# Theory of volume photo-emission from condensed media

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Expressions have been obtained for the photo-emission electron current from condensed media by direct summation of quantum-mechanical probability waves from the various centers. Taking into account the coherence of the waves in the crystal relates the photocurrent characteristics to the characteristics of the crystal lattice. Here specific wave effects of photocurrent enhancement arise for certain positions of the crystal surface relative to the crystal faces. The theory is applicable to description of photo-emission from disordered media, metals, and semiconductors. A comparison is made with the experimental results. Here the main attention is devoted to those results which up to the present time do not have a generally accepted natural explanation: the dependence of the photo-effect on the polarization and angle of incidence of the light, the dependence on the orientation of the surface, the frequency dependence of the photo-effect from semiconductors, and the ratio of currents of the one-photon and two-photon effects.

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## 1. INTRODUCTION

The theory of external electron photoemission from condensed media has a lengthy history. The first calculations were carried out in the single-particle approximation with use of effective potentials broken off at the surface of the medium.[1,2] Recently in discussion of metals investigators have begun to take into account the possibility of excitation by light of volume and surface plasmons.[2,3] However, conditions exist (corresponding usually to threshold energies) in which direct excitation of collective motions plays a minor role. Nevertheless, even in these comparatively simple cases until recently no natural generally accepted explanations were obtained for a number of experimental facts. In this connection we can mention, first of all, the absence of a clear explanation of the observed form of the dependence of the photoeffect on polarization and angle of incidence of the light.[4,5] Second, it is difficult to explain the dependence, carefully measured in recent years,[6,7] of the photocurrent from semiconductors on the frequency of the light. The complicated expressions for the density of states used to explain this dependence are extremely artificial. Third, we have left to the end the unexplained dependence of the photoeffect on the location of the crystal surface relative to the crystal symmetry axes. In concluding this list, which could be considerably extended, we will point out the interesting fact that the ratio measured in mercury[4] of the two-photon quantum yield to the one-photon yield has turned out to be greater than the calculated value by two orders of magnitude.

To resolve the difficulties of the theory and to explain the experimental data, a number of authors have recently turned to the so-called three stage model, in which the emission is represented as consisting of the following three stages: optical excitation in the volume,[1)] motion to the surface, and passage through this surface. Berglund and Spicer[6] are usually cited as the first developers of the model. In this and similar studies only the first stage is treated as a quantum transition, while the motion to the surface is represented as diffusion or random walks. This treatment was sharply criticized by Mahan,[8] who contended that all stages must be considered as a single quantum-mechanical process. This criticism obviously is not always justified; in particular, the approach of Ref. 6 is undoubtedly applicable in discussion of the photoemission from semiconductors with a negative affinity, when the electrons undergo a large number of inelastic and incoherent scattering events before reaching the boundary. However, in many cases when the thickness of the layer contributing to emission is small, it is actually more correct to describe all stages of the photoemission in a unified manner. The means of carrying out this program in Ref. 8 has aroused serious objections. Without going into detail, we note that Mahan[8] used an incorrect asymptote of the emitted-electron wave function at large distances. In addition, as noted by Powell et al.[7] Mahan's conclusion[8] that the photoeffect corresponds to direct interband transitions in which quasimomentum is conserved is not in agreement with experiment.

In the present article we discuss the theory of photoemission from condensed media, constructing a general scheme of the stationary quantum-mechanical scattering problem. The starting point is the integral equation for the electron wave function $\Psi_S(\mathbf{x})$ corresponding to an optically excited state. Using the single-particle and dipole approximations for the one-photon component $\Psi_S^{(1)}$ outside the sources, we have ($\hbar = 1$)

$$\begin{aligned}\Psi_s^{(1)}(\mathbf{x}) &= \frac{e}{2\omega}\int G_s(\mathbf{x},\mathbf{x}')\mathbf{E}(\mathbf{x}')\mathbf{p}\Psi_i(\mathbf{x}')d^3\mathbf{x}' \\ &\approx \frac{e}{2\omega^2}\int G_s(\mathbf{x},\mathbf{x}')\mathbf{E}(\mathbf{x}')[\mathbf{H}\times\mathbf{p}]\Psi_i(\mathbf{x}')d^3\mathbf{x}' \\ &= \frac{e}{2\mu_s\omega^2}\int G_s(\mathbf{x},\mathbf{x}')\mathbf{E}(\mathbf{x}')\frac{\partial V}{\partial \mathbf{x}'}\Psi_i(\mathbf{x}')d^3\mathbf{x}'.\end{aligned} \tag{1}$$

Here $\omega$ is the frequency of the light, V is the potential, $\mathbf{E}(\mathbf{x})$ is the field strength of the electromagnetic wave which falls off in the interior of the medium, $\Psi_i$ is the initial wave function of an electron with energy $\mathscr{E}_i$, $G_S(\mathbf{x},\mathbf{x}')$ is the Green's function corresponding to diverging waves with energy $\mathscr{E}_i + \omega$, and $\mu_S$ is the mass of the particle in the medium. The main contribution to Eq. (1), from which the desired current is constructed, is from the region of the most rapid change of the potential V. A similar result exists for many-photon transitions, as will be evident from Eq. (15). This fact, which is related to the conservation of momentum, sharply distinguishes the problem discussed from the problem of finding the spectrum of a crystal. In considering bounded condensed media there are two main causes of variation of the potential V. The first of these is due to the presence of the surface; the contribution to Eq. (1) corresponding to it we will not take into account, since the corresponding effect has been discussed

in detail in a number of calculations of the surface photoeffect[2] and can be excluded in principle in experiments with s-polarized light. We will present below reasoning on how this effect is included in the scheme considered. We will concentrate our discussion on the second cause of variation of V, which is due to the presence in the volume of ion core potentials, self-consistent potential wells for excess electrons, defects, and so forth.

The discussion begins with a solution of model problems, the first of which (Sec. 2) corresponds to the case of an isolated center, and the second (Sec. 3) to a crystal lattice. In Sec. 4 the formulas obtained are put in a form suitable for comparison with experiment.

## 2. ISOLATED CENTER IN A MEDIUM

Let us consider first the following model quantum-mechanical problem. Let there be at some point $\mathbf{x}^0$ of the half-space $x_3 < 0$ a source of spherical waves with a certain angular momentum $l_S$ and its projection $m_S$ on the $x_3$ axis. Outside the source we assume a potential $V_S$ satisfying the Schrödinger equation of the form

$$V_s(x_3) = -V_s\theta(-x_3) + \delta V_s(x_3)\theta(x_3). \tag{2}$$

Here $\theta(x)$ is a step function and the boundary layer potential $\delta V_S$ is assumed to go to zero as $x_3 \to \infty$. The constant $V_S$ is assumed to include a positive imaginary part taking into account damping: $V_S$ u + iu. The problem[2)] consists of finding the probability flux in the $x_3$ direction for $x_3 > 0$. We will look for a wave function $\psi$ in the form

$$\psi = \begin{cases} \psi_s + \psi_r, & x_3 < 0 \\ \psi_f, & x_3 \to \infty. \end{cases} \tag{3}$$

Here $\psi_S$ is the wave emitted by the source, $\psi_r$ is the wave reflected by the surface, and $\psi_f$ is the wave which has passed through the surface. The quantity $|x_3^0|$ is assumed greater than the wavelength. In accordance with the formulation of the problem we shall write $\psi_S$ in the form

$$\psi_s(\mathbf{x}-\mathbf{x}^0) = iA_{l_s m_s}\left(\frac{\pi\mu_s}{2|\mathbf{x}-\mathbf{x}^0|}\right)^{1/2} H^{(1)}_{l_s+1/2}(k_s|\mathbf{x}-\mathbf{x}^0|)\, Y_{l_s m_s}\left(\frac{\mathbf{x}-\mathbf{x}^0}{|\mathbf{x}-\mathbf{x}^0|}\right), \tag{4}$$

where $A_{l_S m_S}$ is a constant characterizing the source, $H^{(1)}_{l_S+1/2}$ is a Hankel function, $Y_{l_S m_S}$ is a spherical harmonic,[11] and

$$k_s^2 = 2\mu_s(\mathscr{E}_f + V_s),\ \mathscr{E}_f = \mathscr{E}_i + \omega. \tag{5}$$

We expand $\psi_S(\mathbf{x}-\mathbf{x}^0)$ in plane waves for $0 > x_3 > x_3^0$:

$$\psi_s(\mathbf{x}-\mathbf{x}^0) = \int e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}^0)}\psi_s(\mathbf{k}^{\parallel})\, d^2\mathbf{k}^{\parallel}, \tag{6}$$

where $\mathbf{k}^{\parallel} = (k_1, k_2)$ and $k_3 = (k_S^2 - k^{\parallel 2})^{1/2}$. Using the formula for expansion of a plane wave in spherical waves and carrying out one integration by means of the theory of residues, we obtain[12]

$$\psi_s(\mathbf{k}^{\parallel}) = -i\frac{(2l_s+1)^{1/2}}{2\pi}\left(\frac{\mu_s}{|k_s|}\right)^{1/2} A_{l_s m_s} Y_{l_s m_s}(\vartheta_k, \varphi_k)\frac{1}{k_3}; \qquad \cos\vartheta_k = \frac{k_3}{k_s},\quad \operatorname{tg}\varphi_k = \frac{k_2}{k_1}. \tag{7}$$

Equations (6) and (7) permit us to write down the desired expression for $\psi_f$:

$$\psi_f \underset{x_3\to\infty}{=} \int B(k_3')\psi_s(\mathbf{k}^{\parallel})\exp\{i[\mathbf{k}^{\parallel}(\mathbf{x}-\mathbf{x}^0)^{\parallel} - k_3 x_3^0 + k_3' x_3]\}\theta(k_3'^2)\, d^2\mathbf{k}^{\parallel}; \qquad k'^2 = 2\mu_f\mathscr{E}_f;\ k_3'^2 = k'^2 - k^{\parallel 2}. \tag{8}$$

Here $\mu_f$ is the mass in vacuum and $B(k_3^f)$ is the amplitude of the transmission coefficient of the one-dimensional potential barrier (2) for a wave incident from the medium with momentum $k_3$, At the threshold the quantity $|B|^2$ behaves in the simplest cases as follows[12, 13]:

$$\text{a)}\quad |B|^2 = C_1 + O\left(\frac{k_3'}{k_3}\right) \quad \text{for}\quad \delta V_s(x_3) < O(x_3^{-3}); \qquad \text{b)}\quad |B|^2 = C_2\frac{\eta_\alpha}{k_3'} + O(1) \quad \text{for}\quad \delta V_s(x_3) \underset{x_3\to\infty}{\longrightarrow} -\alpha x_3^{-4}; \qquad \eta_\alpha = 2\pi\mu_f\alpha. \tag{9}$$

Case b) corresponds to the existence of image forces. In the opposite limiting case $\mathscr{E}_f \gg u$, $k_3^f \approx k_3$, the equality $|B|^2 = 1$ applies. We note that the form of Eq. (8) is preserved for a non-one-dimensional transition layer $\delta V_S(\mathbf{x})$. Calculation of $B(k_3^f)$ in such a case was carried out in Ref. 14, where we also considered the further terms of the expansion (9) corresponding to the effective-range approximation of scattering theory. From the function (8) we construct the total current I passing through the surface:

$$I = -\frac{ie}{2\mu_f}\int d^2\mathbf{x}^{\parallel}\left(\psi_f\frac{\partial\psi_f^*}{\partial x_3} - \psi_f^*\frac{\partial\psi_f}{\partial x_3}\right) = -\frac{(2\pi)^2 e}{\mu_f}\int d^2\mathbf{k}^{\parallel}\{|B(k_3')\psi_s(\mathbf{k}^{\parallel})|^2 k_3' \exp\{2x_3^0\operatorname{Im}k_3\}\theta(k_3'^2)\}. \tag{10}$$

Using the well known expansions of associated Legendre polynomials near zero for small $k^{\parallel}/|k_S|$ we obtain from Eq. (10) with inclusion of Eq. (7)

$$\text{a)}\ I = a_{l_s m_s}\frac{2^{|m_s|}(|m_s|)!}{(2|m_s|+3)!!}C_1\left(\frac{k'}{|k_s|}\right)^{2|m_s|+3}, \qquad \text{b)}\ I = a_{l_s m_s}\frac{1}{|m_s|+1}C_2\frac{\eta_\alpha}{|k_s|}\left(\frac{k'}{|k_s|}\right)^{2|m_s|+2}, \qquad a_{l_s m_s} = -\frac{e|A_{l_s m_s}|^2\mu_s}{4\mu_f}\left[\frac{(2l_s+1)(l_s+|m_s|)}{2^{|m_s|}(|m_s|)!(l-|m_s|)!}\right]^2\exp\{2x_3^0\operatorname{Im}k_s\}. \tag{11}$$

The discussion presented can easily be generalized to the case in which a superposition of spherical waves is emitted from the point $\mathbf{x}^0$:

$$\psi_s(\mathbf{x}-\mathbf{x}^0) = \sum_{l_s m_s} iA_{l_s m_s}\left(\frac{\pi\mu_s}{2|\mathbf{x}-\mathbf{x}^0|}\right)^{1/2} H^{(1)}_{l_s+1/2}(k_s|\mathbf{x}-\mathbf{x}^0|)\, Y_{l_s m_s}\left(\frac{\mathbf{x}-\mathbf{x}^0}{|\mathbf{x}-\mathbf{x}^0|}\right). \tag{12}$$

For example, instead of the first of the formulas (11) we find that

$$I \sim (k'/|k_s|)^{2m_s^0+3}. \tag{13}$$

Here $m_S^0$ is the smallest of the values of $m_S$ occurring in the sum (12). Sums of the form of (12) are obtained for optical transitions in a centrally symmetric potential $v_i$ from an initial state with angular momentum $l_i$ and its projection $m_i$. Considering Eq. (1) outside the region of action of $v_i$, we obtain in the usual manner[11] for a one-photon transition

$$A_{l_s m_s} = A^{(1)}_{l_s m_s}(l_i, m_i) = \frac{eE_0 e^{\beta x_3^0}}{\mu_s\omega^2}\left(\frac{2l_i+1}{2l_s+1}\right)^{1/2} \times \sum_{m=-1}^{m=1}\left\{\varepsilon_m C(l_i, 1, l_s; m_i, m, m_s)\, C(l_i, 1, l_s; 0, 0, 0)\int_0^\infty \varphi_s^*(x)\frac{\partial v_i}{\partial x}\varphi_i(x)\, dx\right\}. \tag{14}$$

Here the factor $e^{\beta x_3^0}$ takes into account damping in the interior of the medium of a field with intensity $E_0$ at the surface, $\epsilon$ is a vector giving the direction of $\mathbf{E}_0$ in the spherical basis, $C(l_i, l, l_S; m_i, m, m_S)$ are Clebsch-Gordan coefficients,[11] $\varphi_{i,S}(x)$ are radial wave functions regular at zero. In what follows we will need the expression for a two-photon transition, which for simplicity we will write only for the case $l_i = 0$:

$$A_{l_s m_s}=\frac{e^2E_0^2e^{2\beta z_s^0}}{\mu_s^2\omega^4}\left(\frac{3}{2l_s+1}\right)^{1/2}\sum_{m_1,m_2}\Big\{\varepsilon_{m_1}\varepsilon_{m_2}C(1,1,l_s;m_1,m_2,m_3)$$
$$\times C(1,1,l_s;0,0,0)\left[\frac{1}{2}\int_0^\infty\varphi_s^*(x)\frac{\partial v_i}{\partial x}\varphi_i(x)\,dx\right. \qquad (15)$$
$$\left.-\int_0^\infty\int_0^\infty\varphi_s^*(x)\frac{\partial v_i(x)}{\partial x}G_1(x,x')\frac{\partial v_i(x')}{\partial x'}\varphi_i(x')\,dx\,dx'\right]\Big\},$$

where now $\varphi_S$ is a radial wave function with energy $\mathcal{E}_i + 2\omega$ and $G_1(x,x')$ is a radial Green's function with angular momentum equal to unity and energy $\mathcal{E}_i + \omega$. In the limit when $k_S^{-1}$ is much less than the localization parameter $R_0$ of the function $\varphi_i(x)$, it is possible to replace $\varphi_S$ by $k_S^{-1/2}\sin(k_S x + l_S\pi/2)$. Here

$$|A^{(1)}_{l_s m_s}(l_i,m_i)|^2\sim\omega^{-(l_i+7/2)},\quad |A^{(2)}_{l_s m_s}(l_i,m_i)|^2\sim\omega^{-(l_i+11/2)}. \qquad (16)$$

We now consider the question of how suitable are the formulas which we have written out for description of emission from independent centers located inside a condensed medium. The choice of the solution occurring in the Green's function outside the range of $v_i(\mathbf{x})$ in the form of waves (3) moving in a constant potential $V_S$ can be motivated not only by the fact that the corresponding energies usually lie substantially above the bottom of the conduction band, but also by the arguments used in the theory of the pseudopotential.[15] Actually, replacement of $\varphi_S$ on the right-hand side of Eq. (6) by plane waves from which any superposition of wave functions of localized states has been subtracted does not change the expression for the current as $x_3 \to \infty$. At the same time the wave functions occurring in the matrix elements (14) and (15) depend very substantially on $v_i(\mathbf{x})$. However, this dependence appears in the final formula only in the form of a coefficient, and also through the value of $m_S^0$. The value of $m_S^0$ is determined simply by the conservation laws entering into the Clebsch-Gordan coefficients.

## 3. EMISSION FROM A CRYSTAL

In discussing the emission from a crystal, the first problem to arise is taking into account the coherent addition of waves emitted from the different lattice sites. In order to clarify the corresponding effects we shall consider the model problem of departure from the half-space of waves created at the lattice centers with definite phase differences. We shall introduce instead of the function $\psi_S$ from Sec. 2 the function

$$\Psi_s=\sum_{\mathbf{g},g_3<0}e^{i\mathbf{q}\mathbf{g}+\beta g_3}\psi_s(\mathbf{x}-\mathbf{g}), \qquad (17)$$

where $\psi_S(\mathbf{x}-\mathbf{g})$ is given as before by Eq. (4) but from the coefficients $A_{l_S m_S}$ we have separated the factor $e^{\beta g_3}$ providing attenuation of the electromagnetic wave. In Eq. (17) the quantity $\mathbf{q}$ corresponds to quasimomentum; $\mathbf{g} = \mathbf{g}^i n_i$, i = 1, 2, 3, and $\mathbf{g}^i$ are the basis vectors of the three-dimensional lattice. The limitation of the summation to $g_3 < 0$ corresponds to filling of the half-space by the sources. Expanding the functions $\psi_S(\mathbf{x}-\mathbf{g})$ in Eq. (17) in a Fourier integral (6), after calculations similar to those carried out in Sec. 2 we obtain, using the old designations, an expression for the wave function $\psi_f$ outside the medium:

$$\Psi_f\underset{x_3\to\infty}{=}\int d^2\mathbf{k}^\parallel\Big\{B(k_3')\psi_s(\mathbf{k}^\parallel)\exp[i(\mathbf{k}^\parallel\mathbf{x}^\parallel+k_3'x_3)]\theta(k_3'^2)$$
$$\times\sum_{\mathbf{g},g_3<0}\exp[i(\mathbf{q}-\mathbf{k})\mathbf{g}+bg_3]\Big\},\qquad b=\beta+\mathrm{Im}\,k_3. \qquad (18)$$

After averaging in the $x_1x_2$ plane, the current j constructed from Eq. (18) from a unit surface S is written in the form

$$j=-\frac{e}{\mu_f S}\int d^2\mathbf{k}^\parallel\Big\{k_3'|B(k_3')\psi_s(\mathbf{k}^\parallel)|^2\theta(k_3'^2)$$
$$\times\sum_{\mathbf{g},\tilde{\mathbf{g}},g_3,\tilde{g}_3<0}\exp[i(\mathbf{q}-\mathbf{k})(\mathbf{g}-\tilde{\mathbf{g}})+b(g_3+\tilde{g}_3)]\Big\}. \qquad (19)$$

A strict treatment of Eq. (19) requires consideration first of the finite volume and a subsequent transition to an infinite limit. However, the same result is obtained without these tiresome operations and without strict observation of the rules for interchange of summation and integration if the following two prescriptions are used. First, infinite sums must be understood as limits of the form

$$\lim\sum_{m=-j+\nu}^{m=j}f(m),\quad j\to\infty, \qquad (20)$$

where $\nu$ is any finite number. Second, the square of the two-dimensional $\delta$ function of the form $[\delta(k_1)\delta(k_2)]^2$ contained under the integral sign in Eq. (19), as will soon become clear, must be replaced, as is usually done, by $(2\pi)^{-2}S[\delta(k_1)\delta(k^2)]$. We then need to introduce the greatest common measure $g_3^0$ of the quantities $g_3^i$ (i = 1, 2, 3). Here $g_3^i = l_i g_3^0$, where $l_i$ are relatively prime integers or zero. For values of $g_3^i$ which are in an irrational relation, it is assumed that $g_3^0 = 0$. A rational ratio between the $g_3^i$ exists when the normal to the boundary coincides with some special direction of crystal symmetry. In this case the lattice forms layers parallel to the crystal surface with a distance between them equal to $g_3^0$.

We shall transform Eq. (9) to the form

$$j=-\frac{e}{(2\pi)^2S\mu_f}\int d^2\mathbf{k}^\parallel\Big\{k_3'|B(k_3')\psi_s(\mathbf{k}^\parallel)|^2\theta(\mathbf{k}_3'^2)$$
$$\times\gamma\sum_{\mathbf{g},\tilde{\mathbf{g}}}\exp[i(\mathbf{q}-\mathbf{k})(\mathbf{g}-\mathbf{g})]\iint d\alpha\,d\tilde{\alpha}\,\frac{\exp[-i(\alpha g_3-\alpha\tilde{g}_3+{}^1\!/_2(\alpha-\tilde{\alpha})g_3^0)]}{(\alpha-ib)(\tilde{\alpha}+ib)}\Big\}$$
$$\gamma=\exp(-bg_3^0). \qquad (21)$$

The summation over $\mathbf{g}, \tilde{\mathbf{g}}$ is now carried out without limitation. The last factor, which contains $g_3^0$, was separated in order to be able to close the integration contour over $\alpha$ and $\tilde{\alpha}$ by a large semicircle in the complex plane in terms corresponding to $g_3 = 0$ or $\tilde{g}_3 = 0$, which is important only for $g_3^0 \neq 0$. In Eq. (21) we can carry out the summation over $\mathbf{g}, \tilde{\mathbf{g}}$, obtaining the sums of products of $\delta$ functions:

$$\sum_{\mathbf{g},\tilde{\mathbf{g}}}\exp\{i(\mathbf{q}-\mathbf{k})(\mathbf{g}-\tilde{\mathbf{g}})-i(\alpha g_3-\tilde{\alpha}\tilde{g}_3)\} \qquad (22)$$
$$=(2\pi)^6\sum_{n^i,\tilde{n}^i}\prod_{j=1}^{j=3}[\delta(\mathbf{q}-\mathbf{k})\mathbf{g}^j-\alpha g_3^j+2\pi n^i)\delta(-(\mathbf{q}-\mathbf{k})\mathbf{g}^j+\tilde{\alpha}g_3^j+2\pi\tilde{n}^i)].$$

Going over to $\delta$ functions of the variables of integration in (21), we obtain

$$\sum_{\mathbf{g},\tilde{\mathbf{g}}}\exp\{i(\mathbf{q}-\mathbf{k})(\mathbf{g}-\mathbf{g})-i(\alpha g_3-\tilde{\alpha}\tilde{g}_3)\}$$
$$=(2\pi)^6\mathcal{V}_g^{-2}\sum_{\mathbf{G},\tilde{\mathbf{G}}}\Big\{\delta((q_3-k_3)+G_3-\alpha)\delta(-(q_3-k_3)+\tilde{G}_3+\tilde{\alpha}) \qquad (23)$$
$$\cdot\prod_{j=1}^{j=2}\delta(q_j-k_j+G_j)\delta(q_j-k_j+\tilde{G}_j)\Big\},$$

where $\mathcal{V}_g$ is the volume of the unit cell, and $\mathbf{G}$ and $\tilde{\mathbf{G}}$ are the vectors of the reciprocal lattice over which the summation is carried out. In the integrand it is suffici-

ent to retain only the terms in which $G_1 = \tilde{G}_1$ and $G_2 = \tilde{G}_2$, since the remaining terms disappear on division by $S \to \infty$. Using the representation of squares of δ functions mentioned above and abbreviating it by S, we obtain

$$j=-\frac{(2\pi)^2 e}{\gamma^2 g^2 \mu_f}\sum_{\mathbf{G},\tilde{\mathbf{G}}}\Big\{ k_3'|B(k_3')\psi_s(\tilde{\mathbf{k}}^{\parallel})|^2\theta(k_3'^2) \cdot\frac{\exp[-bg_3^0+{}^1/_2 ig_3^0(G_3-\tilde{G}_3)]}{(q_3-k_3+G_3-ib)(q_3-k_3+\tilde{G}_3+ib)}\Big\}, \tag{24}$$

$$\tilde{\mathbf{k}}^{\parallel}=\mathbf{q}^{\parallel}+\mathbf{G}^{\parallel},\quad \tilde{k}_3^2=k_s^2-\tilde{\mathbf{k}}^{\parallel 2},\quad \tilde{k}_3'^2=k'^2-\tilde{\mathbf{k}}^{\parallel 2}.$$

In place of the summation over **G** and $\tilde{\mathbf{G}}$ with the condition $\mathbf{G}^{\parallel} = \tilde{\mathbf{G}}^{\parallel}$ we introduce the summation over all **G** and $\mathbf{G}^{**} = \mathbf{G}^{**}(n_i^{**}) = \mathbf{G} - \tilde{\mathbf{G}}$ with the condition $\mathbf{G}^{**\parallel} = 0$, which is equivalent to the equality

$$n_1^{**}g_3^2g_3^3=n_2^{**}g_3^3g_3^1=n_3^{**}g_3^1g_3^2. \tag{25}$$

In the case $g_3^0 = 0$, the equality (25) is satisfied only for $n_i^{**} = 0$ and the summation over $G_3^{**}$ is actually taken. For $g_3^0 \neq 0$, $g_3^1 = l^1 g_3^0$, the equality (25) is satisfied for $n_i^{**} = nl^i$ for any integral n. In this case the sum over $G_3^{**}$ reduces to expansion of cosec z in elementary fractions[16] and we arrive at the formula

$$j(\mathbf{q})=\sum_{\mathbf{G}} j_p(\mathbf{q}+\mathbf{G}),$$

$$j_p(\mathbf{q})=\frac{-(2\pi)^2 e}{\gamma^2 g^2 \mu_f}k_3'|B(k_3')\psi_s(\mathbf{k}^{\parallel})|^2\theta(k_3'^2)\frac{1}{(q_3-k_3)^2+b^2} \times \mathrm{Re}\Big\{\frac{\gamma g_3^0(q_3-k_3-ib)}{\sin[{}^1/_2(q_3-k_3-ib)g_3^0]}\Big\}\Big|_{\mathbf{k}^{\parallel}=\mathbf{q}^{\parallel}}. \tag{26}$$

The θ function occurring in (26) limits the summation over **G** only if $g_3^0 = 0$. In the opposite case it is possible to choose the vectors $\mathbf{g}^i$ such that $G_1^3 = G_2^3 = 0$, $G_3 = 2\pi(g_3^0)^{-1}n$. Here the sum over $G_3$ gives

$$j(\mathbf{q})=\frac{-(2\pi)^2 e}{\gamma^2 g^2 \mu_f}\sum_{\mathbf{G}^{\parallel}}\frac{k_3'|B(k_3')\psi_s(\tilde{\mathbf{k}}^{\parallel})|^2\theta(k_3'^2)}{(\gamma+\gamma^{-1})-2\cos[g_3^0(q_3-\tilde{k}_3)]}. \tag{27}$$

In the threshold region the expressions for $j_p(\mathbf{q})$ are greatly simplified. By analogy with Eq. (11) we obtain from Eqs. (9) and (26), for example, for the case (9a)

$$j_p(\mathbf{q}) \underset{k'\to 0}{=} -\frac{(2\pi)^2 e}{\gamma^2 g^2 \mu_f}k_3'C_1|\psi_s(\mathbf{k}_{\parallel})|^2\theta(k_3'^2)\frac{1}{(q_3-k_3)^2+b^2} \times \mathrm{Re}\Big\{\frac{\gamma g_3^0[q_3-\mathrm{Re}\,(2\mu_s V_s)^{1/2}-ib]}{\sin[{}^1/_2[q_3-\mathrm{Re}\,(2\mu_s V_s)^{1/2}-ib]g_3^0]}\Big\}\Big|_{\mathbf{k}^{\parallel}=\mathbf{q}^{\parallel}}. \tag{28}$$

Here we have separated the resonance denominators $(q_3 - k_3)^2 + b^2$, whose behavior may turn out to be important near threshold. In the case $g_3^0 \neq 0$ the general structure of Eq. (28) remains unchanged,[3)] but the quantity b is replaced in accordance with (27) by $2(g_3^0)^{-1}\mathrm{sh}(bg_3^0/2)$.

Let us consider the connection between the quantities $|\psi_S(\mathbf{q}^{\parallel})|^2$ occurring in (28) and the characteristics of the initial wave functions $\Psi_i$ by means of Eqs. (14) and (15). Since the main contribution to the matrix elements, to which $\psi_S(\mathbf{q}^{\parallel})$ are proportional, is in this case from the region of the ionic cores, then $\Psi_i$ can be chosen in the form[15]

$$\Psi_i(\mathbf{x})=\sum_{\mathbf{g}} e^{i\mathbf{q}\mathbf{g}}\sum_{l_i m_i}\frac{\varphi_{l_i m_i}(\mathbf{x}-\mathbf{g})}{|\mathbf{x}-\mathbf{g}|}Y_{l_i m_i}\Big(\frac{\mathbf{x}-\mathbf{g}}{|\mathbf{x}-\mathbf{g}|}\Big), \tag{29}$$

where the relation between $\varphi_{l_i m_i}(\mathbf{x})$ with different $l_i m_i$, which is determined by the crystal symmetry, is simplest if we choose the projection $m_i$ on one of the symmetry axes.

Let us consider the general structure of the expressions for the current. They contain, first, the conservation of quasimomentum $\mathbf{q}^{\parallel}$ parallel to the separation boundary with accuracy to the corresponding projections of the reciprocal-lattice vector. This result is in no way trivial and is obtained only as the result of averaging over the surface, without which additional oscillating terms are retained. In the second place, there is no conservation of the third component of quasimomentum $q_3$. Instead of the corresponding δ function in Eq. (26) we have the characteristic factor

$$[(k_3-q_3-G_3)^2+b^2]^{-1}\underset{b\to 0}{\longrightarrow}\frac{\pi}{b}\delta(k_3-q_3-G_3). \tag{30}$$

As $b \to 0$ the total current approaches infinity as $b^{-1}$, since the entire crystal volume begins to be effective. On the other hand, in the energy and momentum region far from the interval where the third component of quasimomentum is conserved

$$(k_3-q_3)^2>b^2, \tag{31}$$

the current ceases to depend substantially on the damping b. Here it is natural to assume that the volume effect goes over to a surface effect.[4)] Special interest is presented by the factor under the Re sign in Eq. (26). This factor takes into account the change in current as the result of the specific wave effect of addition of waves from emitter layers parallel to the crystal surface. In the absence of parallelism ($g_3^0 = 0$) the waves reach the surface with varying phases and partially extinguish each other. From Eq. (26) we can obtain an expression for the total current by summation of the contributions of the various initial states. For the contribution to the photocurrent from one band we obtain

$$j_i=\sum_{\mathbf{G}}\int_{\gamma^2\mathbf{G}} j_p(\mathbf{q}+\mathbf{G})\frac{\rho(\mathbf{q})}{\exp[(\mathscr{E}_i(\mathbf{q})-\zeta)/T]+1}d^3\mathbf{q} =\int j_p(\mathbf{q})\frac{\rho(\mathbf{q})}{\exp[(\mathscr{E}_i(\mathbf{q})-\zeta)/T]+1}d^3\mathbf{q}. \tag{32}$$

The integration in the last equality extends over all **q**, and at the same time we carry out the summation over **G**; the symbol ζ designates the chemical potential; the factor $\rho(\mathbf{q})$ takes into account possible degeneracy.

## 4. COMPARISON WITH EXPERIMENT

The expressions obtained can be compared with experiment. Here we are limited to three cases, which with a certain degree of arbitrariness we can classify as follows: 1—emission from centers chaotically located in a transparent dielectric; 2—emission from simple metals; 3—emission from semiconductors. Case 1 corresponds, in particular, to emission from solutions of solvated electrons[18] and impurity molecules.[19] Here the formula for the current (14) must simply be summed over all independent emitters. In the threshold region for incidence of light normal to the boundary we obtain for the initial s state

$$j_i\sim b^{-1}|A_{11}|^2C_1\rho_e(\omega-\omega_0)^{3/2},\quad \omega_0=2\mu_s u, \tag{33}$$

where $\rho_e$ is the volume density of emitters. The dependence obtained for the photocurrent as a function of $(\omega - \omega_0)$ is in good agreement with experiment.[12]

In case 2, which corresponds to the simplest conditions of emission from metals, we will assume that the transition occurs within a single band when $k_3 \neq q_3$, $k_3^2 - q_3^2 \approx m_S\omega$. Here for T = 0 instead of Eq. (32) we can write

$$j_i = \int_{-\infty}^{\zeta} d\mathscr{E}_i \int_0^{k^f} q^{\parallel} dq^{\parallel} \int_0^{2\pi} d\varphi_q \left[ j_p(\mathbf{q}^{\parallel}, \mathscr{E}_i) \rho(\mathbf{q}^{\parallel}, \mathscr{E}_i) \right], \tag{34}$$

where $\varphi_q$ is the angle in the plane $q_3$ = const and $\rho(\mathbf{q}^{\parallel}, \mathscr{E}_i)$ is the density of states with given $\mathbf{q}^{\parallel}$ and $\mathscr{E}_i$. The expression under the integral over $d\mathscr{E}_i$ gives the distribution of emitted electrons in energy. The current $j_p$ as $k^f \to 0$ is determined by the expressions (28), in which we can assume the denominators are constant, since here $(k_3 - q_3)^2 \approx m_s\omega \gg b^2$. As a result, omitting the cumbersome coefficients, we have

$$\begin{aligned} &\text{a)}\ j_i \sim \omega^{-r}(\omega-\omega_0)^{m_s^0+1/2}\theta(\omega-\omega_0), \\ &\text{b)}\ j_i \sim \omega^{-r}(\omega-\omega_0)^{m_s^0+2}\theta(\omega-\omega_0), \end{aligned} \tag{35}$$

where $\omega_0 = -\zeta$. In the case of the two-photon effect the expression for the photocurrent retains the form of Eq. (35), but $(\omega - \omega_0)$ must be replaced by $(2\omega - \omega_0)$.

We have also retained the asymptotic dependence $\omega^{-r}$, where according to Eq. (16) $r + l_{i0} + 7/2$ for the one-photon effect and $r = l_{i0} + 13/2$ for the two-photon effect, and $l_{i0}$ is the smallest of the values of $l_i$ in the sum (29). In carrying out the integral (34) we assumed that the quantities not containing the factor $\omega - \omega_0$ were constant, which is justified if the density of states does not have a singular behavior near the Fermi surface. For $m_s^0 = 0$ the formulas reproduce the well known regularities: the quadratic Fowler law and the five-halves law. These same laws were derived[2] in the threshold approximation for the surface photoeffect. However, the results obtained by us also contain a number of important differences.

First, the case $m_s^0 \neq 0$ is a special case which is strictly realized if the product of the representations of the initial symmetry group and the vector product do not contain representations corresponding[20] to $m_s = 0$. In particular, for normal incidence of the light $m_s^0 = 1$ if $l_i = 0$. Accordingly the exponent of the factor $\omega - \omega_0$ is increased[5] by $m_s^0$. Special interest is presented by the ratio of the one-photon and two-photon effects. If the light is not circularly polarized, then for the two-photon effect $m_s^0 = 0$ even if for the one-photon effect $m_s^0 \neq 0$. As a result the relation turns out to be proportional,

$$\frac{j_t^{(1)}}{j_t^{(2)}} \approx \frac{\omega^2\mu_s}{e^2E^2R_0^2}\left(\frac{\omega-\omega_0}{u}\right)^{m_s^0}.$$

If we take into account a still greater number of paths contained in sums of the form of Eq. (15), the difference in the relation considered from that calculated in the model of the surface effect can become very significant, which evidently was observed by Babenko et al.[4] In the second place, a substantial difference lies in the appearance of a peculiar sharp dependence on the position of the surface relative to the symmetry axes. The form of this dependence is determined by Eq. (27). It is necessary to separate the effect cited of photocurrent enhancement for surfaces with $g_3^0 \neq 0$, which up to this time has apparently not been observed. A third important feature is associated with the form of the dependence on the angle of incidence and polarization of the light. This dependence turns out to be rather complex. The photocurrent should not go to zero for s polarization of the light, as is found in the calculation of surface photoemission in the free electron model. At the same time when Eq. (31) is satisfied there is no conservation of total quasimomentum, i.e., the effect cannot be considered strictly a volume effect. For illustration we will give the dependence of one-photon emission on the angle of transmission of the light $\kappa$ for the simplest case $l_i = 0$ respectively for s and p polarized light:

$$j_t^{(s)} = -\frac{eC_2\eta_\alpha\rho(-\omega_0,0)}{4\mathscr{V}_g^2\omega(2\mu_s u)^{1/2}}|M_{s,i}|^2\frac{2\mu_i(\omega-\omega_0)^3}{3\mu_s u}, \tag{36a}$$

$$\begin{aligned} j_t^{(p)} &= -\frac{eC_2\eta_\alpha\rho(-\omega_0,0)}{4\mathscr{V}_g^2\omega(2\mu_s u)^{1/2}}|M_{s,i}|^2(\omega-\omega_0)^2 \\ &\cdot\left[\sin^2\varkappa + \frac{2}{3}\cos^2\varkappa\frac{\mu_i(\omega-\omega_0)}{\mu_s u}\right]; \\ |M_{s,i}|^2 &= \left|\frac{eE_0}{\mu_s\omega^2}\int_0^{\infty}\varphi_s^*(x)\frac{\partial v_i}{\partial x}\varphi_i(x)\,dx\right|^2. \end{aligned} \tag{36b}$$

Thus, in the case of p polarization (36a), an additional dependence of the current on the angle $\kappa$ arises. For the two-photon effect the proportionality of absorption of the light generally does not exist. These conclusions are confirmed by the results of Babenko et al.[4]

In case 3 (which corresponds to the simplest situation realized for semiconductors) we shall consider a transition from the valence band + the conduction band, from which emission is energetically possible. Here the emission threshold corresponds to the upper boundary of the valence band, whose location we designate as $-\omega_0$. The quantity $-u$ corresponds now to the location of the bottom of the conduction band. We will assume that $-u > -\omega_0$. In this case in the current formula similar to Eq. (34) the upper limit with respect to $d\mathscr{E}_i$ will contain $-\omega_0$ rather than $\zeta$. In addition, there are further differences due first to the special nature of the density of states near the edge of the valence band and, second, to the important role of the resonance denominators in Eq. (28) in view of the possible equality $k_3(q^{\parallel}) = q_3$. We shall use the simplest dispersion laws in the conduction band and near the surface of the valence band, respectively:

$$\begin{aligned} \mathscr{E}_s &= \mathscr{E}_i + \omega = -u + \frac{1}{2\mu_s}(q_{\parallel}^2 + k_3^2), \\ \mathscr{E}_i &= -\omega_0 - \frac{1}{2\mu_i}q^2. \end{aligned} \tag{37}$$

Here we have taken into account the conservation of energy and of the projections of quasimomentum $\mathbf{q}^{\parallel}$. From Eq. (36) we find the energy $\mathscr{E}_i^0$ at which $k_3 = q_3$:

$$\mathscr{E}_i^0 = -\omega_0 - \frac{\mu_s}{\mu_i+\mu_s}(\omega-\omega_0+u). \tag{38}$$

Usually $\mu_i \gg \mu_s$, so that $\mathscr{E}_i^0$ lies in the immediate vicinity of $-\omega_0$ and, consequently, the contribution of the resonance denominators turns out to be extremely important even in the threshold region.[6] When these remarks and and Eqs. (34) and (37) are taken into account, the expression for the current can be written in the threshold region in the form

$$\begin{aligned} j_t &= j_1 + j_2, \\ j_1 &= \int_{-\infty}^{-\Omega} d\mathscr{E}_i \int_0^{2\mu_s(\mathscr{E}_i+\omega)} F(\mathscr{E}_i, q^{\parallel})\,d(q^{\parallel})^2, \\ j_2 &= \int_{-\Omega}^{-\omega_0} d\mathscr{E}_i \int_0^{-2\mu_i(\mathscr{E}_i+\omega_0)} F(\mathscr{E}_i, q^{\parallel})\,d(q^{\parallel})^2, \\ \Omega &= \frac{\mu_s\omega+\mu_i\omega_0}{\mu_i+\mu_s} \end{aligned} \tag{39}$$

$$F(\mathscr{E}_i, q^{\parallel}) = \frac{\pi\mu_i j_p(q^{\parallel}, \sqrt{-2\mu_i(\mathscr{E}_i+\omega_0)})}{\sqrt{-2\mu_i(\mathscr{E}_i+\omega_0)} - q^{\parallel}}.$$

The breakdown of $j_t$ into two parts is due to the fact

that in different energy intervals different inequalities of the group $k_3^{f2} \geq 0$ and $q_3^2 \geq 0$ are more limiting. Here a separation of the point $\mathscr{E}_i = \mathscr{E}_i^0$ entering into $j_1$ occurs. For $\mu_i \gg \mu_s$, in general $j_1 \gg j_2$ and we are then limited to one term $j_1$. After integration for $m_s^0 = 0$ (image forces not taken into account, $g_3^0 = 0$) we obtain

$$j_l \approx -\frac{e\mu_i\mu_s J(\omega-\omega_0)}{12\mu_i\mathscr{V}_s^2(2\mu_s u)^{3/2}} \sum_s \sum_{l_s'} (2l_s+1) \cdot (2l_s'+1)\,(A_{l_s 0}\dot{A}_{l_s' 0}+\dot{A}_{l_s 0}A_{l_s' 0}), \tag{40}$$

$$J(\omega-\omega_0) = \int_{-\omega}^{-\omega_0} d\mathscr{E}_i \frac{[2\mu_s(\mathscr{E}_i+\omega)]^{1/2}}{[-2\mu_i(\mathscr{E}_i+\omega_0)]^{1/2}\{[-2\mu_i(\mathscr{E}_i+\omega_0)]^{1/2}-(2\mu_s u)^{1/2}]^2+b^2\}}.$$

The integral (40) is obtained in elementary functions but has a complicated form. For illustration of the structure of the expression obtained, we give the function $J(\omega)$ for different frequency regions in the limiting case of small damping $b^2 \ll 2\mu_i(\omega-\omega_0)$:

$$\begin{aligned} J(\omega) &\approx \frac{3\pi}{8}\left(\frac{\mu_s}{\mu_i}\right)^{1/2}\frac{(\omega-\omega_0)^2}{u} \quad \text{for} \quad \frac{\mu_i(\omega-\omega_0)}{\mu_s u} \ll 1, \\ J(\omega) &\approx \frac{3\pi+8}{2}\left(\frac{\mu_s}{\mu_i}\right)^{1/2}(\omega-\omega_0) \quad \text{for} \quad |\omega+\mathscr{E}_i^0| \sim \frac{b^2}{2\mu_i}, \\ J(\omega) &\approx 2\pi\left(\frac{\mu_s}{\mu_i}\right)^{1/2}\frac{(\omega+\mathscr{E}_i^0)^{1/2}}{(2\mu_i)^{-1/2}b} \quad \text{for} \quad \omega+\mathscr{E}_i^0 \gg \frac{b^2}{2\mu_i}. \end{aligned} \tag{41}$$

The functions (41) agree qualitatively with the experimental results on photoemission from semiconductors.[7] We note also that the shape of the energy distribution obtained by Powell et al.[7] for the photoelectrons corresponds to the integrand in Eq. (39). With increase of $\mathscr{E}_i$, first a slow rise is observed, which then goes over to a characteristic bell-shaped behavior. Unfortunately the accuracy of the data, which were presented[7] in the form of graphs, does not permit a quantitative analysis.

The cases discussed above do not exhaust the possibilities of the theory developed in Secs. 2 and 3. It would be possible to consider in addition the effect of overlapping bands, magnetic field (which reduces the symmetry), more complex surface-transmission laws, and so forth. We have limited ourselves to cases which have a sufficiently interesting field of application and at the same time are described by reasonable formulas.

We should also make some remarks on the exponential damping law chosen. This law exists if the final energies $\mathscr{E}_f$ correspond to the forbidden band. Here b increases with departure from the edge of the band $\mathscr{E}_n$ as $|\mathscr{E}_f - \mathscr{E}_n|^{1/2}$ (Ref. 23). For energies $\mathscr{E}_f$ lying in the allowed band, the exponential law corresponds to a realistic approximation for the threshold region, according to which in collisions the loss of energy and of the momentum directed toward the surface are so great that the scattered and secondary electrons cannot pass through the surface barrier. In this article we assumed that the damping b is a rather smooth function of energy. If collective oscillation frequencies fall in the threshold region, then appropriate obvious changes are necessary.

[1)] It is necessary to mention the discussion in the literature of whether volume or surface excitation is dominant. No unanimous opinion [5] based on interpretation of the entire set of experimental data exists on this question up to the present time.

[2)] Sommerfeld [9] has discussed the problem in the optical analogy; see also Weyl. [10]

[3)] There is actually a continuous transition between the cases $g_3^0 = 0$ and $g_3^0 \neq 0$, since for $g_3^0 \neq 0$ and $|G^{3\parallel}| \ll |G^{1\parallel}|, |G^{2\parallel}|$ in the sum (26) will contain rather a large number of terms even in the narrow threshold region and the corresponding expression will be close to Eq. (27).

[4)] If we take into account the variation in the functions $\varphi_i(x)$ in Eq. (14) near the surface as a result of introduction of the so-called generalized Wannier functions, [17] then we will include that part of the surface effect which is due to the change in V at the surface. According to the discussion presented, experiments on the emission from thin films do not always determine, as is often assumed, the mean free path of the excited electrons.

[5)] The increase in the degree of $\omega - \omega_0$ to three in the expression for the photocurrent for normal incidence of light has recently been observed by Gartland et al. [5]

[6)] The relation between the resonance and nonresonance contributions has not been taken into account in the work of Gurevich. [21] Unfortunately, his results have been carried over into the book. [2] The important influence of the resonance denominators has also not been taken into account in a number of studies in which the electronic density of states in semiconductors has been established from the energy distribution of photoelectrons. [22]


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