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Abstract

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ON THE NEUTRALIZATION OF SLOW IONS AND THE DEACTIVATION OF METASTABLE ATOMS NEAR THE SURFACE OF METALS

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The question of the neutralization of slow ions and the deactivation of slow metastable atoms by a collision of the second kind near metallic surfaces is of substantial importance for understanding elementary processes in a gas discharge. Theoretical treatment of this question is the subject of papers ([1–5]). In them the interaction of an ion or metastable atom with a metal is treated as a collision and is described by the method of stationary states of perturbation theory. As a result of a number of significant simplifications of the problem, the results obtained in this way can claim, in essence, only to establish the general characteristics of the processes under consideration.

It is possible, however, to obtain results possessing qualitatively, and to a significant extent also quantitatively, the same features as the results of papers ([1–5]) by a simpler method, not connected with cumbersome calculations in collision theory. The process of pulling electrons out of a metal by ions and metastable atoms in a collision of the second kind can be interpreted as a peculiar "cold emission" in the electric fields of ions and atoms that have approached close to the metal surface ([6]). Then the well-known Fowler–Nordheim method ([7]) can be applied to the description of this process.

The transparency of the potential barrier at the boundary between the metal and the vacuum for electrons is given by the expression:

$$D \approx e^{-2K}, \tag{1}$$

where

$$K = \frac{\sqrt{2m}}{\hbar} \int_{x_1}^{x_2} \sqrt{V(x) - E}\, dx; \tag{2}$$

E is the energy of the electron in the metal; x_1 and x_2 are the coordinates of the boundaries of the potential barrier at the metal surface; $V(x)$ is the potential energy of the electron in the field of the ion, which we take in the form

$$V(x) = \begin{cases} -E, & \text{for } x < 0, \\ -\dfrac{e^2}{4x} - \dfrac{e^2}{s-x}, & \text{for } x > 0; \end{cases} \tag{3}$$

here the first term corresponds to the "image force" ; s is the distance from the ion to the metal surface. It is assumed that this distance considerably exceeds the ion' s own dimensions.

In terms of classical physics, the potential energy $V_{\max}(s)$ lowers the effective height of the potential barrier until, finally, at $V_{\max}(s_{\text{cl}}) = w$, where w is the work function of electrons from the metal, the barrier becomes classically permeable. Finding $V_{\max}(s)$ from (3), we obtain for the indicated distance:

$$s_{\text{cl}} = \frac{33}{w\,(\text{eV})}\ \text{Å}.$$

For example, for $w = 5$ eV, the value is $s_{\text{cl}} = 6.6$ Å.

As a result of the tunnel effect, one should expect a considerable probability of electrons being pulled out of the metal by ions as they approach the metal to distances $s \gtrsim s_{\text{cl}}$.

Determination of the limits of integration in (2) gives $x_1 = -e^2/4E$, $x_2 = s + e^2/E$. Since we are interested in the neutralization of ions by electrons pulled out of the metal, without substantial error one may take $x_1 = 0$, $x_2 = s$. The integral (2) converges at each of these limits.

Following (7), we first calculated the integral (2) without the "image force," $K = K_0$, and then took the corresponding term into account with the aid of the multiplier $\varphi(V_{\max}(s)/E)$, which is equal to 1 for $s = \infty$ and equal to 0 for $s = s_{\text{cl}}$. This gives:

$$K_0 = \frac{\sqrt{2m}}{\hbar}\frac{e^2}{\sqrt{E}}\left(\frac{\sqrt{1+Q}}{Q} - \ln\frac{-1+\sqrt{1+Q}}{\sqrt{Q}}\right), \tag{4}$$

where $Q = e^2/sE$. Then $K = K_0\varphi$, where φ is the exponential Nordheim factor (7). In calculating the barrier penetrability without taking account of the "image force" (D_0) and with it taken into account (D), in these formulae we used for E the value of the work function w, i.e., we neglected the "tail" of the Fermi distribution at $T > 0$°K. The results obtained for different values of the ion distance from the metal surface s are given in Table 1, which also lists the values of the field strength produced by the ion in the direction normal to the metal surface.

Table 1

s, Å	$\frac{e}{s^2}$, 10^6 V/cm	$E =$ 5 eV		$E =$ 4 eV		$E =$ 3 eV	
		D_0	D	D_0	D	D_0	D
20	3.6	$2.5 \cdot 10^{-26}$	$1{\cdot}10^{-23}$	$1.3 \cdot 10^{-21}$	$6.5 \cdot 10^{-19}$	$8{\cdot}10^{-18}$	$4{\cdot}10^{-17}$
18	4.45	–	–	–	–	$6.5 \cdot 10^{-17}$	$1{\cdot}10^{-14}$
16	5.63	–	–	–	–	$2{\cdot}10^{-15}$	$2{\cdot}10^{-12}$
15	6.40	$2.5 \cdot 10^{-21}$	$1{\cdot}10^{-17}$	$1{\cdot}10^{-17}$	$2.5 \cdot 10^{-13}$	$1{\cdot}10^{-14}$	$8{\cdot}10^{-10}$
14	7.35	–	–	–	–	$1{\cdot}10^{-13}$	$5 \cdot 10^{-9}$
12	10.0	$3{\cdot}10^{-18}$	$1{\cdot}10^{-13}$	$5{\cdot}10^{-15}$	$8{\cdot}10^{-10}$	$7{\cdot}10^{-11}$	$1 \cdot 10^{-6}$
10	14.4	$6.5 \cdot 10^{-16}$	$1{\cdot}10^{-10}$	$2.5 \cdot 10^{-13}$	$8 \cdot 10^{-7}$	–	1
8	22.5	$6.5 \cdot 10^{-12}$	$1 \cdot 10^{-6}$	–	1	–	1
6.6	33.8	–	1	–	1	–	1

It is seen from Table 1 that taking account of the "image force" considerably increases the barrier penetrability and that $D(s)$ increases very rapidly near $s = s_{\text{cl}}$, which is generally characteristic of tunnel effects.

The quantity $\lambda(s) = vD(s)$, where for an electron in the metal one may approximately take $v \simeq E/\hbar$, may be interpreted as the probability for an electron to leave the metal per unit time, i.e., in our approach to the problem, as the probability of ion neutralization per unit time at small distances from the metal surface. In this sense $\lambda(s)$ is analogous to the basic quantity that was calculated in (1-4). The total probability of ion neutralization $P(s)$ at a distance s from the metal surface also depends on whether the ion undergoes neutralization in the gas on its way to the metal. A comparison of the dependences $\lambda(s)$ and $P(s)$ obtained by us with the corresponding dependences in (2, 3) shows good qualitative, as well as significant quantitative, agreement. Thus, the peak of the curve $P(s)$ in (2) for $s = s_{\max}$ corresponds in our case to the peak at $s \simeq s_{\text{cl}}$; it is explained by the fact that for $s < s_{\text{cl}}$, despite the probability of ion neutralization being equal to 1, the quantity $P(s)$ rapidly decreases owing to the reduction in the number of remaining ions, since the majority of them are neutralized already as $s \to s_{\text{cl}}$.

The method set forth can also be attempted for extension to the process of deactivation of metastable atoms near the surface of a metal. Here this process is considered as the transition of an electron from the metal to the corresponding level of the metastable atom, accompanied by the emission from the atom of an electron which had previously been on the metastable level. Thus, the most probable, according to ([1,2]), exchange variant is automatically taken into account here. In doing so we assume that at small distances from the metal

surface the field of the metastable atom may, in first approximation, be represented as the sum of the fields of the atomic core and of the excited electron relatively far from it, i.e., as the field of a "quasi-dipole" :

$$-\frac{e^2}{s}+\frac{e^2}{s+a}=-\frac{e^2}{s}\frac{a}{s+a}, \tag{5}$$

where a is the mean distance between the charges of the "quasi-dipole." For an unexcited atom, obviously, $a=0$; for an ion $a\to\infty$.

Substitution of the effective field (5) into the expression for the potential energy (3) leads to the result (4), where now

$$Q=\frac{e^2}{sE}\frac{a}{s+a}.$$

The determination of the classical value s_{cl}, at which the barrier becomes transparent for electrons, is in this case performed by solving the equation

$$f(k)=\frac{k-3}{4k(k+1)}\left(\frac{1}{1-\sqrt{\frac{4}{k+1}}}-\frac{1}{1+\sqrt{\frac{k+1}{4}}}\right)=-\frac{Ea}{e^2}, \tag{6}$$

where $k=s_{\text{cl}}/a$.

We shall illustrate this method for metastable atoms by calculating the probability of deactivation of a metastable mercury atom 6^3P_0 near the surface of tungsten ($w=4.6$ eV). We determine

$$a=\frac{3n^2-l(l+1)}{2Z^*}a_0\approx 0.82\text{ Å},\qquad s_{\text{cl}}\approx 1.80\text{ Å}\approx 3.4\,a_0,$$

where n and l are the quantum numbers of the metastable state of the mercury atom, Z^* is the effective nuclear charge for the level, and a_0 is the Bohr radius. The corresponding values of D_0 and D for various values of s are given, together with the effective field strength of the metastable atom, in Table 2.

Table 2

s, Å	$\left(\frac{e}{s^2}\sqrt{\frac{a}{s+a}},\ \text{V/cm}\right)$	D_0	D	s, Å	$\left(\frac{e}{s^2}\sqrt{\frac{a}{s+a}},\ \text{V/cm}\right)$	D_0	D
10	$3.96\cdot 10^6$	$5\cdot 10^{-11}$	$1\cdot 10^{-10}$	3	$7.45\cdot 10^7$	$1\cdot 10^{-4}$	$6\cdot 10^{-3}$
8	$6.85\cdot 10^6$	$4\cdot 10^{-9}$	$1\cdot 10^{-8}$	2	$1.94\cdot 10^8$	$6\cdot 10^{-4}$	$1.5\cdot 10^{-1}$

s, Å	$\left(\frac{e}{s^2}\sqrt{\frac{a}{s+a}}, \text{V/cm}\right)$		D	s, Å	$\left(\frac{e}{s^2}\sqrt{\frac{a}{s+a}}, \text{V/cm}\right)$		D
6	$1.38 \cdot 10^7$	$4 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	1	$9.62 \cdot 10^8$	$3 \cdot 10^{-3}$	1
4	$3.71 \cdot 10^7$	$7 \cdot 10^{-5}$	$3 \cdot 10^{-4}$				

The dependences $\lambda(s)$ and $P(s)$ constructed from these data are also in agreement with the corresponding curves obtained in ([2,4]). The relation between the mean distances of neutralization and deactivation, $s_{\text{meta}} < s_{\text{ion}}$, is also satisfied, this being a criterion for the validity of the theory ([2,5]).

The question arises of how the specificity of the ion (metastable atom) and of the metal is taken into account in the method under consideration. We note first of all that in the existing calculations based on collision theory the specificity of the metal surface is not taken into account (the approximation of free electrons in the metal is used), while the specificity of the atom (ion) is taken into account by the choice of wave functions of the stationary states. For our calculation, essen-

but that the electron-transition processes under consideration are resonant: an electron from some level of the metal (we have everywhere assumed $E = \omega$) passes to a level of equal energy of the ion or metastable atom. The specificity of the ion will thus be taken into account by introducing into the calculation particular values of E for the transition level (with possible allowance for the distribution of electrons over energies near the boundary of the Fermi distribution at $T > 0°\text{K}$). The specificity of metastable atoms is, in addition, taken into account by the quantity a, determined by the effective charge of the corresponding nucleus Z^*, and also by the quantum numbers n and l, which make it possible to distinguish between a number of metastable states of one and the same atom.

The method described, owing to the comparative simplicity of the calculations, makes it possible to calculate rapidly the quantities $D(s)$, $\lambda(s)$, and $P(s)$ for various possible levels of electron transition from the metal to an ion or metastable atom, and to find the corresponding probabilities of their neutralization or deactivation with transition both to the ground state and to excited states. The obtaining of approximate data of this kind, not connected with cumbersome calculations in collision theory, is of considerable interest.

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Note: Figure translations are in progress. See original paper for figures.