IONIZATION OF HIGHLY EXCITED ATOMS NEAR A METALLIC SURFACE

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The probability for ionization of an highly excited atom that passes slowly near a metallic surface is calculated. It is assumed that the distance from the metal greatly exceeds the orbit of the excited electron.

KUPRIYANOV[1] observed in recent experiments that a metal grid placed in the path of a thermal beam of strongly excited atoms causes the atoms to be ionized. In principle, two essential ionization mechanisms are possible for an atom moving near a metal. The first is detachment of an electron as a result of the time-dependent perturbation, that is, an inelastic collision of the atom and the metal. The necessary energy is drawn from the kinetic energy of the atom, and a free electron is produced in the final state. Such a process begins with a certain value of the atom velocity (in the experiments of[1] this threshold was quite high, ~0.3 eV in energy). The ionization probability should decrease rapidly with decreasing velocity, as is usual in a non-adiabatic transition.

The second mechanism consists of a unique process of "charge exchange" between the atom and the metal. This mechanism is of the non-activation type if the state of the atom corresponds to the region of the allowed band of the metal above the Fermi level. In this case the transition of the electron into the metal is not forbidden by the statistics. For strongly excited atoms such a situation is quite probable. Under the experimental conditions of[1] the second mechanism apparently prevails, owing to the low velocity of the atoms in the beam.

The purpose of the present paper was to calculate the probabilities of the described "charge exchange" process at low atom velocities. It is first necessary to find the ionization probability (per unit volume) of an atom resting at a given distance from the surface of the metal. We choose the origin at the center of the atom, and the boundary of the metal is assumed to be plane and defined by the equation $z = -R$. We shall henceforth consider, for concreteness, the hydrogen atom; this does not limit the generality of the analysis, since highly excited levels of complicated atoms correspond to hydrogenlike states. The Hamiltonian of the electron should include, besides the Coulomb field of the nucleus, also the polarization of the metal. The characteristic period of motion of the electron in the hydrogen atom and a state with principal quantum number $n \gg 1$ is of the order of n^3 (we use atomic units). This is much longer than the relaxation time of the electrons of the metal relative to the electromagnetic perturbation. We can therefore neglect the retardation effects and determine the polarization of the metal by electrostatic methods. It is then necessary to add to the Hamiltonian of the hydrogen atom the potential of the electrostatic image forces of the electron and of the nucleus, $H = H_0 + H_1$, and in the region $z > -R$ (outside the metal) we have

$$H_0 = -\frac{1}{2}\Delta - \frac{1}{r}, \tag{1}$$

$$H_1 = -\frac{1}{2(z+R)} + [x^2 + y^2 + (z+2R)^2]^{-1/2}. \tag{2}$$

In the region $z < -R$ (inside the metal) the potential energy of the metal is constant and is equal to the work function taken with a minus sign. When $z + R \sim 1$, expression (2) is not valid, since the macroscopic description becomes meaningless at such short distances from the metal. We shall henceforth consider only distances greatly exceeding the radius of the atom in the n-th state, that is, $R \gg n^2$. The details of the behavior of the potential in the direct vicinity of the metal turn out to be insignificant in this case. As can be seen from the foregoing, the problem under consideration in perfectly analogous to the problem of ionization of an atom by a external electric field (see[2]).

We confine ourselves for simplicity to the axially symmetrical states of the atom, in which the magnetic quantum number m is equal to zero. (The case $m \neq 0$ can be considered similarly). It is convenient to use the parabolic coordinates $\xi = r + z$ and $\eta = r - z$. The splitting of the degenerate level $E^{(0)}(n) = -1/2n^2$ can be obtained from perturbation theory. Indeed, the effective region of values of ξ and η in the integrals of H_1 with unperturbed hydrogen functions is of the order n^2, that is, much smaller than R. Expanding H_1 in ξ/R and η/R, we obtain in the first nonvanishing approximation $H_1 = (\xi - \eta)/8R^2$. A similar form is possessed by the perturbation operator in the case of a homogeneous electric field. The results for this purpose is known[2]. The correct zeroth-approximation functions are the "parabolic" wave functions $f_{n_1}(\xi)$ and $f_{n_2}(\eta)$, where n_1 and n_2 are the quantum number of the Coulomb problem in parabolic coordinates $(n_1 + n_2 + 1 = n)$. In the first perturbation-theory approximation we get

$$E^{(1)}(n_1, n_2) = -\frac{1}{2n^2} + \frac{3}{8R^2} n(n_1 - n_2). \tag{3}$$

The lifting of the degeneracy described by formula (3) is complete for the states with $m = 0$. The total splitting is of the order of n^2/r^2 and is much smaller than the binding energy of the electron $1/n^2$. This is sufficient for the applicability of perturbation theory to high levels (see[2]). Thus, (3) determines the instantaneous terms of an atom that moves slowly near the metal.

The ionization process, however, is connected with the transition of the electron into the region of large η ($\eta \sim R$). Here perturbation theory cannot be used at all, since $H_1 \gtrsim H_0$ when $\eta \gtrsim R$. To find the ionization probability we can proceed in the same manner as in the case of a strong homogeneous field[2]. An important role is played here by large values of η and relatively small values of ξ:

$$\sqrt{x^2+y^2} = \sqrt{\xi\eta} \sim n^2, \quad \eta \sim R \gg n^2, \quad \xi \sim n^4/\eta \ll R,$$

that is, a narrow cylindrical region near the z axis. In this region the Schrödinger equation can be written from

$$\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right)+\frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)+\beta_1+\beta_2+\right.$$
$$\left.+\frac{\eta}{2(2R-\eta)}-\frac{\eta}{4R-\eta}-\frac{k^2}{4}(\xi+\eta)\right]\psi = 0, \qquad (4)$$

where $k^2 \equiv -2E$, and β_1 and β_2 are the variable-separation constants with $\beta_1 + \beta_2 = 1$. Equation (4) follows from the Hamiltonian (1) and (2), if we neglect in it the quantity ξ compared with η. This means that the dependence of the total wave function on ξ is the same as in the unperturbed atom:

$$\psi_{k,n_1} = \mathrm{const}\cdot f_1(\xi)f_2(\eta);$$
$$f_1(\xi) = \sqrt{k}\exp(-{}^1\!/_2 k\xi)F(-n_1, 1; k\xi), \qquad (5)$$

where F is the confluent hypergeometric function. To determine the dependence on η we obtain from (4) the equation

$$\frac{\partial}{\partial\eta}\left(\eta\frac{\partial f_2}{\partial\eta}\right)+\left[\beta_2-\frac{k^2}{4}\eta+\frac{\eta}{2(2R-\eta)}-\frac{\eta}{4R-\eta}\right]f_2 = 0. \qquad (6)$$

We are interested in the probability of ionization of the atom in the state n_1, n_2. In the case (6) should be solved under the condition that for small η the function $f_2(\eta)$ goes over into the unperturbed wave function of the hydrogen atom with quantum number n_2:

$$f_2(\eta \to 0) \to \sqrt{k}\exp(-{}^1\!/_2 k\eta)F(-n_2, 1; k\eta). \qquad (7)$$

Then the normalization constant in (5) equals $(\sqrt{\pi}n)^{-1}$. Another requirement imposed in the solution (6) is that its asymptotic form must not contain waves incident from the metal on the atom, that is, traveling in the direction of negative η.

Introducing the function $\chi(\eta) = \sqrt{\eta}f_2(\eta)$, we obtain from (6) an equation of the type of the one-dimensional Schrodinger equation:

$$\chi'' + \left[-\frac{1}{4}\cdot k^2+\frac{\beta_2}{\eta}+\frac{1}{4\eta^2}+\frac{1}{2(2R-\eta)}-\frac{1}{4R-\eta}\right]\chi = 0. \qquad (8)$$

Equation (8) cannot be solved exactly. It is possible, however, to use the large value of the distance R and solve (8) in three different regions. Then, joining together the obtained solutions, we get the wave function outside the barrier near the metal, from which we determine the ionization probability.

Let a be a certain value of η, such that $k^{-2} \ll a \ll R$. In the region $0 \leq \eta \lesssim a$ in (8) we can neglect η compared with R in the last two terms. Then the solution $\chi_1(\eta)$ satisfying the foregoing condition as $\eta \to 0$ is

$$\chi_1(\eta) = \sqrt{k\eta}\exp\left(-\frac{1}{2}k\eta\right)F\left(\frac{1}{2}-\frac{\beta_2}{k}, 1; k\eta\right). \qquad (9)$$

Under the barrier, at $k^2\eta \gg 1$, the asymptotic form of $\chi_1(\eta)$ is

$$\chi_1 \approx \frac{(k\eta)^{-\beta_2/k}}{\Gamma(1/2-\beta_2/k)}\exp\left(\frac{k\eta}{2}\right)+\frac{(k\eta)^{\beta_2/k}}{\Gamma(1/2+\beta_2/k)}\exp\left(\frac{i\pi\beta_2}{k}-\frac{i\pi}{2}-\frac{k\eta}{2}\right). \qquad (10)$$

On the complex plane of the variable η it is necessary to make two cuts along the real axis: $[-\infty, 0]$ and $[2R + \infty]$. Let us define $\arg\eta = \arg(2R - \eta) = 0$ on the segment $[0, 2R]$. The values of $(-\eta)$ are taken by definition on the upper edge of the left cut, that is, $-\eta = |\eta|e^{i\pi}$.

In the region under the barrier, $a \leq \eta \leq 2R - a$, Eq. (8) can be solved in the quasiclassical approximation. Indeed, putting

$$p^2(\eta) = \left[-\frac{1}{4}k^2+\frac{\beta_2}{\eta}+\frac{1}{4\eta^2}+\frac{1}{2(2R-\eta)}-\frac{1}{4R-\eta}\right]$$

and calculating the parameter of the quasiclassical theory $d(1/p)/d\eta$, we get

$$\max\left|\frac{d}{d\eta}\left(\frac{1}{p}\right)\right| \sim (a^2k^3)^{-1} \ll k \ll 1.$$

Thus, the condition of the quasiclassical theory is satisfied, and we obtain the solution in the internal region (B and C are arbitrary constants):

$$\chi_2(\eta) = \frac{B}{\sqrt{|p(\eta)|}}\exp\left(\int_a |p(\eta)|d\eta\right)+\frac{C}{\sqrt{|p(\eta)|}}\exp\left(-\int_a^\eta |p(\eta)|d\eta\right). \qquad (11)$$

In the interval under consideration the term with k^2 in $p(\eta)$ is much larger than the remaining ones, so that we can expand $|p(\eta)|$ in (11). When $\eta \sim a$, the solution $\chi_2(\eta)$ should be "joined" with the asymptotic value of $\chi_1(\eta)$ (formula 10)). Calculating the integrals in (11) and comparing with (10), we obtain the values of the coefficients B and C:

$$B = \sqrt{\frac{k}{2}}e^{\varphi_1}\frac{k^{\beta_2/k}}{\Gamma(1/2-\beta_2/k)},$$

$$C = \sqrt{\frac{k}{2}}e^{-\varphi_1}\frac{k^{\beta_2/k}\exp\{i\pi\beta_2/k - i\pi/2\}}{\Gamma(1/2+\beta_2/k)} \qquad (12)$$

where $\varphi_1 = ka/2 - \beta_2 k^{-1}\ln a$.

In the region $2R - a \lesssim \eta < 2R$ Eq. (8) takes the form1)

$$\chi_3'' + \left[-\frac{1}{4}k^2+\frac{1}{2(2R-\eta)}\right]\chi_3 = 0 \qquad (13)$$

(we neglect terms of order $1/R$ compared with k^2 and $1/a$). The general solution of (13) is expressed in terms of Whittaker functions (D and E are integration constants):

$$\chi_3 = DW_{1/2k,\,1/2}(kx) + EW_{-1/2k,\,1/2}(-kx), \quad x = 2R - \eta. \qquad (14)$$

In accordance with the definition given above for $\arg(-\eta)$, we should assume that $\arg(-x) = -\pi$ when η lies outside the segment $[0, 2R]$. The asymptotic value of (14) under the barrier when $kx \gg 1/k \gg 1$ (argument larger than the index) is:

$$\chi_3^{(1)}(x) \approx De^{-kx/2}(kx)^{1/2k} + Ee^{kx/2}(kxe^{-i\pi})^{-1/2k}.$$

This expression has the same form as $\chi_2(\eta)$ from (11)

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1) As already indicated, the region $z + R \approx R - \eta/2 \sim 1$ is excluded from consideration. Therefore Eq. (13) holds for the interval $(2r - a, 2r - l)$, where $l \sim 1$.

as $\eta \to 2R - a$; from this we determine the coefficients D and E;

$$D = \sqrt{\frac{2}{k}}\, k^{-1/2k} B e^{-\varphi_2} \exp\left(\int_a^{2R-a} |p|\, d\eta\right),$$

$$E = \sqrt{\frac{2}{k}} (k e^{-i\pi})^{1/2k} C e^{\varphi_2} \exp\left(-\int_a^{2R-a} |p|\, d\eta\right), \quad \varphi_2 = -\frac{ka}{2} + \frac{\ln a}{2k}. \tag{15}$$

Finally, let us find the asymptotic value of χ_3 outside the barrier when $1/k \gg kx \gg 1$ (index larger than the argument)[3]:

$$\chi_3^{(2)} \approx -D(8k^2 x)^{1/4} \exp\left(-\frac{1}{2k} + \frac{1}{2k}\ln\frac{1}{2k}\right) \sin\left(\sqrt{2x} - \frac{\pi}{2k} - \frac{\pi}{4}\right)$$
$$+ E\left(\frac{1}{2}k^2 x\right)^{1/4} \exp\left(\frac{1}{2k} - \frac{1}{2k}\ln\frac{1}{2k} - \frac{i\pi}{4} + i\sqrt{2x}\right). \tag{16}$$

In (16) there should remain only the wave traveling in the direction of positive η, that is, negative x. This requirement determines the allowed values of the parameter β_2:

$$iD \exp(-i\pi/2k) + E(2ek)^{1/k} = 0. \tag{17}$$

Using (12), (14), and (17), we calculate $\int_a^{2R-a} |p(\eta)|\, d\eta$, expanding $p(\eta)$ in inverse powers of k. As expected, the quantity a drops out of the result. The parameter β_2 is determined by the equation

$$\frac{\Gamma(1/2 + \beta_2/k)}{\Gamma(1/2 - \beta_2/k)} = \left(\frac{ek}{2}\right)^{1/k} e^{i\pi\beta_2/k} (2kR)^{(2\beta_2+1)/k} e^{-2kR}. \tag{18}$$

Since $kR \sim R/n \gg 1$, the right side of (18) is small; consequently the root of the equation is close to the pole $\Gamma(1/2 - \beta_2/k)$. We put $1/2 - \beta_2/k = -n_2 + \epsilon$, where n_2 is a non-negative integer, and $\epsilon \ll 1$. From (18) we get in the first approximation

$$\varepsilon = i\left(\frac{ek}{2}\right)^{1/k} \frac{1}{(n_2!)^2} (2kR)^{1/k+2n_2+1} e^{-2kR}. \tag{19}$$

The ionization probability $w(n_1, n_2)$(per unit time) of an atom in the state n_1, n_2 is equal to the integral of the z-component of the current density over the plane perpendicular to the z axis and located near the metal (the region $1/k \gg kx \gg 1$).

$$w(n_1, n_2) = \int |\psi_{n_1 n_2}|^2 v_z 2\pi\rho\, d\rho$$
$$\approx \int \frac{1}{n^2} f_1^2(\xi) |\chi_3^{(2)}(\eta)|^2 \sqrt{\frac{2}{x}}\, d\xi = \frac{k|D|^2}{n^2} (2ek)^{-1/k}, \tag{20}$$

$v_z = \sqrt{2/x}$ is the electron velocity.

With the aid of (12), (15), and (18) we obtain finally

$$u(n_1, n_2) = \frac{k}{n^2} |\varepsilon(n_1, n_2)| = \frac{k}{n^2} \left(\frac{ek}{2}\right)^{1/k} \frac{1}{(n_2!)^2} (2kR)^{1/k+2n_2+1} e^{-2kR}. \tag{21}$$

The dependence of k on $n_{1,2}$ is determined by the formula (3):

$$k \approx \frac{1}{n} - \frac{3}{8} \frac{n^2(n_1 - n_2)}{R^2}.$$

When $R \gg n^3$ we can confine ourselves in (21) to the zeroth approximation

$$w(n_1, n_2) = \frac{1}{n^3} \left(\frac{e}{2n}\right)^n \frac{1}{(n_2!)^2} \left(\frac{2R}{n}\right)^{2n_2+n+1} e^{-2R/n}$$
$$n = n_1 + n_2 + 1. \tag{22}$$

Let us now take into account the motion of the atom in the adiabatic approximation. We assume that the atom moves in a classical trajectory, so that R is a specialized function of the time. The state of the incoming atom must be described by the spherical quantum numbers n, l, and m, since the perturbations in the atomic Hamiltonian, which lift the hydrogen degeneracy, have spherical symmetry. As before, we assume that m = 0. The wave function of the state n, l, m = 0 must be expanded in parabolic functions

$$\psi_{nl0}(r, \theta, \varphi) = \sum_{n_1+n_2=n-1} c(n_1 n_2) (\sqrt{\pi}\, n)^{-1} f_{n_1}(\xi) f_{n_2}(\eta) \text{for } t \to -\infty.$$

At finite values of t we get $\psi(t)$ in the adiabatic approximation.

The parabolic wave functions are regular zeroth-approximation functions, that is, they are weakly distorted by a small perturbation. In the adiabatic approximation we obtain

$$\psi_{nl0}(r, \theta, \varphi, t) = \sum_{n_1+n_2=n-1} c(n_1, n_2) (\sqrt{\pi} n)^{-1} f_{n_1}(\xi)$$
$$\times f_{n_2}(\eta) \exp\left[-i \int_{-\infty}^{t} E(n_1, n_2; t)\, dt\right]. \tag{23}$$

The total current in the direction of the z axis is equal to

$$W(t) = \frac{i}{2} \int \left[\psi_{nl0}^* \frac{\partial}{\partial z} \psi_{nl0} - \text{c.c.}\right] 2\pi\rho\, d\rho$$
$$\approx i \int \sum_{\substack{n_1+n_2= \\ n_1'+n_2'=n-1}} c(n_1, n_2) c^*(n_1', n_2') f_{n_1}(\xi) f_{n_1'}(\xi)$$
$$\times \left[f_{n_2}(\eta) \frac{\partial f_{n_2}(\eta)}{\partial \eta} - \text{c.c}\right] \exp\left\{i \int_{-\infty}^{t} [E(n_1' n_2') - E(n_1, n_2)]\, dt\right\} \eta \frac{d\xi}{n^2}. \tag{24}$$

We have used here the relations $\partial/\partial z \approx 2\,\partial/\partial y$ and $d\rho^2 \approx \eta\, d\xi$, which are valid when $\eta \gg \xi$. By virtue of the orthogonality of the functions $f_n(\xi)$ with different n_1 and identical n (see[2], only the diagonal terms in the double sum (24)

$$W(t) = \sum_{n_1+n_2=n-1} |c(n_1, n_2)|^2 w[n_1, n_2; R(t)], \tag{25}$$

where $w(n_1, n_2; R)$ is determined by formulas (21) and (22). Thus, the contributions of the different states are summed independently in the total ionization probability; no interference terms that oscillate in time arise.

Let us consider in greater detail the case when the incoming atom is in the state ns. The initial wave function is of the form

$$\psi_{n00} = (\sqrt{\pi}\, n^{5/2})^{-1} e^{-r/n} L_{n-1}^{1}\left(\frac{2r}{n}\right),$$

where L is a Laguerre polynomial and $2r = \xi + \eta$. Using the theorem for the addition of Laguerre polynomials[3],

$$\sum_{i=0}^{j} L_i^{\alpha}(x) L_{j-i}^{\beta}(y) = L_j^{\alpha+\beta+1}(x + y),$$

we obtain the expansion coefficients: $c(n_1, n_2) = (n_1 + n_2 + 1)^{-1/2} = n^{-1/2}$.

The ionization probability of the state ns per unit time is

$$W[R(t)] = \frac{1}{n} \sum_{n_2=0}^{n-1} w(n_1, n_2; R) = \frac{1}{n^4} \left(\frac{e}{2n}\right)^n \left(\frac{2R}{n}\right)^{n+1} e^{-2R/n} \sum_{n_2=0}^{n-1} \frac{(2R/n)^{2n_2}}{(n_2!)^2}. \tag{26}$$

Once W(t) is obtained, it is easy to get a formula for the dimensionless ionization probability per passage (for example, passage past a wire forming the grid). We denote by $P(t)$ the fraction of the atoms that are ionized at the instant t. In the adiabatic approximation, this quantity satisfies the differential equation $dP = [1 - P(t)]W(t)\,dt$ with initial condition $P = 0$ when $t = -\infty$. The atom moves on a classical trajectory, so that $R(t)$ is a specified function of the time. The ionization probability per passage is $P(\infty)$ and is equal to

$$P(\infty) = 1 - \exp\Bigl(-\int_{-\infty}^{+\infty} W\,dt\Bigr) = 1 - \exp\Bigl(-2\int_{R_{\min}}^{\infty} W(R)\,v_R^{-1}\,dR\Bigr) \qquad (27)$$

where v_R is the atom velocity component normal to the metallic surface and $R_{\min}$ is the distance from the metal to the nearest point of the trajectory ($v_R = 0$ when $R = R_{\min}$)[2)].

In conclusion we note the following. If we use in our problem, or in the inverse problem of recombination of ions at a metallic surface, a simplified model that does not take into account the polarization of the metal, when we obtain the same argument of the exponential $W \sim \exp(-2kR)$, but the pre-exponential factor will be incorrect. As seen from (21) and (22), the pre-exponential factor depends on the quantum number n in an exponential manner. Therefore the errors in the simplified model are particularly large for strongly excited states.

[2)] Although our problem involves dimensions that are large on an atomic scale, they are, of course, much smaller than the macroscopic quantities, say the radius of curvature of the metallic surface. Therefore, substitution of a plane for a bent surface cannot lead to an appreciable error.

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