\theta\cos\theta\cos^2\phi$$
$$+\frac{\pi a_0\kappa\gamma^2}{\lambda qq^*}(q+q^*)\sin^2\theta\cos\theta\cos^2\phi+\frac{2\pi i\gamma^2}{\lambda qq^*}(q-q^*)\sin^2\theta\cos\theta\cos^2\phi$$
$$+\frac{a_0 i\gamma p}{2}(q^*-q)\sin^2\theta\cos^2\phi-\frac{12\pi^2}{\lambda^2(qq^*)^2}(q^2+q^{*2})\sin^2\theta\cos^2\theta\cos^2\phi$$

[16] G. Wentzel, l. c.

$$
\begin{aligned}
&-\frac{2\pi\gamma a_0}{\lambda}(1-p)\sin^2\theta\cos\theta\cos^2\phi \\
&+\frac{2\pi\gamma p}{\lambda}\left(\frac{q+q^*}{qq^*}\right)\sin^2\theta\cos\theta\cos^2\phi+\frac{i\gamma pa_0}{2}(q-q^*)\sin^2\ \ \cos\ \phi \\
&+\frac{\pi a_0\gamma}{2}\sin^2\theta\cos^2\phi+\frac{6\pi^2 i(q^{*2}-q^2)}{\lambda^2(qq^*)^2}\gamma p\sin^2\theta\cos^2\theta\cos^2\phi \\
&-\frac{4\pi^2}{\lambda^2}a_0 p\left(\frac{q+q^*}{qq^*}\right)\sin^2\theta\cos^2\theta\cos^2\phi+\frac{2\pi^2}{\lambda^2}\frac{a_0 i\gamma}{qq^*}(q^*-q)\sin^2\theta\cos^2\theta\cos^2\phi \\
&+\frac{32i\pi^3}{\lambda^3(qq^*)^3}(q^3-q^{*3})\sin^2\theta\cos^3\theta\cos^2\phi \\
&+\frac{48i\pi^3}{\lambda^3 qq^*}\left(\frac{1}{q}-\frac{1}{q^*}\right)\sin^2\theta\cos^2\theta\cos^2\phi\cdot
\end{aligned}
\tag{132}
$$

If the notations used by Sommerfeld are adopted, then

$$a_0=a/Z\ ;\ q=Z/a+i\kappa\ ;\ \gamma=\alpha Z \tag{133}$$

and so

$$
\begin{aligned}
&q+q^*=2Z/a\ ; \qquad q-q^*=2i\kappa\ ; \qquad qq^*=Z^2/a^2+\kappa^2\ ; \\
&q^2-q^{*2}=4i\kappa Z/a\ ;\ q^2+q^{*2}=2(Z^2/a^2-\kappa^2)\ ;\ q^3-q^{*3}=2i\kappa(3Z^2/a^2-\kappa^2)\ ;
\end{aligned}
\tag{134}
$$

Moreover, according to Eq. (55)

$$p=\frac{B}{A}=\left(\frac{E'-mc^2}{E'+mc^2}\right)^{1/2}=\frac{\kappa}{A^2}\cong\frac{\kappa h}{4\pi mc}=\frac{\alpha\kappa a}{2} \tag{135}$$

but $E'-mc^2$ is equal to the kinetic energy of the photoelectron, $E'\sim mc^2$ and therefore

$$p\cong\left(\frac{mv^2}{4mc^2}\right)^{1/2}=\frac{v}{2c}\cdot \tag{136}$$

Substitution of these values into Eq. (132) leads

$$
\begin{aligned}
\phi\psi\sim&\sin^2\theta\cos^2\phi\left(1+p^2+\frac{\pi a\alpha}{\lambda}\right)+\sin^2\theta\cos\theta\cos^2\phi\left\{\frac{8\pi\kappa}{\lambda(Z^2/a^2+\kappa^2)}\right. \\
&\left.+\frac{2\pi\alpha Z^2}{\lambda(Z^2/a^2+\kappa^2)}\cdot\frac{p}{a}-\frac{2\pi\kappa\gamma^2}{\lambda(Z^2/a^2+\kappa^2)}-\frac{2\pi a\alpha}{\lambda}(1-p)\right\}+\sin^2\theta\cos^2\theta\cos^2\phi \\
&\cdot\left\{\frac{48\pi^2\kappa^2}{\lambda^2(Z^2/a^2+\kappa^2)^2}-\frac{8\pi^2}{\lambda^2(Z^2/a^2+\kappa^2)}+\frac{4\pi^2 a\alpha\kappa}{\lambda^2(Z^2/a^2+\kappa^2)}-\frac{24\pi^2 pa\alpha\kappa Z^2/a^2}{\lambda^2(Z^2/a^2+\kappa^2)^2}\right. \\
&\left.-\frac{8\pi^2 p}{\lambda^2(Z^2/a^2+\kappa^2)}\right\}+\sin^2\theta\cos^3\theta\cos^2\phi\left\{\frac{256\pi^3\kappa^3}{\lambda^3(Z^2/a^2+\kappa^2)^3}-\frac{96\pi^3\kappa}{\lambda^3(Z^2/a^2+\kappa^2)^2}\right\} \\
&+\frac{\pi^2 a^2}{Z^2\lambda^2}-\frac{\pi a\alpha p}{\lambda}\cos\theta+\frac{a^2\alpha^2 p^2}{4}\left(\frac{Z^2}{a^2}+\kappa^2\right)\cos^2\theta.
\end{aligned}
\tag{137}
$$

According to Sommerfeld and to the Eqs. (47)

$$\kappa=\frac{2\pi mv}{h(1-v^2/c^2)^{1/2}}\,; \qquad a=\frac{h^2}{4\pi^2mc^2} \tag{138}$$

$$\frac{Z^2}{a^2}+\kappa^2=\frac{8\pi^2m\nu}{h} \tag{139}$$

furthermore

$$p^2 \cong \epsilon/2mc^2=(h\nu-I_0)/2mc^2 \quad (I_0\text{—ionization potential}) \tag{140}$$

and

$$\pi a\alpha/\lambda = h\nu/2mc^2. \tag{141}$$

If these values are substituted into Eq. (137) then

$$\begin{aligned}\phi\psi=\sin^2\theta\cos^2\phi\left(1+\frac{h\nu}{mc^2}-\frac{I_0}{2mc^2}\right)+\frac{2v}{c}\left(1-\frac{\alpha^2z^2}{8}+\frac{v^2}{c^2}+\frac{h\nu}{4mc^2}\right.\\ \left.-\frac{h\nu}{c^2mv}\right)\sin^2\theta\cos\theta\cos^2\phi+\frac{3v^2}{c^2}\left(1-\frac{h\nu}{3mv^2}\right)\sin^2\theta\cos^2\theta\cos^2\phi\\ +\frac{4v^3}{c^3}\left(1-\frac{3h\nu}{4mv^2}\right)\sin^2\theta\cos^3\theta\cos^2\phi+\frac{\pi^2a^2}{Z^2\lambda^2}-\frac{h\nu}{4mc^2}\cdot\frac{v}{c}\cos\theta\\ +\frac{h\nu}{8mc^2}\,\frac{v^2}{c^2}\cos^2\theta.\end{aligned} \tag{142}$$

The term $-\alpha^2Z^2/4$ in the parenthesis after $3v^2/c^2$ was omitted, because other terms of the same order have been also omitted for the present approximation.

If the right side of the Eq. (142) is divided by $1+h\nu/mc^2-I_0/2mc^2$ then to the same degree of approximation

$$\begin{aligned}\phi\psi=\sin^2\theta\cos^2\phi\left\{1+\frac{2v}{c}\left(1-\frac{\alpha^2Z^2}{8}+\frac{I_0}{2mc^2}+\frac{v^2}{2c^2}-\frac{3h\nu}{4mc^2}-\frac{1}{2}\,\frac{h\nu}{cmv}\right)\cos\theta\right.\\ \left.+\frac{3v^2}{c^2}\left(1-\frac{h\nu}{3mv^2}\right)\cos^2\theta+\frac{4v^3}{c^3}\left(1-\frac{3h\nu}{4mv^2}\right)\cos^3\theta\right\}\\ +\frac{\pi^2a^2}{Z^2\lambda^2}-\frac{h\nu}{4mc^2}\,\frac{v}{c}\cos\theta+\frac{h\nu}{8mc^2}\,\frac{v^2}{c^2}\cos^2\theta\end{aligned} \tag{143}$$

On the basis of Eq. (143) one can calculate, as Sommerfeld has done, the angle of the cone surrounding the z axis inside of which half of the electrons are emitted. Then to Sommerfeld's degree of approximation

$$\theta=\pi/2-v/2c. \tag{144}$$

This result agrees with the elementary calculation of the basis of the quantum hypothesis.[17] Sommerfeld's result differs by the factor 9/5 before

[17] A. H. Compton, X-rays and Electrons, London, 1927, p. 240.

$-v/2c$ which is due, as can be seen by repeating his calculations, to the neglecting of the normalizing factors for the spherical harmonics. Thus, instead of the harmonics

$$P_k{}^m(\cos\theta) \tag{145}$$

in the formula (4) on the 210th page of the "Wellenmechanisches Ergänzungsband," the functions

$$\left[\frac{(k-m)!}{(k+m)!}\,\frac{2k+1}{2}\right]^{1/2} P_k{}^m(\cos\theta) \tag{146}$$

ought to be used, otherwise the formula (7) on the page 212 is not correct. The same remark applies to the result of Carrelli.

To calculate the angle θ with a higher degree of accuracy one can start from the equation given by Sommerfeld

$$\int_0^{2\pi}\int_0^{\theta}\phi\psi\sin\theta d\theta d\phi=\int_0^{2\pi}\int_0^{\pi}\phi\psi\sin\theta d\theta d\phi. \tag{147}$$

To simplify the notations the relation (143) can be written in the form

$$\phi\psi=\sin^2\theta\cos^2\phi(1+b\cos\theta+c\cos^2\theta+d\cos^3\theta)+A-B\cos\theta+C\cos^2\theta. \tag{148}$$

Eq. (147) leads then to

$$2\cos\theta+4A\cos\theta+b\cos^2\theta-\frac{2\cos^3\theta}{3}=\frac{b}{2}+\frac{d}{6}-2B. \tag{149}$$

If it is supposed that θ is equal to $\pi/2-x$, then from (149) it follows that

$$\sin x=\frac{b}{4}+\frac{d}{12}-B-\frac{5b^3}{192}-\frac{Ab}{2} \tag{150}$$

whence, on account of (143)

$$\sin x=\frac{v}{2c}\left(1-\frac{\alpha^2Z^2}{8}+\frac{I_0}{2mc^2}+\frac{3v^2}{4c^2}-\frac{7h\nu}{4mc^2}-\frac{1}{2}\,\frac{h\nu}{cmv}-\frac{2\pi^2a^2}{Z^2\lambda^2}\right). \tag{151}$$

If it is supposed that the photoelectrons are emitted from the K-level only, which conforms with the initial assumptions in this paper then

$$\frac{I_0}{2mc^2}=\frac{RhZ^2}{2mc^2}=\frac{\alpha^2Z^2}{4} \tag{152}$$

and so Eq. (151) can be written in the following form

$$\sin x=\frac{v}{2c}\left(1-\frac{5\alpha^2Z^2}{8}-\frac{h\nu}{4mc^2}-\frac{1}{2}\,\frac{h\nu}{cmv}-\frac{2\pi^2a^2}{Z^2\lambda^2}\right). \tag{153}$$

According to Birge[18] $\alpha=7.283\times10^{-3}$ and $h/mc=0.02428$A. If moreover the value of λ is given in Ångström units, then finally

[18] R. T. Birge, Phys. Rev. Suppl., July 1929.

$$\sin x = \frac{v}{2c}\left(1 - 3{,}53.10^{-5}Z^2 - \frac{v}{4c} - \frac{0.006}{\lambda} - \frac{5.50}{Z^2\lambda^2}\right). \tag{154}$$

Eq. (154) shows that the increase of the frequency of the incident radiation causes a decrease of $\sin x$ from the value $v/2c$. However, this effect becomes appreciable only for very high frequencies such as correspond to very hard x-rays, and γ-rays. This does not apply to the last term in the brackets, namely $5.50/Z^2\lambda^2$, which becomes of importance even for ordinary x-rays in the case of low values of Z. Therefore for helium and especially for hydrogen the value of $\sin x$ should be markedly less than $v/2c$. For both these gases and for x-rays of the order of 1Å the coefficient A in Eq. (149) becomes of the order of unity and so instead of Eq. (159) it follows that

$$\sin x = \frac{b}{4(1+2A)}\left\{1 + \frac{d}{36} - \frac{4B}{6} - \frac{b^2}{48}\frac{(5+12A)}{(1+2A)^3}\right\} \tag{155}$$

whence finally

$$\sin x = \frac{v}{2c(1+2A)}\left\{1 - 3.77\times 10^{-5}Z^2 - \frac{v}{4c} - \frac{0.002}{\lambda} - \frac{v^2}{12c^2}\frac{5+12A}{(1+2A)^3}\right\} \tag{156}$$

where

$$A = \frac{\pi^2 a^2}{Z^2\lambda^2} = \frac{2.75}{Z^2\lambda^2}\cdot \tag{157}$$

The formulas (154) and (156) do not agree with the results obtained recently by Williams, Nuttall and Barlow[19] but they represent fairly well the results of other authors.[20] However, the experimental methods used to find the spatial distribution of photoelectrons cannot as yet claim a high degree of accuracy and it seems therefore well to wait for a final decision till more experimental data are available.

It is to be noted that the angle of the maximum emission of photoelectrons does not coincide with the above computed $\theta = \pi/2 - x$. This angle can be calculated from the formula

$$\frac{d}{d\theta}(\phi\psi) = 0. \tag{158}$$

In the first approximation this leads to the value

$$\theta_1 = \pi/2 - v/c \tag{159}$$

which differs from the corresponding value of Sommerfeld

$$\theta_1 = \pi/2 - 9v/5c \tag{159'}$$

by the disappearance of the factor 9/5.

[19] E. J. Williams, Nature, **121**, 134 (1928). E. J. Williams, J. M. Nuttall and H. S. Barlow, Proc. Roy. Soc. **121**, 611 (1928).

[20] A. Sommerfeld, l.c. p. 225, fig. 20.

In the second approximation it can be found that according to Eqs. (158) and (148)

$$\theta_1 = \pi/2 - x_1$$

where

$$\sin x_1 = \frac{b}{2} + \frac{cb}{2} - \frac{5b^3}{16} - \frac{B/\cos^2\phi}{2} \qquad (160)$$

or according to Eqs. (148) and (143)

$$\sin x_1 = \frac{v}{c}\left\{1 - \frac{11h\nu}{4mc^2} + \frac{5\alpha^2 Z^2}{8} + \frac{1}{2}\ \frac{h\nu}{cmv} - \frac{h\nu}{8mc^2}\ \frac{1}{\cos^2\phi}\right\}. \qquad (161)$$

Hence finally by using the formerly given values of h/mc and α

$$\sin x_1 = \frac{v}{c}\left(1 + 3{,}53.10^{-5}Z^2 - \frac{v}{4c} - \frac{0.067}{\lambda} - \frac{0.003}{\lambda \cos^2\phi}\right). \qquad (162)$$

It can be readily seen from this formula that for very hard x-rays the value of $\sin x_1$ begins to be appreciably smaller than v/c, but for the same values of v and λ the values of $\sin x_1$ increases with the increase of Z.

The independence of the maximum of photoelectric emission from the value of A can be readily understood with regard to the fact that Eq. (148), if coefficients B and C are neglected represents a superposition of an emission given by the term

$$\sin^2\theta \cos^2\phi(1 + b\cos\theta + c\cos^2\theta + d\cos^3\theta)$$

which shows a pronounced maximum and an emission independent from the direction in space, represented by the term A.

The values of the angles of maximum photoelectric emission which follow from the data of Loughridge[21] agree fairly well with the formula (162). This formula ceases to be valid for ϕ nearly equal $\pi/2$ or $3\pi/2$.

The author wishes to express his gratitudes to the International Education Board for the granting of a fellowship.

Note added during the proof. The average forward momentum of the photoelectrons can be calculated readily from the Eq. (148). It appears to be equal to $bmv/5$ or, if the ionization energy is neglected, so that

$$b = \frac{4h\nu}{c}/mv$$

equal to $0.8h\nu/c$. According to Williams (Proc. Roy. Soc. **121,** 611, 1928) an average momentum $0.8h\nu/c$ of photoelectrons in the direction of the x-ray beam corresponds to a constant momentum $5/4\ (0.8h\nu/c)$ in the direction of the x-ray beam, superimposed on the radial momenta of the photo-

[21] D. H. Loughridge, Phys. Rev. **30,** 488 (1927).

electrons distributed proportionally to $\sin^2\theta\cos^2\phi$. It follows that this additional component of momentum is equal to the momentum of the photon.

It is to be noted that all the results of this paper were obtained by neglecting the term $-i\delta\log r$ in the exponential of the formula (56). The value of δ is according to Eq. (57)

$$\delta=\frac{\gamma^2}{2}\left(\frac{A}{B}+\frac{B}{A}\right)=\gamma^2\frac{c}{v}\cdot \tag{163}$$

The smaller the value of δ, the smaller the effect of its neglect. It follows that the results of this paper are more exact, the greater the velocity of the photoelectrons and the smaller the atomic number.

The calculations of this paper can be repeated taking δ into account, which causes the wave functions representing the photoelectrons to take the form

$$\psi\sim r^{-i\delta}e^{-i\kappa r}/r\cdot \tag{164}$$

The calculations are easy but rather long; they lead to the result that to the first approximation

$$\phi\psi\sim\sin^2\theta\cos^2\phi\left\{1+\frac{2v}{c}\left(1+\frac{\delta Z}{2a\kappa}\right)\cos\theta\right\}\cdot \tag{165}$$

It follows that for $\delta Z/2a\kappa\ll 1$ or $(v/c)^2\gg(\alpha Z)^3/2$ the terms with δ can be neglected and the formula (143) is then valid.

Thus for comparatively slow photoelectrons and high atomic numbers the formula (165) is to be applied instead of (143), whereas this latter formula is valid for high speed photoelectrons and low atomic numbers. Eq. (165) ceases to be valid for very slow photoelectrons, because the use of the asymptotic formula (164) is then not justified.