

Electron escape and photoemission in the threshold region

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The formula giving the probability of electron escape is generalized to the case of electron excitation involving two conduction bands in the vicinity of the Brillouin-zone boundary when the gap between the bands is of critical importance. The escape probability in this case can be significantly larger than that found for excitation from the occupied states lying well within the first Brillouin zone. It is also shown that the Fowler law (commonly used to describe photoemission in the threshold region) is not restricted to the usually accepted assumption of indirect, momentum nonconserving, electron transitions but is a consequence of the linear dependence of the escape function on the electron energy near threshold and is valid for both direct and indirect electron transitions.

The basis of the theory of photoemission was mostly developed in the 1960s and 1970s.¹⁻³ The process has been successfully described in terms of a three-step model consisting of excitation of the photoelectrons, migration to the surface with inelastic collisions en route, and escape overcoming the appropriate potential barriers.¹ More recent progress in photoemission is connected with such problems as multiphoton excitation,⁴ surface states,⁵ and photoemission enhancement due to the surface plasmons excitation.^{6,7} However, there are some important points remained in the theory which need to be examined in more detail. In particular, we show in this paper that the well-known formula for the probability of electron escape must be modified when excitation occurs in vicinity of the first Brillouin-zone boundary. We also demonstrate that the Fowler law, which describes the spectral dependence of photoemission in the threshold region, is more generally valid than one might expect based on the well-known assumptions used to obtain this law.

Let us consider first escape of excited electrons from a surface. Our main hypothesis is the following: In order to escape over the surface barrier the electrons must have a component of momentum normal to the surface, p_n , greater than a critical value p_c .¹ Here p_c is defined by the equation $E_2(p_c) = E_F + \Phi$, where E_F is the Fermi energy, Φ the work function, and $E_2(\mathbf{p})$ the energy of the excited electron with total momentum \mathbf{p} . We assume that the distribution of excited electrons is isotropic, as is the case for polycrystals. If θ is the angle between the direction of electron momentum upon excitation with respect to the normal of the photoemitting surface, z , the electron must move a distance $z/\cos\theta$ to reach the surface. The probability of electron escape without loss of energy following excitation to energy $E_2 = E_1 + \hbar\omega'$ ($E_1 \equiv E$ and $\hbar\omega'$ are the initial electron energy and the total photon energy, respectively) is $\frac{1}{2} \int_0^{\cos^{-1}(p_c/p)} e^{-(z/\cos\theta)} \sin\theta d\theta$ if $p \geq p_c$ and is 0 otherwise.¹ Here l is the mean free path for inelastic scattering which is a function of electron energy. For n -photon excitation ($\hbar\omega' = n\hbar\omega$) the energy distribution of the photoelectrons per unit surface and time, $D(E)$, is given by

$$D(E) = \frac{1}{2} \int_0^\infty dz e^{-n\alpha z} P(E) \times \int_0^{\cos^{-1}(p_c/p)} e^{-(z/\cos\theta)} \sin\theta d\theta, \quad (1)$$

where $P(E)$ is the energy distribution of the excited electrons per unit time and volume, and α is the linear absorption coefficient.

The energy dependence of the excited electrons on its momentum, $E_2(\mathbf{p})$, near the bottom of the upper band, E_0 , can be presented in general as $E_2(\mathbf{p}) \equiv E(\mathbf{p}) + \hbar\omega' \simeq E_0 + \gamma p^2$ ($\gamma \equiv \hbar^2/2m^*$ where m^* is the effective mass; see below). We restrict ourselves to consideration of the photoemission in the threshold region when $\hbar\omega' - \Phi \ll E_F + \Phi - E_0$ (the condition $E_F + \Phi > E_0$ is assumed to be fulfilled) and, therefore, $|p - p_c| \ll p_c$. From the latter condition the following relation is valid for the upper limit of the integral in (1): $\cos^{-1}(p_c/p) \simeq [2(1 - p_c/p)]^{1/2} \ll 1$. Using this approximation and performing the integration in (1) one obtains

$$D(E) = t(E)T(E)[P(E)R_s/n], \quad (2)$$

where

$$t(E) = \frac{nl/R_s}{1 + nl/R_s} \quad (3)$$

is the transmission function and

$$T(E) = \frac{1}{2} \left(1 - \frac{p}{p_c}\right) \quad (4)$$

is the escape function and $R_s \equiv \alpha^{-1}$ is the light penetration depth. For $n = 1$ formulas (2)–(4) were obtained in Ref. 1 (see also Ref. 3). Note that in the frame of our consideration $T(E) \ll 1$. The energy distribution $P(E)$ for one-photon excitation is found in Ref. 2 and for two-photon excitation in Ref. 8. In the threshold region only electrons within a narrow energy interval are excited and, therefore, one can neglect the energy dependence of $P(E)$ and $t(E)$. This allows us to put $P(E) \simeq P(E_F)$ and $t(E) \simeq t(E_F)$ in (2). Thus, all energy dependence

in the energy distribution curve of photoelectrons [$D(E)$] is controlled by the escape function [$T(E)$] alone. Note that the first term of the decomposition of $T(E)$ is zero [$T(E + \hbar\omega' = E_F + \Phi) = 0$] and therefore the energy dependence of $T(E)$ is of critical importance. Let us now find the form of $T(E)$.

Assuming the excited electrons follow the free-electron model perfectly, then

$$E + \hbar\omega' = \beta\mathbf{p}^2, \quad (5)$$

and one has for the critical momentum $p_c = \beta^{-1/2}(E_F + \Phi)^{1/2}$, where $\beta \equiv \hbar^2/2m$ and m is the electron mass. Accordingly, from (4) and (5) one obtains for the escape function the commonly used formula³

$$T_c(E) = \frac{1}{2} \left[1 - \left(\frac{E_F + \Phi}{E + \hbar\omega'} \right)^{\frac{1}{2}} \right], \quad (6)$$

if $E + \hbar\omega' > E_F + \Phi$ and 0 otherwise. However, it is clear that the validity of the above escape function (6) is restricted to the perfectly free-electron model [or one orthogonalized plane wave (OPW)] with dispersion relation (5).

Below we obtain the escape probability within the frame of the two-OPW approximation taking into account electron reflection at the Bragg plane. Electron transitions between the two conduction bands can be successfully described on the basis of this approximation.^{2,8} In particular, photoemission from some noble metals in the threshold region occurs mostly due to transitions between conduction bands near the L -symmetry point.²

The electron energies in the two conduction bands are given by⁹

$$2E_2(\mathbf{k}) = \beta[(\mathbf{k} - \mathbf{G})^2 + \mathbf{k}^2] + \{\beta^2[(\mathbf{k} - \mathbf{G})^2 - \mathbf{k}^2]^2 + 4V_G^2\}^{\frac{1}{2}}, \quad (7)$$

$$2E_1(\mathbf{k}) = \beta[(\mathbf{k} - \mathbf{G})^2 + \mathbf{k}^2] - \{\beta^2[(\mathbf{k} - \mathbf{G})^2 - \mathbf{k}^2]^2 + 4V_G^2\}^{\frac{1}{2}},$$

where \mathbf{G} is the reciprocal-lattice vector which generates the second band and $2V_G$ is the energy gap between the bands.

If the condition

$$\beta(\mathbf{G}^2 - 2\mathbf{k}\mathbf{G}) \gg 2V_G \quad (8)$$

is fulfilled, then from (7) one finds that

$$E_1(\mathbf{k}) = \beta\mathbf{k}^2, \quad E_2 = \beta(\mathbf{k} - \mathbf{G})^2. \quad (9)$$

Using the substitution $\mathbf{p} = \mathbf{G} - \mathbf{k}$, one obtains from (9) the dispersion relation of excited electrons in the form of Eq. (5) and, therefore, in this case the escape function has the form of Eq. (6). Thus, condition (8) identifies the region of validity of the escape function $T_c(E)$. The escape function T_c is valid for solids with no gap such as the alkali metals. In those metals the occupied states lie well within the first Brillouin zone and one may ignore the gaps at the zone boundaries.

Let us now consider electron escape upon excitation in the vicinity of the first Brillouin-zone boundary ($\mathbf{k}_0 = \mathbf{G}/2$) when $\hbar\omega' - 2V_G \ll \hbar\omega'$ and $p = |\mathbf{G}/2 - \mathbf{k}| \ll G/2$ so that $\beta p^2 \ll 2V_G$. Under these conditions, with substitution of $\mathbf{p} = \mathbf{G}/2 - \mathbf{k}$, it follows from (7) that

$$E_1(\mathbf{p}) = \frac{1}{4}\beta G^2 - V_G + [1 - (\beta G^2/2V_G)]\beta\mathbf{p}^2 \quad (10)$$

and

$$E_2(\mathbf{p}) = \frac{1}{4}\beta G^2 + V_G + [1 + (\beta G^2/2V_G)]\beta\mathbf{p}^2. \quad (11)$$

We also restrict our consideration to photoemission from noble metals such as Ag and Cu with work functions typically close to the energy gap. For those metals only electron transitions in the vicinity of $L_2' \rightarrow L_1$ contribute to the near-threshold photoemission and the work function just slightly exceeds the energy gap. Of course, the present considerations are appropriate for other solids as well if the work function is pulled down close to the value of the energy gap. Then electrons at the Brillouin-zone boundary dominate in near-threshold photoemission.

Substitution of the critical energy $E_F + \Phi$ for E_2 in (11) gives $p_c = \gamma^{-1/2}(E_F + \Phi - \frac{1}{4}\beta G^2 - V_G)^{1/2}$, where $\gamma = \beta[1 + (\beta G^2/2V_G)]$. The distinction of γ from β reflects the renormalization of the electron mass near the bottom of the upper energy band. It follows from (4) and (11) that the escape probability of electrons upon excitation in the threshold region is given by

$$T(E) = \frac{1}{2} \left[1 - \left(\frac{E_F + \Phi - \frac{1}{4}\beta G^2 - V_G}{E + \hbar\omega' - \frac{1}{4}\beta G^2 - V_G} \right)^{\frac{1}{2}} \right], \quad (12)$$

if $E + \hbar\omega' > E_F + \Phi$ and 0 otherwise. If the electron excitation occurs near the L -symmetry point one should put $\frac{1}{4}\beta G^2 + V_G = E_{L_1}$, where E_{L_1} is the bottom energy of the second band. This gives

$$T(E) = \frac{1}{2} \left[1 - \left(\frac{E_F + \Phi - E_{L_1}}{E + \hbar\omega' - E_{L_1}} \right)^{\frac{1}{2}} \right]. \quad (13)$$

Recall that we assumed that $E_F + \Phi > E_0$, where $E_0 \equiv \frac{1}{4}\beta G^2 + V_G$ for the escape function (12) and $E_0 \equiv E_{L_1}$ for the escape function (13) [see the paragraph preceding formula (2)].

Note that the difference between the escape probabilities given by (13) [or (12)] and (6) is important. For example, using values for the parameters² $E_F = 5.5$ eV, $\Phi = 4.3$ eV, $E_{L_1} = 9.4$ eV, $E + \hbar\omega' = 10$ eV, one finds for the escape probability in the threshold region $T(E) \simeq 0.1$ while the value $T_c = 5 \times 10^{-3}$ found on the basis of (6) significantly underestimates electron escape.

Let us consider now a spectral dependence of photoemission in the threshold region. Since one can neglect the energy dependence of $P(E)$ and $t(E)$ in the threshold region, the total photoelectric yield J is approximated by

$$J \simeq t(E_F)[P(E_F)R_s/n]K, \quad (14)$$

where

$$K \equiv \int_{E_F + \Phi - \hbar\omega'}^{E_F} T(E) dE = \frac{1}{2} (\hbar\omega' - \Phi) - (E_F + \Phi - E_0) \left[\left(\frac{\hbar\omega' + E_F - E_0}{\Phi + E_F - E_0} \right)^{\frac{1}{2}} - 1 \right]. \quad (15)$$

Near the threshold $\hbar\omega' - \Phi \ll E_F + \Phi - E_0$ and K has the form

$$K = \frac{1}{8} \frac{(\hbar\omega' - \Phi)^2}{E_F + \Phi - E_0}. \quad (16)$$

For comparison, the factor K_c found on the basis of the escape function (6) is given by

$$K_c = \frac{1}{8} \frac{(\hbar\omega' - \Phi)^2}{E_F + \Phi}. \quad (17)$$

It is clear that the total yield J determined by substitution of K_c for K in (14) would significantly underestimate photoemission in the threshold region.

According to (14) and (16) the total photoyield depends quadratically on $\hbar\omega' - \Phi$ in the threshold region. This dependence constitutes the essence of the Fowler law¹⁰ and it is widely apparent in the literature (see, for example, Ref. 3). The usual way to obtain this law is based on integration over all k states satisfying the conditions $\beta k_n^2 > \Phi + E_F - \hbar\omega'$ and $\beta(k_p^2 + k_n^2) \leq E_F$ (k_p and k_n are the parallel and normal to the surface components of the total electron momentum):

$$J \propto \int_{(E_F + \Phi - \hbar\omega')^{\frac{1}{2}}}^{E_F^{\frac{1}{2}}} dk_n \int_0^{(E_F - \hbar^2 k_n^2 / 2m)^{\frac{1}{2}}} k_p dk_p. \quad (18)$$

In the threshold region one obtains from (18) that $J \propto (\hbar\omega' - \Phi)^2$. Formula (18) is based on the energy conservation requirement only. The reduction of the part of k space contributing to photoemission due to the requirement of momentum conservation is not taken into account (see below). In other words, the assumption that photoemission is dominated by indirect transitions, where electron momentum is not conserved, is implied. With the present analysis we have shown that the Fowler law has a wider range of applicability. Since we did not make any assumptions in (14) and (16) about the character of electron excitation (direct or indirect), the law remains valid for photoemission governed by direct transitions. Note that since the light penetrates hundreds of atomic layers, while translational invariance is broken only for few atomic layers near the boundary, one anticipates a strong volume rather than a surface effect. Photon momentum is negligible compared to electron momentum. Accordingly, photoemission from smooth (warmly deposited) films can be successfully interpreted in terms of direct (vertical) transitions within the bulk.^{2,8} For direct electron transitions the surface of constant interband energy at $\hbar\omega'$ is determined by $E_2(\mathbf{k}) - E_1(\mathbf{k}) - \hbar\omega' = 0$ or, in accordance with (7), by

$$\beta(G^2 - 2\mathbf{kG}) - [(\hbar\omega')^2 - 4V_G^2]^{\frac{1}{2}} = 0. \quad (19)$$

For the perfectly free-electron model, with energy dependence (9), one should put in (19) $2V_G = 0$. Only

the electrons that have momenta satisfying (19) can be excited via direct transitions. Equation (19) defines the plane normal to \mathbf{G} (i.e., parallel to the zone boundary). It means that for direct electron transitions, in contrast with (18), one of the momentum components, namely, the projection on \mathbf{G} , is fixed. Thus, the momentum conservation requirement reduces the volume of k space determined by the limits of integration in (18) to the surface defined by (19) and by the condition $E \leq E_F$.² But, still, the Fowler law is valid in accordance with (14) and (16).

An important issue in this paper is that the Fowler law has nothing to do with the direct or indirect character of electron excitation: It is purely a consequence of the linear dependence of the escape function near threshold, and this is valid in general. $T(E)$ must be equal to zero at $E + \hbar\omega' = E_F + \Phi$ and, therefore, for small values of $(E + \hbar\omega' - E_F - \Phi)$ the first nonzero term of the decomposition of $T(E)$ gives

$$T(E) \propto (E + \hbar\omega' - E_F - \Phi). \quad (20)$$

The linear dependence (20) of the escape function near threshold ultimately results in a quadratic dependence of the total photoyield on $(\hbar\omega' - \Phi)$ regardless of the character of electron excitation:

$$J \propto \int_{E_F + \Phi - \hbar\omega'}^{E_F} T(E) dE \propto (\hbar\omega' - \Phi)^2. \quad (21)$$

In Ref. 7 Fowler plots were reported for one-photon ($\hbar\omega' = 4.5$ eV) and two-photon ($\hbar\omega = 2.3$ eV) photoemission for rough (coldly deposited) and smooth (warmly deposited) silver films. The two-photon photoemission from rough films was strongly enhanced and dominated by indirect transitions due to localized surface plasmons while photoemission from smooth films was mostly due to direct electron transitions for both one-photon and two-photon excitation.⁸ Thus, in accordance with the present considerations for these very different films (smooth and rough) the quadratic dependence near the photoemission threshold was obtained independently of the character of electron excitation: direct or indirect.^{7,8} This experimental observation supports our conclusion about more general validity of the Fowler law than one can expect based on the well known assumptions used to obtain this law.

There are two important points in this paper. First, we generalized the formula giving a probability of electron escape for the case of the electron excitation in the vicinity of the first Brillouin-zone boundary when a large gap between two conduction bands is of importance. Second, we showed that the Fowler law is not restricted to the usually accepted assumption of nonconservation of the electron momentum but, rather, is a consequence of the linear dependence of the escape function on electron energy, and is valid independently of the detailed character of electron excitation.

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