Electron emission by auto-detachment in collisions of He$^+$ ions with metal surfaces

M. Pamperin, F. X. Bronold, and H. Fehske
Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, 17489 Greifswald, Germany
(Dated: April 5, 2017)

Using a semi-empirical correlated Anderson-Newns model, containing two ionization levels and one affinity level, and a quantum-kinetic derivation of coupled rate equations for the probabilities for electron emission and the occurrence of the electronic configurations of the projectile, we present a scenario for electron emission in charge-transferring collisions of He$^+$ ions with metal surfaces which does not depend on Auger processes. Instead it is based on two sequential single-electron transfers. The first produces a metastable He$^+$ atom while the second turns the metastable atom into a metastable He$^{+\ast}$ ion which auto-detaches an electron by relaxing back to He$^+$. We demonstrate that the sequence, which leads to rather efficient electron emission with yields for Au surfaces on the order experimentally observed, is only open because of the non-adiabaticity encoded in the transition rates. In the golden rule approximation leading to adiabatic transition rates the channels are closed which could be the reason why they have not been explored in detail so far.

PACS numbers: 34.35.+a, 79.20.Rf, 72.10.Fk

I. INTRODUCTION

Charge-transferring collisions between atomic or molecular projectiles and surfaces are of great importance in applied science. Various surface diagnostic methods, for instance, secondary ion mass spectrometry$^{[1]}$ or metastable atom de-excitation spectroscopy$^{[2]}$ utilize these processes as well as technological devices such as the plasma display panel$^{[3]}$ or the negative hydrogen ion source in the pre-stage of the neutral gas heating of nuclear fusion reactors$^{[4]}$. The subject has been reviewed several times$^{[5–13]}$ since the early studies$^{[14–19]}$ dating back to the very beginning of modern condensed matter physics and there can be no doubt that the basic mechanisms have been by now identified.

Of particular interest are collisions leading to the emission of an electron. Typically these are Auger processes$^{[5–8]}$ where the Coulomb interaction between an electron from the projectile and an electron from the target promotes either a target or projectile electron into an unbound state. Auger neutralization of a positive ion at a surface, for instance, occurs because an electron scatters from an occupied state of the target into the lowest unoccupied state of the projectile. Since the states involved are usually non-degenerate energy is released and taken up by another electron either from the projectile or the surface. If the energy gain is large enough the electron scatters into an unbound state. At the end of the ion-surface collision it is thus free to leave the scattering zone. In addition to the (two-electron) Auger processes there are also one-electron processes$^{[9–13]}$ transferring an electron to-and-fro the projectile and the target. They are driven by the overlap of wave functions leading to a hybridization of the electronic states. The mixing of the states per se does not lead to the emission of an electron. It may produce however a transient electronic configuration from which an electron gets ejected either due to an Auger process or due to auto-detachment.

Although the basic mechanisms are well understood to disentangle how they become operative in a particular collision is still a great challenge and subject of on-going experimental as well as theoretical research$^{[20–38]}$. There are many pathways the collisional system can take. Figure 1 indicates the main processes for a He$^+$ ion hitting a metal surface. The processes marked in orange are studied in this paper and will be commented upon in more detail in the next paragraph. Besides Auger neutralization (AN), there is single-electron transfer (SET), Auger de-excitation (AD), and auto-detachment (AuD). Which one to include in a theoretical analysis depends on energetic as well as dynamic considerations. Usually it is assumed that pathways via He configurations which are energetically far away from the relevant electronic states of the metal can be ignored. However, quantum-dynamical effects beyond simple energetic considerations arising from the position- and hence time-dependent coupling between the He projectile and the target surface may open up some of those channels. Without a quantum-kinetic analysis of the scattering process it is hard to anticipate which channels are open and which are not.

In this paper we focus on the charge-transfer processes marked by orange arrows in Fig. 1. Auger processes will be included in a follow-up paper. Our purpose is to show, without the masking by Auger processes which preliminary calculations showed not to knock out the scenario we investigate, that in the collision of a He$^+$ (1s) ion with a metal surface an electron can get efficiently ejected by two sequential single-electron transfer processes producing first a metastable He$^+$ (1s2s) atom and then a He$^+\ast$ (1s2s2p) ion which auto-detaches the electron by falling back to the He$^+$ (1s2s) state. To the best of our knowledge, this channel of electron ejection, in which the He$^+\ast$ (1s2s2p) ion acts as a relay state, has not been investigated so far because the large energy mismatch of the He$^+$ (1s2s) and He$^+\ast$ (1s2s2p) configurations with the occupied states of the metal suggests that the channel is closed. A crude kinetic description of the collis-
FIG. 1: (Color online) Schematic representation of possible charge transfer processes which may take place during a collision of a He$^+$ ion with a metal surface, depending on the occupancies of the electronic states, their coupling, and the collision dynamics. The ion may capture electrons from the metal by single-electron transfer (SET) changing its configuration from He$^+(1s)$ to He$^+(1s2s)$ or even to He$^{++}$(1s2s2p) if two sequential SET processes occur. SET processes may however also work in the other direction, that is, the projectile may also lose electrons. Auto-detachment may lead to an electron loss and a reconfiguring of He$^{++}$(1s2s2p) to either He$^+(1s2s)$ or He$^+(1s^2)$. In addition, Auger neutralization (AN) and Auger de-excitation (AD) due to the Coulomb interaction between two electrons may take place pushing the projectile to its ground state configuration He(1s$^2$). Processes marked in orange will be investigated in this paper. The labeling $(n+1)e^-$ is a reminder that when the projectile relaxes back to He$^+(1s2s)$ via AuD an electron is released and the charge of the target is formally increased by one.

When a He projectile approaches a metal surface direct and exchange Coulomb interactions not only redistribute electrons between the atom and the surface they also modify the electronic structure of the atom and the surface. Since the projectile and the target are composite systems to analyze these processes from first principles is a complicated many-body problem. To describe the charge transfer between the He$^+$ (1s) ion and the metal surface we follow therefore Gadzuk’s semi-empirical approach. It uses classical image charges to mimic the long-range exchange interactions (polarization interactions) and a multichannel scattering theory to account for the non-orthogonality of the target and projectile wave functions. To furnish the formalism with wave functions simple models are used for the surface potential and the electronic structure of the projectile parameterized however in such way to reproduce measured ionization energies and electron affinities. From our previous work on the de-excitation of metastable nitrogen molecules on surfaces and the neutralization of alkaline-earth ions on gold surfaces we expect the Gadzuk approach also to provide reasonable matrix elements for an Anderson-Newns Hamiltonian describing electron ejection from metal surfaces due to impacting He$^+$ (1s) ions.

To analyze the chain of processes outlined in orange in Fig. 1 we consider the following electronic configurations for the He projectile: He$^+$ (1s), He$^+(1s2s)$, and He$^{++}$(1s2s2p). Without loss of generality we assume the electron of the He$^+$ (1s) ion to have an up-spin. This leaves us with two non-degenerate metastable levels He$^+(1s2s)$, a triplet $2^3S_1$ and a singlet $2^1S_0$ state with a spin-up and spin-down electron, respectively, in the 2s level. The term symbol of the positive ion is $1^2S_{1/2}$. Following this line of thought we have four negative ion...
levels \( \text{He}^{++}(1s^22p) \), two where the spins of the two electrons in the \( 2s \) and \( 2p \) levels are parallel and two where the spins are anti-parallel. For a free \( \text{He}^{++}(1s^22p) \) ion it is known that only the quartet state \( 2^3P_{3/2} \), where the spins of all three electrons points in the same direction, is metastable having lifetimes on the order of \( 10^{-4} \) s at cryogenic temperatures. Since the atom-surface collision time is extremely short, on the order of \( 10^{-14} \) s, we do not want to rule out other spin orientations to play also a role allowing therefore for the \( 2s \) and \( 2p \) electrons all four spin configurations. The metastable negative ion state is thus simply denoted by \( \text{He}^{+} \) (2P). In total we consider thus seven configurations for the projectile: a single non-degenerate ion state, two-fold degenerate singlet and triplet metastable states, and a two-fold degenerate negative ion state. Note, the groundstate \( \text{He}(1s^2) \) is not included. We neglect therefore the possibility of Auger de-excitation and Auger neutralization which will be the subject of a follow-up work. The metastable state \( \text{He}^{+}(1s^22p) \) is also not included since at the distances metastable states become occupied they strongly hybridize into a single effective state. To have a wave function for this state to be used in the calculation of the matrix elements we assumed the metastable state to have mostly s-character.

In view of the considerations of the previous paragraph we model the projectile by a spin-dependent two-level system where each level can host either one spin-up (\( \sigma = \uparrow \)) or one spin-down (\( \sigma = \downarrow \)) electron. If two electrons are present one has thus to occupy the upper and one the lower level. The upper level, denoted by \( \varepsilon_{\sigma\sigma}(t) \), will be hence the affinity level required for constructing the negative ion state and the lower, denoted by \( \varepsilon_{\sigma\sigma}(t) \), will be the ionization level associated with the singlet and the triplet metastable state depending on the spin of the electron. Due to the polarization-induced image interaction, the ionization (affinity) level shifts upward (downward) when the He projectile approaches the metal. Hence, \( \varepsilon_{\sigma\sigma}(t) = -\varepsilon_{0\sigma} + \frac{e^2}{4(z(t) - z_i)} \), \( \varepsilon_{\sigma\sigma}(t) = \varepsilon_{0\sigma} - \frac{e^2}{4(z(t) - z_i)} \), where \( \varepsilon_{0\sigma} > 0 \) and \( \varepsilon_{0\sigma} > 0 \) are, respectively, the ionization and the affinity level of the He projectile far away from the surface and

\[
z(t) = z_{TP} + v_{\perp}|t|
\]

with \( v_{\perp} \) the projectile’s velocity component perpendicular to the surface and \( z_{TP} \) the turning point of the scattering trajectory. The position of the image plane \( z_i \) is used as a fitting parameter to make the energy shifts approximately 2 eV at the turning point \( z_{TP} \) in accordance with jellium-edge calculations of the shifts. The 2p level \( \varepsilon_{p\sigma}(t) \) shifts downward as it is required for an affinity level. In our model it does not act as an ionization level because we do not keep the \( \text{He}^{+}(1s2p) \) metastable state. Hence, the 2p level enters the scattering process only when the 2s level is occupied. This will be ensured by using projection operators. In addition to the energy levels of the projectile we also need the energy of an electron in front of the surface. Taking again into account the image interaction it is given by

\[
\varepsilon_{\tilde{q}\sigma}(t) = \varepsilon_{q\sigma} - \frac{e^2}{4(z(t) - z_i)}.
\]

In Fig. 2 we show the essence of the model with distances and energies on scale using the parameters listed in Table I. To set up the Anderson-Newns Hamiltonian for the scattering we are interested in finally require the hybridization matrix elements describing the mixing of the projectile states with the states of the surface. Denoting the position of the projectile by \( \vec{r}_P(t) = z(t)\hat{e}_z \) with \( z(t) \) defined in and following Gadzuk and our earlier work we write

\[
V_{s\tilde{k}\sigma}(t) = \int d^3r \psi_k^*(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}_P(t)|} \psi_{s\sigma}(\vec{r} - \vec{r}_P(t)),
\]

\[
V_{p\tilde{k}\sigma}(t) = \int d^3r \psi_k^*(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}_P(t)|} \psi_{p\sigma}(\vec{r} - \vec{r}_P(t)).
\]
TABLE I: Material parameters used in our calculations. The energy $\varepsilon^0$ denotes the ionization (affinity) level of the indicated helium configuration.$\text{[31,32]___33}$ $Z_{\text{eff}}$ is the effective charge used in the hydrogen-like wave functions $\psi_{\sigma\alpha}(\vec{r})$ and $\psi_{\sigma\rho}(\vec{r})$ to reproduce these energies, $z_i$ is the fitting parameter to guarantee an image shift of roughly 2 eV to reproduce these energies, $E_F$ and $m_e$ are the Fermi energy and the conduction band electron mass of the metal surface.$\text{[15,31,34]___35}$

for the coupling of the metal states with the ionization and affinity levels of the projectile and

$$V_{\text{p}q}(t) = \int d^3r \, \psi_{\vec{q}}^*(\vec{r}) \, \frac{-e^2}{4(z - z_i)} \psi_{\text{p}n}(\vec{r} - \vec{r}_p(t)) \tag{7}$$

for the coupling of the affinity level with the projectile’s continuum states. As demonstrated by Gadzuk,$\text{[33]}$ the matrix elements (5) and (6) take the non-orthogonality of the target and projectile states into account. In (7) no fundamental orthogonality problem arises because the continuum and the bound level belong to the same Hamiltonian. The calculation of the matrix elements is carried out in the same way as in our previous work.$\text{[33]}$ For the metal we use wave functions of a step potential $\psi_{k}(\vec{r})$ whereas for the bound states of the projectile hydrogen wave functions $\psi_{\sigma\alpha}(\vec{r})$ and $\psi_{\sigma\rho}(\vec{r})$ are used with effective charges $Z_{\text{eff}}$ adjusted to reproduce, respectively, the ionization energy $\varepsilon_{\sigma\alpha}^0$ and the electron affinity $\varepsilon_{\sigma\rho}^0$ far away from the surface. The projectile’s continuum states are approximated by plane waves $\psi_{\vec{q}}(\vec{r})$. Although these are strong assumptions for the wave functions, we stick to it because they allow us to pursue the calculation of the hybridization matrix elements to a large extent analytically by means of lateral Fourier transformation, which in turn substantially reduces the numerical effort when it comes to the solution of the kinetic equations.

To proceed we combine the projectile states included in our modeling to a completeness relation,

$$|00\rangle\langle00| + \sum_\sigma |\sigma0\rangle\langle\sigma0| + \sum_\sigma'| |0\sigma'\rangle\langle0\sigma'|$$

$$+ \sum_\sigma |\sigma\sigma'\rangle\langle\sigma\sigma'| = 1, \tag{8}$$

where the first position in the state vectors labels the 2s electron and the second the 2p electron. Hence, $|00\rangle$ stands for He$^+(1s)$, $|\sigma0\rangle$ for He$^+(1s2s)$, $|0\sigma'\rangle$ for He$^+(1s2p)$, and $|\sigma\sigma'\rangle$ for He$^-(1s2s2p)$. The spin labels $\sigma$ and $\sigma'$ indicate the spin orientation of the electron. As pointed out before the metastable configuration He$^+(1s2p)$ will not appear in the collision process. The 2p level acts as an affinity level and will thus be only occupied when the 2s level is also occupied. To guarantee this we introduce operators projecting the Anderson-Newns Hamiltonian into the correct subspace of the spin-dependent two-level system,

$$P_{n_s,n_p} = |n_s\sigma\rho\rangle\langle n_s\sigma\rho| \tag{9}$$

with indices $n_s$ and $n_p$ taking on values from the set $\{0, \sigma, \sigma'\}$.

We are now in a position to write down the Anderson-Newns Hamiltonian for the chain of processes indicated in orange in Fig. 1. With the energy shifts and matrix elements given above it reads

$$H(t) = \sum_{\sigma\sigma'} (P_{\sigma\sigma} + P_{\sigma\sigma'}) \varepsilon_{\sigma\alpha}(t) c_{\sigma\alpha}^\dagger c_{\sigma\alpha}$$

$$+ \sum_{\sigma\sigma'} P_{\sigma\sigma'} \varepsilon_{\sigma\rho}(t) c_{\sigma\rho}^\dagger c_{\sigma\rho'}$$

$$+ \sum_{\sigma} \varepsilon_{\sigma\alpha} k_{\sigma} c_{\sigma\alpha}^\dagger c_{\sigma\alpha} + \sum_{\sigma} \varepsilon_{\sigma\rho} q_{\sigma} c_{\sigma\rho}^\dagger c_{\sigma\rho}$$

$$+ \sum_{\sigma\sigma'} [P_{\sigma\sigma} + P_{\sigma\sigma'}] V_{s\sigma\alpha}(t) c_{\sigma\alpha}^\dagger c_{\sigma\alpha} + \text{H.c.}$$

$$+ \sum_{\sigma\sigma'} [P_{\sigma\sigma} + P_{\sigma\sigma'}] V_{p\sigma\rho}(t) c_{\sigma\rho}^\dagger c_{\sigma\rho} + \text{H.c.}$$

$$+ \sum_{\sigma\sigma'} [P_{\sigma\sigma} + P_{\sigma\sigma'}] V_{q\sigma\rho}(t) c_{\sigma\rho}^\dagger c_{\sigma\rho} + \text{H.c.} \right) \tag{10}$$

where the operators $c_{\sigma\alpha}^\dagger$ and $c_{\sigma\rho}^\dagger$ annihilate or create an electron with spin $\sigma$ in the first respectively second position of any given state $|n_s\sigma\rho\rangle$. The operators $c_{\sigma\alpha}^\dagger$ and $c_{\sigma\rho}^\dagger$ annihilate or create, respectively, an electron with spin $\sigma$ in the surface state $|k\rangle$ or the projectile’s continuum state $|q\rangle$. The physical meaning of the various terms is as follows: The first two terms describe the bound projectile levels, the third and fourth term denote the continuum of surface states and the continuum of unbound projectile states, while the next two terms describe the hybridization of the surface states with the bound projectile states. The last term finally encodes the auto-ionization of the negative ion.

Working directly with the Hamiltonian (10) is cumbersome because it is not suited for a diagrammatic analysis which on the other hand is a powerful tool to derive kinetic equations as shown by Langreth and coworkers.$\text{[36,37]}$ We rewrite therefore the states making up the projection operators in terms of pseudo-particle operators $e^\dagger$, $s^\dagger$, $p^\dagger$, and $d^\dagger$, defined by

$$|00\rangle = e^\dagger |\text{vac}\rangle, \quad |\sigma0\rangle = d_{\sigma\sigma'}^\dagger |\text{vac}\rangle,$$

$$|\sigma0\rangle = s_{\sigma}^\dagger |\text{vac}\rangle, \quad |\sigma\sigma'\rangle = p_{\sigma\sigma'}^\dagger |\text{vac}\rangle. \tag{11}$$

Since the positive ion carries an electron in the 1s shell the operators $e^\dagger$ and $d^\dagger$ representing, respectively, the
positive ion (empty 2s and empty 2p level) and the negative
ion (singly occupied 2s and single occupied 2p level) behave fermionic
while the operators \( s^{(1)} \) and \( p^{(1)} \) standing for metastable states (either singly occupied 2s or
single occupied 2p level) behave bosonic. The relation be-
tween the original operators \( c_{\sigma\sigma} \) and \( c_{\sigma\sigma}' \) and the pseudo-
operators can be found by letting the pseudo-operators act on the comple-
teness (9),

\[
c_{\sigma\sigma} = c_{\sigma\sigma} \ast 1 = \langle 0 | \langle 0 | - \sum_{\sigma'} | 0 \sigma' \rangle \langle 0 \sigma' |,
\]

(12)

\[
c_{\sigma\sigma}' = c_{\sigma\sigma}' \ast 1 = | 0 \sigma \rangle \langle 0 | - \sum_{\sigma'} | 0 \sigma' \rangle \langle 0 |,
\]

(13)

\[
c_{\sigma\sigma}' = c_{\sigma\sigma}' \ast 1 = | 0 \sigma \rangle \langle 0 | + \sum_{\sigma'} | 0 \sigma' \rangle \langle 0 \sigma' |,
\]

(14)

\[
c_{\sigma\sigma}' = c_{\sigma\sigma}' \ast 1 = | 0 \sigma' \rangle \langle 0 | + \sum_{\sigma'} | 0 \sigma' \rangle \langle 0 \sigma' |,
\]

(15)

where the minus sign in (12) and (13) is produced by com-
mutation. Inserting this in the Anderson-Newns Hamiltonian (10)
yields

\[
H(t) = \sum_{\sigma} \varepsilon_{\sigma}(t) c_{\sigma\sigma}^\dagger c_{\sigma\sigma} + \sum_{\sigma' \sigma} \left( \varepsilon_{\sigma}(t) + \varepsilon_{\sigma'}(t) \right) d_{\sigma\sigma'}^\dagger d_{\sigma\sigma'}
\]

\[
+ \sum_{k \sigma \sigma^\prime} \varepsilon_{k \sigma} c_{k \sigma}^\dagger c_{k \sigma} + \sum_{k \sigma \sigma^\prime} [V_{p k}(t)c_{k \sigma}^\dagger s_{\sigma'}^\dagger d_{\sigma \sigma'} + \text{H.c.}]
\]

\[
+ \sum_{q \sigma q^\prime} \varepsilon_{q \sigma} c_{q \sigma}^\dagger c_{q \sigma} + \sum_{q \sigma q^\prime} [V_{p q}(t)c_{q \sigma}^\dagger s_{\sigma'}^\dagger d_{\sigma \sigma'} + \text{H.c.}] 
\]

\[
+ \sum_{k \sigma} [V_{s k}(t)c_{k \sigma}^\dagger e_{\sigma}^\dagger s_{\sigma} + \text{H.c.}]
\]

(16)

when all projections are carried out. The physical mean-
ing of the various terms is now particularly transparent. Consid-
er, for instance, the second last term. It describes the cre-
dation and annihilation of the metastable He\(^{+}(1s2s)\) state by, respec-
tively, surface-mediated auto-detachment of the He\(^{−}(1s2s2p)\) state and surface-mediated capture
of an unbound electron by the He\(^{+}(1s2s)\) state. Since
the energy of the He\(^{+}(1s)\) configuration is zero the op-
erators \( e^{(1)} \) representing the positive ion show up only
in the last term describing the annihilation/creation of the
metastable atom by loosing/capturing an electron from/to the surface. As intended the operators \( p^{(1)} \) are
absent. The metastable configuration He\(^{+}(1s2p)\) is not
allowed in our modeling.

## III. QUANTUM KINETICS

With the electronic configurations of the He projectile
encoded in a spin-dependent two-level system holding ei-
ther none, one, or two electrons we can now calculate the probability with which an electron is emitted via the
sequence of single-electron transfers leading to an auto-

detaching He\(^{+}(1s2s2p)\) state as shown in Fig. 1. For
that purpose we use the quantum-kinetic method de-
veloped by Langreth and coworkers.\cite{19,20} In our case, the

\[
iE(t, t') = \langle T_c e(t) e^\dagger(t') \rangle,
\]

(17)

\[
iS_{\sigma}(t, t') = \langle T_c s_{\sigma}(t) s_{\sigma}^\dagger(t') \rangle,
\]

(18)

\[
iD_{\sigma\sigma'}(t, t') = \langle T_c d_{\sigma\sigma'}(t) d_{\sigma'\sigma}^\dagger(t') \rangle,
\]

(19)

\[
iG_{\sigma}(t, t') = \langle T_c c_{\sigma}(t) c_{\sigma}^\dagger(\bar{q})(t') \rangle,
\]

(20)

where the first three functions describe the empty, the
 singly, and the doubly occupied projectile, while the fourth refers to an electron in the unbound states of the
projectile. The operators making up the Green functions
evolve in time with the full Hamiltonian \( H \) and the
brackets denote the statistical average with respect to the
initial density matrix describing surface electrons in
thermal equilibrium and an empty projectile.

Following the lead of Langreth and coworkers\cite{19,21,22} we
use the Dyson equations for these functions to derive a set
of equations for the occurrence probabilities/occupancies
of the bound and unbound projectile states. Introducing
self-energies \( \Pi_{\sigma}(t, t') \), \( \Pi_{\sigma\sigma'}(t, t') \), \( \Sigma_{\sigma}(t, t') \) and \( \Sigma_{\sigma\sigma'}(t, t') \) for the four Green functions
given above, we obtain \((\hbar = 1)\)

\[
\frac{d}{dt} n_{n_{\sigma}}(t) = 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle
\]

\[
- 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle,
\]

(21)

\[
\frac{d}{dt} n_{s_{\sigma}}(t) = 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle
\]

\[
- 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle,
\]

(22)

\[
\frac{d}{dt} n_{d_{\sigma\sigma'}}(t) = 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle
\]

\[
- 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle,
\]

(23)

\[
\frac{d}{dt} n_{\sigma_{\bar{q}}}(t) = 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle
\]

\[
- 2 \text{Im} \int_{-\infty}^{\infty} d\bar{E} \langle \bar{E}, \bar{t} | \Pi_{\sigma}(\bar{t}, \bar{t}) \rangle.
\]

(24)

The equations are exact but of course not closed in
terms of the occupation number \( n_{\sigma_{\bar{q}}}(t) \) and the occurrence
probabilities \( n_{n_{\sigma}}(t) \), \( n_{s_{\sigma}}(t) \), \( n_{d_{\sigma\sigma'}}(t) \), and \( n_{\sigma_{\bar{q}}}(t) \).

In order to close the set of equations we proceed as
follows: First, we calculate the self-energies in the
non-crossing approximation. Heading towards linear rate
equations we approximate in the self-energies the dressed
propagators \( G_{\sigma}(\bar{r}, \bar{r}', t) \), associated with the projectile’s
continuum, by their undressed counterparts \( G_{\sigma}(\bar{r}, \bar{r}', t) \).
This strategy we also applied in our work on surface-
induced de-excitation of metastable nitrogen molecules\cite{23} where it was successful. The resulting expressions
for the self-energies are listed in the Appendix. Second, prepar-
ing the equations for the application of the semiclassical
approximation\cite{32,34,35,36,37} which in essence is a saddle-point integration in time, we split off the Green functions the trivial parts of the time dependence by defining reduced Green functions (indicated by an overbar),

$$H^R(t, t') = -i\Theta(t - t') \exp \left(-i \int_{t'}^{t} dt' \varepsilon(t')\right) \bar{H}^R(t, t') ,$$

(25)

$$H^\Xi(t, t') = \exp \left(-i \int_{t'}^{t} dt' \varepsilon(t')\right) \bar{H}^\Xi(t, t') ,$$

(26)

for any one of the four Green functions, dressed or undressed. The energy $\varepsilon(t)$ stands either for zero, $\varepsilon_{\sigma\sigma}(t)$, $\varepsilon_{\sigma\sigma}(t) + \varepsilon_{\rho\sigma}(t)$, or $\varepsilon_{q\sigma}(t)$ depending on the Green function. Third, we perform the saddle-point integration in time. It utilizes the fact that the bare Green functions associated with the states of the metal surface and the continuum of the projectile lead to functions in the self-energies strongly peaked at equal times which in effect sets on the rhs of Eqs. \ref{eq:21}–\ref{eq:24} the time variables of the projectile’s (reduced) Green functions (also the ones inside the self-energies) to equal times. Identifying reduced less-than functions at equal times with occurrence probabilities/occupancies and realizing that retarded reduced functions at equal times are simply equal to unity we obtain the rate equations

$$\frac{d}{dt} n_\sigma(t) = -n_\sigma(t) \sum_\alpha \Gamma_{\sigma\sigma}^<(t) + \sum_\alpha n_{\sigma\sigma}(t) \Gamma_{\sigma\sigma}^>(t) ,$$

(27)

$$\frac{d}{dt} n_{\sigma\sigma}(t) = -n_{\sigma\sigma}(t) \left[ \Gamma_{\rho\sigma}^>(t) + \Delta_{\rho\sigma}(t) \right] + n_{\sigma}(t) \Gamma_{\sigma\sigma}^<(t) ,$$

(28)

$$\frac{d}{dt} n_{\sigma}(t) = -n_{\sigma}(t) \left[ \Gamma_{\sigma\sigma}^<(t) + \sum_\alpha \Gamma_{\rho\sigma}(t) \right]$$

$$+ n_{\sigma}(t) \Gamma_{\sigma\sigma}^>(t)$$

$$+ \sum_\alpha n_{\sigma\sigma}(t) \left[ \Gamma_{\rho\sigma}^>(t) + \Delta_{\rho\sigma}(t) \right] ,$$

(29)

$$\frac{d}{dt} n_{\gamma}(t) = \frac{1}{2} \sum_\sigma n_{\sigma\sigma}(t) \Delta_{\rho\sigma}(t)$$

(30)

with transition rates $\Gamma_{\sigma\sigma}^<(t)$, $\Gamma_{\rho\sigma}^>(t)$, and $\Delta_{\rho\sigma}(t)$ given by \cite{32,34,35,36,37} in the Appendix and

$$n_{\gamma\sigma}(t) = \sum_q n_{\varphi\sigma}(t)$$

(31)

the $q\bar\sigma$-integrated occupancy of unbound projectile states. Except for the replacement of $G_{\varphi\sigma}^{R,A}(t, t')$ by $G_{\varphi\sigma}^{R,A}(t, t')$, which enabled us to employ in all terms on the rhs of \ref{eq:21}–\ref{eq:24} the saddle-point integration in time (semiclassical approximation), the derivation of the rate equations follows exactly the approach of Langreth and coworkers\cite{32,34,35,36,37} It is thus not reproduced step-by-step. Instead only the final result \ref{eq:27}–\ref{eq:30} is given.

The occurrence probabilities of the projectile’s electronic configurations at the end of the collision as well as the probability of having at the end an electron emitted into the unbound states of the projectile can be obtained by integrating the rate equations from $t = -\infty$ to $t = \infty$ with the initial condition $n_{e}(\infty) = 1$ and $n_{\sigma\sigma}(\infty) = n_{\rho\sigma}(\infty) = n_{\gamma\sigma}(\infty) = 0$ Before we do this we simplify however the transition rates \cite{32,34,35,36,37} by utilizing the fact that the hybridization matrix elements $V_{\varphi\sigma}(t)$, $V_{p\rho}(t)$, and $V_{pq\varphi}(t)$ factorize approximately in $t$ and $\vec{k}$ respectively $\vec{q}$. It is then possible to express the transition rates \cite{32,34,35,36,37} in the from

$$\Gamma_{\varphi\sigma}(t) = 2\text{Re} \int_{-\infty}^{t} d\tau \sqrt{\Gamma_{\varphi\sigma}(t) \Gamma_{\varphi\sigma}(\tau) \bar{f}_{\varphi\sigma}(t, \tau)} ,$$

(32)

$$\Gamma_{p\rho}(t) = 2\text{Re} \int_{-\infty}^{t} d\tau \sqrt{\Gamma_{p\rho}(t) \Gamma_{p\rho}(\tau) \bar{f}_{p\rho}(t, \tau)} ,$$

(33)

$$\Delta_{p\rho}(t) = 2\text{Re} \int_{-\infty}^{t} d\tau \sqrt{\Delta_{p\rho}(t) \Delta_{p\rho}(\tau) \bar{h}_{p\rho}(t, \tau)} ,$$

(34)

with

$$\Gamma_{\varphi\sigma}(t) = 2\pi \sum_{\vec{k}} \left| V_{\varphi\sigma}(t) \right|^2 \delta(\varepsilon_{\sigma\sigma}(t) - \varepsilon_{\varphi\sigma}(t)) ,$$

(35)

$$\Gamma_{p\rho}(t) = 2\pi \sum_{\vec{k}} \left| V_{p\rho}(t) \right|^2 \delta(\varepsilon_{\rho\sigma}(t) - \varepsilon_{\varphi\sigma}(t)) ,$$

(36)

$$\Delta_{p\rho}(t) = 2\pi \sum_{\vec{q}} \left| V_{pq\varphi}(t) \right|^2 \delta(\varepsilon_{\rho\sigma}(t) - \varepsilon_{\varphi\sigma}(t)) ,$$

(37)

one-electron adiabatic (golden rule type) expressions for the level widths and

$$\bar{f}_{\varphi\sigma}(t, \tau) = \int \frac{dk}{2\pi} f_{\varphi\sigma}(\varepsilon) \exp \left[-i \int_{\tau}^{t} d\tau' [\varepsilon(\tau') - \varepsilon(t)]\right] ,$$

(38)

$$\bar{h}_{\varphi\sigma}(t, \tau) = \int \frac{dk}{2\pi} h_{\varphi\sigma}(\varepsilon) \exp \left[-i \int_{\tau}^{t} d\tau' [\varepsilon(\tau') - \varepsilon(t)]\right] ,$$

(39)

generalized Fourier-transforms of the functions describing the initial occupancies of the two continua. The functions $f_{\varphi\sigma}(\varepsilon)$ and $f_{p\rho}(\varepsilon) = 1 - f_{\varphi\sigma}(\varepsilon)$ encode, respectively, the initially occupied and empty states in the conduction band of the metal. Hence, $f_{\varphi\sigma}(\varepsilon)$ is a Fermi-Dirac distribution function. The function $h_{\varphi\sigma}(\varepsilon)$ describes initially occupied states in the continuum of unbound projectile states. Hence, it is identically zero leading to $h_{\varphi\sigma}(\varepsilon) = 1$ and also to $h_{\varphi\sigma}(\varepsilon) = h_{\varphi\sigma}(\varepsilon) - h_{\varphi\sigma}(\varepsilon) = 1$ which is needed in \ref{eq:20} and \ref{eq:21}.

The essential points of the derivation of \cite{32,34,35,36,37} can be found in the appendix of Ref. \cite{34}, where we used the same strategy to construct the integral kernels for the Dyson equations describing the neutralization of strontium ions on gold surfaces. Despite the approximations and the saddle-point integrations already performed, the
transition rates (32)–(34) still account for the quantum-mechanical non-adiabaticity of the collision because the time integrals convolute along the collision trajectory hybridization matrix elements at the actual time with their values at all previous times. It is this non-adiabaticity which will opening up, as we shall see, charge-transfer channels which otherwise would be closed. We call the transition rates (32)–(34) therefore non-adiabtic in contrast to the adiabatic rates (35)

\[
\Gamma_{\sigma\sigma}^\xi (t) = \Gamma_{\varepsilon_{\sigma\sigma}}(t) f^\xi(\varepsilon_{\sigma\sigma}(t)) ,
\]

\[
\Gamma_{\sigma\sigma}^\rho (t) = \Gamma_{\varepsilon_{\sigma\rho}}(t) f^\rho (\varepsilon_{\sigma\rho}(t)) ,
\]

\[
\Delta_{\sigma\sigma}^>/A (t) = \Delta_{\varepsilon_{\sigma\sigma}}(t) h^>/A(\varepsilon_{\sigma\sigma}(t)),
\]

which follow from (32)–(34) by applying once more a saddle-point integration in time. The adiabatic approximation to the transition rates can be justified as follows: If the functions \( f^\xi(t,\tilde{t}) \) and \( h^>/A(t,\tilde{t}) \) are sufficiently strongly peaked for equal times the two hybridization matrix elements under the square roots can both be evaluated at the actual time \( t \) and hence pushed in front of the integrals. Applying the identities (36)

\[
2\text{Re} \int_{-\infty}^{t} dt' f^\xi(t,\tilde{t}) = f^\xi(\varepsilon) ,
\]

\[
2\text{Re} \int_{-\infty}^{t} dt' h^>/A(t,\tilde{t}) = h^>/A(\varepsilon) ,
\]

which hold under the same strong-peaking assumption, yields then the transition rates (40)–(42). It should be however noted that the identities depend on a number of conditions (35) which are almost never rigorously satisfied. We thus expect the adiabatic transition rates to describe reality only in rather advantageous situations.

Solutions of the rate equations, with either adiabatic or non-adiabatic transition rates, will be presented in the next section. To get an idea of what to expect let us first discuss the physical content of the equations. Three points are worth of mentioning.

(i) The adiabatic rates are positive definite. Using them in the rate equations (27)–(30) enables one to interpret terms on the rhs with an overall positive sign as gain processes and terms with an overall negative sign as loss processes. Except of the rate equation (30) for the occupancy of the unbound projectile states all rate equations have the gain-loss structure. The absence of this structure in (30) is due to the replacement of the dressed continuum propagators \( G^{R,A,\xi}_{\sigma\sigma}(t, t') \) by the undressed ones leading to a transition rate for loss processes \( \Delta_{\sigma\sigma}(t) \) proportional to \( G^{R,A}_{\sigma\sigma}(t, t') \) which vanishes however due to the initial condition \( n_{\sigma\sigma}(-\infty) = 0 \). To complete the discussion of the structure of the rate equations we mention that the factor 1/2 on the rhs of (30) takes into account that an electron ejected into the projectile’s continuum, which we model by plane waves, can either move towards the surface or away from it. Only electrons moving away from the surface contribute to electron emission. Hence, the factor 1/2 in the rate equation for \( n_{\sigma\sigma}(t) \).

(ii) The functions \( f^\xi(t,\tilde{t}) \) and \( h^>/A(t,\tilde{t}) \) defined in (38) and (39) make the non-adiabatic transition rates (32)–(34) no longer positive definite. Hence, using them in the rate equations destroys the simple interpretation in terms of gain and loss processes. It is thus hard to anticipate how the interplay of the various terms in the rate equations determines the final outcome of the ion-surface collision. Since the adiabatic transition rates result from the non-adiabatic ones by an additional saddle-point integration we expect them moreover to be smaller in magnitude. The numerical calculations presented in the next section verify this expectation. The quantum-mechanical collision dynamics included in the non-adiabatic transition rates enhances therefore the rates enabling thereby the projectile to trace a path of charge-transfer reactions a reasoning based on adiabatic rates would suggest to be closed and thus irrelevant.

(iii) The adiabatic rates are symmetric with respect to the turning point, the non-adiabatic rates are not. The time integrals in the exponent of the functions \( f^\xi(t,\tilde{t}) \) and \( h^>/A(t,\tilde{t}) \) destroy the symmetry. For the incoming branch, where \( \tilde{t} \) is negative, the variable \( \tilde{t} \) is also always negative. Whereas for the outgoing branch, where \( t \) is positive, the variable \( \tilde{t} \) can be positive as well as negative. The collision dynamics along the two branches should thus be different. Finally, one should also realize that the adiabatic transition rates are independent of the projectile’s velocity while the non-adiabatic transition rates depend on it. This can be seen by rewriting the time integrals in (38) and (39) as integrals over the spatial variable \( z \). The integrals turn then out to be proportional to \( v_{\perp}^{\beta} \), the inverse of the projectile’s normal velocity.

Having discussed the physical content of the formalism we now know what to expect from the numerics: Non-adiabaticity should lead to potentially larger rates which are however no longer positive definite and symmetric with respect to the turning point. Before implementing the equations numerically we modify them however slightly. The interpretation of the formalism given in the previous paragraphs is not affected by the modification.

Surface scattering experiments typically occur under conditions of grazing incidence (23). The lateral velocity \( v_{\parallel} \) of the projectile is thus very large. To account in our calculations for the smearing of the metal’s Fermi-Dirac distribution induced by the lateral motion of the projectile, in addition to the thermal smearing of the distribution function due to the surface temperature \( T_s \), we replaced for the numerical calculations in the formulas given above the function \( f^<(\varepsilon) \) by an angle-averaged velocity-shifted distribution (32)

\[
f^<(\varepsilon, v_{\parallel}) = \frac{\ln (1 + e^{-\beta(\varepsilon + \Phi - \delta)}) - \ln (1 + e^{-\beta(\varepsilon + \Phi + \delta)})}{2\beta \delta}
\]

with \( \Phi \) the work function of the surface, \( \beta = 1/k_B T_s \), and \( \delta = k_F v_{\parallel} \), where \( k_F \) the surface’s Fermi wave number.
From the projectile’s perspective the velocity smearing populates surface states above the Fermi energy thereby potentially strengthening charge-transfer processes from the metal to the He metastable states which, due to image shifting, are well above the Fermi energy.

Let us finally say a few words about the numerics we applied. The calculation of the level widths requires a two-dimensional integration of the solid angle of \( \vec{k} \) or \( \vec{q} \). This is done by a MPI parallelized Monte Carlo Vegas code for a discrete number of different times. To obtain the matrix elements at times in between we utilized linear interpolation. Since the level widths are very smooth a better interpolation method like splines does not necessarily yield a better result. The interpolation is required to perform the time integration in the non-adiabatic transition rates with an adaptive 61-point Gauss-Kronrod rule provided by the GNU scientific library. To solve the rate equations, finally, we employed the explicit embedded Runge-Kutta Cash-Karp method also provided by GNU. We have put importance on a reasonable error propagation resulting in a relative numerical error of the calculated occurrence/occupation probabilities of less than \( 10^{-4} \).

IV. RESULTS

In this section we present numerical results calculated for the material parameters listed in Table I. We use atomic units measuring length in Bohr radii and energy in Hartrees. The surface is assumed to be on room temperature leading to a thermal broadening of the Fermi-Dirac distribution which is much less than the velocity-induced smearing. In the calculations we used therefore (45) in the limit \( T' \rightarrow \infty \).

We start the discussion by looking at the non-adiabatic and adiabatic transition rates defined respectively in (32)-(34) and (40)-(42). The goal is to find out whether dynamical quantum-mechanical effects included in the non-adiabatic transition rates are strong enough to significantly influence the charge transfer to-and-fro the atomic projectile and the target surface. Figures 3 and 4 show for the purpose of demonstration the rates \( \Gamma_{s \uparrow}^\pm \) and \( \Gamma_{s \downarrow} \) for a He\(^+\)\((1^2S_1/2)\) ion hitting a tungsten surface with \( E_{\text{kin}} = 200 \text{ eV} \) and an incident angle, measured from the surface, \( \varphi = 2^\circ \). The abscissas show the separation of the projectile from the surface. Starting on the left at a distance \( z = 40 \), it moves along the incoming branch of the trajectory towards the turning point \( z_{TP} = 2.27 \), indicated by the thin vertical line, where it is specularly reflected to move back to the distance \( z = 40 \) along the outgoing branch of the trajectory shown on the right. With the exception of Fig. 7 all figures have to be read like that.

During the projectile’s movement the non-adiabatic transition rates tend to oscillate strongly, in particular, along the outgoing branch of the trajectory making their comparison with the adiabatic rates complicated. For guidance of the eye we smoothened therefore in Figs. 3 and 4 the non-adiabatic rates by a third-order centered binomially weighted moving average. For the same reason the instantaneous occurrence and occupation probabilities shown in Fig. 6 are also calculated with smoothened non-adiabatic rates. We found however the smoothening to have little impact on the occurrence/occupation probabilities for \( t \rightarrow \infty \). It just makes the interpretation of the data at intermediate times easier. The smoothening is not required and hence not performed in plots showing only data for \( t \rightarrow \infty \), as in Fig. 7 where we depict the angular dependence of the final occurrence/occupation probabilities.

The magnitudes of the non-adiabatic and adiabatic transition rates shown, respectively, by the solid and dashed lines in Figs. 3 and 4 increase or less exponentially towards the turning point as a consequence of the exponential dependence of the wave function of the metal electrons on the wave vector \( \vec{k} \). For the adiabatic rates, however, this trend is present only as long as the shifted ionization levels \( \varepsilon_{s \uparrow}(t) \) and \( \varepsilon_{s \downarrow}(t) \) are degenerate with the states of the surface. Is this no longer the case, the adiabatic rates collapse as in panel (a) of Fig. 4, where the adiabatic approximation to \( \Gamma_{s \downarrow}^\pm \) is larger than \( 10^{-10} \) only around \( z = 20 \). Only in this very narrow range overlaps \( \varepsilon_{s \downarrow}(t) \) to some extent with the occupied tail of the velocity-broadened Fermi-Dirac distribution. Even if the adiabatic rates are finite, they are in general much smaller than the non-
adiabatic rates. Only in some cases, which are however hard to anticipate in advance, the two rates may be close to each other or even equal. For instance, the adiabatic approximation works well for the rate $\Gamma_{s<}^{-}$ plotted in panel (b) of Fig. 4. In this case it can be rigorously justified by an asymptotic analysis of the involved integrals. In general, however, the adiabatic rates are for the electron transfer processes investigated in this work at least two orders of magnitude smaller than the non-adiabatic rates. Based on them one would think the processes to be inefficient or even closed. In reality, however, they are open because of the non-adiabaticity of the quantum-mechanical collision dynamics.

The asymmetry of the non-adiabatic rates with respect to the turning point, arising from the time integrals in (38) and (39), can be also seen in Figs. 3 and 4. It is most apparent by the fact that the sign of the rates may change when the projectile switches from the incoming to the outgoing branch of the trajectory. The same rate may thus describe in some parts of the trajectory a gain process whereas in others it describes a loss process. For instance, the non-adiabatic rate $\Gamma_{s<}^{-}$ plotted in panel (a) of Fig. 4 describes a gain process throughout most parts of the incoming branch (only close to the turning point it becomes the rate of a loss process) whereas on the outgoing branch it describes a loss process over a wide range of distances. Adiabatic transition rates, on the other hand, are symmetric around the turning point, hence, equal for in- and outgoing branches, as well as always positive. Similar features and differences are also found for the other transition rates.

In view of the data shown in Figs. 3 and 4 it should be clear that the solutions of the rate equations (27)–(30) depend strongly on whether adiabatic or non-adiabatic rates are used. In Figs. 5 and 6 we plot the instantaneous occurrence probabilities for the electronic configurations of the He$^+(1^2S_{1/2})$ projectile and the instantaneous probability of electron emission arising from the solution of the rate equations with, respectively, adiabatic and non-adiabatic rates. For better readability we relabelled the probability $n_e(t)$ for the occurrence of the empty two-level system, that is, the probability for the occurrence of an positive ion to $n_+(t)$ and introduced the variables $n_-(t) = \sum_{\sigma}\gamma_\sigma(t)$ and $\gamma_\sigma(t) = \sum_{n}\gamma_{n\sigma}(t)$ to measure, respectively, the probability that a He$^−(2P)$ ion occurs in any spin configuration and that an electron is emitted with an arbitrary spin. The occurrence probabilities of the metastable configurations, that is, the triplet He$^*(2^3S_1)$ and singlet He$^*(2^1S_0)$ state are still identified by $n_\uparrow(t)$ and $n_{s\uparrow}(t)$.

Let us first turn to Fig. 5 showing the occurrence probabilities obtained from the rate equations using the adiabatic transition rates (40)–(42). The only channel open is the channel creating the triplet He$^*(2^3S_1)$ state reducing thereby the probability for obtaining a He$^+(1^2S_{1/2})$ configuration at the end of the collision to approximately 0.7. Neither the singlet He$^*(2^1S_0)$ state nor the He$^−(2P)$ state are occupied. The electron capture channels leading to them are closed in the adiabatic approximation. Without a negative ion an electron cannot be auto-detached. Hence, $\gamma_e = 0$ in the adiabatic approximation. Recall that we neglect Auger processes. Had we included them we would have found small probabilities for electron emis-
FIG. 6: (Color online) Instantaneous occurrence probabilities for the electronic configurations of the initial He$^+$($1^3S_{1/2}$) projectile and the probability for emitting an electron in the course of the collision using non-adiabatic transition rates (32)–(34) but smoothening them for guidance of the eye (see main text for an explanation). Panel (a) shows data for the axis of the $p$-orbital involved in the He$^{-}$($2P$) configuration perpendicular to the surface while panel (b) plots data for the axis parallel to the surface. The He$^+$($1^3S_{1/2}$) ion hits in both cases the tungsten surface with $E_{\text{kin}} = 200$ eV and an angle of incident $\varphi = 2^\circ$. The turning point $z_{TP} = 2.27$ and is indicated by the thin vertical line.

The solutions of the rate equations with the non-adiabatic transition rates (32)–(34) are plotted for the same parameters in Fig. 6. Since the negative ion state He$^{-}$($2P$) enters now the collision dynamics, having the $p$-orbital either oriented perpendicular or parallel to the surface, we distinguish the two orientations. Panel (a) shows data for the axis of the $p$-orbital oriented perpendicular to the surface whereas panel (b) shows data for the axis of the $p$-orbital parallel to the surface. In both cases negative ions are formed leading to a significant probability for emitting an electron via auto-detachment. For perpendicular orientation electron emission is some-what more efficient because of the larger overlap of the $p$-orbital with the states of the metal. The electron capture channels kept closed by the adiabatic transition rates are thus now open due to the non-adiabaticity of the quantum-mechanical collision dynamics included in the non-adiabatic transition rates. It can be also seen that the collision dynamics is different for the incoming and the outgoing branch of the trajectory, as expected from the asymmetry of the non-adiabatic rates with respect to the turning point. The He$^+$($2P$) state responsible for the emission of the electron is formed along the incoming branch. As a result, the probability for emitting an electron via the sequence of electron capture processes shown in orange in Fig. 1 is determined by the collision dynamics along the incoming branch. The final occurrence probabilities of the electronic configurations of the He$^+$($1^3S_{1/2}$) projectile, on the other hand, are determined by the dynamics along the outgoing branch.

Tracing the collision dynamics in Fig. 6 more closely and correlating it with the level shifts induced by the image-interaction reveals that the dynamics along the incoming branch is indeed driven by the non-adiabaticity of the scattering process which cannot be anticipated by simply looking at the energies of the projectile and target states while the dynamics along the outgoing branch shows some resemblance to what one would expect from the energies. The electron transfer in the active region of the incoming branch of the trajectory occurs despite the fact that the mismatch between the involved energy levels is large. In fact, it is the large mismatch which leads to the absence of electron emission when adiabatic rates are used in the rate equations. For instance, the affinity level $\varepsilon_{pe}(t)$ never touches the highest occupied state of the metal even with velocity-induced smearing of the Fermi-Dirac distribution taken into account which for the parameters of Fig. 6 pushes the highest occupied metal state to the energy $E = \Phi - k_F v_0 = 4.5$ eV − 0.87 eV = 3.63 eV. Similarly the ionization level $\varepsilon_{i1}(t)$ representing the singlet metastable state He$^+$($2^1S_0$) crosses this energy, that is, the highest occupied metal state, at $z_c = 18.6$. In Fig. 6 it can be however seen that its occurrence probability still increases for $z < z_c$. It is thus not the degeneracy of projectile levels with surface states which drives along the incoming branch the electron capture processes leading to metastable and negatively charged electronic configurations of the He$^+$($1^3S_{1/2}$) projectile and thus eventually causing the emission of an electron by auto-detachment but the non-adiabaticity of the quantum-mechanical collision dynamics encoded in the rates. Along the outgoing branch the situation is different. The He$^{-}$($2P$) state is not realized anymore, as expected from the large energy mismatch between the affinity level and the occupied metal states, while the metastable states He$^+$($2^3S_1$) and He$^+$($2^1S_0$) appear most prominently after the ionization levels $\varepsilon_{e1}(t)$ and $\varepsilon_{a1}(t)$ crossed from above (since it is the outgoing branch) the highest occupied state of the metal surface at $z_c = 4.7$ and $z_c = 18.6$, respectively.
After the collision is completed the He\(^{+}\)\((2S_{1/2})\) ion finds itself with almost equal probability either in its original state or in a metastable triplet He\(^{+}\)\((2S_{1})\) state. For perpendicular orientation, for instance, the probabilities—fixed along the outgoing branch of the trajectory—are \(n_{+}(\infty) \approx 0.45\) and \(n_{+}\uparrow(\infty) = 0.55\) while \(n_{-}(\infty)\) and \(n_{-}\uparrow(\infty)\) are both less than \(10^{-3}\) and thus negligible. At the same time an electron gets emitted with probability \(\gamma_{\epsilon}(\infty) \approx 0.05\) due to the auto-detachment of the He\(^{+}\)\((2P)\) ion temporarily realized along the incoming branch. The loss of memory which usually implies that the final occurrence probabilities do not depend on the collision dynamics along the incoming branch does thus not apply to the electron emission probability.

Since we included the velocity-induced smearing of the Fermi-Dirac distribution it is of interest to study the angle dependence of the auto-detachment scenario. In Fig. 7 we plot therefore for the two principal orientations of the \(p\)-orbital the emission and occurrence probabilities for \(t \to \infty\), that is, the final probabilities after the collision is completed for a He\(^{+}\)\((2S_{1/2})\) ion with \(E_{\text{kin}} = 50\) eV and \(E_{\text{kin}} = 150\) eV scattering off a tungsten surface with the parameters given in Table 1. To obtain the results we solved the rate equations with unsmoothed non-adiabatic rates (32)–(34) without smoothening.

FIG. 7: (Color online) Final probabilities \(\gamma_{\epsilon}, n_{+},\) and \(n_{+}\uparrow\) for electron emission and the occurrence of the He\(^{+}\)\((2S_{1/2})\) and the He\(^{+}\)\((2S_{1})\) configurations as a function of the incident angle. The kinetic energy of the initial He\(^{+}\) ion scattering off the tungsten surface is \(E_{\text{kin}} = 50\) eV [panel (a) and (b)] and \(E_{\text{kin}} = 150\) eV [panel (c) and (d)]. Note, only the positive ion and the triplet metastable state occur at the end of the collision. Negative ion and singlet metastable states occur only temporarily and do thus not show up in these plots. Panels (a) and (c) apply to the case where the \(p\)-orbital required for the temporary formation of the negative ion is oriented perpendicular to the surface whereas panels (b) and (d) apply to the case where the orientation is parallel. The data shown are obtained by solving the rate equations (27)–(30) for the probabilities using the non-adiabatic transition rates (32)–(34) without smoothening.
TABLE II: Angle-averaged electron emission probability resulting from the auto-detachment of the transiently formed He$^{+*}$ (2P) ion for different metal surfaces hit by a He$^{+}$ (1S$^1/2$) ion with $E_{kin} = 50$ eV. The $p$-orbital of the He$^{+*}$ (2P) ion is either oriented parallel or perpendicular to the surface.

|               | Tungsten (W) | Gold (Au) | Aluminum (Al) |
|---------------|-------------|-----------|--------------|
| $\gamma_e^1$  | 0.007       | 0.243     | 0.07         |
| $\gamma_e^\perp$ | 0.041       | 0.439     | 0.228        |

A numerical solution of the rate equations showed moreover that the probability for electron emission is determined by the collision dynamics along the incoming branch of the scattering trajectory whereas the probabilities for the final occurrence of the electronic configurations of the projectile are fixed by the collision dynamics along the outgoing branch. The loss of memory, which usually makes the collision dynamics along the incoming branch of the trajectory irrelevant for the final outcome of the collision, does thus only apply to the occurrence probabilities but not to the electron emission probability. Grazing incident of the He$^+$ (1S$^1/2$) ion is beneficial for the auto-detachment scenario because the large energy mismatch between the ionization/affinity levels and the metal states is then partially compensated by the velocity-induced broadening of the metal’s Fermi-Dirac distribution function due to the lateral motion of the ion. It should be however noted that even for perpendicular incident the auto-detachment scenario is open indicating that the non-adiabaticity of the collision dynamics is more important than reducing the energy mismatch by smearing-out the Fermi edge.

V. CONCLUSIONS

In this work we showed that it is possible that an electron gets ejected in the course of a collision between a He$^+$ (1S$^1/2$) ion and a metal surface not because of Auger processes but because of the formation of an auto-detaching He$^{+*}$ (2P) state. Excluding Auger transitions altogether we focused on the two sequential single-electron transfer processes leading first to the triplet metastable state He$^+$ (2S$^1$) and then to the He$^{+*}$ (2P) state which ejects the electron by relaxing back to the He$^+$ (2S$^1$) configuration. Electron ejection via this channel is rather efficient yielding, for instance, for Au surfaces emission probabilities on the order experimentally found.

We based our work on a semi-empirical correlated Anderson-News model containing an image-shifted affinity level standing for the He$^{+*}$ (2P) ion and two image-shifted ionization levels representing, respectively, the singlet He$^+$ (2S$^0$) and the triplet He$^+$ (2S$^1$) metastable state. After expressing the electronic configurations of the projectile and hence the Hamiltonian in terms of pseudo-operators we applied contour-ordered Green functions to derive a set of rate equations for the probabilities with which an electron gets emitted and the projectile can be found in any of the electronic configurations included in the model. It was essential to use rate equations with non-adiabatic transition rates, as they arise from the quantum kinetics, and not adiabatic transition rates a golden rule calculation would produce. The electron transfer processes required for the auto-detachment scenario are only open due to the non-adiabaticity of the collision dynamics. For adiabatic rates they are closed because of the large energy mismatch between the ionization/affinity levels and the occupied states of the metal.

We did not attempt a detailed comparison with experimental data because we did not yet fully work out the consequences Auger processes may have on the auto-detachment scenario and also because we did not calculate electron emission spectra. Both will be the subject of a forthcoming work. Exploratory calculations showed however that Auger processes do not destroy the auto-detachment scenario because they either take place at a distance where the auto-detachment is already over or they are blocked by spin conservation. Both we expect to remain valid also for collision Hamiltonians which do not depend on the semi-empirical arguments we employed. Electron emission via the auto-detaching He$^{+*}$ (2P) state should thus turn out to be also strong in calculations based on first principle Hamiltonians provided the collision dynamics is treated non-adiabatically.
Acknowledgements

M. P. was funded by the federal state of Mecklenburg-Western Pomerania through a postgraduate scholarship within the International Helmholtz Graduate School for Plasma Physics. In addition, support from the Deutsche Forschungsgemeinschaft through project B10 of the Transregional Collaborative Research Center SFB/TRR24 is greatly acknowledged.

Appendix

Applying the non-crossing approximation to the Hamiltonian of the conduction band and 0 the Fermi-Dirac distribution for the metal's conduction band electrons at temperature \( T_s \). The function \( h^>(\epsilon_{\vec{q}\sigma}) = 1 - h^<(\epsilon_{\vec{q}\sigma}) \) denote the occupancies of the two continua prior to the charge transfer as encoded in the initial density matrix. Assuming the surface to be in thermal equilibrium \( f^>(\epsilon_{\vec{k}\sigma}) = 1 - f^<(\epsilon_{\vec{k}\sigma}) \) with \( f^<(\epsilon_{\vec{k}\sigma}) = 0 \), implying \( h^>(\epsilon_{\vec{q}\sigma}) = 1 \), since initially there is no electron in the unbound states of the projectile. In the formulae above it is understood that the variable \( \epsilon_{\vec{k}\sigma} \) runs over the width of the conduction band and \( 0 < \epsilon_{\vec{q}\sigma} < \infty \).

To obtain from the self-energies the transition rates entering the rate equations for \( n_{\sigma}(t) \), \( n_{\sigma\sigma}(t) \), \( n_{\sigma\sigma'}(t) \), and \( n_{\gamma\sigma}(t) \) we perform the steps explained in the paragraph prior to Eqs. \( 27 \) - \( 30 \) and find

\[
\Pi^R_{d\sigma\sigma'}(t,t') = \sum_{k} V^*_{p\vec{k}\sigma}(t) V_{p\vec{k}\sigma'}(t') G^>_{0\vec{k}\sigma}(t',t) S^R_{\sigma}(t,t')
\]

\[
+ \sum_{\vec{q}} V^*_{p\vec{q}\sigma'}(t) V_{p\vec{q}\sigma}(t') G^>_{0\vec{q}\sigma}(t',t) S^R_{\sigma}(t,t')
\]  

\[
(51)
\]

\[
\Sigma^R_{d\sigma}(t,t') = \sum_{k} V^*_{p\vec{k}\sigma}(t) V_{p\vec{k}\sigma}(t') G^>_{0\vec{k}\sigma}(t',t) E^R_{\sigma}(t,t')
\]

\[
+ \sum_{\vec{q}} V^*_{p\vec{q}\sigma'}(t) V_{p\vec{q}\sigma}(t') G^>_{0\vec{q}\sigma}(t',t) D^R_{\sigma\sigma'}(t,t')
\]

\[
+ \sum_{q\sigma'} V_{p\vec{q}\sigma'}(t) V^*_{p\vec{q}\sigma}(t') G^<_{0\vec{q}\sigma}(t',t) D^R_{\sigma\sigma'}(t,t'),
\]  

\[
(52)
\]

\[
\Sigma^R_{\gamma\sigma}(t,t') = \sum_{\sigma'} V_{p\vec{q}\sigma'}(t) V^*_{p\vec{q}\sigma}(t') S^R_{\sigma'}(t',t) D^R_{\sigma'\sigma}(t),
\]

\[
(53)
\]

\[
\Pi^R_{\gamma}(t,t') = \sum_{k\sigma} V_{\vec{k}\sigma}(t) V^*_{\vec{k}\sigma}(t') G^<_{0\vec{k}\sigma}(t',t) S^R_{\sigma}(t,t'),
\]

\[
(50)
\]

with

\[
G^<_{0\vec{k}\sigma}(t,t') = f^<_{\vec{k}\sigma}(\epsilon_{\vec{k}\sigma}) e^{\epsilon_{\vec{k}\sigma}(t-t')},
\]

\[
(54)
\]

\[
G^<_{0\vec{q}\sigma}(t,t') = h^<_{\vec{q}\sigma}(\epsilon_{\vec{q}\sigma}) e^{\epsilon_{\vec{q}\sigma}(t-t')},
\]

\[
(55)
\]
The non-adiabaticity of the transition rates arises from the time integrals which convolute the hybridization matrix elements $V_\gamma(t)$ at the actual time $t$ with the matrix elements $V_{\gamma\delta}(\tilde{t})$ at all the previous times $\tilde{t} < t$ along the collision trajectory.