Intermediate stages of the neutralization of multiply charged ions interacting with solid surfaces

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Abstract.
We consider the electron capture (neutralization) into Rydberg states of multiply charged ions interacting with solid surface in the normal (escaping) and in the grazing incidence geometry. The time-symmetrized two-state vector model is used to investigate the intermediate stages of the population dynamics. For the fixed initial and final states of the active electron, the two wave functions which evolve simultaneously in two opposite directions of time (by two scenarios), are used to describe the transitional electron state. In both considered geometries, the main idea is to obtain the information about the position and the magnitude of the population process for the fixed initial and final states of the active electron. The results are compared with the classical overbarrier predictions and the measured kinetic energy gain due to the image acceleration of the ions. It is demonstrated that the ionic velocity influences the ion-surface distance at which the formation of the particular intermediate Rydberg state is mainly localized, as well as the probability of this formation.

1. Introduction
The interaction of ions/atoms with solid surfaces has been intensively studied both theoretically and experimentally [1,2]. The basic process in the system is the electron exchange between the atomic projectile and the solid surface, which can be described by several theoretical models. In order to elucidate the intermediate stages of the electron exchange dynamics, we developed the two-state vector model (TVM); the model has been introduced in [3] in which the proton neutralization was considered and has been developed ever since in our group.

In the present article we report the TVM analysis of the intermediate stages of the neutralization process for the multiply charged ions interacting with conducting solid surfaces. The transitional electron state is described simultaneously by two state vectors $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ evolving in two opposite directions in time. The first state vector evolves, in the first scenario, from the initial state (electron in the solid) ”preselected” at the initial time $t = t_{\text{in}}$ towards the future, while the second state vector evolves, in the second scenario, from the fixed final state (electron bound to the ion), ”postselected” at the final time $t = t_{\text{fin}}$.

The ions SVI, ClVII, ArVIII, KrVIII, and XeVIII, escaping solid surfaces in the normal direction, at low perpendicular velocity $v_{\perp} \ll 1$ a.u. [4,5], and the ions Ar$^{Z+}$, Kr$^{Z+}$ and Xe$^{Z+}$ for $Z \in [5,35]$ (in a.u.) [6] colliding with solid surface at velocity $v$ with parallel component $v_{||} < v_F$, where $v_F$ is the Fermi velocity of the solid, and with low perpendicular component
(v_\perp \ll 1 \text{ a.u.})$, are considered as an example.

The TVM developed in [4,5] has been devoted to the normal emergency case. The neutralization probability $P_{\nu_A}(t)$, resulting in the formation of the Rydberg state $|\nu_A\rangle$, has been considered as a "sum" over the initial quantum numbers $\mu_M$ of the transition probability density $T_{\mu_M,\nu_A}(t)$; for description of the intermediate stages of the process we used the normalized probability $P_{\nu_A}(t) = P_{\nu_A}/P_{\nu_A}^{\text{fin}}$ and the corresponding rate $\tilde{\Gamma}_{\nu_A}(t)$. The quantity $P_{\nu_A}(t)$ represents the neutralization probability at time $t$ under the condition that the state $|\nu_A\rangle$ is populated at time $t = t_{\text{fin}}$, i.e. $P_{\nu_A}(t_{\text{fin}}) = 1$. In [6] we adapted the model to the scattering geometry. Under the grazing incidence geometrical conditions we calculated the intermediate transition probability density $T_{\mu_M,\nu_A}(t)$ for shifted initial quantum numbers $\mu_M$, the velocity dependent intermediate transition probability $T_{\nu_A}(t) = \sum_{\mu_M} \langle f | \Omega_k' | \mu_M,\nu_A \rangle$, and the population probability $P_{\nu_A}^P(t) = 1 - \exp[-T_{\nu_A}(t)]$. We note that, in the scattering geometry, the Fermi-Dirac distribution $f$ of the electron momenta in solid is kinematically modified ($k \rightarrow k' = k - v_\parallel$), and averaged.

2. Calculation of the population probability $P_{\nu_A}^P(t)$

2.1. Formulation of the problem

The present report is mainly devoted to the scattering geometry. That is, we consider the intermediate stages of the Rydberg state population of multiply charged ions (core charge $Z \gg 1$) impinging a solid surface at velocity $v = v_\perp + v_\parallel$, where $v_\perp$ and $v_\parallel$ are the perpendicular and parallel velocity components, respectively, see figure 1. At the initial time $t_{\text{in}}$ the ion is on the ion-surface distance $R_{\text{in}} \rightarrow \infty$, which decreases in time according to the law $v_\perp = -dR/dt$. The neutralization of the multiply charged ions interacting with solid surface in the escaping geometry can be considered as a special case $v_\parallel = 0$.

![Figure 1. The TVM description of the population dynamics under the scattering conditions. At ion-surface distance $R$ the electron can be resonantly captured by the ion (and recaptured by the solid) with probability $P_{\nu_A}^P(t)$.](image)

The TVM analysis of the population process in the scattering geometry requires some new elements in comparison to the normal emergency case. We formulate the problem in the system $S$ which moves with velocity $v_\parallel$ along the surface, with $z$ axis along the instant ion-surface direction, see figure 1. At the time $t$ the quantum behaviour of the active electron in the system $S$ is simultaneously described by two state vectors $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$. The kinematic modification can be used to connect the state $|\Psi_1(t)\rangle$ in the $S$ and the state $|\Psi_1^{(0)}(t)\rangle$ in the system $S^{(0)}$ in rest (for $v_\parallel = 0$): $|\Psi_1(t)\rangle = |\Psi_1^{(0)}(t)\rangle/|k_\rightarrow k'||k_\rightarrow k' - v_\parallel|$, where $k$ is the momentum of the electron in solid. This transformation induces an effective change of the Fermi-Dirac distribution $f$ of the vectors $k$, which becomes dependent on the intensity and orientation of $k'$; using the angle averaging $\langle f | \Omega_k' \rangle$ we obtain the necessary $k'$-distribution for our model. The
state \(|\Psi_2(t)\rangle\) in the S and the state \(|\Psi_2^A(t)\rangle\) in the rest frame \(S_A\) of the moving ion (which moves at velocity \(v_\perp\) in respect to \(S\)) are connected by the relation \(|\Psi_2(t)\rangle = \exp(i\hat{G}_\perp)\)|\(\Psi_2^A(t)\rangle\), where \(\hat{G}_\perp = v_\perp \cdot r - v_\perp^2 t/2\) is the Galilei translation factor.

Within the framework of the TVM we take into account both the initial and the final conditions: \(|\Psi_1^{(0)}(t_\text{in})\rangle = |\mu_M\rangle\) and \(|\Psi_2^A(0)\rangle = |\nu_A\rangle\). The parabolic state \(|\mu_M(R)\rangle = |\gamma_M, n_{1M}, m_{1M}\rangle\) is the eigenstate of the in-Hamiltonian \(\hat{H}_1(R)\) of the first scenario and the spherical state \(|\nu_A(R)\rangle = |n_A, l_A, m_A\rangle\) is the eigenstate of the out-Hamiltonian \(\hat{H}_2(R)\) of the second scenario. For \(R \to \infty\), the state \(|\mu_M(R)\rangle \to |\mu_M\rangle\) describes the electron localized in solid, and for \(R = R_\text{fin}\) the state \(|\nu_A(R)\rangle \to |\nu_A\rangle\) describes the electron that is completely localized around the ionic core. The energy spectrum of the Hamiltonian \(\hat{H}_1(R)\) in the system \(S^{(0)}\) is continuous \(E_M = -\gamma_M^2/2\) (measured from the vacuum level of the ion-surface system). Note that the energy \(E_M = k^2/2\) (measured from the bottom level \(U_0\) of the solid) is connected with \(E_M\) by the relation \(\gamma_M^2/2 + k^2/2 = U_0\); the same relation holds for the shifted energies \(E'_M = -\gamma_M'^2/2\) and \(E'_M = k^2/2\), relevant for \(v_\parallel \neq 0\). The operator \(\hat{H}_2(R)\) has a discrete spectrum \(E_A(R) = -\gamma_A^2(R)/2\).

State \(|\Psi_1^{(0)}(t)\rangle\) evolves by the first scenario according to the law \(|\Psi_1^{(0)}(t)\rangle = \exp(-i\int_0^t \hat{H}_1(R)dt)|\mu_M\rangle\). The second state \(|\Psi_2^A(t)\rangle\) evolves teleologically toward the fixed final state (by the second scenario). It means that the final state evolves backward in time: \(|\Psi_2^A(t)\rangle = \exp(-i\int_{t_\text{in}}^t \hat{H}_2(R)dt)|\nu_A\rangle\). The form of the Hamiltonians \(\hat{H}_1(R)\) and \(\hat{H}_2(R)\) is independent of the scattering geometry \([4,5,6]\). The ionic core polarization is taken into account using the Simons-Bloch potential.

2.2. Basic expressions of the TVM

The intermediate stages of the neutralization in the considered scattering geometry are described by two-state probability amplitude \(A_{\mu_M,\nu_A}(t) = \langle \Psi_2(t) | \hat{P}_A(t) | \Psi_1(t) \rangle\), where \(\mu_M = (\gamma_M, n_{1M}, m_{1M})\) and \(\hat{P}_A(t) = \int_{V_A} |r_A\rangle \langle r_A|dV\) is the projection operator onto the "ionic" region \(V_A\) (right from the Firsov plane \(S_F\) in figure 1). The intermediate probability per unit energy parameter \(\gamma_M\) is given by relation: \(T_{\mu_M,\nu_A}(t) = |A_{\mu_M,\nu_A}(t)|^2\). The corresponding intermediate transition probability \(T_{\nu_A}(t)\), in which the overall effectively extended conduction band participates, represents a "sum" over \(\mu_M\):

\[
T_{\nu_A}(t) = \int \sum_{\mu_{1M},m_{1M}} \langle f | \Omega_{k'} \rangle T_{\mu_{1M}',\nu_A}(t) d\gamma_{1M}'.
\]  

(1)

The intermediate population probability \(P_{\nu_A}^P(t)\) of the Rydberg state that will evolve into the final state \(|\nu_A\rangle\) is given by

\[
P_{\nu_A}^P(t) = 1 - \exp[-T_{\nu_A}(t)].
\]  

(2)

In (1) the quantity \(\langle f | \Omega_{k'} \rangle = \int_{4\pi} f d\Omega_{k'}/4\pi\) is the angle averaged (over all orientations of \(k'\) inside the solid) Fermi-Dirac distribution \(f = I_{0,E_F}(k'/2)^2\). By \(E_F = v_F^2/2\) we denoted the Fermi energy, where \(v_F\) is the Fermi velocity; in what follows we shall restrict our consideration to the case \(v_\parallel < v_F\). In that case we have: \(\langle f | \Omega_{k'} \rangle = 1\) for \(\phi_\parallel < \gamma_M'^2/2 < U_0\), and \(7,8\)

\[
\langle f | \Omega_{k'} \rangle = \frac{v_F^2 - \left(\sqrt{2U_0 - \gamma_M'^2} - v_\parallel\right)^2}{4\sqrt{2U_0 - \gamma_M'^2} v_\parallel}, \phi_\parallel < \gamma_M'^2/2 < \phi_\parallel.
\]  

(3)

In the expressions for \(\langle f | \Omega_{k'} \rangle\) we use the notation \(\phi_\downarrow = U_0 - (v_F + v_\parallel)^2/2\) and \(\phi_\uparrow = U_0 - (v_F - v_\parallel)^2/2\). In the case of \(v_\parallel = 0\) we have \(\phi_\downarrow = \phi_\uparrow = \phi\), where \(\phi\) is the solid work function.
The TVM is based on the mixed flux \( I_{\nu'_{A',\nu'_{A}}} (t) \) through the Firsov plane \( S_{F} \), which represents a specific entanglement of the wave functions \( \Psi_{1}(r,t) \) and \( \Psi_{2}(r,t) \), i.e., we have \( T_{\nu'_{A',\nu'_{A}}} (t) = \int_{t_{m}}^{t} I_{\nu'_{A',\nu'_{A}}} (t') dt' \). The advantage of the model is that for the calculation of the mixed flux it is sufficient to know these wave functions on the Firsov plane only, which is, during the most intensive electron transition, positioned sufficiently far from both the surface and the ionic core. Therefore, taking into account that the electron transitions occur at large ion-surface distances \( R \), we can apply the appropriate asymptotic methods. The wave functions \( \Psi_{1}^{(0)} (r,t) = \Phi_{MA,\rho M} \exp [ f_{M} + i (\gamma_{M}^{2}/2) t ] \) and \( \Psi_{2}^{(0)} (r,t) = \Phi_{AM,\nu A} \exp [ f_{A} + i (\gamma_{A}^{2}/2) t ] \) are expressed as space-time modifications of the eigenfunctions \( \Phi_{MA,\rho M} \) and \( \Phi_{AM,\nu A} \) [9,10] of the Hamiltonians \( H_{1} \) and \( H_{2} \), respectively. For the function \( \Phi_{MA,\rho M} \), we use the expression analytically continued from the metallic region (through the barrier) into the ionic region [11] by the phase-integral method [12], using the appropriate JWKB connection formulas [13], obtained from the eigenfunctions \( \Phi_{AM,\nu A} \) of the atomic Hamiltonian \( H_{2} \).

The explicit expression for the mixed flux in the considered scattering geometry is given by [6]:

\[
I_{\nu'_{M},\nu'_{A}} (t) = \frac{i}{2} e^{w(R) t} \left[ \gamma_{M}' + \gamma_{A}(R) \right] e^{f_{M}' t} + f_{M} \int_{S_{F}} \Phi_{AM,\nu A}^{*} \Phi_{MA,\nu'_{M}} dS,
\]

(4)

where \( f_{M}' = f_{M}/\gamma_{M} \rightarrow \gamma_{M}' \) and

\[
w(R) = \frac{\gamma_{M}^{2}}{2} - \frac{\gamma_{A}(R)^{2}}{2}
\]

is the energy difference considered from the system \( S \). Using the expression for the mixed flux and taking into account that in the considered case the electron capture is determined by the resonant condition \( \gamma_{M}' = \gamma_{A}(R) \), for the transition probability we get:

\[
T_{\nu_{A}} (t) = T_{\nu_{A}}^{(0)} (f) \Omega_{e} f_{\gamma} (\gamma_{M}') e^{2} \left[ \gamma_{M} + \gamma_{A}(R) \right]^{2} \frac{\gamma_{M}^{2}}{\gamma_{M}'^{2}} \left( 1 + \frac{2\tilde{\alpha}}{\beta} \frac{1}{R} \right) R^{2\tilde{\alpha}} e^{-2R}.
\]

(6)

The quantities \( T_{\nu_{A}}^{(0)} \) and \( f_{\gamma} (\gamma_{M}') \) and the parameters \( \tilde{\alpha} \) and \( \tilde{\beta} \) are explicitly given in reference [6]. The population probability \( P_{\nu_{A}}^{P} (t) \) is given by (2). The population rates \( P_{\nu_{A}}^{P} (t) = dP_{\nu_{A}}^{P} (t)/dt \), change sign during the ionic motion, which can be interpreted as interplay of the population and reionization processes. The position of the positive maximum of the rate determine the neutralization distances \( R_{N} \), at which the population process is mainly localized.

3. RESULTS

3.1. Selectivity of the population process and the role of the projectile velocity

As an illustrative example, in figure 2 we present the quantities \( P_{\nu_{A}}^{P} (t) \) for the population of some characteristic Rydberg states of the ions ArVIII and XeXIII slowly impinging the Al-surface. The most important fact that can be recognized from figure 2 is the selectivity of the population process: the larger \( n_{A} \) states are populated with lower \( P_{\nu_{A}}^{\text{max}} \). Moreover, the Rydberg states \( n_{A} > n_{c} \) are populated with very low probabilities (considering the maxima); the values \( n_{c} \) are characteristic for the particular ion-solid system and the kinematic conditions. It means that, within the framework of the TVM, one can estimate the Rydberg states \( n_{A} = n_{c} \) that will be populated first during the grazing incidence of multiply charged ions on solid surface.

The role of parallel projectile velocity \( v_{||} \) is discussed in figure 3 in which we consider the population dynamics of the ion ArX. In figures 3(a) and 3(b) we present the intermediate population probability \( P_{\nu_{A}}^{P} (t) \) via ion-surface distance \( R \) for the population of the Rydberg states with \( n_{A} = 10 \) and \( n_{A} = 12 \), respectively, for \( t_{A} = 1 \). We consider the population curves
for some characteristic values of the projectile parallel velocity \(v_\parallel \leq 0.16\) a.u. and for \(v_\perp = 0.005\) a.u.

The essential difference between the results presented in these two figures is that the Rydberg state \(n_A = 10\) of the ArX ion considered in figure 3(a) could be populated in the normal incidence case \((v_\parallel = 0)\), while the state \(n_A = 12\) presented in figure 3(b) could not. The common property of the presented population curves is the \(v_\parallel\)-behaviour: the distributions are shifted toward smaller ion-surface distances \(R\) with increasing \(v_\parallel\). However, the behavior of the probability maxima is different. In the first case we recognize a decrease of \(P_{n_A}^{\text{max}}\) with increasing \(v_\parallel\) for \(v_\parallel \leq 0.5\) a.u. and increase of probability maxima with further increase of \(v_\parallel\), while in the second case the values \(P_{n_A}^{\text{max}}\) increase with increasing \(v_\parallel\) for all considered parallel velocities.

### 3.2. TVM and comparison with experiments

Direct observation of the neutralization distances \(R_c^\text{N}\) has not yet been investigated experimentally in the case of multiply charged ions. However, an indirect insight into the neutralization dynamics is possible if we compare the measured projectile kinetic energy gain \(\Delta E^{\text{ZD}}\) [14,15] with the corresponding quantity calculated on the base of the TVM \(R_c^\text{N}(n_c)\) values, where the \(n_c\) represents the principal quantum number of the "highest" Rydberg level that can be populated with probability \(P_{n_A}^{\text{max}} \geq 0.2\).
All data are for $Z = 15$ and open circles are the TVM conditions. Solid circles represent the experimental data taken from [15] and closed circles are the TVM values. All data are for $v_\perp = v \sin 1.5^\circ$, for $\phi = 4.3$ eV, and for $U_0 = 15$ eV. Dashed curve is the COB quantity $\Delta E^{(Z)} \approx \phi Z^{3/2}/3\sqrt{2}$ for $\phi = 4.3$ eV [16].

Figure 4. Kinetic energy gain $\Delta E^{(Z)}$ via ionic core charge $Z$ of the ions $\text{Xe}^{Z+}$, under the experimental conditions. Solid circles represent the experimental data taken from [15] and open circles are the TVM values. All data are for $v_\perp = v \sin 1.5^\circ$, for $\phi = 4.3$ eV, and for $U_0 = 15$ eV. Dashed curve is the COB quantity $\Delta E^{(Z)} \approx \phi Z^{3/2}/3\sqrt{2}$ for $\phi = 4.3$ eV [16].

For the surface parameters in figure 4 we use the values $\phi = 4.3$ eV and $U_0 = 15$ eV; the work function $\phi = 4.3$ eV is taken in accordance with experimental conditions. By dashed curve in figure 4 we present the corresponding COB expression $\Delta E^{(Z)}$ [16]. For $v_\perp$ we take the experimental data $v_{\perp} \approx v_{\text{in}}$, where $v_{\text{in}}$ is the initial projectile velocity; perpendicular ionic velocity is given by $v_\perp = v \sin \Phi$, where $\Phi = 1.5^\circ$. We point out that, according to experimental conditions, the projectile velocity is 0.087 a.u. for the ions of low charge $Z \leq 11$; the ions of higher charge ($20 \leq Z \leq 33$) have been extracted through a fixed potential difference, and the corresponding projectile energies depended of the ionic charge: $E = 3.7Z$ keV, i.e. $v \in [0.15$ a.u., 0.2 a.u.][15]. According to figure 4 we conclude that the TVM results are in accord with the experimental values including the experimentally observed saturation for $Z \gg 1$. The COB curve is in a good agreement with experimental values for low $Z$ values, while in the large $Z$ region the COB values are systematically larger in comparison to the experimental data. The obtained agreement of the TVM with available experimental results in the large $Z$ case should be addressed to parallel velocity effect.

4. Concluding remarks

In this article we report the TVM study of the intermediate stages of the Rydberg state population of multiply charged ions impinging a conducting solid surface under the grazing incidence geometry. Within the framework of the model, the population probability distributions $P_{nA}^P(t)$ are represented by the the velocity dependent peak-shaped curves [6]. This is the specific feature of the scattering geometry; the corresponding physical picture of the population process is different in comparison to the normal incidence geometry case considered in [4,5]. The analytical form of the obtained population probabilities enables us to discuss the localization and the
selectivity of the processes expressed via neutralization distances $R^N_c$ and probability maxima $P_{v_A}^{\text{max}}$, for various relevant parameters of the ion-surface system.

The TVM results are compared indirectly with the existing theoretical (COB) and experimental results [15]. Due to the $v_{\parallel}$-dependence of the quantity $R^N_c(n_c)$, the obtained kinetic energy gain also depends on the projectile parallel velocity in accordance with experimental findings.

Few additional comments may be relevant for further investigations of population dynamics of multiply charged ions interacting with solid surfaces, based on the TVM.

First, the TVM treatment of the present paper can be used to analyze the other ions as well as other solid surfaces in comparison to those considered in references [4,5,6]. Also, by varying the value of the parallel velocity $v_{\parallel}$ one can obtain a more complete insight into the population dynamics; the extension of our model to the ionic velocities close to Fermi velocity $v_F$ and the larger values is also possible. The influence of the angle of incidence on the population dynamics can be analyzed using the obtained $v_{\perp}$-dependence of the population probability.

Second, the TVM developed in the present paper for the grazing incidence of multiply charged ions with population of the low-$l_A$ Rydberg states can be extended into the large-$l_A$ region, by taking into account that the corresponding electron transitions do not take place in the vicinity of the $z$ axis [17].

Acknowledgments
This work was supported in part by the Ministry of Education and Science, Republic of Serbia (Project 171016).

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