The non-resonant neutralization dynamics of the multiply charged Rydberg ions escaping solid surfaces

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Abstract. We investigate the intermediate and final population of the Rydberg states \((n_A \gg 1, l_A = 0 - 3, m_A)\) of multiply charged ions escaping solid surfaces by using the two-state vector model. All our calculations have been carried out for intermediate projectile velocities \((v \approx 1\) a.u.). The electron capture is non-resonant and characterized by the selective population of the ionic Rydberg states. The final population probabilities enable us to elucidate the role of the ionic core polarization and to analyze the \(n_A, l_A\) and \(v\) probability distributions. We consider the ions SVI, ClVII and ArVIII with core charges \(Z = 6, 7\) and \(8\), respectively, and the ions KrVIII and XeVIII with \(Z = 8\). The model is applied on two different ion-surface systems in order to emphasize the influence of the solid work function. We discuss the appearance of resonances (pronounced maxima) in the probability distributions. The resonances are explained by means of the electron tunneling in the very vicinity of the ion-surface potential barrier top. It is demonstrated that the resonances are characteristic only for some combination of the surface and ionic characteristics (argon anomaly), in agreement with available beam-foil experimental data.

1. Introduction
The electron exchange during the interaction of ions with solid surfaces has been intensively studied in the last two decades both theoretically [1] and experimentally [2]. This kind of problem, concerning the neutralization dynamics of multiply charged ions, has been also considered within the framework of two-state vector model (TVM) [3, 4, 5, 6, 7, 8, 9, 10, 11], for wide range of projectile velocities \(v\).

In the present article we report the TVM of the non-resonant electron capture from the solid conducting band into the Rydberg states \((n_A, l_A, m_A)\) of multiply charged ionic projectiles \((v \approx 1\) a.u.) [4, 5], by taking into account the ionic core polarization [10, 11]. The state of a single active electron is simultaneously described by two state vectors \(|\Psi_1(t)\rangle = \hat{U}_1(t_{\text{in}}, t)|\Psi_1(t_{\text{in}})\rangle\) and \(|\Psi_2(t)\rangle = \hat{U}_2(t_{\text{fin}}, t)|\Psi_2(t_{\text{fin}})\rangle\), within the first and the second scenarios, respectively, where \(\hat{U}_1\) and \(\hat{U}_2\) are the corresponding evolution operators. An entanglement of these states at intermediate stages of the ion-surface interaction is described by a mixed electron flux through the moving Firsov plane \(S_F\) used to define the ionic region. Model is almost independent of the form of the near-surface potential, and a dynamical response of the surface can be neglected, so that the classical electrostatic image potentials can be used outside the surface. The interaction of the active electron with polarized ionic core in the first scenario is the Coulomb interaction.
However, in the second scenario the active electron moves closer to the charge cloud of the electrons already bound to the nucleus. In that case, the Simons-Bloch potential [12] can be used: \( \hat{U} = -Z/r_\Lambda + \sum_{l=0}^\infty (c_l/r_\Lambda^l) \hat{P}_l \), where \( \hat{P}_l = \langle l' | l \rangle \) is the projection operator onto the subspace of a given angular momentum \( l' \). This effective potential accounts for the experimentally observed quantum defects of the energy spectra \( \tilde{E}_\Lambda = -\gamma_\Lambda^2/2 \) through the constants \( c_l \).

2. The non-resonant Rydberg state population

2.1. Intermediate stages of the population dynamics

Our attention is focused on the electron capture into the Rydberg states of multiply charged Rydberg ions (core charge \( Z \)) escaping solid surfaces at intermediate velocities \( v = dR/dt \approx 1 \) a.u., where \( R \) is the ion-surface distance. In order to take into account the ionic core polarization, the TVM developed in [4, 5] is appropriately modified [10, 11], following the idea of [8]. Within the framework of the TVM, the neutralization probability density \( \tilde{T}_{\mu M, \nu_A} (t) = |A_{\mu M, \nu_A} (t)|^2 \) (per unit energy parameter \( \gamma_M \) of the energy \( E_M = -\gamma_\Lambda^2/2 \)) is defined using the two-amplitude \( A_{\mu M, \nu_A} = \langle \Psi_2 (t) | \hat{P}_A | \Psi_1 (t) \rangle \); the quantity \( \hat{P}_A \) represents the projection operator onto the ionic region. For description of the intermediate stages of the process we use the normalized probability density \( \tilde{T}_{\mu M, \nu_A} (t) = T_{\mu M, \nu_A} (t)/T^{\text{fin}}_{\mu M, \nu_A} \), where \( T^{\text{fin}}_{\mu M, \nu_A} = \lim_{t \to t_{\text{fin}}} T_{\mu M, \nu_A} (t) \).

Appropriate analytical expression for the normalized probability in the considered intermediate velocity region is given by [13]

\[
\tilde{T}_{\mu M, \nu_A} (t) \approx \left| 1 - B(R)e^{-\left(\beta - \frac{1}{v}R\right)} \right|^2 ,
\]

where \( B(R) = 1 + (\beta R)^{\alpha+1}/\Gamma(\alpha+2) \), \( \alpha = Z/\gamma_\Lambda - 3/2 + 1/(4\gamma_M) \) and \( \beta = \tilde{\beta} - i\omega/v = \gamma_M + (\gamma_\Lambda - \gamma_M)g - i\omega/v \). The quantity \( \omega \) in equation (1) is defined by \( \omega = (\gamma_\Lambda^2 - \gamma_\Lambda^2)/2 - v^2 (1 - 2g)/2 \), where \( g = a/R \), whereas \( a \) represents the position of the Firsov plane \( S_F \) in respect to the ionic core [4]. The population of the Rydberg states is mainly localized at the ion-surface distances \( R = R^N \); the distances \( R^N \) can be considered as neutralization distances under the fixed initial and final states of the active electron. Within the framework of TVM, the quantities \( R^N = R^N (\mu_M, \nu_A) \) are defined as a positions of maxima of the total rates \( \Gamma_{\mu M, \nu_A} = dT_{\mu M, \nu_A} / dt \); in the explicit form (scaled by velocity \( v \)) we have

\[
\tilde{\Gamma}_{\mu M, \nu_A} (t) = \frac{2(\alpha + 1)}{R} R e^{-\beta R} \cos K(R) \\
+ 2 f(R) \left\{ \left( \frac{\alpha + 1}{R} - \beta \right) \left[ f - \cos K(R) \right] + \frac{w}{v} \sin K(R) \right\} - \frac{(\alpha + 1)}{R} e^{-\beta R} ,
\]

where \( K(R) = wR/v + \arg B(R) \) and

\[
f(R) \approx 1 + \left| \frac{\beta^{\alpha+1}}{\Gamma(\alpha+2)} R^{\alpha+1} \right| e^{-\beta R} .
\]
In figure 2 we analyzed the normalized intermediate rate $\tilde{\Gamma}_{\mu_M,\nu_A}$ for the population of the Rydberg states of the ArVIII ion with the $n_A = 8$, for $l_A = 0, 1$ and 2, and for $v = 1$ a.u. and $v = 2$ a.u. As we can see, the neutralization distances are slowly shifted toward larger ion-surface distances by increasing $l_A$. In the absence of core polarization, i.e. in the the pointlike core case (dashed curves) we obtain almost the same curve as for $l_A = 3$. Also, from figure 2 we conclude that the velocity dependence of $R^N$ in the intermediate velocity region is practically negligible.

![Figure 1](image1.png)

**Figure 1.** Normalized intermediate (a) probability density $\tilde{T}_{\mu_M,\nu_A}(t)$ and (b) rate $\tilde{\Gamma}_{\mu_M,\nu_A}(t)$ (scaled by $v$) via ion-surface distances $R$ for the population of the Rydberg states $n_A = 6, 8, 10$, $l_A = 1$ of the ArVIII ion escaping the solid surface with velocity $v = 1$ a.u. Dashed curves correspond to the pointlike core case.

![Figure 2](image2.png)

**Figure 2.** The last peak of the normalized intermediate rate $\tilde{\Gamma}_{\mu_M,\nu_A}(t)$ (scaled by $v$) via ion-surface distances $R$ for the population of the Rydberg states $n_A = 8$, $l_A = 0, 1, 2$ of the ArVIII ion escaping the solid surface with velocity (a) $v = 1$ a.u. and (b) $v = 2$ a.u. Dashed curves correspond to the pointlike core case.

### 2.2. The regular population of the final Rydberg state

First we consider the population of the Rydberg states $n_A < n_{res}$, which occur via tunnelling mechanism. We shall consider the term ”regular population” for this type of the population process to distinguish from the population of the Rydberg states $n_A = n_{res}$, populated in the very vicinity of the potential barrier top [4, 10]. By $n_{res}$ we denoted the resonant quantum numbers. A specific feature of the TVM (independently of the type of electron transitions) is
the use of the mixed flux $I_{\mu M,\nu_A}(t)$ through the Firsov plane defined by the following surface integral:

$$I_{\mu M,\nu_A}(t) = \frac{1}{2} \int_{S_M} \left[ \nabla \Psi_1 - \frac{\nabla \Psi_2^*}{\Psi_2} - 2iv \left( 1 - \frac{da}{dR} \right) e_z \right] \Psi_2^*(r, t) \Psi_1(r, t) dS.$$

The kinematic factor $g$ of the Firsov plane dynamics is given by equation (4.20) in reference [4]. The final transition probability follows directly from the mixed flux, i.e.

$$T_{\nu_A}^{\text{fin}} = \sum_{\mu M} T_{\mu M,\nu_A}^{\text{fin}} = \int_{\gamma_M} \sum_{n_1 M, m_M} \lim_{t \to t\text{lim}} \left| \int_{t\text{lim}}^t I_{\mu M,\nu_A}(t) dt \right|^2 d\gamma_M.$$

The final population probability $P_{\nu_A}^{\text{fin}}$ (that can be compared with experiments) for the principal quantum numbers $n_A \leq n_{\text{res}} - 1$ and for $l_A = 1$ and 2 is given by [4]

$$P_{\nu_A}^{\text{fin}} = \left[ 1 - \exp(-T_{\nu_A}^{\text{fin}}) \right] \exp \left( -\sum_{n_A' \neq n_A} T_{\nu_A'}^{\text{fin}} \right),$$

where $\nu_A' = (n_A', l_A' = 1, m_A' = 0)$.

In figure 3 we present the quantities $T_{\nu_A}^{\text{fin}}$ and $P_{\nu_A}^{\text{fin}}$ for the ions SVI, ClVII and ArVIII escaping the solid surface at velocities $v = 1.94 \text{ a.u.}$, $v = 2.50 \text{ a.u.}$ and $v = 1.42 \text{ a.u.}$, respectively, relevant for the beam-foil experiments. We consider the surface with the solid work function $\phi = 3 \text{ eV}$ and with the bottom level of the solid $U_0 = 10 \text{ eV}$. Comparing the $T_{\nu_A}^{\text{fin}}$ and $P_{\nu_A}^{\text{fin}}$ curves in figure 3, we recognize the importance of the multichannel description of the population process. Indeed, the distances between Rydberg levels are small and all channels participate simultaneously. This is of particular importance in the case of ArVIII ion for $v = 1.42 \text{ a.u.}$, which is characterized by the higher population probabilities. Also, one can recognize that the core polarization induce the lowering of the probability distribution (compare the full curves with the dashed curves in figure 3).

The final population probabilities $P_{\nu_A}^{\text{fin}}$ with core polarization taken into account (solid curves in figure 3) reflect the selective character of the Rydberg level population. That is, the Rydberg levels with $n_A = n_0 = 6, 7, 9$ (for $l_A = 1$ and $m_A = 0$) of the ions SVI, ClVII and ArVIII, respectively, are populated with maximal probabilities. The selective population (with $n_0 = 6, 7$ and 8) appears also in the point-like core approximation. For the ArVIII (which is, considering the electronic structure, close to the hydrogen-like ions) the probability distributions with the ionic core polarization taken into account and those obtained for the pointlike ionic cores are similar. The relatively close relation between the TVM theoretical final population probabilities for $n_A < n_{\text{res}}$ and $l_A = 1$ and the corresponding experimental findings (dots) is also demonstrated in figure 3. However, due to the relative character of the experimental output, the results reveals the agreement of both probabilities (for the polarized and pointlike core cases) with beam-foil experiment (for SVI and ClVII [14] and for ArVIII [15]). The same agreement with experimental data can be obtained for other low-$l_A$ values, $l_A = 0$ and $l_A = 2$ [15, 16].

In figure 4(a) we present the final population probabilities $P_{\nu_A}^{\text{fin}}$ of the Rydberg states with $n_A < n_{\text{res}}$ and $l_A = 1$ of the ions ArVIII, KrVIII and XeVIII escaping solid surface ($\phi = 3 \text{ eV}$ and $U_0 = 10 \text{ eV}$) at velocity $v = 1.42 \text{ a.u.}$. The theoretical results presented in figure 4(a) are compared with available beam-foil experimental data [15] for ArVIII ion (dots). Experimental data for KrVIII and XeVIII do not exist in the low-$l_A$ region, and for the Rydberg states with $n_A \approx Z$. The experimental data for KrVIII ionic projectiles exist only for the large-$l_A$ Rydberg states ($l_A \geq 5$) [15]. Also, the recently obtained data for ArVIII ion interacting with microcapillary foil are in the large-$l_A$ region, and for somewhat lower ionic velocities ($v = 0.2$
Figure 3. Final transition probabilities $T^{fin}_{n_A}$ and final population probabilities $P^{fin}_{n_A}$ via $n_A < n_{res}$ for the Rydberg states with $l_A = 1$ of the ions (a) SVI, (b) ClVII and (c) ArVIII escaping the solid surface ($\phi = 3$ eV, $U_0 = 10$ eV) with the velocities $v = 1.94$ a.u., $v = 2.50$ a.u. and $v = 1.42$ a.u., respectively. Dashed curves correspond to the pointlike core case. Dots are the results of the beam-foil experiments taken from [14] for SVI and ClVII ions and [15] for ArVIII ions.

Figure 4. (a) Final population probabilities $P^{fin}_{n_A}$ via $n_A < n_{res}$ for the Rydberg states with $l_A = 1$ of the ions ArVIII, KrVIII and XeVIII escaping the solid surface ($\phi = 3$ eV and $U_0 = 10$ eV). In (b) and (c): probabilities $T^{fin}_{n_A}$ and $P^{fin}_{n_A}$ for $n_A < n_{res}$ and $n_A \geq n_{res}$ of the ArVIII ion, for surfaces with $\phi = 3$ eV, $U_0 = 10$ eV and $\phi = 5$ eV, $U_0 = 15$ eV, respectively. Dashed curves correspond to the pointlike core case. Dots represent the experimental results [15].
a.u.) [17]. From figure 4(a) we recognize that, due to the core polarization, the final population probabilities for KrVIII and XeVIII species are significantly lower in comparison to the ArVIII case. Because of the absence of the experimental data for KrVIII and XeVIII ions, for the considered Rydberg states, the obtained trends in the behavior of the population probabilities can not be directly experimentally verified.

2.3. Resonances in the final Rydberg state population

It is intriguing to discuss [5, 11] the population curves in the vicinity of the resonant quantum numbers $n_{res} > n_0$, i.e., for $n_A \in \mathcal{N}_r$, where the set $\mathcal{N}_r$ is complementary to the set $\mathcal{N}$ considered in section 2.2. We are looking for the existence of an extra pronounced maximum (resonance) in the final population distribution at $n_A = n_{res}$. Such a situation has been experimentally recognized [15] for the ArVIII ions, for $n_A = n_{res} = 11$ and $l_A = 1$ and $l_A = 2$.

In order to obtain appropriate analytical form for the final transition probabilities $T_{fin}^{f A}$ and the final population probabilities $P_{fin}^{f A}$ for $n_A \in \mathcal{N}_r$, we adapt the wave function $\Psi_2$ to the case of the tunneling in the very vicinity of the ion-surface potential barrier top [5]. The etalon equation method (EEM) for the calculation of the appropriate wave function $\Psi_1$ contains a scaling parameter $\alpha_s$, through which one can express the fact that the corresponding electron transition are characterized by the close turning point configuration. In the considered case, the two-large-parameter asymptotic form of the wave function $\Psi_1$ is necessary. The case $n_A \in \mathcal{N}$, in which the one-large-parameter asymptotic form of the function $\Psi_1(t)$ is sufficiently accurate, follows in the limit $\alpha_s \to \infty$. The wave function $\Psi_2$, corresponding to the state $|\Psi_2(t)\rangle$ that evolves teleologically (in the second scenario) toward the final state $|\Psi_A\rangle$ with $n_A \in \mathcal{N}_r$, can be obtained analogously as in the case of the regular population of the final Rydberg state. The explicit analytical form of these two functions is given in [11].

In figures 4(b) and 4(c) we present (full curves) the final transition probabilities $T_{fin}^{f A}$ and the final population probabilities $P_{fin}^{f A}$ for the Rydberg states of the ArVIII ion escaping the conducting solid surface at $v = 1.42$ a.u. We consider the population of the Rydberg states with principal quantum numbers $n_A \in \mathcal{N}$ and $n_A \in \mathcal{N}_r$, for angular momentum quantum number $l_A = 1$ and $m = m_A = 0$. The final distributions are discussed for two types of the surfaces. Dashed curves are the final probabilities obtained in the absence of core polarization, i.e., in the pointlike core approximation. Solid circles in Figure 4(b) are the properly normalized beam-foil experimental results [15]. The existence of the resonances is theoretically confirmed only for the ArVIII ion and the type of the surface considered in figure 4(b).

3. Concluding remarks

We analyzed the electron capture into Rydberg states of multiply charged Rydberg ions escaping solid surfaces at intermediate velocity, investigating the neutralization dynamics within the time interval between initial and final "measurement" within the framework of the TVM. At intermediate stages of the process, the main output of this analysis from the standpoint of an experiment is the neutralization distances $R_s^{\mathcal{N}}$ for the ions finally detected in a given Rydberg state. We also discussed the final low-$l_A$ Rydberg state population distributions for $n_A \in \mathcal{N}$ of the SVI, CIVIII, ArVIII, KrVIII and XeVIII multiply charged ions, escaping conduction solid surfaces at intermediate velocities, by using the nonresonant multichannel TVM. It was concluded that the core polarization (included via the Simons-Bloch potential [12]) systematically suppress the final population probabilities $P_{fin}^{f A}$, comparing with the pointlike core approximation. This effect become essential when we consider the KrVIII and XeVIII ions. In addition, we find out a strong connections between the surface parameters ($\phi$ and $U_0$) and the position of maxima of the population distributions for a given ion and projectile velocity.

In order to elucidate the appearance of the extra pronounced maxima (resonances) in the population curves, the TVM has been adapted to the complemental case $n_A \in \mathcal{N}_r$. The
resonances are treated by using the appropriate EEM accompanied by the scaling parameter $\alpha_s$ for the calculation of the wave function $\Psi_1$. The pronounced maxima in the final population distribution are obtained for the ArVIII ion interacting with solid surface with the lower valued of the work function and with angular momentum quantum numbers $l_A = 1$ and $l_A = 2$. We recognize that the resonances are observable only for the compatible combination of the ionic core structure and the solid surface band structure. We point out that the TVM population distributions (including resonances) are in agreement with available beam-foil experimental data.

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