# Auger neutralization rates of multiply charged ions near metal surfaces

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Transition rates for the Auger neutralization processes of multiply charged ions on metal surfaces are calculated in closed analytical form. The core potential of a multiply charged ion is represented by a pseudopotential, which accounts for the electron screening effects and allows transition to the pure Coulomb case (fully stripped ions). The relative importance of various neutralization channels in slow-ion-surface collisions is discussed for the examples of  $He^{2+} + Mo(100)$  and  $C^{3+} + Mo(100)$  collisional systems.

#### I. INTRODUCTION

Recent development of new types of ion sources able to produce intense beams of low-energy, multiply charged ions<sup>1</sup> has opened the possibility of extending the studies of low-energy ion-surface inelastic processes into the region of higher ion charge states.<sup>2</sup> The first experimental results in this field of research have already emerged.<sup>3</sup> Besides their intrinsic scientific interest, the low-energy collision processes of multiply charged ions with solid surfaces also play an important role in the edge plasmas of present-day magnetic fusion devices.<sup>4</sup>

In the present article we shail study the Auger neutralization processes occurring in a slow collision of multiply charged ions  $(A^{Z+})$  with metal surfaces (M). The system  $A^{Z+} + M(Z >> 1)$ , at relatively small ion-surface distances R, can be regarded as a "superexcited" complex in which the upper (metallic) electron levels are filled, and the lower (ionic) levels are vacant. The complex can relax nonradiatively through a host of Auger-type processes, which involve simultaneous (partial) neutralization of the ion and emission of electrons into continuous spectrum. Although when the charge Z is high, where Auger relaxation processes with capture and emission of many electrons are possible, in the present work we shall consider only those processes in which only two electrons are involved. The most prominent two-electron Auger processes are (i) proper Auger neutralization,

$$A^{Z+} + M(e_1, e_2) \rightarrow A^{(Z-1)+}(e_1) + M + \overline{e}_2$$
, (1.1)

(ii) one-electron capture into an excited ionic state, followed by Auger relaxation with emission of either a metallic electron or the captured electron itself.

$$A^{Z+} + M(e_1, e_2) \to (A^{(Z-1)+})^*(e_1) + M(e_2)$$
  

$$\to A^{(Z-1)+}(e_1) + M + \overline{e}_2 , \qquad (1.2a)$$

$$\rightarrow A^{(2-1)+}(e_2) + M + \overline{e}_1$$
, (1.2b)

and (iii) two-electron capture into a doubly excited ionic state, followed by its autoionization decay

$$A^{Z+} + M(e_1, e_2) \rightarrow (A^{(Z-2)+})^{**}(e_1, e_2) + M$$
  
$$\rightarrow A^{(Z-1)} + (e_1) + M + \overline{e}_2 , \qquad (1.3)$$

where by  $e_1, e_2$  we have denoted the two active electrons, and by  $\overline{e_i}$  (i = 1, 2) the emitted electron. The first step of the reaction (1.2) is a resonant process whose probability at low collision velocities becomes unity already at large ion-surface distances.<sup>5</sup> For this reason, the Auger relaxation channels (1.2) can effectively compete with the proper Auger neutralization (1.1). The same is true also for the Auger channel (1.3), when the charge Z is sufficiently high.

The two-electron capture channel (1.3), however, differs from the Auger channels (1.1) and (1.2). Namely, the Auger relaxation dominantly takes place in the isolated ion while in reactions (1.1) and (1.2) the relaxation occurs during the collision. Since the autoionization of doubly excited ionic states is a sufficiently well-known process,<sup>6</sup> and since the two-electron capture in ionsurface collisions requires a separate study unrelated to the dynamic Auger neutralization, in the present paper we shall confine ourselves to processes (1.1) and (1.2). We note that the proper Auger neutralization (1.1) and the second step of the reaction (1.2b) have already been studied<sup>7,8</sup> under the assumption that ion  $A^{Z+}$  is fully stripped. For an incompletely stripped ion, the shortrange, non-Coulomb part of the ionic potential may have a significant effect on the Auger transition matrix elements, which, as we shall see in the following sections, are dominantly influenced by the behavior of electron wave functions in the vicinity of the ion. The field of the incompletely stripped ion shall be described by a pseudopotential which includes the short-range screening effects and has a proper asymptotic behavior. The known eigenfunctions and eigenvalues for this potential and the dipole approximation for the interelectron interaction in the configuration space giving the main contribution to Auger matrix elements will allow us to calculate the transition rates for processes (1.1) and (1.2) in closed analytical form.

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The article is organized as follows. In Sec. II, we shall calculate the matrix elements and the associated Auger rate for the neutralization channel (1.1), while the analogous calculations for processes (1.2a) and (1.2b) will be done in Sec. III. In Sec. IV we discuss the relative role of the considered Auger neutralization channels as multicharged ion approaches to a metal surface. Finally in Sec. V some concluding remarks will be given.

Atomic units  $(m_e = \hbar = e^2 = 1)$  will be used throughout this work, unless otherwise explicitly stated.

### **II. PROPER AUGER NEUTRALIZATION**

#### A. Transition rate and relevant wave functions

The electron transitions taking place in the proper Auger neutralization channel (1.1) are schematically shown in Fig. 1(a), from where it follows that the following energy conditions apply for this process:

$$\phi < -E_i < U_0, \quad i = 1 \text{ and } 2,$$
 (2.1a)

$$-E_0 > -E_i$$
,  $i = 1$  and 2, (2.1b)

$$E_{\rm fin} - E_{\rm in} \equiv E_2' - E_0 - (E_1 + E_2) = 0$$
, (2.1c)

where  $\phi$  is the metallic work function,  $U_0$  is the depth of the metal potential well (the metal being treated in the Sommerfeld model),  $E_i$  is the energy of the *i*th metallic electron,  $E'_2$  is the energy of the emitted electron,  $E_0$  is the energy of the captured electron in the ground state of ion  $A^{(Z-1)+}$ , and  $E_{fin}$ ,  $E_{in}$  are the total final- and initialstate energies. We place the coordinate origin in the center of the ion and define the position of the metallic surface by z = -R. Denoting by  $\mathbf{r}_i$  and  $\mathbf{r}_{iM}$  the radius vectors of the *i*th electron with respect to coordinate origin (0,0,0) and the point (0,0,-R), respectively, one has  $\mathbf{r}_{iM} = \mathbf{R} + \mathbf{r}_i$ . As shown in Ref. 7(a) (see also below) the dominant contribution to the Auger matrix element comes from the region of configuration space in which  $r_{2M} \sim 1$ ,  $r_1 \sim 1/Z$ , and  $r_{1M} \sim R \gg r_{2M}$ . Bearing this in mind, the two-electron Hamiltonian of the  $A^{Z+} + M$  system can conveniently be written in the form

$$H(1,2) = H(1) + H(2) + V_{int}(1,2) , \qquad (2.2)$$

where H(i) is the Hamiltonian of the *i*th electron in the field of the ionic core and the metal,

$$|H_M(i), z_i < -R \tag{2.3a}$$

$$H(i) = \begin{cases} H_A(i) + V_i(i) + V_i(A) & z_i \ge -R + \delta R \end{cases}, \quad (2.3b)$$

with i = 1 and 2

$$|0, z_{1,2}| < -R$$
 (2.4a)

$$V_{\text{int}} = \begin{cases} V_{12}, & z_1(z_2) \ge -R + \delta R, & z_2(z_1) < -R \end{cases}$$
 (2.4b)

$$V_1(2) + V_2(1) + V_{12}, \quad z_{1,2} \ge -R + \delta R \quad .$$
 (2.4c)

In Eqs. (2.3) and (2.4),  $H_A(i)$  and  $H_M(i)$  are the Hamiltonians of the *i*-th electron in the ionic and metal field at  $R \to \infty$ , respectively,  $V_i(j)$  and  $V_i(A)$  are the interaction



FIG. 1. Schematic representation of energy levels of an ionsurface system involved in the two-electron Auger neutralization processes: (a) proper Auger neutralization [reaction (1.1)]; (b) resonant electron capture, followed by a dipole-allowed deexcitation [reaction (1.2a)]; (c) resonant electron capture, followed by Auger deexcitation [reaction (1.2b)].

potentials of the *i*-th electron with the electrostatic images of the *j*th electron and of the ion  $A^{Z+}$ , respectively, and  $V_{12}$  is the interelectron interaction. The distance  $\delta R$  (~1) defines a near-surface layer in which the image potential representation breaks down. The repulsive forces arising from the interpenetration of electronic clouds at small ion-surface distances (and due to the Pauli exclusion principle) are also restricted to this layer. We shall see, however, that the uncertainty of potential interactions in the region  $\delta R$  is not essential for determination of the Auger neutralization rate.

In the chosen coordinate system, the specific forms of  $H_A(i)$  and  $H_M(i)$  and potential interactions<sup>9</sup> are (i, j = 1, 2)

(2.5a)

$$H_A(i) = -\frac{1}{2}\nabla_i^2 + V_A(i), \quad V_A(i) \sim -\frac{Z}{r_i} \text{ as } r_i \to \infty$$
.

$$H_{M}(i) = -\frac{1}{2}\nabla_{i}^{2} + V_{M}^{\text{eff}}(i) \equiv -\frac{1}{2}\nabla_{i}^{2} - U_{0}, \quad z_{i} < -R ,$$
(2.5b)

$$V_i(i) = -\frac{1}{4}(z_i + R)^{-1}, \qquad (2.5c)$$

$$V_i(A) = Z[x_i^2 + y_i^2 + (z_i + 2R)^2]^{-1/2}, \qquad (2.5d)$$

$$[V_{i}(j)]_{(i\neq j)} = -[(x_{i} - x_{j})^{2} + (y_{i} - y_{j})^{2} + (z_{i} + z_{i} + 2R)^{2}]^{-1/2}, \qquad (2.5e)$$

$$V_{12} = \frac{\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (2.5f)$$

Note that in some previous papers<sup>5</sup> the electron image potential was erroneously a factor of 2 larger than in Eq. (2.5c).

There are many ways to represent the interaction of an electron with the screened Coulomb potential of an incompletely stripped ion (e.g., use of the Thomas-Fermi potential, Yukawa-type model potentials, etc.). A convenient representation of the type  $V_A = -Z/r + \sum_l V_{al} \hat{P}_l$  has been proposed by Simons:<sup>10</sup>

$$V_A(\mathbf{r}) = -\frac{Z}{r} + \sum_{l=0}^{\infty} \frac{c_l}{r^2} \hat{P}_l$$
, (2.5g)

where  $\hat{P}_l$  is the projection operator projecting onto the subspace of a given orbital angular momentum l.

The transition probability per unit time for the proper Auger neutralization is

$$W_{I}(R) = 2\pi \int \int \int |V_{if}|^{2} n(\mu_{1}) n(\mu_{2}) g(\mu'_{2}) \\ \times \delta(E_{fin} - E_{in}) d\mu_{1} d\mu_{2} d\mu'_{2}, \qquad (2.6)$$

$$V_{if} = \langle \psi_{\mu_0}(1)\psi_{\mu'_2}(2) | V_{\text{int}} | \psi_{\mu_1}(1)\psi_{\mu_2}(2) \rangle , \qquad (2.7a)$$

where  $n(\mu_i)$  (i = 1 and 2) and  $g(\mu'_2)$  are the population numbers and statistical weight of the metallic and continuum electrons, respectively,  $\mu_i$  (i = 1 and 2) and  $\mu'_2$  are sets of quantum numbers (discrete and continuous) defining the state of the metallic and ejected electrons, and the integration symbols in Eq. (2.6) include summation over the discrete quantum numbers. The wave functions entering in Eq. (2.7a) are normalized as ( $\mu_0$  is the set of ground-state quantum numbers for  $A^{(Z-1)+}$ )

$$\langle \psi_{\mu_0} | \psi_{\mu_0} \rangle = 1 ,$$

$$\langle \psi_{\mu_i} | \psi_{\bar{\mu}_i} \rangle = \delta(\mu_i - \bar{\mu}_i), \quad \dot{l} = 1 \text{ and } 2 ,$$

$$\langle \psi_{\mu'_2} | \psi_{\bar{\mu}'_2} \rangle = g^{-1}(\mu'_2)\delta(\mu'_2 - \bar{\mu}'_2) ,$$

$$(2.7b)$$

in which the  $\delta$  function reduces to a Kronecker symbol for discrete values of  $\mu_i, \tilde{\mu}_i$ . We note that Eq. (2.6) for  $W_I$  takes into account the identity of two metal electrons. [The result follows after antisymmetrization, averaging over the initial and summing over the final spin states, and keeping in mind that the matrix element (2.6) includes integration over the states of both electrons in the metal.]

Due to the inequality (2.1b) and  $\gamma_0 R \gg 1$   $[E_0 = -\gamma_0^2/2 + O(1/R)]$ , the product  $\psi_{\mu_0}(1)\psi_{\mu'_1}(1)$  in Eq. (2.7a) is localized dominantly in the ionic region  $(r_1 \sim 1/Z)$ , while due to exponential decay of the function  $\psi_{\mu_2}(2)$  outside the metal, the product  $\psi_{\mu_2}(2)\psi_{\mu'_2}(2)$  is localized in the region  $r_{2M} \sim 1$ . In this region of twoelectron configuration space, the wave functions  $\psi_{\mu_0}(1)$ ,  $\psi_{\mu_2}(2)$ , and  $\psi_{\mu'_2}(2)$  can be well represented by their unperturbed forms.<sup>7(a),8(a)</sup> However, the wave function  $\psi_{\mu_1}(1)$ of the metallic electron in the region  $r_1 \sim 1/Z$  is strongly perturbed by the field of ion  $A^{Z+}$ , and it has to be determined by solving the eigenvalue problem of Hamiltonian H(1) given by Eq. (2.3).

The wave functions  $\psi_{\mu_0}(1)$  and  $\psi_{\mu_1}(1)$  in the atomic region are the eigenfunctions of the Hamiltonian  $H \approx H_A + \Delta E$ , where  $\Delta E$  is the first term in the expansion of the image force potential  $V_i(i) + V_i(A)$  into the inverse powers of R:  $\Delta E = (2Z - 1)/4R$ . The variables in the Schrödinger equation

$$(H_A + \Delta E)\psi = E(R)\psi \qquad (2.8a)$$

separate in the spherical coordinates  $(r, \theta, \varphi)$ ,

$$\psi = R(r)Y_{lm}(\theta,\varphi) . \qquad (2.8b)$$

Eigenenergies of the Hamiltonian  $H_A + \Delta E$  are

$$E(R) = -\frac{\gamma^2}{2} + \Delta E , \qquad (2.8c)$$

and  $R = f_l(r)/r$ , where  $f_l$  satisfies the radial Schrödinger equation

$$\left[-\frac{d^2}{dr^2} - \frac{2Z}{r} + \frac{2c_l}{r^2} + \frac{l(l+1)}{r^2} + \gamma^2\right] f_l(r) = 0. \quad (2.9)$$

 $Y_{lm}(\theta, \varphi)$  are the spherical harmonics.

The solutions of the above equation, regular at zero and exponentially decreasing when  $r \rightarrow \infty$ , correspond to a discrete spectrum:

$$\gamma = \frac{Z}{\mu}, \quad \mu = p + 1 + s_l, \quad p = 0, 1, 2, \dots,$$
 (2.10a)

$$s_l = -\frac{1}{2} + \left[ (l + \frac{1}{2})^2 + 2c_l \right]^{1/2} .$$
 (2.10b)

where  $\mu$  is the effective quantum number. The coefficients  $c_l$  in Eq. (2.5g) can be determined by fitting the lowest energies  $E_l = -\gamma_l^2/2$ , (2.10a), for each *l* series and a given spin to the experimental data

$$c_l = \frac{1}{2} \left[ \frac{Z}{\gamma_l} + l \right] \left[ \frac{Z}{\gamma_l} - l - 1 \right], \quad l = 0, 1, 2, \dots \quad (2.10c)$$

The normalized wave functions of the potential (2.5g) for the discrete spectrum are given by<sup>10</sup>

$$\psi_{\gamma lm}(\mathbf{r}) = R_{pl}(\gamma, \mathbf{r}) Y_{lm}(\theta, \varphi), \quad \gamma = \frac{Z}{\mu} \quad . \tag{2.11a}$$

$$R_{pl}(\gamma, r) = B_p r^{s_l} e^{-\gamma r} {}_1 F_1(-p, 2s_l + 2; 2\gamma r) , \qquad (2.11b)$$

$$B_{p} = (2\gamma)^{s_{l}+3/2} \left[ \frac{(s_{l}+1)(2s_{l}+2)_{p}}{(s_{l}+p+1)p!\Gamma(2s_{l}+3)} \right] , \quad (2.11c)$$

$$(a)_p = a(a+1) \times \cdots \times (a+p-1), \text{ with } (a)_0 = 1,$$
  
(2.11d)

where  ${}_{1}F_{1}(x,y;z)$  is the confluent hypergeometric function.

The regular solution  $f_l(r)$  of the radial equation (2.9) that satisfy the asymptotic condition

$$f_l(r) \sim r^{-Z/\gamma} e^{\gamma r} + \text{const} \times r^{Z/\gamma} e^{-\gamma r} \text{ as } r \to \infty$$
, (2.12)  
is

$$f_{l}(r) = (2\gamma)^{s_{l}+1+Z/\gamma} \frac{\Gamma(1+s_{l}-Z/\gamma)}{\Gamma(2s_{l}+2)} r^{s_{l}+1} e^{-\gamma r} \times {}_{1}F_{1}(1+s_{l}-Z/\gamma, 2s_{l}+2; 2\gamma r) , \qquad (2.13)$$

where  $s_l$  is given by Eq. (2.10b) and  $\gamma$  belongs to the continuous spectrum  $(\gamma \neq \mathbb{Z}/\mu)$ .

The wave function  $\psi_{\mu_0}(1)$  is the eigensolution (2.11) of the atomic Hamiltonian (corrected by  $\Delta E$ ). The wave function  $\psi_{\mu_1}(1)$  is the solution of the Schrödinger equation

$$[H(1) - E_1(R)]\psi_{\mu_1}(1) = 0 \tag{2.14}$$

analytically continued from the metallic region into the atomic region.

In the underbarrier region, where the effects of image potentials  $V_1(1)$  and  $V_1(A)$  on particle motion are comparable with the electron-ion interaction, the electron wave function exponentially decays in the direction perpendicular to the z axis. Therefore, it is sufficient to solve Eq. (2.14) in a cylindrical region around the z axis (with a radius  $\rho$ ) in which, within an accuracy of  $O(\rho/R)$ , the variables in Eq. (2.14) can be separated in parabolic coordinates.

For the case of the pure Coulomb potential  $V_A$ , the separation of variables in parabolic coordinates can also be done in the atomic region, and, thus, the solution of Eq. (2.14) can be analytically continued from the metallic (through the subbarrier) into the atomic region<sup>11(a)</sup> (or vice versa<sup>5,11(b)</sup>). In the case when  $V_A$  contains a short-range non-Coulomb part, separation of variables in Eq. (2.8) in parabolic coordinates is not anymore possible in the atomic region.

With  $V_A$  given by (2.5g), the variables in Eq. (2.14) in the atomic region can be separated in spherical coordinates  $(r_1, \theta_1, \varphi_1)$ . The connection of  $\psi_{\mu_1}$  from the metallic and subbarrier regions (where it can conveniently be represented in parabolic coordinates) into the atomic region can now be performed by its expansion in the former region in the spherical basis and then smoothly linked to the solution in the atomic region. This procedure is performed in the Appendix. We quote here only the result for  $\psi_{\mu_1}$  for  $n_1 = 0$  in the region  $r_1 \sim 1/Z$  and for convenience designate it by  $\psi_{MA}$  [we note that  $\mu_1 \equiv (\gamma_1, n_1, m)$ , of which  $\gamma_1$  is continuous and  $n_1, m$  are discrete quantum numbers]:

$$\psi_{MA}(\mathbf{r}_{1}) = D_{M}(R; Z, \gamma_{1}, m) \varphi_{MA}(\mathbf{r}_{1}) , \qquad (2.15a)$$

$$\varphi_{MA}(\mathbf{r}_{1}) = \sum_{l=|m|}^{\infty} (-1)^{l} (2l+1) \frac{f_{l}(r_{1})}{r_{1}} \times P_{l}^{|m|} (\cos\theta_{1}) e^{im\varphi_{1}} , \qquad (2.15b)$$

$$D_{M}(R; Z, \gamma_{1}, m) = \frac{(-1)^{m}}{2\pi [2(m!)]^{1/2}} 2^{-Z/\gamma_{1}} (2e)^{1/4\gamma_{1}} \times (2\gamma_{1})^{1/2\gamma_{1}-(m+1)/2} e^{(2Z-1)/4\gamma_{1}} \times Q_{m}(R; Z, \gamma_{1}) \quad (m = |m|), \quad (2.16)$$

$$Q_m(R;Z,\gamma_1) = R^{Z/\gamma_1 + 1/4\gamma_1 - (m+1)/2} e^{-\gamma_1 R} , \qquad (2.17)$$

where the functions  $f_l(r_1)$  in (2.15b) are the regular (in the origin) solutions of the radial Schrödinger equation (2.9), with an exponentially increasing behavior in the subbarrier region [Eq. (2.13)]. The function (2.15a) is normalized by the condition (2.7b).

It should be noted that in the region  $z \gg 1$ , the exponentially small terms in Eq. (2.12) cannot be neglected, since in the summation (2.15b), the exponentially increasing terms in this region cancel each other (if the correct asymptotic form of  $f_l$  valid both for large argument and large index is used). In the case of the pure Coulomb potential ( $V_{Al} \equiv 0$ ),  $f_l(r_1)$  are well-known solutions of the radial Coulomb equation (2.9).<sup>12</sup> In that case, the function  $\psi_{MA}$ , Eq. (2.15b), expressed in parabolic coordinates, is given by Eq. (A1) of the Appendix, and along the z axis and for m = 0 it takes the form

$$\psi_{MA}(z) = D_M(2\gamma_1)^{Z/\gamma_1 + 1} \Gamma(1 - Z/\gamma_1) e^{-\gamma_1 z} h(z)$$
, (2.18a)

$$h(z) = \begin{cases} 1, & z \ge 0\\ {}_{1}F_{1}(Z/\gamma_{1}, 1, 2\gamma_{1}z), & z \le 0 \end{cases}.$$
(2.18b)

In the calculation of the matrix element  $V_{if}$  for the transition of electron 2 from the metal into the continuum, the wave function  $\psi_{\mu_2}(2)$  is taken from the Sommerfeld model for the metal<sup>13</sup> and  $\psi_{\mu'_2}(2)$  is represented by a plane wave.

In that case  $\mu_2 = \mathbf{k}_2$ ,  $\mu'_2 = (E'_2, \Omega'_2)$ ,  $\Omega'_2$  being the solid angle of  $\gamma'_2 = (\gamma'_{2x}, \gamma'_{2y}, \gamma'_{2z})$  with  $E'_2 = \gamma'^2_2/2$ ;  $\mathbf{k}_2 = (k_{2x}, k_{2y}, k_{2z})$ , with  $k^2_{2x} + k^2_{2y} + k^2_{2z} = 2U_0 - \gamma^2_2$ . The vectors  $\mathbf{k}_2$  and  $\gamma'_2$  are the momenta of electron 2 in its initial and final state, respectively. The corresponding wave functions, normalized by the condition (2.7b), are

$$\psi_{\mu_{2}}(\mathbf{r}_{2M}) = \frac{1}{2\pi} \exp(ik_{2x}x_{2M} + ik_{2y}y_{2M}) \\ \times \frac{k_{2z}}{(\pi U_{0})^{1/2}} \begin{cases} \left[\frac{ik_{2z} - p_{2z}}{2ik_{2z}}\right] \exp(ik_{2z}z_{2M}) + \left[\frac{ik_{2z} + p_{2z}}{2ik_{2z}}\right] \exp(-ik_{2z}z_{2M}), & z_{2M} < 0 \\ \exp(-p_{2z}z_{2M}), & z_{2M} \ge 0 \end{cases},$$

$$(2.19)$$

where 
$$p_{2z}^2 = 2U_0 - k_{2z}^2$$
, and  
 $\psi_{\mu_2'}(\mathbf{r}_{2M}) = (2\pi)^{-3/2} \gamma_2' \exp(i\gamma_2' \cdot \mathbf{r}_{2M})$ . (2.20)

Since  $\psi_{\mu'_2}$  is normalized to  $\delta(\gamma'_2 - \tilde{\gamma}'_2)\delta(\Omega'_2 - \tilde{\Omega}'_2)$ , we have

$$g(\mu'_2) = |d\gamma'_2/dE'_2| = \frac{1}{\gamma'_2}$$
.

By a direct calculation, one can show that the partial functions in the sum of Eq. (2.15b) are orthogonal to all eigenfunctions in the potential  $V_A(r_1)$  with absolute value of eigenenergies greater than  $\gamma_1^2/2$ . For that reason, the two-electron wave functions  $\Psi_i = \psi_{\mu_1}(1)\psi_{\mu_2}(2)$  and  $\Psi_f = \psi_{\mu_0}(1)\psi_{\mu_2'}(2)$  of the initial and final states are mutually orthogonal.

#### B. Matrix elements in dipole approximation

In the region  $r_1 \sim 1/Z$ ,  $r_{2M} \sim 1$  which gives the main contribution to the integral (2.7a), the image potentials  $V_1(2)$  and  $V_2(1)$  can be neglected with respect to the interelectron interaction  $V_{12}$ , which in the considered configuration can be expanded in powers of 1/R. Due to the above-mentioned orthogonality of the initial- and final-state wave functions,  $\Psi_i$  and  $\Psi_f$ , the leading term of this expansion is (we present only the terms that give nonzero contribution to the matrix element  $V_{if}$ )

$$V_{\text{int}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \simeq \frac{w}{R^3}$$
$$w = \sum_{\nu = -1}^{+1} (-1)^{\nu + 1} (1 + \delta_{\nu 0}) d_{1\nu}^* d_{2\nu}$$
(2.21a)

where  $d_{iv}$  are multiplicative operators of the form

$$d_{i\nu} = \left(\frac{4\pi}{3}\right)^{1/2} r_i Y_{i\nu}(\theta_i, \varphi_i), \quad i = 1, 2M$$
 (2.21b)

where  $Y_{i\nu}(\theta_i, \varphi_i)$  are the spherical harmonics, and  $(r_i, \theta_i, \varphi_i)$  are the spherical coordinates of vector  $\mathbf{r}_i$ .

Within the dipole approximation (2.21) for  $V_{int}$ , the matrix element (2.7a) is factored

$$V_{if} = \mathcal{L}_{MA}(\gamma_1, Z) R^{-3} Q_0(R; Z, \gamma_1)$$

$$\times \sum_{\nu = -1}^{+1} (-1)^{\nu+1} (1 + \delta_{\nu 0}) \mathcal{F}_{MA}^{(\nu)}(1) \mathcal{F}_{M}^{(\nu)}(2) \qquad (2.22)$$

where

$$\mathcal{L}_{MA}(\gamma_1, Z) = \frac{1}{4\pi} 2^{-Z/\gamma_1 + 1/2\gamma_1} \gamma_1^{1/2\gamma_1 - 1/2} \times (2e)^{1/4\gamma_1} e^{(2Z - 1)/4\gamma_1}, \qquad (2.23)$$

$$\mathcal{F}_{MA}^{(\nu)}(1) = \langle \psi_{\gamma_0 l_0 m_0}(\mathbf{r}_1) \mid d_{1\nu}^* \mid \varphi_{MA}(\mathbf{r}_1) \rangle , \qquad (2.24)$$

 $\mathcal{T}_{M}^{(\nu)}(2) = \langle \psi_{\mu_{2}'}(\mathbf{r}_{2M}) | d_{2\nu} | \psi_{\mu_{2}}(\mathbf{r}_{2M}) \rangle , \qquad (2.25)$ 

and  $Q_0(R; Z, \gamma_1)$  is given by Eq. (2.17).

In writing the expression (2.22) we have taken into account that the main contribution in  $W_{I}(R)$  give electrons with m = 0; the terms with  $m \ge 1$  give corrections on the order of O(1/R), which have also been neglected in the expansion (2.21). Now we turn to calculation of matrix elements  $\mathcal{F}_{MA}^{(\nu)}(1)$  and  $\mathcal{F}_{M}^{(\nu)}(2)$ .

The product  $\psi_{\gamma_0 l_0 m_0} \varphi_{MA}$  is mainly localized in the atomic region, where the function  $\varphi_{MA}$  is given by (2.15b). As the above product exponentially decreases outside of the mentioned region, we may extrapolate its range of validity to the whole space. Analogously, the product  $\psi_{\mu'_2}\psi_{\mu_2}$  is mainly localized in the metallic region, and integration in (2.25) is even this period.

and integration in (2.25) is over this region.

With the functions (2.11a) [with  $(\gamma, l, m) = (\gamma_0, l_0, m_0)$ ], (2.15b) (with  $\gamma = \gamma_1$ ) and (2.13), the matrix element  $\mathcal{F}_{MA}^{(\nu)}(1)$  can be calculated in the form

$$\mathcal{F}_{MA}^{(\nu)}(1) \equiv \mathcal{F}_{MA}^{(\nu)}(\gamma_1;\gamma_0,l_0,m_0;Z) = (4\pi)^{1/2} \sum_{l=l_0\pm 1} (-1)^{l_{\max}} [(2l+1)l_{\max}]^{1/2} \begin{bmatrix} l_0 & 1 & l \\ m_0 & \nu & 0 \end{bmatrix} \mathcal{M}_{p_0l_0}^l(\gamma_0,\gamma_1,Z) , \qquad (2.26)$$

$$M_{P_0l_0}^{l}(\gamma_0,\gamma_1,Z) = B_{p_0}(\gamma_0,s_{l_0})(2\gamma_1)^{s_l+1+Z/\gamma_1} \frac{\Gamma(1+s_l-Z/\gamma_1)}{\Gamma(2s_l+2)} \frac{\Gamma(s_{l_0}+s_l+4)}{(\gamma_0+\gamma_1)^{s_{l_0}+s_l+4}} \times F_2(s_{l_0}+s_l+4;-p_0,1+s_l-Z/\gamma_1;2s_{l_0}+2,2s_l+2;2\gamma_0/(\gamma_0+\gamma_1),2\gamma_1/(\gamma_0+\gamma_1)) ,$$

 $l_{\max} = \max(l_0, l)$ , (2.27)

where () is the 3j Wigner symbol and  $F_2(\ldots;x,y)$  is the Appel hypergeometric function.<sup>14</sup> As can be seen from Eq. (2.26), for  $l_0 = 0$ ,  $\mathcal{F}_{MA}^{(\pm 1)} = 0$ , and in the matrix element  $\mathcal{F}_{MA}^{(0)}$ , the term with  $l = l_0 - 1$  has to be dropped.

In some special cases, the expression (2.27) can be simplified. For the ground state of the ion  $A^{(Z-1)+}$ , when  $p_0=0$ , the expression (2.27) reduces to

$$M_{0l_{0}}^{l} = B_{0}(\gamma_{0}, s_{l_{0}})(2\gamma_{1})^{s_{l}+1+Z/\gamma_{1}} \frac{\Gamma(1+s_{l}-Z/\gamma_{1})}{\Gamma(2s_{l}+2)} \frac{\Gamma(s_{l_{0}}+s_{l}+4)}{(\gamma_{0}+\gamma_{1})^{s_{l_{0}}+s_{l}+4}} \times {}_{2}F_{1}(1+s_{l}-Z/\gamma_{1}, s_{l_{0}}+s_{l}+4; 2s_{l}+2; 2\gamma_{1}/(\gamma_{0}+\gamma_{1})), \qquad (2.28)$$

where  ${}_{2}F_{1}(\alpha,\beta;\gamma;x)$  is the complete hypergeometric function. If, in addition, the ground state of the  $A^{(Z-1)+}$  ion is spherically symmetric  $(l_{0}=0)$ , Eq. (2.28) further simplifies. The entire matrix element in this case is (m=0, l=1)

$$\mathcal{F}_{MA}^{(\nu)}(\gamma_{1};\gamma_{0}00;Z) = -\delta_{\nu0}(4\pi)^{1/2}(2\gamma_{1})^{Z/\gamma_{1}}2^{s_{0}+s_{1}+5/2} \frac{\gamma_{0}^{s_{0}+3/2}\gamma_{1}^{s_{1}+1}}{(\gamma_{0}+\gamma_{1})^{s_{0}+s_{1}+4}} \frac{\Gamma(1+s_{1}-Z/\gamma_{1})\Gamma(s_{0}+s_{1}+4)}{\Gamma^{1/2}(2s_{0}+3)\Gamma(2s_{1}+2)} \times {}_{2}F_{1}(1+s_{1}-Z/\gamma_{1},s_{0}+s_{1}+4;2s_{1}+2;2\gamma_{1}/(\gamma_{0}+\gamma_{1})) .$$
(2.29)

When the ion  $A^{Z+}$  is fully stripped  $[c_l=0 \text{ in Eq. } (2.20)]$ , the corresponding matrix element  $\mathcal{F}_{MA}^{(\nu)}(1)$  can be obtained from expressions (2.26) and (2.27) by setting there  $s_l=l$ ,  $s_{l_0}=l_0$ , and  $\gamma_0=Z/n_0$ , where  $n_0$  is the principal quantum number of the final state. The resulting expression is

$$\mathcal{F}_{MA}^{(\nu)Coul}(\gamma_{1};\gamma_{0},l_{0},0;Z) = \delta_{\nu0}(4\pi)^{1/2}(2\gamma_{1})^{Z/\gamma_{1}}2^{l_{0}+5/2} \frac{\gamma_{1}\gamma_{0}^{l_{0}+3/2}}{(\gamma_{0}+\gamma_{1})^{l_{0}+4}} \left[ \frac{[(l_{0}+n_{0})!]}{2n_{0}(2l_{0}+1)[(n_{0}-l_{0}-1)!]} \right]^{1/2} \frac{1}{[(2l_{0}+1)!]} \\ \times \sum_{l=l_{0}\pm 1} (-1)^{l}l_{\max}(2\gamma_{1})^{l} \frac{\Gamma(1-l-Z/\gamma_{1})[(l_{0}+l+3)!]}{[(2l+1)!](\gamma_{0}+\gamma_{1})^{l}} \\ \times F_{2}(l_{0}+l+4; -(n_{0}-l_{0}-1), 1+l-Z/\gamma_{1}; 2l_{0}+2, 2l+2; 2\gamma_{0}/(\gamma_{0}+\gamma_{1}), 2\gamma_{1}/(\gamma_{0}+\gamma_{1}))) \\ \text{ with } l_{\max} = \max(l, l_{0}) .$$

$$(2.30)$$

For the capture into the ground state of a hydrogenlike ion  $A^{(Z-1)+}(n_0=1,\gamma_0=Z,l_0=0)$ , the above expression reduces to

$$\mathcal{F}_{MA}^{(\nu)Coul}(\gamma_1;\gamma_000;Z) = \delta_{\nu 0}(4\pi)^{1/2} 2^{Z/\gamma_1 + 4} \gamma_1^{Z/\gamma_1 + 1} \Gamma(1 - Z/\gamma_1) \left[\frac{\sqrt{Z}}{\gamma_1 + Z}\right]^5 \left[\frac{Z - \gamma_1}{Z + \gamma_1}\right]^{Z/\gamma_1 - 2}.$$
(2.31)

The calculation of the matrix element  $\mathcal{F}_{\mathcal{M}}^{(\nu)}(2)$  for the dipole transition of electron 2 from the metal into the continuum can be done in a straightforward manner<sup>7(a)</sup> if the wave functions  $\psi_{\mu_2}(2)$  and  $\psi_{\mu'_2}(2)$  are taken in the form (2.19) and (2.20), respectively. The result for  $\mathcal{F}_{M}^{(\nu)}(2)$  is

$$|\mathcal{F}_{M}^{(\nu)}(2)|^{2} = \frac{\gamma_{2}^{\prime 2}}{8\pi^{2}U_{0}} |\Delta_{2}^{(\nu)}|^{2} \delta(k_{2x} - \gamma_{2x}^{\prime}) \delta(k_{2y} - \gamma_{2y}^{\prime}), \qquad (2.32)$$

$$\Delta_{2}^{(\nu)} = 2^{-|\nu|/2} \left[ (-1)^{\nu} \frac{k_{2z} + ip_{2z}}{(k_{2z} - \gamma_{2z}^{\prime} + i\beta)^{2-|\nu|}} + \frac{k_{2z} - ip_{2z}}{(k_{2z} + \gamma_{2z}^{\prime} - i\beta)^{2-|\nu|}} + \frac{2(-i)^{|\nu|}k_{2z}}{(p_{2z} + i\gamma_{2z}^{\prime})^{2-|\nu|}} \right] \times \left[ \frac{1}{k_{2x} - \gamma_{2x}^{\prime} + i\beta} + \frac{1}{k_{2y} - \gamma_{2y}^{\prime} - i\beta} \right]^{|\nu|} \text{ with } \beta \rightarrow 0. \qquad (2.33)$$

The result for v=0 has been obtained previously.<sup>7(a)</sup>

### C. Calculation of the transition rate

Having the analytic expressions for the matrix elements for Auger neutralization, one can calculate the transition probability per unit time  $W_{I}(R)$  by using Eq. (2.6). Let us consider the Auger neutralization process when the metallic electron 1 is captured into an s state of the ion  $A^{(Z-1)+}$ . In this case the matrix elements with v=0 only give a nonzero contribution to the transition rate. Due to the delta function in  $\mathcal{F}_{M}^{(0)}(2)$ , and energy conservation relation

$$\gamma_0^2 - \gamma_1^2 = \gamma_2^2 + \gamma_2'^2 \equiv 2w$$
, (2.34)

the integration over  $\mu_2$  in Eq. (2.6) can be performed directly. The integration over the orientations of the momentum  $\gamma'_2$  of the ejected electron can also be carried out analytically, reducing the integration over  $\mu'_2$  in Eq. (2.6) to an integration over the energy  $E'_2$  of the ejected electron, only. Finally, due to spherical symmetry of the final state, the integration over  $\mu_1$  is reduced to integration over  $\gamma_1$ . Omitting the details of the calculations we give the result

$$W_{I}(R) = 8R^{-6} \int_{\gamma_{1}} \int_{E_{2}'} \mathcal{L}_{MA}^{2}(\gamma_{1}, z) Q_{0}^{2}(R; Z, \gamma_{1}) \\ \times |\mathcal{J}_{MA}^{(0)}(\gamma_{1}; \gamma_{0}, 00; Z)|^{2} \\ \times I(\gamma_{1}, E_{2}') n(\mu_{1}) n(\mu_{2}) \\ \times E_{2}'g(E_{2}') d\gamma_{1} dE_{2}'$$
(2.35)

where the factor  $I(\gamma_1, E'_2)$ , coming from the integration over the orientations of ejected electrons, has the form

$$I(\gamma_{1}, E_{2}') = \int_{\mathcal{O}_{m}}^{1} \frac{1}{2k_{2z}U_{0}} |\Delta_{2}^{(0)}|^{2} d(\cos\theta_{2}')$$

$$= \frac{U_{0}}{2(2E_{2}')^{1/2}w^{2}(w - U_{0})^{2}} \left[ [E_{2}'(E_{2}' - w + U_{0})]^{1/2} \left[ 1 + \frac{(2w - U_{0})(2E_{2}' - w + U_{0})}{(w - U_{0})^{2}} \right] - (3w - 2U_{0}) \ln \left[ \frac{(E_{2}')^{1/2} + (E_{2}' - w + U_{0})^{1/2}}{(w - U_{0})^{1/2}} \right] \right], \qquad (2.36)$$

where

$$\mathcal{O}_{m} = \left[\frac{\max\{0, w - U_{0}\}}{E'_{2}}\right]^{1/2},$$

$$k_{2z} = \left[2(U_{0} - w + E'_{2}\cos^{2}\theta'_{2})\right]^{1/2}.$$
(2.37)

For further evaluation of the integral (2.35), it is necessary to specify the functions  $n(\mu_1)$  and  $n(\mu_2)$ . For  $n(\mu_2)$ one can use the expression

 $n(\mu_2) = 1$ , (2.38)

corresponding to the case of a free-electron gas.

The use of a similar form for  $n(\mu_1)$  would require drastic additional approximations in the evaluation of (2.35). For certain metal surfaces, however, surface-localized states have been observed<sup>15</sup> [for instance W(100) and Mo(100)]. For such surfaces we can take  $n(\mu_1)$  to be sharply peaked at certain energy  $\gamma_1^2/2 = \tilde{\gamma}^2/2$ , and represent it by

$$n(\mu_1) = D_0 \delta(\gamma_1 - \tilde{\gamma}), \quad D_0 = \frac{[2(U_0 - \phi)]^{3/2}}{3\tilde{\gamma}(2U_0 - \tilde{\gamma}^2)^{1/2}}.$$
 (2.39)

The multiplicative factor  $D_0$  is obtained from the condition  $\sum_n (\mu_1) = N$ , N being the total number of electrons.

With the distributions (2.38) and (2.39) the integration in (2.35) can be carried out analytically, and the result is

$$W_{\rm I}(R) = A_{\rm I} R^{-6} Q_0^2(R; Z, \tilde{\gamma}) , \qquad (2.40)$$

$$A_{\mathrm{I}} = \frac{2D_0U_0}{w^2w_3^2} \mathcal{L}^2_{MA}(\tilde{\gamma}, Z) \mid \mathcal{F}^{(0)}_{MA}(\tilde{\gamma}; \gamma_0 00; Z) \mid {}^2f(w, \phi, U_0) ,$$

$$f(w,\phi, U_0) = \frac{1}{2} (w_1 w_2)^{1/2} (w + w_1 + \frac{3}{2} w_3) + \frac{2}{3} (w_1 w_2)^{3/2} (w + w_3) w_3^{-2} - [w_1 (w + 2w_3) - \frac{1}{2} w_3 (w + \frac{3}{2} w_3)] \times \ln \left[ \frac{(w_1)^{1/2} + (w_2)^{1/2}}{(|w_3|)^{1/2}} \right], \qquad (2.42)$$

where w is defined by (2.34), and

$$w_1 = w - \phi, \quad w_2 = U_0 - \phi, \quad w_3 = w - U_0$$
 (2.43)

The expressions for  $\mathcal{L}_{MA}(\tilde{\gamma}, Z)$  and  $Q_0(R; Z, \tilde{\gamma})$  are given by Eqs. (2.23) and (2.17), respectively, and  $\mathcal{F}_{MA}^{(0)}(\tilde{\gamma}; \gamma_0; Z)$  is given by Eq. (2.29) for incompletely stripped ions, and by Eq. (2.30) for fully stripped ions.

Taking expression (2.17) for  $Q_0(R; Z, \tilde{\gamma})$  into account, we represent  $W_1(R)$  in the form

$$W_{\mathrm{I}}(R) = A_{\mathrm{I}}(\gamma_0, Z, w, U_0, \phi, \tilde{\gamma}) R^{2Z/\tilde{\gamma} + 1/2\tilde{\gamma} - 7} e^{-2\tilde{\gamma}R} ,$$
(2.44)

where the constant  $A_{\rm I}$  depends on the parameters of both the ionic and metallic potential wells, but the *R* dependence contains only the energy parameter  $\tilde{\gamma}$  (which also depends on *R*) of the localized surface state  $(E_s = -\tilde{\gamma}^2/2 + \Delta E)$ . From Eq. (2.44) it follows that if there are several surface states with different binding energies, the main contribution to the Auger neutralization comes from the state with the smallest binding energy.

The Auger neutralization rate  $W_{I}(R)$ , as a function of transition energy w, has an extremum (singularity) at  $w = U_0$ . The origin of this singularity is in the matrix element (2.33) which for  $k_{2z} = \gamma'_{2z}$  diverges. In most realistic situations, however,  $w \gg U_0$  and then one has

$$W_{I}(R) \simeq \frac{8}{3} U_{0} D_{0} w^{-7/2} w_{2}^{3/2} \mathcal{L}_{MA}^{2} |\mathcal{F}_{MA}^{(0)}|^{2} \times R^{2Z/\tilde{\gamma} + 1/2\tilde{\gamma} - 7} e^{-2\tilde{\gamma}R} .$$
(2.45)

For a transition into the ground state, the obtained transition rate (2.44) can be compared with the corresponding expression<sup>7(a)</sup> valid for a Coulomb interaction in the atomic region, but calculated with a variational wave function. The present value of the factor  $A_I$  tends to the corresponding expression in Ref. 7(a) if the factor  $\mathcal{F}_{MA}^{(0)Coul}G(Z,Z^*,\gamma_1)$ , where

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$$G(Z, Z^*, \gamma_1) = 2 \left[ 1 - \frac{Z}{2Z^*} \right] \left[ \frac{Z}{Z^*} \right]^{5/2} \times \frac{Z - \gamma_1}{Z^* - \gamma_1} \left[ \frac{Z + \gamma_1}{Z^* + \gamma_1} \right]^5, \quad (2.46)$$

 $Z^*$  being the variational effective charge. Note that the function  $f(w,\phi, U_0)$  in these two papers is somewhat different due to a different averaging procedure used in Ref. 7(a). A mean value of  $D_0 \simeq 1$  has also been used there.

### III. AUGER RELAXATION OF RESONANTLY CREATED EXCITED IONIC STATES NEAR THE SURFACE

#### A. Transition rates in dipole approximation

A multiply charged ion always possesses a number of excited states that are isoenergetic with the metal conduction band and to which metallic electrons can be captured resonantly.<sup>5</sup> An ionic excited state, created by this resonant process usually at large ion-surface distance, is subject to the Auger relaxation processes (1.2a) and (1.2b) [see Figs. 1(b) and 1(c)]. The total relaxation probability per unit time is

$$W_{\rm II} = W_{\rm II}^{(a)} + W_{\rm II}^{(b)}$$
(3.1)

where

$$W_{\rm II}^{(a),(b)} = 2\pi \int \int |V_{if}^{(a),(b)}|^2 n(\mu_1) n(\mu_2) \\ \times \delta(E_{\rm fin} - E_{\rm in}) g(\mu'_{2,1}) d\mu_2 d\mu'_{2,1} ,$$
(3.2a)
$$V_{if}^{(a),(b)} = \langle \psi_{\mu_0}(1,2) \psi_{\mu'_{2,1}}(2,1) | V_{\rm int} | \psi_{\mu_{1r}}(1) \psi_{\mu_{2}}(2) \rangle ,$$

(3.2b)

where indices (a) and (b) refer to the channels (1.2a) and (1.2b), respectively,  $\psi_{\mu_{1r}}$  and  $\psi_{\mu_0}$  are the wave functions of the upper (resonantly created) and lower ionic states,  $\psi_{\mu'_2}(\psi_{\mu'_1})$  is the wave function of the ejected electron from the metal (ion), and  $\psi_{\mu_2}$  is the initial metallic electron wave function. The functions  $\psi_{\mu_i}$  are normalized by  $\langle \psi_{\mu'_i} | \psi_{\bar{\mu}'_i} \rangle = g^{-1} \delta(\mu_i - \tilde{\mu}_i)$ ,  $\psi_{\mu_2}$  is normalized by the condition (2.7b), and  $\psi_{\mu_0}$  and  $\psi_{\mu_{1r}}$  are normalized to unity. The indices  $\mu_0$ ,  $\mu_{1r}$  and  $\mu'_1$  comprise the set of quantum numbers  $\mu_0 = (\gamma_0 l_0 m_0)$ ,  $\mu_{1r} = (\gamma l m)$ , and  $\mu'_1 = (E'l'm')$ , while  $\mu'_2 = (E'_2, \Omega'_2)$  and  $\mu_2 = \mathbf{k}_2$  for the channel (a) and  $\mu_2 = (\gamma_2 n_2 m_2)$  for the channel (b).

Eq. (3.1) [together with Eq. (3.2) for  $W_{\rm II}$ ] takes into account the identity of two metallic electrons. This result follows from arguments similar to those applied in writing  $W_{\rm I}$ , with the exception that the averaging procedure (as well as summation in the final state) is performed over the spin state of electron 2 only. The other electron is resonantly captured into a given atomic spin state without changing its spin projection. In writing Eq. (3.1) we neglect the "interference" between the direct (a) and

exchange (b) channel.

For the channel (b), the wave function  $\psi_{\mu_2}$  is given by Eq. (2.15a) [written as  $\psi_{MA}(\mathbf{r}_2)$ ], and for channel (a) it may be taken (in the zeroth approximation) in the form of Eq. (2.19). The population numbers  $n(\mu_1)$  and  $n(\mu_2)$  are

$$n(\mu_1) = n(\mu_2) = 1$$
 (3.3a)

for channel (a).

$$n(\mu_1) = 1, \quad n(\mu_2) = D_0 \delta(\gamma_2 - \tilde{\gamma}),$$
 (3.3b)

for channel (b). The second condition of Eqs. (3.3b) has the same meaning as Eq. (2.39), i.e., we assume that underbarrier transition takes place from a surface state with energy  $E_s = -\tilde{\gamma}^2/2 + \Delta E$ .

The functions  $\psi_{\mu_0}$  and  $\psi_{\mu_{1r}}$  are the ground-state and the excited-state atomic functions, respectively [Eq. (2.11a)]. The function  $\psi_{\mu'_2}(2)$  for channel (a) is represented by an outgoing wave [Eq. (2.20)]. The function  $\psi_{\mu'_1}(1)$ , which belongs to the continuous spectrum of the model potential (2.20) (corrected by the image force factor  $\Delta E$ ), has the form of Eq. (2.11a):

$$E' = \frac{k^2}{2} + \Delta E , \qquad (3.4a)$$
  

$$\psi_{\mu_1'}(1) \equiv \psi_{E'l'm'} = R_{E'l'}(k,r)Y_{l'm'}(\theta,\varphi) , \qquad (3.4a)$$
  

$$R_{E'l'}(k,r) = B_{E'}(k,s_{l'})r^{s_{l'}}e^{-ikr} \times {}_1F_1(s_{l'}+1+i(Z/k),2s_{l'}+2;2ikr) , \qquad (3.4b)$$
  

$$B_{E'}(k,s_{l'}) = \frac{(2k)^{s_{l'}}}{\Gamma(2s_{l'}+2)} \left[\frac{2k}{\pi}\right]^{1/2} e^{(\pi Z/2k)}$$

$$\times |\Gamma(s_{l'}+1+i(Z/k))| , \qquad (3.4c)$$

where k is the wave vector  $(E' = k^2/2 + \Delta E)$  and

$$S_{l'} = -\frac{1}{2} + \left[ (l' + \frac{1}{2})^2 + 2c_{l'} \right]^{1/2}$$

In the dipole approximation (2.21),  $V_{if}^{(a)}$  can be written as

$$V_{if}^{(a)} = R^{-3} \sum_{\nu=-1}^{+1} (-1)^{\nu+1} (1+\delta_{\nu_0}) \mathcal{F}_{A}^{(\nu)}(1) \mathcal{F}_{M}^{(\nu)}(2) , \quad (3.5a)$$

where

$$\mathcal{F}_{A}^{(\nu)}(1) = \left\langle \psi_{\gamma_0 l_0 m_0}(\mathbf{r}_1) \mid d^*_{1\nu} \mid \psi_{\gamma lm}(\mathbf{r}_1) \right\rangle , \qquad (3.5b)$$

and  $\mathcal{J}_{M}^{(\nu)}(2)$  is given by Eq. (2.32). In the calculation of  $V_{if}^{(b)}$ , the main contribution to the integral gives the configuration when electron 2 is already in the vicinity of the ionic core  $(r_2 \sim \gamma_0^{-1})$ , and having in mind that the state  $|\mu_{1r}\rangle$  is a highly excited one  $(r_1 \sim \gamma^{-1} \gg \gamma_0^{-1})$ , the interaction  $V_{\text{int}}$  can be expanded as

$$V_{\text{int}} \simeq \frac{1}{r_{12}} \simeq \frac{1}{r_1} + \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1^3} + \cdots, \quad r_1 \gg r_2 \;.$$
 (3.6)

Using the first two terms of this expansion and the orthogonality of initial- and final-state wave functions, we obtain

$$V_{if}^{(b)} = \mathcal{L}_{MA}(\gamma_2, Z) Q_0(R; Z, \gamma_2) \mathcal{F}_{MA}^{(0)}(\gamma_2; \gamma_0, l_0, m_0; Z)$$

$$\times M_A^{(0)}(E',l',m';\gamma,l,m)$$
, (3.7)

where  $Q_0$  and  $\mathcal{L}_{MA}$  are, respectively, given by Eqs. (2.17) and (2.23), and  $\mathcal{F}_{MA}^{(0)}$  [defined by (2.24)] is given by Eq. (2.26). The matrix element  $M_A^{(0)}$  is

$$M_{A}^{(0)} = \left\langle \psi_{\mu_{1}'}(\mathbf{r}_{1}) \left| \frac{\mathbf{r}_{1} \cdot \mathbf{n}}{r_{1}^{3}} \right| \psi_{\mu_{1r}}(\mathbf{r}_{1}) \right\rangle$$
(3.8a)  
$$= -\frac{w^{2}}{Z} \left\langle \psi_{\mu_{1}'}(\mathbf{r}_{1}) \left| d_{10} \right| \psi_{\mu_{1r}}(\mathbf{r}_{1}) \right\rangle \equiv -\frac{w^{2}}{Z} \widetilde{\mathcal{J}}_{AC}^{(0)}(1) ,$$
(3.8b)

where n = R/R, and the Ehrenfest theorem has been employed in writing (3.8b).

Let us note that dipole approximation (2.21), used in the evaluation of matrix element  $V_{if}$  for channels I and IIa, presumes that  $|\mathbf{r}_1 - \mathbf{r}_{2M}| / R \ll 1$ . For the channel IIb, we assume that  $r_2/r_1 \ll 1$ .

According to Ref. 8(a), the matrix element  $\mathcal{T}_{A}^{(\nu)}(1)$ , Eq. (3.5b), can be represented as

$$\mathcal{F}_{A}^{(\nu)}(1) \equiv \mathcal{F}_{A}^{(\nu)}(\gamma, l, m; \gamma_{0}, l_{0}, m_{0})$$

$$= (-1)^{l_{\max} + m} (l_{\max})^{1/2} \begin{bmatrix} l_{0} & 1 & l \\ -m_{0} & -\nu & m \end{bmatrix}$$

$$\times M_{p_{0}l_{0}}^{pl}(\gamma_{0}, \gamma)$$
(3.9)

where  $l = l_0 \pm 1$ ,  $-m = m_0 + v$ , and  $l_{max} = max(l, l_0)$ . The radial matrix element  $M_{p_0 l_0}^{pl}$ , calculated with the functions (2.11a), has the form

$$M_{p_0l_0}^{pl}(\gamma_0,\gamma) = B_{p_0}(\gamma_0,s_{l_0}) \frac{\Gamma(s_{l_0}+s_l+4)}{(\gamma_0+\gamma)^{s_{l_0}+s_l+4}} B_p(\gamma,s_l) F_2(s_{l_0}+s_l+4;-p_0,-p;2s_{l_0}+2,2s_l+2;2\gamma_0/(\gamma_0+\gamma),2\gamma/(\gamma_0+\gamma)),$$
(3.10)

where  $F_2(...)$  is the Appel hypergeometric function.<sup>14</sup> Note that since  $p_0$  and p are positive integers, the function  $F_2(...)$  reduces to a polynomial. For transitions into the ground state  $(p_0=0)$ , Eq. (3.10) reduces to

$$M_{0l_0}^{pl}(\gamma_0,\gamma) = B_0(\gamma_0,\gamma) B_p(\gamma_0,\gamma) \frac{\Gamma(s_{l_0} + s_l + 4)}{(\gamma_0 + \gamma)^{s_{l_0} + s_l + 4}} {}_2F_1(-p,s_{l_0} + s_l + 4;2s_l + 2;2\gamma/(\gamma_0 + \gamma)) .$$
(3.11)

In the case of a hydrogenlike ion, one sets  $s_{l_0} = l_0$  and  $s_l = l$  in the above expressions. Finally, for the  $l = 1(m=0) \rightarrow l_0 = 0(m_0=0)$  transition in a hydrogenlike ion, from (3.9) and (3.11) one obtains the well-known result<sup>16</sup>

$$\mathcal{F}_{A}^{(0)}(\gamma 10, \gamma_{0} 00) = \frac{2^{4}}{(3Z^{2}n^{3})^{1/2}} \left(\frac{n^{2}}{n^{2}-1}\right)^{5/2} \left(\frac{n-1}{n+1}\right)^{n}$$
(3.12)

where  $\gamma_0 = Z$ , and  $\gamma = Z/n$ , *n* being the principal quantum number of the excited state.

The reduced matrix element  $\tilde{\mathcal{F}}_{AC}^{(0)}(1)$  for the  $\mu_{1r}(\gamma, l, m) \rightarrow \mu'_{1}(E', l', m')$  has a form similar to  $\mathcal{F}_{A}^{(v)}(1)$ :

$$\widetilde{\mathcal{F}}_{AC}^{(0)}(1) \equiv \widetilde{\mathcal{F}}_{AC}^{(0)}(\gamma, l, m; E', l', m') = (-1)^{l_{\max} + m} (l_{\max})^{1/2} \begin{bmatrix} l & 1 & l' \\ -m & 0 & m' \end{bmatrix} M_{pl}^{E'l'}(\gamma, k)$$
(3.13)

where  $l_{\max} = \max(l, l'), l' = l \pm 1, m' = -m$ , and

$$M_{pl}^{E'l'}(\gamma,k) = \langle R_{E'l'}(k,r) | r | R_{pl}(\gamma,r) \rangle$$

is the radial matrix element. For the model potential (2.5g),  $R_{pl}$  is given by Eq. (2.11b) while  $R_{E'l'}(k,r)$  has the form of Eq. (3.4b).

The matrix element  $M_{pl}^{E'l'}$  can be calculated analytically and has the form

$$M_{pl}^{E'l'}(\gamma,k) = B_{p}(\gamma,s_{l})B_{E'}(k,s_{l'}) \frac{\Gamma(s_{l}+s_{l'}+4)}{(\gamma+ik)^{s_{l}+s_{l'}+4}} \times F_{2}(s_{l}+s_{l'}+4;-p,s_{l'}+1-i(Z/k);2s_{l}+2,2s_{l'}+2;2\gamma/(\gamma-ik),-2ik/(\gamma-ik)) .$$
(3.14)

The results for hydrogenlike ions are obtained by setting in Eqs. (3.13) and (3.14)  $s_l = l$ ,  $s_{l'} = l'$ .

# **B.** Expressions for transition rates

With the matrix elements calculated in the preceding subsection, the relaxation rate for channel (1.2a) is (we

take only the 
$$v=0$$
 contribution)

$$W_{II}^{(a)} = 8R^{-6} |\mathcal{F}_{A}^{(0)}(\gamma, l, m; \gamma_{0}l_{0}, m_{0})|^{2} \\ \times \int I(\gamma_{1}, E_{2}')E_{2}'g(E_{2}')dE_{2}'$$
(3.15)

where  $I(\gamma_1, E'_2)$  is given by Eq. (2.36). The integration in

Eq. (3.15) over the energies  $E'_2$  of ejected electrons can be carried out analytically (see Sec. II), and the result is

$$W_{\rm II}^{(a)} = 2R^{-6} |\mathcal{J}_A^{(0)}(\gamma, l, m; \gamma_0, l_0, m_0)|^2 \\ \times \frac{U_0}{w^2 (w - U_0)^2} f(w, \phi, U_0)$$
(3.16)

where the function  $f(w, \phi, U_0)$  is given by Eq. (2.42).

The transition rate for the Auger relaxation channel (1.2b) can similarly be calculated from Eq. (3.2). Introducing the photoionization cross section,

$$\sigma_{\rm ph}(\gamma, l, m; E'_2) = \frac{4\pi^2 w}{3c} \sum_{l', m'} |\tilde{\mathcal{J}}^{(0)}_{AC}(\gamma, l, m; E'_2, l', m')|^2$$
(3.17)

(c being the speed of light), the transition rate  $W_{II}^{(b)}$  can be represented in the form

$$W_{\mathrm{II}}^{(\mathrm{b})} = D_0 \frac{3cw^3}{2\pi Z^2} \sigma_{\mathrm{ph}}(\gamma, l, m; E'_2) \mathcal{L}^2_{MA}(\tilde{\gamma}, Z)$$

$$\times |\mathcal{F}_{MA}^{(0)}(\tilde{\gamma}; \gamma_0 l_0, m_0)|^2 R^{2Z/\tilde{\gamma} + 1/2\tilde{\gamma} - 1} e^{-2\tilde{\gamma}R} .$$
(3.18)

It has to be noted that the R dependence of  $W_{II}^{(a)}$  and  $W_{\rm II}^{(b)}$  written down explicitly in Eqs. (3.16) and (3.18) are the dominant ones, but not the only ones. Due to the image forces, the energy of an excited electron at a distance R is shifted upwards, Eq. (2.8c), E $=-\gamma^2/2+(2Z-1)/4R$ , and through the energy conservation relation (2.1c), the transition energy contains also an R dependence. However, in the region of large R, where the concept of image forces is meaningful, the Rdependence of w is weak compared to those which are already indicated in Eqs. (3.16) and (3.18). This remark holds also for the rate  $W_{I}(R)$  of the direct Auger neutralization channel. The R dependence of  $\tilde{\gamma}$  $(E_s = -\tilde{\gamma}^2/2 + \Delta E, E_s)$  being the considered surface energy level) is important only in the exponen- $\exp(-2\tilde{\gamma}R) = \exp(-2\gamma_s R) \exp[-(2Z-1)/2\tilde{\gamma}],$ tial:  $\gamma_s = (-2E_s)^{1/2}$ . (Note that the second exponential factor cancels with the corresponding factor in  $\mathcal{L}^2_{MA}$ . Except in the exponential factor, for the parameter  $\tilde{\gamma}$  in the expressions for  $W_{\rm I}$  and  $W_{\rm II}^{(b)}$  one can take [to within an accuracy of O(1/R)]  $\tilde{\gamma} = \gamma_s$ . Now the rates of all the three Auger neutralization channels can be written as [cf. Eqs. (2.45), (3.16), and (3.18)]

$$W_{\rm I} = A_{\rm I} R^{\alpha-6} \exp(-2\tilde{\gamma} R) . \qquad (3.19a)$$

$$W_{\rm II}^{(a)} = A_{\rm II}^{(a)} R^{-6}$$
 (3.19b)

$$W_{\rm II}^{\rm (b)} = A_{\rm II}^{\rm (b)} R^{\alpha} \exp(-2\tilde{\gamma}R) . \qquad (3.19c)$$

$$\alpha = \frac{2Z}{\tilde{\gamma}} + \frac{1}{2\tilde{\gamma}} - 1 , \qquad (3.19d)$$

and  $A_{\rm I}$ ,  $A_{\rm II}^{(a)}$ ,  $A_{\rm II}^{(b)}$  may be considered as constants. Since the typical values of  $\gamma_s$  are around 0.5, the exponents in (3.19a) and (3.19c) will dominate the *R* behavior of the rates  $W_{\rm I}$  and  $W_{\rm II}^{(b)}$  only at very large ion-surface distances. For smaller distances, the rate  $W_{\rm I}$  will be about  $R^{-6}$  times smaller than  $W_{\rm II}^{(b)}$ . With increasing ionic charge *Z*, the region of *R* in which the rate  $W_{\rm II}^{(a)}$  is appreciable becomes smaller.

# IV. AUGER NEUTRALIZATION PROBABILITIES FOR He<sup>2+</sup> AND C<sup>3+</sup> IONS ON THE Mo(100) SURFACE

In order to characterize more specifically the relative role of the considered Auger neutralization processes when an ion  $A^{Z+}$  slowly approaches a metal surface, it is convenient to introduce the probability  $P_k(R, v_0)$  that  $A^{Z+}$  will undergo neutralization along the Auger channel k in the interval from infinity to R. Since the transition rates for different Auger channels are usually dominantly localized in the separate R intervals (due to the different exponential decay factors), the corresponding transition probabilities P can be treated independently. Thus, the transition probability for channel I can be written as

$$P_{\rm I}(R,v_0) = 1 - \exp\left[-\frac{1}{v_0} \int_R^\infty W_{\rm I}(R') dR'\right], \quad (4.1)$$

where  $v_0$  is the ion velocity component perpendicular to the surface. In the case when Auger neutralization goes through the channels (1.2a) and (1.2b), the probability  $P_{II}(R, v_0)$  is given by

$$P_{\mathrm{II}}^{(a),(b)}(R,v_0) = P^{\mathrm{RN}}(R) \left[ 1 - \exp\left[ -\frac{1}{v_0} \int_R^\infty W_{\mathrm{II}}^{(a),(b)}(R') dR' \right] \right],$$
(4.2)

where  $P^{RN}(R)$  is the resonant neutralization probability.

In Eq. (4.2), the resonant transition probability  $P^{\text{RN}}(R)$ and the Auger neutralization probability are given in a multiplicative form. The resonant neutralization is a process "localized" far from the surface while the Auger neutralization channels become operative closer to the surface where  $P^{\text{RN}}(R)$  is close to unity. The approximation (4.2) implies that the resonant neutralization has already been (almost) finished when the Auger process begins. The resonant neutralization probability is given by

$$P^{\mathrm{RN}}(R) = g_s \left[ 1 - \exp \left[ -\frac{1}{v_0} \int_R^\infty W^{\mathrm{RN}}(R') dR' \right] \right],$$
(4.3)

where  $W^{RN}$  is the resonant neutralization rate and  $g_s$  is the statistical weight of the state to which the electron is captured. The expression for  $W^{RN}$  has been derived earlier<sup>5,11</sup> and has the form<sup>11</sup>

$$W^{\rm RN}(R) = A_{\gamma l}^{\rm RN} R^{2Z/\gamma + 1/2\gamma - 1} e^{-2\gamma R} . \qquad (4.4a)$$

$$A_{\gamma l}^{\text{RN}} = (2l+1) \left| \left( \begin{array}{cc} v & v & l \\ -v & v & 0 \end{array} \right) \right|^2 A_c^{\text{RN}}, \quad v = \frac{1}{2} (Z/\gamma - 1) ,$$
(4.4b)

$$A_{c}^{RN} = 2^{1/\gamma - 1} \Gamma^{-2} \left[ \frac{Z}{\gamma} \right] \gamma^{2Z/\gamma + 1/\gamma - 1} (2e)^{1/2\gamma} \times (2U_{0} - \gamma^{2}) e^{(2Z - 1)/2\gamma} , \qquad (4.4c)$$

where  $E(R) = -\gamma^2/2 + (2Z-1)/4R$  is the energy of the state  $|\gamma lm\rangle$  of the captured electron at ion-surface distance R. The above transition rate  $W^{RN}$  was obtained for electron capture in the pure Coulomb ionic field. The same expression remains also valid when a short-range potential is added to the Coulomb one. [The corresponding  $\gamma = Z/\mu$ ,  $\mu$  being the effective quantum number, Eq. (2.10a).] Namely,  $W^{RN}$  is determined as the probability current flux through a surface lying in the atomic asymptotic region where  $\psi_{MA}$  goes over into the parabolic function which describes the electronic motion in the Coulomb field.

Note that the excited atomic level E(R) can be resonantly populated only for  $R > R_F$  where  $E(R_F) = -\phi$ . For  $R < R_F$ , the resonant neutralization probability is given by  $P^{\text{RN}}(R) = P^{\text{RN}}(R_F)$ .

A rigorous multichannel treatment of the considered ion-surface collision problem takes into account a coherent superposition of the incoming and outgoing channels, which includes also the backcoupling to the initial state. The dominant occurrence of Auger processes at different R distances leads, however, to an effective decoupling of the channels. Moreover, predominance of one of the reaction channels makes other channels inoperative or even "closed." If a given process effectively takes place at  $R \ge R_0$ , the corresponding backcoupling process is "closed" for  $R < R_0$ . These statements apply to the specific processes discussed below.

As two illustrative examples for the considered Auger neutralization processes, we take the collisions of He<sup>2+</sup> and C<sup>3+</sup> ions with the Mo(100) surface. There is a localized surface state on Mo(100) having energy of  $E_s = 4.85$ eV (Ref. 15) (i.e.,  $\gamma_s = 0.597$ ) which participates predominantly in the underbarrier transitions within the He<sup>2+</sup> + Mo(100) and C<sup>3+</sup> + Mo(100) colliding systems. In the case of He<sup>2+</sup> projectiles, isoenergetic to the conduction band of the metal is the He<sup>+</sup>(n = 3) level only (with  $\gamma = \frac{2}{3}$ ), while in the case of a C<sup>3+</sup> ion the lowest isoenergetic levels with the conduction band are the  $C^{2+}(p=2, l=0)$  and  $C^{2+}(p=2, l=1)$  levels, with  $\gamma$  determined by Eq. (2.10a).  $[\gamma(2,0)=0.833 \text{ and } \gamma(2,1)=0.776$ , respectively.] The last two theoretical levels correspond to the experimental  $C^{2+}(2s4s \ S)$  and  $C^{2+}(2s4p \ P^0)$  levels, with  $\gamma_{4s}=0.825$  and  $\gamma_{4p}=0.763$ , respectively. The ground-state levels of neutralized ions. He<sup>+</sup>(1s) and  $C^{2+}(2s^2 \ S)$  have  $\gamma_0$  values equal to  $\gamma_0(\text{He}^+)=2$  and  $\gamma_0(C^{2+})=1.876$ . In the resonant neutralization deexcitation channel (1.2a), only the He<sup>+</sup>(3p) $\rightarrow$ He<sup>+</sup>(1s) and  $C^{2+}(2s4p \ P^0) \rightarrow C^{2+}(2s^2 \ S)$  transitions participate within the dipole approximation. The parameters  $c_l$  (l=0 and 1) of the pseudopotential (2.5g) for the  $C^{2+}$  ion have been determined by using the expression (2.10c) with  $\gamma_0=1.876$  and  $\gamma_1=1.608 \ [\gamma_1 \ corresponds to the <math>C^{2+}(2s2p \ P)$  electron configuration]. The constants  $A_I$ ,  $A_{II}^{(a,b)}$ , and  $A_{\gamma_0}^{RN}$  of the rates  $W_k$  [see Eqs. (3.19) and (4.4a)] are given in Table I. The probabilities  $P_k$  and  $P^{RN}$  for He<sup>2+</sup> + Mo(100) and

The probabilities  $P_k$  and  $P^{\text{RN}}$  for  $\text{He}^{2+} + \text{Mo}(100)$  and  $C^{3+} + \text{Mo}(100)$  systems, colliding with a velocity  $v_0 = 0.01$  a.u., are shown in Figs. 2(a) and 2(b), respectively. For channel (1.2b), transitions through both  $\text{He}^+(3s)$  and  $\text{He}^+(3p)$ , [respectively  $C^{2+}(4s)$ ,  $C^{2+}(4p)$ ], are shown in Figs. 2(a) and 2(b), respectively. It is seen from these figures that for low collision velocities, the resonant-capture-Auger-deexcitation channel is by far the most dominant neutralization process down to ion-surface distances of the order of  $R \sim 2$ .

Auger neutralization processes may be characterized by the radial rates  $P_{k,t}$  of probabilities  $P_k$ , defined by

$$P_{k,t}(R,v_0) = \frac{W_k(R)}{v_0} S_k(R,v_0) , \qquad (4.5)$$

where  $S_k(R, v_0)$  is the survival probability for the kth channel

$$S_{I}(R,v_{0}) = \exp \left[-\frac{1}{v_{0}}\int_{R}^{\infty}W_{I}(R')dR'\right],$$
 (4.6a)

$$S_{\mathrm{II}}^{(\lambda)}(R,v_0) = P^{\mathrm{RN}}(R) \exp\left[-\frac{1}{v_0} \int_R^\infty W_{\mathrm{II}}^{(\lambda)}(R') dR'\right],$$
  
$$\lambda = (a) \text{ and } (b). \qquad (4.6b)$$

Radial probability  $P_{k,t}$  is taken [as was the case for the probabilities (4.1) and (4.2)] for the inward trajectory where  $P_{k,t} \approx -dP/dR$ .

For the  $He^{2+} + Mo(100)$  and  $C^{3+} + Mo(100)$  collision systems at  $v_0 = 0.01$  a.u., we have calculated the probabil-

TABLE I. Values of constants A in transition rates  $\hbar W_k$ , Eqs. (3.19), and (4.4), expressed in units of eV (with R expressed in units of Å).  $a[\pm x]$  means  $a \times 10^{\pm x}$ .

$A^{Z+}$ + Mo	$(A^{(Z-1)+})^*$	A_1	A (a)	A (b)	$A_l^{\rm RN}$
$He^{2+} + Mo$	3p 3s	1.29[-4] 1.29[-4]	1.24[-4]	2.65[-2] 4.60[-2]	1.61[+2] 1.07[+2]
$C^{3+} + Mo$	4p 4s	8.25[-7] 8.25[-7]	1.87[-5]	6.39[-5] 3.86[-5]	1.24[+2] 7.25[+1]

ity rates  $P_{k,t}$  of the Auger neutralization channels, and they are shown in Figs. 3(a) and 3(b). The corresponding probabilities  $P_t^{\text{RN}}(R, v_0)$  are also shown in these figures. All the probability rates  $P_{k,t}$  exhibit a maximum at a certain ion-surface distance  $R_{k,m}$ , around which the whole neutralization along the kth channel practically takes place. The figures show that the resonant-capture-



FIG. 2. (a) Auger neutralization probabilities vs ion-surface distance for the reaction channels (1.1)  $(P_{\rm I})$ , (1.2a)  $(P_{\rm II}^{(a)})$ , and (1.2b)  $(P_{\rm II}^{(b)})$  in the He<sup>2+</sup> + Mo(100) collisions at ion velocity  $v_0$ =0.01 a.u. The curves 3s and 3p for  $P_{\rm II}^{(b)}$  correspond to Auger deexcitation of [He<sup>+</sup>(3s)]<sup>\*</sup> and [He<sup>+</sup>(3p)]<sup>\*</sup> states. (b) Same as (a), except for C<sup>3+</sup> + Mo(100) collisional system. The curves 4s and 4p for  $P_{\rm II}^{(b)}$  correspond to Auger deexcitation of [C<sup>2+</sup>(2s4s)]<sup>\*</sup> and [C<sup>2+</sup>(2s4p)]<sup>\*</sup> states.

Auger-deexcitation process occurs dominantly at large R  $[R_{II,m}^{(b)}(\text{He}^{2+}) \sim 6-7$  a.u. and  $R_{II,m}^{(b)}(\text{C}^{3+}) \sim 8-9$  a.u.], and most of the ions are neutralized at these distances (for the given values of  $v_0$ ). The rest of the ions, which survive, undergo neutralization very near to the surface through the proper Auger neutralization and the capture-resonant deexcitation processes. These considerations show that the Auger electrons from these colliding systems will predominantly be ejected from the moving ion and will have a relatively sharp energy distribution. The energy width of the Auger electron distribu-



FIG. 3. (a) Probabilities  $P_{k,t}$ , Eq. (4.5), vs ion-surface distance for different Auger neutralization channels in He<sup>2+</sup> + Mo(100) collisions at  $v_0 = 0.01$  a.u. (See the text.) (b) Same as (a), except for C<sup>3+</sup> + Mo(100) collisional system.

tion will be determined by the width of the localized surface state, as well as by the dynamical (broadening) effects introduced by the finite value of ion velocity.<sup>17</sup> At higher collision velocities, the relative role of proper Auger neutralization and capture-resonant deexcitation processes is expected to be more pronounced.

### V. CONCLUDING REMARKS

In the present paper we have considered three channels of Auger neutralization of multiply charged ions slowly colliding with metal surfaces: direct (or proper) Auger neutralization, resonant capture of one electron into an excited ion state, with emission of either a metallic electron (resonant deexcitation) or of the captured electron itself (Auger deexcitation). The screening effects in the incompletely stripped ionic core are taken into account through a suitable model potential. The rates of the above Auger neutralization channels have been calculated in closed analytical form within the dipole approximation for the interelectron interaction, the use of which is justified for the considered processes. On the examples of  $He^{2+} + Mo(100)$  and  $C^{3+} + Mo(100)$  collision systems at a velocity of 0.01 a.u. it has been demonstrated that the resonant-capture-Auger-deexcitation process is the dominant neutralization channel in the low-velocity collision regime. This process takes place at large R and is characterized by a high probability. The other two Auger neutralization channels are operative at very small ionsurface distances. These conclusions, although derived from a direct comparison of the corresponding probabilities  $P_k$  and  $P_{k,t}$  [see Eqs. (4.1), (4.2), and (4.5)], remain valid even in a coupled kinetic-equation description of the three processes. Both Fig. 2 and Fig. 3 show that the probability of direct (proper) Auger neutralization is at least 3 orders of magnitude smaller than the leading neutralization channel. The probability of the captureresonant deexcitation channel becomes comparable to that of capture-Auger deexcitation only in a very narrow region near the surface, but by the time this region is reached, the excited ions created by single-electron resonant capture will almost entirely be deexcited by the Auger deexcitation mechanism.

## APPENDIX

The continuation of metallic wave function in the vicinity of a perturbation Coulomb center, placed at a distance R from the surface, has been accomplished by Nedeljković.<sup>11(a)</sup> In the asymptotic atomic region, where the electron interaction with the multicharged ion can be approximated by a Coulomb potential, the obtained function can be expanded in a spherical basis and then analytically continued in the vicinity of the ion. In the considered asymptotic region, the main contribution to electron transition gives a narrow cylindrical region around the z axis, where the separation of variables is approximately possible in the parabolic coordinates  $\xi$ ,  $\eta$ , and  $\varphi$ . The wave function that corresponds to the continuous negative energy spectrum with an energy E(R) $=-\gamma^2/2+(2Z-1)/4R, -\gamma^2/2$  being different from any of the ionic levels  $(\gamma \neq Z/n)$ , and for a parabolic quantum number  $n_1 = 0$ , is (up to the unimportant phase factor) given by

$$\psi_{MA} = \frac{\Gamma(-(Z/\gamma) + m + 1)}{\pi m! (2m!)^{1/2}} (2\gamma)^{1/2\gamma - (m+1)/2} (2e)^{1/4\gamma} \gamma^{Z/\gamma + 1 + m} \times Q_m(R;Z,\gamma) (\xi\eta)^{m/2} e^{-(1/2)\gamma(\xi-\eta)} {}_1F_1(Z/\gamma,m+1;-\gamma\eta) e^{im\varphi} .$$
(A1)

The above function is normalized to a  $\delta$  function of  $\gamma$ . For our further purposes, it is convenient to use the integral representation of confluent hypergeometric function  $_1F_1(\alpha,\beta;z)$  for noninteger values of  $\alpha$ , and for integer values of  $\beta$  (>0) (Ref. 18):

$${}_{1}F_{1}(\alpha,\beta;z) = (1 - e^{-2\pi i\alpha})^{-1} \frac{\Gamma(\beta)}{\Gamma(\alpha)\Gamma(\beta - \alpha)} \times \int_{\Gamma_{\alpha}} e^{zt} t^{\alpha - 1} (1 - t)^{\beta - \alpha - 1} dt , \qquad (A2)$$

where  $\Gamma_0$  is a counter enclosing the points t = 0 and t = 1in an opposite clockwise direction. In the parabolic coordinates  $\xi = r + z$ ,  $\eta = r - z$ , Eq. (A2) takes the form

$$F_{1}(Z/\gamma, m+1; -\gamma\eta)$$

$$= e^{(\gamma/2)(\xi-\eta)}(1-e^{-(2\pi Z/\gamma)i})^{-1}$$

$$\times \frac{m!}{\Gamma(Z/\gamma)\Gamma(m+1-Z/\gamma)}J(Z,\gamma) ,$$
(A3)

where

$$J(Z,\gamma) = \int_{\Gamma_0} e^{-\gamma z(1-t)} e^{-\gamma r t} t^{(Z/\gamma-1)} (1-t)^{m-Z/\gamma} dt .$$
(A4)

The function  $\exp[-\gamma z(1-t)]$  can be expanded as

$$e^{-\gamma z(1-t)} = \frac{(-1)^m}{\gamma^m (\xi\eta)^{m/2}} (1-t)^{-m} \\ \times \sum_{l=m}^{\infty} (2l+1)(-i)^l \\ \times j_l [i\gamma(1-t)r] P_l^m(\cos\theta) , \quad (A5)$$

where  $P_l^m$  are the associated Legendre polynomials ( $\theta$  being the spherical polar angle) and  $j_l(\rho) = (\pi/2\rho)^{1/2}J_{l+1/2}(\rho)$  are the spherical Bessel functions. The later functions are related to  ${}_1F_1(\alpha,\beta;z)$  by<sup>14</sup>

$$j_{l}(i-\gamma(1-t)r) = \frac{2^{l}l!}{(2l+1)!}(i\gamma r)^{l}(1-t)^{l}e^{-\gamma r(1-t)} \times {}_{1}F_{1}(l+1,2l+2;2\gamma(1-t)r) .$$
 (A6)

Expanding  ${}_{1}F_{1}(\alpha,\beta;z)$  in a power series, and inserting Eq. (A5) into Eq. (A4), we obtain

$$J(Z,\gamma) = \frac{(-1)^m e^{-\gamma r}}{\gamma^m (\zeta\eta)^{m/2}} \sum_{l=m}^{\infty} (2l+1)i^l P_l^m (\cos\theta) (2i\gamma r)^l \sum_{p=0}^{\infty} \frac{[(l+p)!](2\gamma r)^p}{[(2l+p+1)!](p!)} \int_{\Gamma_0} t^{Z/\gamma-1} (1-t)^{l+p-Z/\gamma} dt .$$
(A7)

In the calculation of the contour integral in Eq. (A7), we can use again the integral representation (A2). Finally,

$${}_{1}F_{1}(Z/\gamma, m+1; -\gamma\eta) = \frac{(-1)^{m}m!}{\gamma^{m}(\zeta\eta)^{m/2}} \frac{\exp[(\gamma/2)(\zeta-\eta)]}{\Gamma(m+1-Z/\gamma)} \sum_{l=m}^{\infty} (-1)^{l}(2l+1)P_{l}^{m}(\cos\theta) \frac{\Gamma(l+1-Z/\gamma)}{\Gamma(2l+2)} (2\gamma r)^{l} e^{-\gamma r} \times {}_{1}F_{1}(l+1-Z/\gamma, 2l+2; 2\gamma r) .$$
(A8)

Inserting Eq. (A8) into Eq. (A1) and using Eq. (2.13) (with  $s_l = l$ ) to introduce  $f_l$ , we obtain the expression (2.15a).

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