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# Transition absorption as a mechanism of surface photoelectron emission from metals

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*Transition absorption* of electromagnetic field energy by an electron passing through a boundary between two media with different dielectric permittivities is considered both classically and quantum mechanically. It is shown that transition absorption can make a substantial contribution to the process of electron photoemission from metals due to the surface photoelectric effect.

Transition *emission*, first theoretically predicted in the work of Ginzburg and Frank in 1946 [1], takes place when an electron passes through a boundary between two media with different dielectric permittivities. Transition emission was studied in a large number of papers and was applied, e.g., for charged particle detection in high energy physics [2]. It is obvious than the inverse process of transition *absorption* should also exist, i.e., an electron passing through a boundary between two media with different permittivities should be able to absorb the energy of electromagnetic field if such field exists at the boundary. Transition absorption is particularly interesting in relation to the problem of electron photoemission from metallic nanoparticles or nanoantennas [3–9]. One of the photoemission mechanisms (the surface photoelectric effect) was found to depend both on the potential step and on the dielectric permittivity step at the interface between a metal and another medium (dielectric, semiconductor, or vacuum) [4, 5]. The dependence on the permittivity step suggests that transition absorption can play an important role in photoelectric processes and should be carefully investigated.

In this Letter, we perform a qualitative analysis of transition absorption and derive simple expressions that characterize this effect both classically and quantum mechanically. We start by considering the electromagnetic field energy absorption by a classically described electron passing through a boundary between two media, following a method used earlier for the analysis of the anomalous skin effect [10, 11]. Then we calculate the quantum mechanical probability for such an electron to absorb a photon from the electromagnetic field and show that the quantum mechanical results for the absorbed energy converge to the classical ones in the limit $\hbar \to 0$. Finally, we identify the role of transition absorption in the surface photoelectric effect at a metal boundary, and demonstrate that this role is important.

We note that Brodsky and Gurevich in Refs. [12, 13] presented general formulas for the probability amplitudes of electron photoemission, which included the roles of both potential step and dielectric permittivity step, as well as accounted
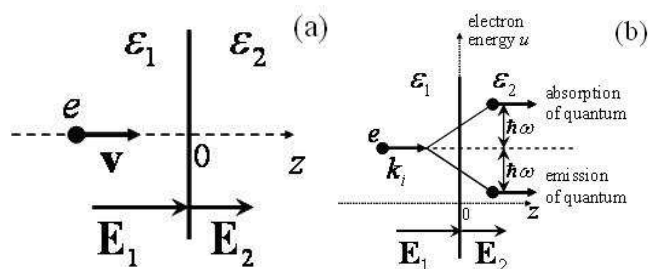


Figure 1. (a) An electron (a classical charged particle) moves along a straight line normal to the boundary between two media with different permittivities and passes through that boundary. (b) The energy diagram of a corresponding quantum mechanical problem: an electron impinging upon a boundary between two media can either absorb or emit a quantum $\hbar\omega$ as it passes through the boundary.

for the change of effective electron mass at the metal boundary. However, they did not perform any specific study of the permittivity step influence and only used their general formulas to arrive at more specific expressions, which only took into account the influence of the potential step. Therefore Refs. [12, 13] did not touch upon the subject of transition absorption, nor upon its role in photoemission.

Consider first the classical description of transition absorption, following the model in [6, 7]. We suppose that the half-space $z < 0$ is filled with medium 1 with dielectric permittivity $\varepsilon_1$ and the half-space $z > 0$ is filled with medium 2 with permittivity $\varepsilon_2$, as shown in Fig. 1(a). We further assume that electric field $E_1$ and $E_2$ exists in the medium 1 and 2, respectively, and that the field is time-harmonic with frequency $\omega$, uniform in the $x$–$y$ plane, and polarized along the $z$-axis in both media:

$$\mathbf{E}_{1,2}(t,\mathbf{r}) = \hat{\mathbf{z}}E_{1,2}(t,z) = \hat{\mathbf{z}}E_{1,2}(z)e^{-i\omega t} + \text{c.c.} \qquad (1)$$

The complex field amplitudes $E_1$ and $E_2$ satisfy the boundary condition at $z = 0$:

$$\varepsilon_1 E_1 = \varepsilon_2 E_2. \qquad (2)$$

It is obvious that the field in both media can be represented as

$$E(t,z) = [E_1(z) + (E_2(z) - E_1(z)) \cdot \Theta(z)] e^{-i\omega t} + \text{c.c.,} \quad (3)$$

where $\Theta(z)$ is the Heaviside unit step function.

Suppose that the electron is moving in the field given by Eq. (3) from $z = -\infty$ to $z = \infty$, passing the interface between the media at $z = 0$. The electron motion is described by the equations

$$\begin{aligned}\dot{v} &= eE[t,z(t)] m^{-1}, \\ \dot{z} &= v(t),\end{aligned} \quad (4)$$

where $E[t,z(t)]$ is the field acting on the electron located at $z(t)$ at time $t$, $m$ is the electron mass, and $e = -|e|$ is its charge. At $t = -\infty$ (or $z = -\infty$) the electron moves at the constant initial velocity $v_0$. We assume that the field is adiabatically switched on and off along the $z$-axis, i.e., $E_1(z) = E_1 e^{\kappa_1 z}$ for $z < 0$ and $E_2(z) = E_2 e^{-\kappa_2 z}$ for $z > 0$, applying the limits $\kappa_{1,2} \to 0$ at the final step. For sufficiently weak fields in Eq. (3) so that the electron velocity is only weakly affected, the solution of Eqs. (4) can be found using the perturbation theory by expanding the variables $z(t)$ and $v(t)$ in terms of the weak field amplitudes:

$$\begin{aligned}v(t) &= v_0 + v_1(t) + v_2(t) + \ldots, \\ z(t) &= z_0(t) + z_1(t) + z_2(t) + \ldots,\end{aligned} \quad (5)$$

where

$$z(t), v(t) \propto |E_{1,2}|^n, \quad n = 0,1,2,\ldots \quad (6)$$

In the zero-order approximation we get

$$z_0(t) = v_0(t - t_s), \quad (7)$$

where $t_s$ is the moment of time when the electron would pass the boundary if no field were present. Without loss of generality we can assume that $t_s = 0$ [6, 7].

One can find that the difference between the electron's energy in the two media (the energy change as the electron passes through the boundary) is non-vanishing starting from the second order of the perturbation series and has the form

$$\begin{aligned}\Delta W_{\text{classic}} &= \langle mv^2(+\infty)/2 - mv_0^2(+\infty)/2 \rangle \\ &\approx (m/2) \langle v_1^2(+\infty) \rangle + mv_0 \langle v_2(+\infty) \rangle,\end{aligned} \quad (8)$$

where $\langle \ldots \rangle$ denotes the averaging with respect to the phase $\phi_1$ of the complex amplitude $E_1 = |E_1| e^{-i\phi_1}$ [6, 7].

Substituting the expansions in Eqs. (5) into Eqs. (4), in the first order of the perturbation theory we find

$$v_1(+\infty) = \frac{ie|E_1|}{m\omega} \left[ e^{-i\phi_1} \left( 1 - \frac{\varepsilon_1}{\varepsilon_2} \right) - e^{+i\phi_1} \left( 1 - \frac{\varepsilon_1^*}{\varepsilon_2^*} \right) \right], \quad (9)$$

and therefore,

$$\langle v_1^2(+\infty) \rangle = \frac{2e^2}{m^2\omega^2} |E_1|^2 \left| \frac{\varepsilon_1}{\varepsilon_2} - 1 \right|^2. \quad (10)$$

In the second order the expression for $v_2(+\infty)$ turns out to be rather bulky, so we only give the explicit form of its average:

$$\langle v_2(+\infty) \rangle = \frac{e^2}{m^2\omega^2 v_0} |E_1|^2 \left| \frac{\varepsilon_1}{\varepsilon_2} - 1 \right|^2. \quad (11)$$

Substituting Eqs. (10) and (11) into Eq. (8), we finally get

$$\Delta W_{\text{classic}} = \frac{2e^2}{m\omega^2} |E_1|^2 \left| \frac{\varepsilon_1}{\varepsilon_2} - 1 \right|^2 = \frac{2e^2}{m\omega^2} |E_2 - E_1|^2. \quad (12)$$

Equation (12) shows that the average energy absorbed by the electron passing from medium 1 to medium 2 is proportional to the square of the dielectric permittivity difference, i.e., $\Delta W \propto |\varepsilon_1 - \varepsilon_2|^2$. This constitutes the effect of transition absorption. It exists irrespective of the sign of $\varepsilon_1 - \varepsilon_2$, i.e., irrespective of whether the electron passes from medium 1 to medium 2 or the other way around. As will be shown below, the classical expression (12) remains valid in the quantum case if the quantum energy is much less than the electron energy ($\hbar\omega \ll u_i$).

Note that the first-order correction to the electron velocity is sufficient for the description of the anomalous skin effect [12, 13] because it is typically considered for the normal incidence of light on the metal boundary, so light causes the electrons to oscillate parallel to the boundary. In such a case, at least for electrons normally incident on the boundary and experiencing specular reflection from it, the expression for $\Delta W$ similar to Eq. (8) contains no term proportional to $v_2(+\infty)$, since the initial velocity $\mathbf{v}_0$ and the velocity $\mathbf{v}_2(+\infty)$ are perpendicular to each other. On the contrary, for the transition absorption in the geometry shown in Fig. 1(a) the term proportional to $\langle v_2(+\infty) \rangle$ in Eq. (8) is non-vanishing and equal to the term proportional to $\langle v_1^2(+\infty) \rangle$. The substantial contribution of both these terms requires the application of the regular perturbation theory up to the second order.

Now let us consider the transition absorption effect quantum mechanically, showing that quantum mechanical calculations also converge to Eq. (12). Figure 1(b) shows the setup of the problem. An electron with energy $u_i = \hbar^2 k_i^2/2m$ ($k_i$ being the electron wave number) is normally incident on the boundary between two media. When passing through the boundary, the electron can either absorb or emit a quantum of electromagnetic energy $\hbar\omega$ with probabilities $p_+$ and $p_-$, respectively. The energy of the electron then becomes $u_\pm = \hbar^2 k_\pm^2/2m = u_i \pm \hbar\omega$. The probabilities $p_\pm$ can be found using the Fermi golden rule as

$$p_\pm = p_\pm(k_o) = \frac{m}{\hbar^3} \cdot \frac{1}{k_\pm} \cdot |\langle i| H_\pm' |f_\pm \rangle|^2, \quad (13)$$

where the initial and final wave functions of the electron are,

$$|i\rangle = v_i^{-1/2} e^{+ik_i z}, \quad |f_\pm\rangle = e^{+ik_\pm z}, \quad (14)$$

the subscripts $+$ and $-$ corresponding to photon absorption and emission, respectively. The interaction Hamiltonians $H_\pm'$ are

$$H_+' = \frac{i\hbar e}{2m} \frac{\partial A_z(z)}{\partial z} + \frac{i\hbar e}{m} A_z(z) \frac{\partial}{\partial z}, \quad H_-' = (H_+')^*. \quad (15)$$
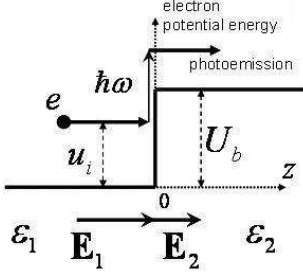
Figure 2. Photoelectron emission from metal: an electron with energy $u_i$ absorbs a photon with energy $\hbar\omega$ during collision with the potential barrier $U_b$ at the metal boundary, overcomes the barrier and leaves the metal.



Figure 3. Spectrum of the photoemission coefficient $c_{\text{out}}$ defined in Eq. (21) for Au/GaAs interface with $u_i = 5.5\,\text{eV}$ and $U_b = u_i + 0.8\,\text{eV}$. Full contribution taking into account both the inverse bremsstrahlung term and the transition absorption term in Eq. (19) (curve *1*, solid line) is compared with the result of keeping only the inverse bremsstrahlung term (curve *4*, dashed line) and only the transition absorption term (curve *3*, chain line); the dotted line (curve *2*) shows the special case of $E_1 = E_2$ (neglecting the dielectric permittivity step at the boundary). The inset shows the behavior of curves *1* and *4* near the photoemission threshold.

Here the vector potential component of the electromagnetic field $A_z(z)$ is equal to $A_1$ for $z < 0$ and to $A_2$ for $z > 0$; this potential is related to the electric field $E_z(z)$ as $A_z(z) = -iE_z(z)/\omega$. Using Eqs. (14)–(15), Eq. (13) results in

$$p_\pm = \frac{e^2 u_i}{2m\hbar^2\omega^4} \cdot \frac{\left(1 + \sqrt{1 \pm \frac{\hbar\omega}{u_i}} \pm \frac{\hbar\omega}{2u_i}\right)^2}{\sqrt{1 \pm \frac{\hbar\omega}{u_i}}} \cdot |E_2 - E_1|^2. \quad (16)$$

Similarly to the classical analysis, we assume adiabatically smooth variation of the field (on-off switching) along the $z$-axis during the integration over $z$ needed to evaluate the matrix element in Eq. (13).

Now we can use Eq. (16) to derive the average energy transferred from the field to the electron passing through the boundary between two media:

$$\Delta W_{\text{quantum}} = \hbar\omega \cdot [p_+ - p_-]. \quad (17)$$

In the classical limit $\hbar\omega/u_i \ll 1$ Eqs. (16) and (17) result in

$$\Delta W_{\text{quantum}} \approx 2\frac{e^2}{m\omega^2}|E_2 - E_1|^2, \quad (18)$$

which coincides with the classical result given by Eq. (12).

Now let us show how transition absorption influences the electron photoemission from metals. In the surface photoelectric effect scenario investigated, e.g., in [4, 5, 12, 13], an electron with the wave number $k_i$ and energy $u_i = \hbar^2 k_i^2/2m$ is normally impinging on a potential step with height $U_b$, which models a boundary between a metal and some adjacent medium (semiconductor, dielectric or vacuum), into which electrons can be emitted from metal, as seen in Fig. 2. The structure contains a light wave with electric field amplitudes $E_1$ and $E_2$ in medium 1 (metal) and medium 2 (e.g. semiconductor), respectively. As an electron collides with the potential step, it can absorb a photon with energy $\hbar\omega$. If the electron's resulting energy $u_i + \hbar\omega$ exceeds $U_b$, then the electron can leave the metal. Following, e.g., the steady-state perturbation theory [4], one can derive the probability of photoelectron emission
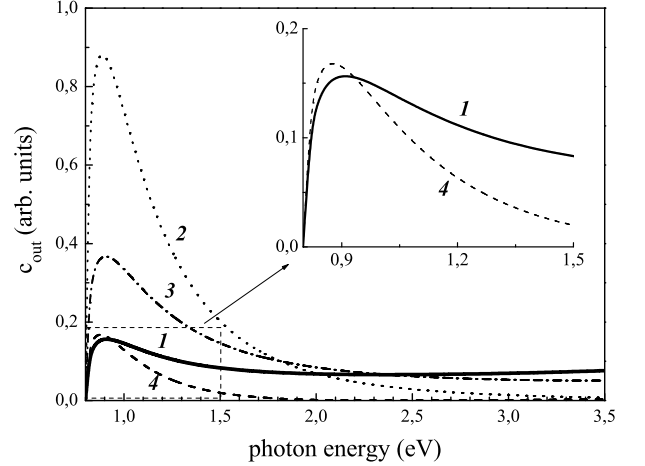
$$p_{\text{PE}} = 0.25 K_{\text{PE}} \sqrt{u_i + \hbar\omega - U_b}$$

$$\times \left| (E_2 + E_1) U_b - (E_2 - E_1) \left( \sqrt{u_i + \hbar\omega} + i\sqrt{U_b - u_i} \right)^2 \right|^2, \quad (19)$$

where

$$K_{\text{PE}} = \frac{8e^2}{m\hbar^2\omega^4 U_b^2} \cdot \frac{\sqrt{u_i} \cdot \left| \sqrt{u_i} - i\sqrt{U_b - u_i} \right|^2}{\left| \sqrt{u_i + \hbar\omega} + \sqrt{u_i + \hbar\omega - U_b} \right|^2}. \quad (20)$$

The first term inside the modulus on the second line of Eq. (19), $(E_2 + E_1) U_b$, describes the contribution to photoemission stemming from the process of electron collision with the potential step, the so-called inverse bremsstrahlung [14]. This term disappears for $U_b \to 0$ and contains the sum of the field amplitudes, $E_2 + E_1$, i.e., the inverse bremsstrahlung persists if the two media have equal permittivities ($\varepsilon_1 = \varepsilon_2$). On the contrary, the remaining second term in Eq. (19) is proportional to $E_2 - E_1$, and thus vanishes if $\varepsilon_1 = \varepsilon_2$. It is this term that corresponds to the contribution of the transition absorption to photoemission; one can see that it converges to $p_+$ in Eq. (16) in the limit $U_b \to 0$. One can also see from Eq. (19) that the contributions from these two terms are not additive but undergo quantum interference of their complex probability amplitudes.

Consider an example when photoelectrons are emitted from a metal into a semiconductor [8, 9]. The incident electron energy is taken to be $u_i = 5.5\,\text{eV}$ (the typical Fermi energy

in gold and silver), and the potential step is $U_b = u_i + 0.8\,\text{eV}$ (meaning that $p_{\text{PE}} > 0$ only for $\hbar\omega > 0.8\,\text{eV}$). The dielectric permittivity of the semiconductor is $\varepsilon_2 = 13$ (GaAs), whereas for the metal the Drude model is assumed so that $\varepsilon_1 = 1 - (\hbar\omega_p)^2/[(\hbar\omega)^2 + i(\hbar\gamma_p)(\hbar\omega)]$ with $\hbar\omega_p = 8.9\,\text{eV}$ and $\hbar\gamma_p = 0.07\,\text{eV}$, which are typical values for gold.

The calculation results are presented in Fig. 3 in the form of the spectral dependence of the surface photoemission coefficient defined as

$$c_{\text{out}}(\hbar\omega, U_b, u_i, E_1/E_2) = p_{\text{PE}}/|E_2|^2. \quad (21)$$

This coefficient is convenient because it does not depend on the field strength (unlike the probability $p_{\text{PE}}$) and thus characterizes only the media properties as well as the electron and photon energies. The solid line in Fig. 3 shows the full $c_{\text{out}}$ calculated according to Eqs. (19)–(20), taking both effects (inverse bremsstrahlung and transition absorption) into account. The dashed line shows the case when only the inverse bremsstrahlung is retained, i.e., only the first term is kept inside the modulus in Eq. (19). The chain line similarly shows the case when only the transition absorption [the second term in Eq. (19)] is retained.

The comparison between these three curves shows that transition absorption contribution to the overall photoemission is generally the strongest. Interestingly, the account for transition absorption causes the total photoemission coefficient to decrease close to the threshold value of $\hbar\omega$ (slightly over 0.8 eV, see inset in Fig. 3). This results from destructive interference of probability amplitudes in Eq. (19) caused by the minus sign between the two terms. As $\hbar\omega$ increases further away from the threshold, the inverse bremsstrahlung contribution becomes vanishingly small. Indeed, the Drude formula predicts that the absolute value of $\text{Re}\,\varepsilon_1$ decreases with the increase of $\hbar\omega$, and that $\text{Re}\,\varepsilon_1$ remains negative. As a result, the first term inside the modulus in Eq. (19) has a minimum when

$$\text{Re}\,(\varepsilon_1) + \varepsilon_2 = 0, \quad (22)$$

which takes place at the values of $\hbar\omega$ around 2.5 eV for the chosen parameters. Nevertheless, the full photoemission coefficient is non-zero in that range, decreasing to an almost constant value after the peak at 0.9 eV instead. Such behavior is the direct consequence of transition absorption. Therefore we can conclude that transition absorption makes a dominant contribution to photoelectron emission throughout the entire considered spectral range for the chosen parameters.

Note that the vanishing of the inverse bremsstrahlung contribution given by Eq. (22) takes place in the optical range ($\hbar\omega \simeq 2\ldots 3\,\text{eV}$) for the internal photoelectric effect when the medium 2 has a relatively large $\varepsilon_2$, as considered here. For the external photoelectric effect when that medium is vacuum, Eq. (22) is satisfied for photon energies larger by 3–4 times. In such a case the frequency dependence of all curves in Fig. 3 would be dominated by the coefficient in front of the modulus in Eq. (19), so all the three lines (solid, dashed and chain) would become approximately congruent to each other.

Finally, the dotted line in Fig. 3 shows a frequently used approximation (see, e.g., [13] and references therein) assuming that the fields inside the metal $E_1$ and outside the metal $E_2$ are equal ($E_1 = E_2$). Comparing this curve to the accurate result of Eq. (19), we see that this approximation overestimates the coefficient $c_{\text{out}}$ very substantially (by a factor of about 4) for the values of $\hbar\omega$ such that $|\varepsilon_2/\varepsilon_1| \ll 1$, and underestimates $c_{\text{out}}$ for higher photon energies. So, we see that the approximation $E_1 = E_2$ can be regarded as only qualitatively correct.

To summarize, we have addressed the problem of transition absorption of light wave energy by an electron as it passes through a boundary between two media, and have solved this problem both classically and quantum mechanically. In the limit when the photon energy is much less than the electron energy, the classical and quantum results converge to each other. We have also shown that transition absorption makes a substantial contribution to the process of surface photoelectron emission from metallic nanoparticles.

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