Pseudo-particle approach for charge-transferring molecule-surface collisions

Johannes Marbach, Franz Xaver Bronold, and Holger Fehske
Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, 17489 Greifswald, Germany
(Dated: May 22, 2014)

Based on a semi-empirical generalized Anderson-Newns model we construct a pseudo-particle description for electron emission due to de-excitation of metastable molecules at surfaces. The pseudo-particle approach allows us to treat resonant charge-transfer and Auger processes on an equal footing, as it is necessary when both channels are open. This is for instance the case when a metastable $N_2(\Sigma_u^+)$ molecule hits a diamond surface. Using non-equilibrium Green functions and physically motivated approximations to the self-energies of the Dyson equations we derive a system of rate equations for the probabilities with which the metastable $N_2(\Sigma_u^+)$ molecule, the molecular ground state $N_2(\Sigma_g^+)$, and the negative ion $N_2^{-}(\Pi_g)$ can be found in the course of the scattering event. From the rate equations we also obtain the spectrum of the emitted electron and the secondary electron emission coefficient. Our numerical results indicate the resonant tunneling process underpinning the source of the Auger channel which therefore contributes only a few percent to the secondary electron emission.

PACS numbers: 34.35.+a, 34.70.+e, 79.20.Fv, 79.20.Hx

I. INTRODUCTION

Charge exchange processes during atom-surface or molecule-surface collisions have been the subject of intense scientific research during the last decade. This type of surface reactions is of fundamental interest. It represents a quantum-impurity problem where a finite many-body system with discrete quantum states couples to an extended system with a continuum of states which essentially acts as a reservoir for electrons. Under appropriate conditions, such an arrangement gives for instance rise to the Kondo effect, originally found in metals containing magnetic impurities or to Coulomb blockades as it is discussed in nanostructures.

Besides of being a particular realization of a quantum impurity problem, atom/molecule-surface collisions are also of technological interest, especially in the field of bounded low-temperature plasmas, where this type of surface collisions is the main supplier of secondary electrons which in turn strongly affect the overall charge balance of the discharge. In dielectric barrier discharges, for instance, secondary electron emission determines whether the discharge operates in a filamentary or a diffuse mode. Only the latter mode is useful for surface modification. Controlling the yield with which secondary electrons are produced is thus of great practical interest. This applies even more so to microdischarges, where the continuing miniaturization gives charge-transferring surface reactions more and more influence on the properties of the discharge.

Depending on the projectile and the target, secondary electron emission usually occurs either in the course of a resonant tunneling process or an Auger transition. In some situations, however, both transitions may be energetically allowed and hence contribute to the yield with which electrons are released. The interplay of the two reaction channels has therefore been studied in the past. Starting with the work of Alvarez et al. a detailed theoretical analysis of the interference of Auger and resonant tunneling processes has been given by Goldberg and coworkers. Their results for $H^+$ and $He^+$ indicate the Auger channel to be active only close to the surface whereas the resonant channel is already efficient at rather large projectile-surface distances. When both channels are coupled together the dynamics of the system is hence controlled by the resonant channel as it destroys the initial species before the Auger channel can become operative. The Auger channel is therefore strongly suppressed in the coupled system albeit the individual efficiencies of the reaction channels are comparable. Onufriev and Marston also investigated the interplay of tunneling and Auger processes for the particular case of Li(2p) atoms de-exciting on a metallic surface. Using a sophisticated many-body theoretical description of the scattering process they concluded that depending on the model parameters the two de-excitation channels interfere either constructively or destructively.

Whereas the previous studies focused on atomic projectiles we will investigate in the following the interplay of Auger and resonant tunneling processes for a molecular projectile. More precisely, we will analyze how these two processes affect secondary electron emission due to de-excitation of metastable molecules. Neutralization of molecular ions will not be discussed. A particularly interesting case is the de-excitation of metastable $N_2(\Sigma_u^+)$ because this molecule de-excites in two primary reaction channels. On the one hand, there is the two-step resonant charge transfer (RCT) reaction

$$e^{-}_k + N_2(\Sigma_u^+) \xrightarrow{RCT} N_2^{-}(\Sigma_g^-) \xrightarrow{RCT} N_2(\Sigma_g^+) + e^{-}_q,$$

where $e^{-}_k$ and $e^{-}_q$ denote an electron within the surface and a free electron, respectively. In this process the metastable $N_2(\Sigma_u^+)$ molecule first resonantly captures an electron from the surface to form the intermediate negative ion shape resonance $N_2^{-}(\Pi_g)$ which then decays into the ground state $N_2(\Sigma_g^+)$ by resonantly emitting an
electron. The decay of the negative ion can be either due to the ion’s natural life time or due to the ion surface interaction. In addition to the RCT channel, there exists an Auger de-excitation reaction also known as Penning de-excitation

$$e_k^- + N_2(3\Sigma_u^+) \xrightarrow{\text{Auger}} N_2(1\Sigma_g^-) + e_q^-.$$  \hspace{1cm} (2)

Here the molecule non-resonantly captures a surface electron and simultaneously releases another electron. Depending on the surface band structure both processes may be possible at the same time. This is for instance the case for diamond as it possesses a rather wide valence band.

In our previous work\cite{27,28} we investigated the two reaction channels separately by a quantum-kinetic approach and a rate equation technique. The molecule was in both cases treated as a semi-empirical two-level system corresponding to the $2\pi_u$ and $2\pi_g$ molecular orbitals, which are the two molecular orbitals whose occupancies change during the de-excitation process. spectator electrons not involved in the processes were neglected. Depending on the process the two levels denoted the upper and lower ionization levels of either the metastable molecule (Auger de-excitation) or the negative ion (resonant charge-transfer). The advantage of a semi-empirical model is that it is based on a few parameters which are relatively easy accessible, either experimentally or theoretically. The difference of the two parameter sets, which arises from intra-molecular Coulomb correlations not included in the model, is not a problem as long as the two processes are treated separately. A simultaneous treatment of them requires however a way to implement both processes dominating the Auger process. The overall secondary electron emission coefficient due to de-excitation of $N_2(3\Sigma_u^+)$ at a diamond surface is on the order of $10^{-1}$.

The outline of the rest of the paper is as follows. In Sec. \[II\] we describe the semi-empirical model on which our investigation of the de-excitation process is based. Thereafter, we explain in Sec. \[III\] the pseudo-particle representation. Afterwards, we conduct in Sec. \[IV\] a second order quantum-kinetic calculation on top of the pseudo-particle model. In Sec. \[V\] we introduce a physically motivated semi-classical approximation that allows us to reduce the set of Dyson equations to a set of rate equations. Finally, we present in Sec. \[VI\] the results for the diamond surface and conclude in Sec. \[VII\] with a brief summary of the main points of the work. Appendix \[A\] lists the Langreth-Wilkins rules\cite{23} as used in our calculation and Appendix \[B\] collects the second order Dyson equations for the molecular Green functions.

\section{II. Model}

The interacting molecule-surface system is characterized by three different types of electronic states: bound and unbound molecular states and states within the solid surface. In the spirit of our previous work\cite{27,28} we restrict the attention to those states whose occupancies change during the molecule-surface collision. For these states and the coupling between them we construct a semi-empirical model. Its matrix elements can be either obtained from quantum-mechanical calculations based on particular assumptions about the electron wave functions and/or experimentally measured ioniza-
tion energies, electron affinities, surface response functions, and electron tunneling rates. Since we are primarily interested in the quantum-kinetic handling of the semi-empirical model we pursue for simplicity the former route. A more realistic parameterization of the model is however in principle possible.

We treat the relevant bound states of the nitrogen molecule in terms of a two-level system consisting of a ground state level "0" and an excited level "1". Within a linear combination of atomic orbital (LCAO) description of the molecule these two levels represent the nitrogen molecule’s 2π_u and 2π_g orbitals. Each of the two orbitals can carry four electrons. We neglect however the three electrons in the 2π_u orbital and the three holes in the 2π_g orbital which are not directly involved in the de-excitation process. They act only as frozen-in spectators. For the same reason we neglect the electron spin and treat the magnetic quantum number m = ± 1 as an initial parameter. Hence, both levels of our model carry at most one electron.

The two-level system represents any of the molecular states depicted in Fig. 1. The positive ion N_2^+(2Π_u), the ground state N_2(3Σ_u^+) , the metastable state N_2(3Σ_u^+) , and the negative ion N_2^−(2Π_g) . Depending on the particular occupation the energies ε_0 and ε_1 correspond therefore to the ionization energies of different molecular states. Due to intra-molecular Coulomb interactions these ionization energies are in general different [35,37]. We have to allow therefore ε_0 and ε_1 to depend on the occupancy of the two-level system, that is, on the molecular state it is supposed to represent. In addition, the ionization energies are also subject to the surface’s image potential V_i(z) and thus vary with time as the molecule moves with respect to the surface. Using the analysis presented in Ref. 28 we find

\[ \varepsilon_{0g}(z) = \varepsilon_{0g} - V_i(z) , \]  
\[ \varepsilon_{1*}(z) = \varepsilon_{1*} - V_i(z) , \]  
\[ \varepsilon_{0-}(z) = \varepsilon_{0-} + V_i(z) , \]  
\[ \varepsilon_{1-}(z) = \varepsilon_{1-} + V_i(z) , \]

where the subscripts g, * and - signal the dependence of the energy levels on the molecular state denoting, respectively, the ground state molecule, the metastable molecule, and the negative ion. The unperturbed molecular energies are given by [36,37]

\[ \varepsilon_{0g} = -17.25 \text{ eV} , \quad \varepsilon_{1*} = -9.67 \text{ eV} , \]
\[ \varepsilon_{0-} = -14.49 \text{ eV} , \quad \varepsilon_{1-} = 1.18 \text{ eV} . \]  

The overall energy scheme of the coupled molecule-surface system is sketched in Fig. 2 for the particular case of a diamond surface. As can be seen the positive ion is neither involved in the RCT nor the Auger process.

For the image potential we employ for simplicity the classical expression,

\[ V_i(z) \approx -\frac{\varepsilon_b^0 - 1}{\varepsilon_b^0 + 1} \frac{e^2}{16\pi\varepsilon_0 z} , \]  

where \( \varepsilon_b^0 \) standing for the surface’s static bulk dielectric constant. Close to the surface the image potential is however truncated according to \( V_i(z_c) = V_0 \) where \( V_0 \) is the
depth of the potential barrier confining the electrons of the solid participating in the de-excitation process. As in our previous investigations,[27,28] we describe the solid by a step potential of depth $V_0$. For a metallic surface,[27] the step depth is the width of the valence band $\Delta \varepsilon_v$, that is, the sum of the work function $\Phi_W$ and the Fermi energy $\varepsilon_F$ whereas for a dielectric surface,[29] it is the sum of the width of the valence band $\Delta \varepsilon_v$, the energy gap $\varepsilon_g$, and the electron affinity $\varepsilon_a$ which can be positive or negative.

In both the RCT and the Auger channel the emitted electron stems from the molecule and, thus, the emission proceeds into the molecular continuum states. We model the latter as free electron states moving along with the molecule and label them with $\vec{q}$. Electrons residing in those states are also affected by the image potential and their energy is thus given by

$$\varepsilon_{\vec{q}}(z) = \varepsilon_0^{\infty} + V_i(z) = \frac{\hbar^2q^2}{2m_e} + V_i(z). \quad (6)$$

The wave function of the emitted electron is a two-center Coulomb wave for the Auger channel[27] and a plane wave for the RCT channel.[23] The latter is a special case of the former which holds for zero effective nuclear charge. Since in the RCT channel the emitted electron leaves a neutral molecule behind the plane wave is the suitable choice for this channel. In the Auger channel however the emitted electron feels the residual two-center Coulomb attraction of the ion core. The two-center Coulomb wave takes this effect into account. To complete the description of the model we note that we use LCAO molecular wave functions for the two-level system and eigenstates of a superposition of a step potential (which somewhat underestimates the exponential tail of the metal electron’s wave functions and hence the absolute value of the matrix elements) and a classical image potential (which is less critical because the turning point turns out to be far in front of the surface) allows us however to write down analytic expressions for the matrix elements. For the quantum kinetics itself the matrix elements are only parameters. Our approach can thus be also furnished with improved matrix elements obtained from more realistic potentials. Based on the work of Kürpick and Thumm[33] we would expect however not too dramatic differences.

We now cast the semi-empirical model just described into a mathematical form. Introducing projection operators

$$P_{n_0n_1} = |n_0n_1\rangle\langle n_0n_1| \quad (7)$$

projecting onto states of the two-level system with $n_0 = 0, 1$ electrons in the lower and $n_1 = 0, 1$ electrons in the upper state, the transitions shown in Fig. 2 give rise to a generalized Anderson-Newns model.[31]

$$H(t) = \sum_{\vec{k}} \varepsilon_{\vec{k}} c_{\vec{k}}^\dagger c_{\vec{k}} + \sum_{\vec{q}} \varepsilon_{\vec{q}}(t) c_{\vec{q}}^\dagger c_{\vec{q}}$$

$$+ \omega_0 b_{\vec{0}}^\dagger b_{\vec{0}} + \omega_1 b_{\vec{1}}^\dagger b_{\vec{1}}$$

$$+ \sum_{n_0,n_1} P_{n_0n_1} \left( \varepsilon_{\vec{k}}^{n_0n_1}(t) c_{\vec{k}}^\dagger c_{\vec{k}} + \varepsilon_{\vec{q}}^{n_0n_1}(t) c_{\vec{q}}^\dagger c_{\vec{q}} + \varepsilon_{1\downarrow}^o c_{\vec{k}}^\dagger c_{\vec{k}} + \varepsilon_{1\downarrow}^e c_{\vec{q}}^\dagger c_{\vec{q}} + h.c. \right)$$

$$+ \sum_{\vec{q}} \left( [P^{10} + P^{11}] V_k(t) c_{\vec{k}}^\dagger b_{\vec{q}} c_{\vec{q}} + h.c. \right)$$

$$+ \sum_{\vec{k}q} \left( [P^{10} + P^{01}] V_{\vec{k}q}(t) c_{\vec{k}}^\dagger c^\dagger_{\vec{q}} c_{\vec{q}} + h.c. \right). \quad (8)$$

where $\varepsilon_{10}^o = \varepsilon_{0g}$, $\varepsilon_{11}^o = \varepsilon_{ks}$, $\varepsilon_{11}^e = \varepsilon_{0e}$, and $\varepsilon_{1\downarrow}^o = \varepsilon_{1\downarrow}^e$.

The remaining energy levels need not be specified further. They drop out in the course of the pseudo-particle representation presented in the next section. The two auxiliary bosons $b_{\vec{0}}(t)$ and $b_{\vec{1}}(t)$ mimic the intra-molecular Coulomb correlations which make the two steps of the RCT channel[14] resonant. This can be accomplished by setting $\omega_0 = \varepsilon_{1\downarrow}^o - \varepsilon_{0}^o$ and $\omega_1 = \varepsilon_{1\downarrow}^e - \varepsilon_{1\downarrow}^e$. The initial energy of the tunneling electron is then resonant respectively with the lower and the upper level of the negative ion. The rest of the Hamiltonian is written in the notation we used in our previous work.[27,28]

The time dependence of the Hamiltonian arises from the trajectory of the molecule’s center of mass $\vec{R}(t)$. For simplicity we assume normal incidence described by the trajectory $\vec{R}(t) = (v_0 t + z_0) \vec{e}_z$, where $v_0$ is a constant velocity and $z_0$ is the molecule’s turning point which can be calculated from a Morse type interaction potential.[22] Employing the trajectory the $z$ dependence of the molecular energies[3] and the energy of the emitted electron[6] transforms into a time dependence. Similarly, the Auger matrix element $V_{\vec{k}\vec{q}}$ and the two resonant tunneling matrix elements $V_k$ and $V_q$ acquire also a time-dependence.

The quantum-kinetic calculation presented below treats the matrix elements of the Hamiltonian as parameters. We are thus not restricted to the specific approximations to the matrix elements derived in our previous work.[27,28] We could as well use matrix elements from ab-initio calculations or experimental measurements. The natural decay of the negative ion, described by the rate $\Gamma_n = 1/\tau_n$ with $\tau_n$ the natural lifetime of the negative ion, is not included in the Hamiltonian[5]. It will be inserted at the end into the final set of rate equations for the molecular occupancies.
III. PSEUDO-PARTICLE REPRESENTATION

The projection operators 7 permit us to describe the transitions 11 and 12 by a single Hamiltonian. Depending on the process and thus the occupancy of the molecular levels different matrix elements can be assigned to the Hamiltonian. The projectors also guarantee that the N$_2^+(2\Pi_u)$ state never occurs. In other words, they ensure that the occupancies of the two molecular levels never vanishes simultaneously. For instance, an electron residing in the upper level can only be released when an electron has been captured in the lower level.

A drawback of the projection operators is that they are not suitable for a diagrammatic treatment which on the other hand is a powerful tool to set up quantum-kinetic equations. To remedy this drawback we now employ a pseudo-particle approach to express the Hamiltonian 5 in terms of slave fields 5, 28, 29, 33. The starting point for this procedure is the completeness condition,

$$|00\rangle\langle00| + |10\rangle\langle10| + |01\rangle\langle01| + |11\rangle\langle11| = 1,$$  

which expresses the fact that the molecule can be only in either one of the configurations depicted in Fig. 1. Introducing pseudo-particle operators $c^\dagger_1$, $c^\dagger_2$, $c_1^\dagger$, and $c_2^\dagger$ that create the positive ion, the ground state molecule, the metastable molecule, and the negative ion from an abstract vacuum state,

$$|00\rangle = c^\dagger_1 |\text{vac}\rangle, \quad |10\rangle = c^\dagger_2 |\text{vac}\rangle, \quad |01\rangle = c_1^\dagger |\text{vac}\rangle, \quad |11\rangle = c_2^\dagger |\text{vac}\rangle,$$  

the completeness condition 5 becomes

$$c^\dagger_1 c_+ + c^\dagger_2 c_g + c^\dagger_1 c_s + c^\dagger_2 c_- = 1.$$  

Using 5 and 10 the operators $c_{0/1}^{(t)}$ creating and destroying an electron in the two states of the two-level system can then be written as

$$c_0 = c_0 \ast 1 = |00\rangle\langle00| - |01\rangle\langle01| - |10\rangle\langle10| + |11\rangle\langle11|, \quad c_0^{\dagger} = c_0^{\dagger} c_g - c_0^{\dagger} c_-,$$  

$$c_1 = c_1 \ast 1 = |00\rangle\langle01| + |01\rangle\langle00| + |10\rangle\langle11| + |11\rangle\langle10|, \quad c_1^{\dagger} = c_1^{\dagger} c_s + c_1^{\dagger} c_-,$$  

$$c_2 = c_2 \ast 1 = |10\rangle\langle00| + |11\rangle\langle01| - |00\rangle\langle11| - |01\rangle\langle10|, \quad c_2^{\dagger} = c_2^{\dagger} c_s + c_2^{\dagger} c_g.$$  

In order to satisfy the anti-commutation relations of the $c_{0/1}^{(t)}$ one has to define $c_0 |11\rangle = - |01\rangle$ and $c_0^{\dagger} |01\rangle = - |11\rangle$ (see also Ref. 39). The anti-commutator relations then reproduce the completeness condition 11 when either the $c_{g/s}$ are bosonic and the $c_{-/+}$ are fermionic or the $c_{g/s}$ are fermionic and the $c_{-/+}$ are bosonic.

Without loss of generality we choose $c_g$ and $c_s$ to be bosonic and declare the labeling conventions

$$c_g^{(t)} \rightarrow b_g^{(t)}, \quad c_s^{(t)} \rightarrow b_s^{(t)}, \quad c_1^{(t)} \rightarrow f_1^{(t)}, \quad c_2^{(t)} \rightarrow f_2^{(t)}. $$

The constraint 11 reduces then to

$$Q = b_g^{(t)} b_g + b_s^{(t)} b_s + f_1^{(t)} f_- + f_2^{(t)} f_+ = 1,$$  

where we have introduced the usual pseudo-particle number operator $Q$ to encapsulate the constraint.

Formally, the auxiliary fermion and boson operators are pseudo-particle operators creating and annihilating molecular configurations. The constraint ensures that at any time only one of the four possible molecular configurations is present in the system. The occupancy of a molecular pseudo-particle state is thus at most unity. Hence, it represents the probability with which the molecular configuration it describes appears in the course of the scattering event.

Inserting the decomposition 12 into the Hamiltonian 5, making the identifications 13, and collecting only terms which are in accordance with 14 is straightforward. The result is

$$H(t) = \sum_k \varepsilon_k c_k^{\dagger} c_k + \sum_{\tilde{q}} \varepsilon_{\tilde{q}}(t) c_{\tilde{q}}^{\dagger} c_{\tilde{q}}$$  

$$+ \omega_0 b_0^{\dagger} b_0 + \omega_1 b_1^{\dagger} b_1$$  

$$+ \varepsilon_g(t) b_g^{\dagger} b_g + \varepsilon_s(t) b_s^{\dagger} b_s + \varepsilon_-(t) f_-^{\dagger} f_-$$  

$$- \sum_k \left( V_k(t) c_k^{\dagger} b_0^{\dagger} b_0 f_+ + h.c. \right)$$  

$$+ \sum_{\tilde{q}} \left( V_{\tilde{q}}(t) c_{\tilde{q}}^{\dagger} b_0^{\dagger} b_0 f_+ + h.c. \right)$$  

$$+ \sum_{\tilde{k}\tilde{q}} \left( V_{\tilde{k}\tilde{q}}(t) c_{\tilde{k}}^{\dagger} c_{\tilde{q}}^{\dagger} b_g b_s + h.c. \right),$$  

where we introduced the abbreviations

$$\varepsilon_g = \varepsilon_{10}^{10}, \quad \varepsilon_s = \varepsilon_{01}^{01}, \quad \varepsilon_- = \varepsilon_{11}^{11} + \varepsilon_{11}^{11}. $$

Notice, no term in the Hamiltonian contains the operator $f_+$ or its adjoint. This is by construction because the positive ion N$_2^+(2\Pi_u)$ is not involved in the two transitions the Hamiltonian is supposed to model. The physical meaning of the various terms in the Hamiltonian is particularly transparent. Consider for instance the last term describing the Auger de-excitation. A metastable molecule and an electron from the surface disappear while a ground state molecule and an Auger electron are created.

The operators $f_-$ and $b_{g/s}$ comply to standard commutation and anti-commutation relations. It is thus possible to conduct a non-equilibrium diagrammatic expansion of the interaction terms in 15. The Hamiltonian 15 conserves the pseudo-particle number $Q$. The quantum-kinetic equations however may contain terms which violate the constraint. The projection onto the physical subspace with $Q = 1$ needs to be therefore carried out explicitly. For this purpose we employ in the next section the Langreth-Nordlander projection technique 31.
IV. QUANTUM-KINETICS

To start the quantum-kinetic calculation we first define a contour-ordered fermion Green function \( G_- \) for the negative ion and contour-ordered boson Green functions \( B_{s/g/0/1} \) for the metastable molecule, the molecular ground state, and the two auxiliary bosons, respectively. Using the notation of Langreth and Nordlander\cite{Langreth1974} we write

\[
\begin{align*}
    iG_- (t, t') &= \langle T_c f_-(t) f_+^\dagger (t') \rangle, \\
    iB_l (t, t') &= \langle T_c b_l (t) b_+^\dagger (t') \rangle,
\end{align*}
\]

where \( l = *, g, 0, 1 \), and define the analytic pieces \( G_\pm \) and \( B_l^\pm \) by

\[
\begin{align*}
    iG_- (t, t') &= \Theta_C (t - t') G_\pm (t, t'), \\
    iB_l (t, t') &= \Theta_C (t - t') B_l^\pm (t, t') \\
        &+ \Theta_C (t' - t) B_l^\pm (t, t').
\end{align*}
\]

The time-ordering operator \( T_c \) and the \( \Theta_c \) function are defined on a complex time contour. The associated retarded Green functions \( G_R \) and \( B_l^R \) are given by

\[
\begin{align*}
    iG_R^R (t, t') &= \Theta (t - t') (G_\pm (t, t') + G_\mp (t, t')), \quad (19a) \\
    iB_l^R (t, t') &= \Theta (t - t') (B_l^\pm (t, t') - B_l^\mp (t, t')), \quad (19b)
\end{align*}
\]

whereas the advanced functions \( G_A \) and \( B_l^A \) may be constructed from \( (19) \) using the relations

\[
\begin{align*}
    G_A (t, t') &= [G_R^R (t', t)]^*, \quad (20a) \\
    B_l^A (t, t') &= [B_l^R (t', t)]^*. \quad (20b)
\end{align*}
\]

The diagrams for the fermionic self-energy \( \Sigma_- \) and the bosonic self-energies \( \Pi_s \) and \( \Pi_g \) are shown in Fig. 3. Mathematically they read

\[
\begin{align*}
    \Sigma_- (t_1, t_2) &= i \sigma_{k\rightarrow q} (t_1, t_2) B_s (t_1, t_2) \\
        &+ i \sigma_{q\rightarrow k} (t_1, t_2) B_g (t_1, t_2), \quad (21a) \\
    \Pi_s (t_1, t_2) &= -i \sigma_{k\rightarrow q} (t_2, t_1) G_- (t_1, t_2) \\
        &+ \sigma_{k\rightarrow q} (t_2, t_1) B_g (t_1, t_2), \quad (21b) \\
    \Pi_g (t_1, t_2) &= -i \sigma_{q\rightarrow k} (t_2, t_1) G_- (t_1, t_2) \\
        &+ \sigma_{q\rightarrow k} (t_2, t_1) B_s (t_1, t_2). \quad (21c)
\end{align*}
\]

The diagrams for the fermionic self-energy \( \Sigma_- \) and the bosonic self-energies \( \Pi_s \) and \( \Pi_g \) are shown in Fig. 3. Mathematically they read

\[
\begin{align*}
    \Sigma_- (t_1, t_2) &= i \sigma_{k\rightarrow q} (t_1, t_2) B_s (t_1, t_2) \\
        &+ i \sigma_{q\rightarrow k} (t_1, t_2) B_g (t_1, t_2), \quad (21a) \\
    \Pi_s (t_1, t_2) &= -i \sigma_{k\rightarrow q} (t_2, t_1) G_- (t_1, t_2) \\
        &+ \sigma_{k\rightarrow q} (t_2, t_1) B_g (t_1, t_2), \quad (21b) \\
    \Pi_g (t_1, t_2) &= -i \sigma_{q\rightarrow k} (t_2, t_1) G_- (t_1, t_2) \\
        &+ \sigma_{q\rightarrow k} (t_2, t_1) B_s (t_1, t_2). \quad (21c)
\end{align*}
\]

With

\[
\begin{align*}
    \sigma_{k\rightarrow q} (t_1, t_2) &= \frac{i}{\hbar^2} \sum_{k/q} V_{k\rightarrow q}^* (t_1) V_{k\rightarrow q} (t_2), \\
    \sigma_{q\rightarrow k} (t_1, t_2) &= -\frac{1}{\hbar^2} \sum_{k/q} V_{q\rightarrow k}^* (t_1) V_{q\rightarrow k} (t_2), \quad (22a)
\end{align*}
\]

and \( G_{k/q}^{(0)} \) and \( B_{0/1}^{(0)} \) denoting, respectively, the contour-ordered Green functions for a free/valence band electron
and an auxiliary boson.

In the self-energies \([21]\) the two reaction channels \([1]\) and \([2]\) are separated. Every term involving \(\sigma_k^\sigma\) or \(\sigma_{\bar{q}}^\sigma\) refers to the RCT channel and every term containing \(\sigma_{k\bar{q}}^\sigma\) pertains to the Auger channel. Due to the dressed Green functions the two channels are however coupled. The Green functions of the auxiliary bosons contained in \(\sigma_k^\sigma\) and \(\sigma_{\bar{q}}^\sigma\) ensure that the two tunneling processes contained in \([1]\) are resonant. Physically, the auxiliary bosons simulate the action of intra-molecular correlations which kick-in when an electron hops to-and-fro the molecule.

Using the Langreth-Wilkins rules for analytic continuation (see Refs. 31–32 and Appendix A) we obtain from the self-energies \([21]\) the set of Dyson equations given in Appendix B. The components of these equations arising from the RCT terms are equivalent to the ones in Ref. 31 but with two bosonic pseudo-particles instead of one and an energy shift caused by the auxiliary bosons. The set of Dyson equations \([B1]\) contains terms which violate the constraint \([14]\). Before physically meaningful information can be extracted the Dyson equations have to be projected onto the physical subspace defined by the constraint \([14]\).

The procedure to achieve this is originally due to Langreth and Nordlander and has been outlined several times.\(^{20,22}\) It is based on inspecting the order of the Green functions in the conserved pseudo-particle number \(Q\). The retarded functions \(\tilde{G}_{\nu}^R(t, t')\) are proportional to \(Q^0\) while the lesser Green functions \(\bar{G}_{\nu}^L(t, t')\) are proportional to \(Q^1\). Thus, we have to omit any terms of higher order than \(Q^0\) from the retarded self-energies and any terms of higher order than \(Q^1\) from the lesser self-energies. This approach is not an additional approximation but an exact projection enforced by the constraint\(^{21}\).

Before carrying out the projection we split off the Green functions’ oscillating factors by means of the decompositions\(^{23}\)

\[
\begin{align*}
\tilde{G}_{\nu}^{R/A}(t, t') &= \tilde{G}_{\nu}^{C/R/A}(t, t') e^{-\frac{i}{\hbar} \int_{t_0}^{t_1} dt_1 \varepsilon_{\nu}(t_1)} , \quad (23a) \\
\bar{G}_{\nu}^{C/R/A}(t, t') &= \bar{G}_{\nu}^{R/A}(t, t') e^{\frac{i}{\hbar} \int_{t_0}^{t_1} dt_1 \varepsilon_{\nu}(t_1)} , \quad (23b) \\
\bar{B}_{\nu}^{C/R/A}(t, t') &= \bar{B}_{\nu}^{R/A}(t, t') e^{-\frac{i}{\hbar} \int_{t_0}^{t_1} dt_1 \varepsilon_{\nu}(t_1)} , \quad (23c)
\end{align*}
\]

and

\[
\begin{align*}
\tilde{G}_{\nu}^R(t, t') &= -i \Theta(t - t') g_-(t, t') , \quad (24a) \\
\tilde{G}_{\nu}^A(t, t') &= i \Theta(t' - t) g_-(t, t') , \quad (24b) \\
\bar{B}_{\nu}^R(t, t') &= -i \Theta(t - t') b_{\nu/g}(t, t') , \quad (24c) \\
\bar{B}_{\nu}^A(t, t') &= i \Theta(t' - t) b_{\nu/g}(t, t') . \quad (24d)
\end{align*}
\]

Using the definition of the retarded and advanced Green functions we find the following relations\(^{23}\)

\[
\begin{align*}
g_-(t, t) &= b_{\nu/g}(t, t) = 1 , \quad (25a) \\
g_-(t, t') &= [g_-(t', t)]^* , \quad (25b) \\
b_{\nu/g}(t, t') &= [b_{\nu/g}(t', t)]^* . \quad (25c)
\end{align*}
\]

Within the Dyson equations the oscillating terms emerging from Eqs. \((23)\) will be absorbed in the functions \(\tilde{\sigma}_k^\sigma\), \(\tilde{\sigma}_{\bar{q}}^\sigma\) and \(\tilde{\sigma}_{k\bar{q}}^\sigma\) which are defined by

\[
\begin{align*}
\tilde{\sigma}_k^\sigma(t, t') &= \tilde{\sigma}_k^\sigma(t, t') e^{\frac{i}{\hbar} \int_{t_0}^{t_1} dt_1 \varepsilon_{+}(t_1)} , \quad (26a) \\
\tilde{\sigma}_{\bar{q}}^\sigma(t, t') &= \tilde{\sigma}_{\bar{q}}^\sigma(t, t') e^{-\frac{i}{\hbar} \int_{t_0}^{t_1} dt_1 \varepsilon_{-}(t_1)} , \quad (26b) \\
\tilde{\sigma}_{k\bar{q}}^\sigma(t, t') &= \tilde{\sigma}_{k\bar{q}}^\sigma(t, t') e^{-\frac{i}{\hbar} \int_{t_0}^{t_1} dt_1 \varepsilon_{+}(t_1)} \cdot \tilde{\sigma}_{k\bar{q}}^\sigma(t, t') . \quad (26c)
\end{align*}
\]

The terms \(\sigma_k^\sigma\), \(\sigma_{\bar{q}}^\sigma\) and \(\sigma_{k\bar{q}}^\sigma\) vanish identically due to the initial conditions \(n_0(t_0) = n_{\bar{q}}(t_0) = 1 \) and \(n_1(t_0) = n_{k\bar{q}}(t_0) = 0\) since

\[
\begin{align*}
\sigma_k^\sigma(t, t') &\sim (1 - n_k(t_0))(1 - n_0(t_0)) = 0 , \quad (27a) \\
\sigma_{\bar{q}}^\sigma(t, t') &\sim n_{\bar{q}}(t_0)n_1(t_0) = 0 , \quad (27b) \\
\sigma_{k\bar{q}}^\sigma(t, t') &\sim n_{k\bar{q}}(t_0) = 0 . \quad (27c)
\end{align*}
\]

Employing the Langreth-Nordlander projection together with the relations \((23)\), \((24)\), \((26)\) and \((27)\) the set of Dyson equations \([B1]\) takes the following form
\[
\frac{\partial}{\partial t} \tilde{G}^< (t, t') = - \int_{-\infty}^{t'} dt_1 \tilde{\sigma}^>_q (t, t_1) b_g (t, t_1) \tilde{G}^< (t_1, t') + \int_{-\infty}^{t'} dt_1 \tilde{\sigma}^>_q (t, t_1) \tilde{B}^<_g (t, t_1) g_- (t_1, t'),
\]

(28a)

\[
\frac{\partial}{\partial t} \tilde{B}^<_g (t, t') = - \int_{-\infty}^{t'} dt_1 \left[ \tilde{\sigma}^>_k (t, t_1) g_- (t_1, t) \tilde{B}^<_g (t_1, t') + i \tilde{\sigma}^>_q (t, t_1) b_g (t, t_1) \tilde{B}^<_g (t_1, t') \right],
\]

(28b)

\[
\frac{\partial}{\partial t} \tilde{B}^<_g (t, t') = \int_{-\infty}^{t'} dt_1 \left[ \tilde{\sigma}^>_k (t, t_1) b_g (t, t_1) g_- (t_1, t') + i \tilde{\sigma}^>_q (t, t_1) \tilde{B}^<_g (t_1, t_1) b_g (t, t_1) b_s (t_1, t') \right],
\]

(28c)

\[
\Theta(t-t') \frac{\partial}{\partial t} g_- (t, t') = - \int_{t'}^{t} dt_1 \tilde{\sigma}^>_q (t, t_1) b_g (t, t_1) g_- (t_1, t'),
\]

(28d)

\[
\Theta(t-t') \frac{\partial}{\partial t} b_s (t, t') = - \int_{t'}^{t} dt_1 \left[ \tilde{\sigma}^>_q (t_1, t) g_- (t, t') b_s (t_1, t') + i \tilde{\sigma}^>_q (t_1, t) b_g (t, t_1) b_s (t_1, t') \right],
\]

(28e)

\[
\Theta(t-t') \frac{\partial}{\partial t} b_g (t, t') = 0.
\]

(28f)

The time evolution of the molecular occupation numbers \( n_- \), \( n_+ \), and \( n_q \) can be calculated from the following relations:

\[
\frac{dn_- (t)}{dt} = \left. \frac{\partial \tilde{G}^< (t, t')}{\partial t} \right|_{t=t'} + \left. \frac{\partial \tilde{G}^> (t, t')}{\partial t'} \right|_{t=t'},
\]

(29a)

\[
\frac{dn_+ (t)}{dt} = \left. \frac{\partial \tilde{B}^<_g (t, t')}{\partial t} \right|_{t=t'} + \left. \frac{\partial \tilde{B}^<_g (t, t')}{\partial t'} \right|_{t=t'},
\]

(29b)

\[
\frac{dn_q (t)}{dt} = \left. \frac{\partial \tilde{B}^<_g (t, t')}{\partial t} \right|_{t=t'} + \left. \frac{\partial \tilde{B}^<_g (t, t')}{\partial t'} \right|_{t=t'}.
\]

(29c)

Hence, we also need the adjoint Dyson equations of the lesser functions which can be calculated in the same manner. The result reads

\[
\frac{\partial}{\partial t} \tilde{G}^< (t, t') = - \int_{-\infty}^{t'} \int dt_1 \tilde{G}^< (t, t_1) \tilde{\sigma}^>_q (t_1, t') b_g (t_1, t')
\]

\[
+ \int_{-\infty}^{t} \int dt_1 \tilde{G}^< (t, t_1) \tilde{\sigma}^>_q (t, t') \tilde{B}^<_g (t, t_1),
\]

(30a)

\[
\frac{\partial}{\partial t} \tilde{B}^<_g (t, t') = - \int_{-\infty}^{t'} \int dt_1 \tilde{B}^<_g (t, t_1) \tilde{\sigma}^>_q (t_1, t') g_- (t_1, t')
\]

\[
+ \int_{-\infty}^{t} \int dt_1 \tilde{B}^<_g (t, t_1) i \tilde{\sigma}^>_q (t, t_1) b_g (t_1, t'),
\]

(30b)

\[
\frac{\partial}{\partial t} \tilde{B}^<_g (t, t') = \int_{-\infty}^{t} \int dt_1 b_g (t, t_1) \tilde{\sigma}^>_q (t, t_1) \tilde{G}^< (t_1, t')
\]

\[
+ \int_{-\infty}^{t} \int dt_1 b_g (t, t_1) i \tilde{\sigma}^>_q (t_1, t') \tilde{B}^<_g (t, t_1, t').
\]

(30c)

Equations (28) and (30) constitute the final projected set of Dyson equations that determines the dynamics of the system within the subspace \( Q = 1 \). The rate-equation-like structure of these equations is already evident. The Dyson equation for the lesser Green function of the negative ion, Eq. (30a), for instance, contains a production term proportional to \( \tilde{\sigma}^>_q \) and \( \tilde{B}^<_g \) and a loss term proportional to \( \tilde{\sigma}^>_q \) and \( \tilde{G}^< \). These terms relate to the production and loss of negative ions by the RCT electron capture and release reaction, respectively.

Since the self-energies are known in terms of the Green functions, Eqs. (28) and (30) constitute a closed set of equations. A numerical solution along the lines pioneered by Shao et al. could thus be attempted. The rather involved numerics of double-time Green functions is however not required for moderate projectile velocities. In that case the semi-classical approximation described in the next section can be employed to reduce Eqs. (28) and (30) to a set of rate equations. As far as possible applications of our approach to plasma walls are concerned, we have to keep in mind however that plasma walls are usually negatively charged with respect to the bulk plasma. Charged projectiles might thus acquire kinetic energies for which the semi-classical approximation and with it the rate equations are no longer valid. The metastable molecules however we are concerned with in the present work approach the surface with thermal energies making the rate equations an excellent approximation to the full two-time equations.

V. SEMI-CLASSICAL APPROXIMATION

The strongly oscillating factors of the projected set of Dyson equations are contained in the functions \( \tilde{\sigma}^>_q \), \( \tilde{\sigma}^>_q \), and \( \tilde{\sigma}^>_q \). If these functions are strongly peaked along the
time diagonal $t = t'$, we can apply a saddle point approximation to the integrals in (28) and (30). For instance,

$$\int_{-\infty}^{t'} dt_1 \tilde{\sigma}_k^-(t, t_1) \tilde{B}_k^+ (t, t_1) g_-(t_1, t') \approx \tilde{B}_k^+ (t, t) g_-(t, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_k^- (t, t_1).$$

(31)

$$\frac{\partial}{\partial t} \tilde{G}_k^-(t, t') \approx -b_g(t, t') \tilde{G}_k^-(t, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_q^+(t, t_1) + \tilde{B}_k^+ (t, t_1) g_- (t_1, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_k^- (t, t_1),$$

(32a)

$$\frac{\partial}{\partial t} \tilde{G}_k^-(t, t') \approx -\tilde{G}_k^-(t, t') b_g(t, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_q^+(t, t_1) + g_- (t_1, t') \tilde{B}_k^+ (t', t) \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_k^- (t, t'),$$

(32b)

$$\frac{\partial}{\partial t} \tilde{B}_k^+ (t, t') \approx -b_g(t, t') \tilde{G}_k^- (t, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_q^+(t, t_1) + \tilde{G}_k^- (t, t_1) \tilde{B}_k^+ (t, t') \int_{-\infty}^{t'} dt_1 i\tilde{\sigma}_k^- (t, t'),$$

(32c)

$$\frac{\partial}{\partial t} \tilde{B}_g^-(t, t') \approx \tilde{G}_k^- (t, t') b_g(t, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_q^+(t, t_1) + \tilde{B}_k^+ (t, t_1) \tilde{B}_g^-(t, t') \int_{-\infty}^{t'} dt_1 i\tilde{\sigma}_k^- (t, t'),$$

(32d)

$$\frac{\partial}{\partial t} \tilde{B}_g^-(t, t') \approx \tilde{B}_g^-(t, t') b_g(t, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_q^+(t, t_1) + \tilde{B}_k^+ (t, t_1) \tilde{B}_g^-(t, t') \int_{-\infty}^{t'} dt_1 i\tilde{\sigma}_k^- (t, t'),$$

(32e)

$$\frac{\partial}{\partial t} \tilde{B}_g^+(t, t') \approx b_g(t, t') \tilde{G}_k^- (t, t') \int_{-\infty}^{t'} dt_1 \tilde{\sigma}_q^+(t, t_1) + b_g(t, t') \tilde{B}_k^+ (t, t') \int_{-\infty}^{t'} dt_1 i\tilde{\sigma}_k^- (t, t'),$$

(32f)

Using Eqs. (29) we then arrive at a set of rate equations for the occupancies of the molecular pseudo-particle states,

$$\frac{dn_-(t)}{dt} \approx -\Gamma_1 (t) n_- (t) + \Gamma_0 (t) n_+ (t),$$

(33a)

$$\frac{dn_+(t)}{dt} \approx -\Gamma_0 (t) n_+ (t) - \Gamma_A (t) n_+ (t),$$

(33b)

$$\frac{dn_0 (t)}{dt} \approx \Gamma_1 (t) n_- (t) + \Gamma_A (t) n_+ (t),$$

(33c)

where the rates are given by

$$\Gamma_0 (t) = \int_{-\infty}^{t} dt_1 2\Re \{ \tilde{\sigma}_k^- (t, t_1) \},$$

(34a)

$$\Gamma_1 (t) = \int_{-\infty}^{t} dt_1 2\Re \{ \tilde{\sigma}_q^+ (t, t_1) \} + \Gamma_n,$$  

(34b)

$$\Gamma_A (t) = \int_{-\infty}^{t} dt_1 2\Re \{ i\tilde{\sigma}_k^- (t, t_1) \}.$$  

(34c)

Note, in Eq. (34b) we incorporated the natural decay of the negative ion by adding the natural decay rate $\Gamma_n = 1/\tau_n$ on the right-hand side.

Similar to what Langreth and coworkers did in the context of the neutralization of atomic ions, we have thus reduced a complicated set of Dyson equations - Eqs. (28) and (30) describing the de-excitation of a metastable molecule via the simultaneous action of the RCT channel (1) and the Auger channel (2) - to an easy to handle system of rate equations (33). The reaction rates (34) entering the rate equations are linked to quantum-kinetic quantities and thus related to the semi-empirical model.

The validity of this approximation, which is also known as the semi-classical approximation, will be demonstrated in Sec. VI.

Within the saddle-approximation the projected Dyson equations for the lesser Green functions become
For a given Auger matrix element $V_{\vec{k},\vec{q}}(t)$ the multi-dimensional integral in [35] can be calculated efficiently using the techniques and approximations outlined in Ref. [27]. The Auger matrix element, originating from the Coulomb interaction between the (active) projectile electron and an electron from the solid, is in general subject to the dynamical response of the target electrons. For metallic surfaces this is an important issue, as discussed for instance by Alvarez et al. [36]. It leads to the screening of the Coulomb interaction and should be at least accounted for by a statically screened Coulomb potential. For the dielectric surfaces we are primarily interested in, however, screening is suppressed by the energy gap. We calculate therefore $V_{\vec{k},\vec{q}}(t)$ from the bare Coulomb interaction. Thereby we overestimate somewhat the strength of the Auger matrix element.

We will now seek an analytic solution to the coupled rate equations [33]. As a starting point we first take a step back and consider the isolated decay channels of resonant electron capture, resonant electron emission, and Auger de-excitation. Singling out the individual reactions in [33] we obtain

\[
\frac{dn^{(0)}_s(t)}{dt} = -\Gamma_0(t) n^{(0)}_s(t), \quad (37a)
\]

\[
\frac{dn^{(-1)}_s(t)}{dt} = -\Gamma_1(t) n^{(-1)}_s(t), \quad (37b)
\]

\[
\frac{dn^{(A)}_s(t)}{dt} = -\Gamma_A(t) n^{(A)}_s(t). \quad (37c)
\]

The superscripts $(0)$, $(1)$, and $(A)$ identify the isolated resonant electron capture, resonant electron emission, and Auger de-excitation, respectively. Since the channels are isolated, each of the decay equations [37] comes with an analogous equation for the species that is produced.

For instance, accompanying [37a] is the equation

\[
\frac{dn^{(0)}_s(t)}{dt} = \Gamma_0(t) n^{(0)}_s(t). \quad (38)
\]

The time derivatives of $n^{(0)}_s(t)$ and $n^{(-1)}_s(t)$ differ however only in sign. Hence, $n^{(0)}_s(t)$ is given through the conservation of particles as $n^{(-0)}_s(t) = 1 - n^{(-0)}_s(t)$ (valid when the channels are isolated). Consequently, the additional equations of type [38] do not contain any additional information and can be omitted. Using the initial condition $n^{(0)}_s(t_0) = n^{(A)}_s(t_0) = 1$ the system [37] can be solved straightforwardly. The result is

\[
n^{(0)}_s(t) = e^{-\int_{t_0}^t dt_1 \Gamma_0(t_1)}, \quad (39a)
\]

\[
n^{(-1)}_s(t) = n^{(-1)}_s(t') e^{-\int_{t'}^t dt_1 \Gamma_1(t_1)}, \quad (39b)
\]

\[
n^{(A)}_s(t) = e^{-\int_{t_0}^t dt_1 \Gamma_A(t_1)}. \quad (39c)
\]

Now we are in position to use these occupancies to calculate the solution of the full, coupled system of rate equations [33]. First we consider the equation for $n_s$. Using the initial condition $n_s(t_0) = 1$, Eq. [33a] can be solved by separation of variables and yields

\[
n_s(t) = e^{-\int_{t_0}^t dt_1 \Gamma_0(t_1) + \Gamma_1(t_1)} = n_s^{(-0)}(0) n_s^{(A)}(t). \quad (40)
\]

To solve [33b] for the occupancy of the negative ion state we first multiply this equation by a factor $\exp(\int_{t_0}^t dt_2 \Gamma_1(t_2))$ and rearrange the terms to obtain

\[
\frac{d}{dt} \left( n_-(t) e^{\int_{t_0}^t dt_2 \Gamma_1(t_2)} \right) = \Gamma_0(t) n_s(t) e^{\int_{t_0}^t dt_2 \Gamma_1(t_2)}. \quad (41)
\]

Relabeling then $t$ as $t_1$ and integrating the equation from $t_1 = t_0$ to $t_1 = t$ while minding the initial condition $n_-(t_0) = 0$ yields after a further rearrangement

\[
n_-(t) = \int_{t_0}^t dt_1 \Gamma_0(t_1) n_s(t_1) e^{-\int_{t_1}^t dt_2 \Gamma_1(t_2)} = \int_{t_0}^t dt_1 \left[ -\frac{dn^{(0)}_s(t_1)}{dt_1} \right] n_s^{(A)}(t_1) n^{(-1)}_s(t_1) n^{(1)}_s(t_1). \quad (42)
\]

Finally, the occupancy of the molecular ground state $n_g$, that is, the solution of Eq. [33c], is given through the particle conservation property of the full system [33],

\[
n_g(t) = 1 - n_s(t) - n_-(t). \quad (43)
\]

Note, the molecular occupancies satisfying the combined rate equation scheme Eqs. [40], [42] and [43] are completely determined by the occupancies $n^{(0)}_s$, $n^{(-1)}_s$ and $n^{(A)}_s$. Moreover, when the Auger channel is disabled by setting $\Gamma_A(t) = 0$, Eqs. [40], [42] and [43] reduce to the rate equations derived by intuitive means for the isolated RCT channel [28]. Hence, the quantum-kinetic treatment justifies a posteriori the intuitive approach taken by us in Ref. [28].

We now turn to the spectrum of the emitted electron. While the evolution of the $\vec{q}$ states has not been considered explicitly in our quantum-kinetic calculation, the occupancy of these states can nevertheless be extracted from the solution of [33].

From the reactions [41] and [2] it is obvious that the probability for emitting an electron $n_e(t)$ is equal to the occupancy of the ground state $n_g(t)$ as every ground state molecule must have resulted from the reaction chain and, hence, must be accompanied by an emitted electron. Consequently, the evolution of $n_e(t)$ is governed by Eq. [33c]. Due to the image potential, however, not every emitted electron can escape the surface. In particular, the escape is only possible when the emitted electron's perpendicular kinetic energy $e_{\perp}^\infty = e_{\perp}^0 \cos^2(q_d)$ is higher than the absolute value of the image potential $V_i$ at the position of emission. The latter can be approximated by the position of the molecule's center of mass at the time of emission.

To incorporate the image potential effect, we adopt a two step strategy. As a start we introduce the spectral
rates $\Gamma_1(t)$ and $\Gamma_A(t)$ which are not restricted by the image potential effect by writing

$$\Gamma_{1/A}(t) = \int_0^\infty d\varepsilon_q^\infty \langle \varepsilon_q^\infty, t \rangle \ ,$$

and afterwards we let $\Gamma_{1/A} \rightarrow \bar{\Gamma}_{1/A}$ with

$$\bar{\Gamma}_{1/A}(\varepsilon_q^\infty, t) = \int_0^\frac{\bar{\pi}}{2} dq \int_0^{2\pi} d\varphi \times \Theta(V_i(z_R(t)) + \varepsilon_q^\infty) \frac{d^2\bar{\Gamma}_{1/A}(\varepsilon_q^\infty, t)}{dq dq \varphi} \ .$$

An explicit expression for the spectral RCT emission rate $\bar{\Gamma}_1$ has been given in Ref. 28. The spectral Auger rate $\bar{\Gamma}_A$ may be calculated from Eq. (43) by stripping out the $q_r$ integral and multiplying the result by $m_e/\hbar^2 q_r$. Introducing the spectral decomposition of the rates in Eq. (33e) and identifying $n_{\varepsilon_q}$ with $\bar{n}_\varepsilon$ we obtain

$$\frac{dn_{\varepsilon_q}(t)}{dt} = \int_0^\infty d\varepsilon_q^\infty \bar{\Gamma}_1(\varepsilon_q^\infty, t)n_-(t)$$

$$\quad + \int_0^\infty d\varepsilon_q^\infty \bar{\Gamma}_A(\varepsilon_q^\infty, t)n_+(t) \ ,$$

where $\bar{n}_{\varepsilon_q}$ denotes the probability for emitting an electron that can escape from the surface. Integrating over the time argument with the initial condition $\bar{n}_{\varepsilon_q}(t_0) = 0$ and taking the derivative with respect to $\varepsilon_q^\infty$ we find for the spectrum of the emitted electron at time $t$

$$\frac{dn_{\varepsilon_q}}{d\varepsilon_q^\infty} \bigg|_{t_0} = \int_{t_0}^t dt_1 \bar{\Gamma}_1(\varepsilon_q^\infty, t_1)n_-(t_1)$$

$$\quad + \int_{t_0}^t dt_1 \bar{\Gamma}_A(\varepsilon_q^\infty, t_1)n_+(t_1) \ .$$

The secondary electron emission coefficient $\gamma_e$, that is, the probability for having emitted an electron after the collision is completed, is given by

$$\gamma_e = \bar{n}_{\varepsilon_q}(\infty) \ .$$

The occupancies of the molecular pseudo-particle states $|40\rangle$, $|42\rangle$, $|43\rangle$ and the spectrum of the emitted electron $|47\rangle$ are the main result of this work. The occupancies fully characterize the temporal evolution of the de-excitation of a metastable N$_2$(3Σ$_u^+$) molecule at a surface when both the RCT and the Auger channel are open. The ingredients required as an input, the occupancies arising from the isolated processes $n^\infty_-$, $n^\infty_+$, $n^\infty_A$ and the image potential adjusted spectral rates $\bar{\Gamma}_1$, $\bar{\Gamma}_A$, can be obtained from the quantum-kinetic calculation and thus from the semi-empirical model.

Assuming the parameters of the model Hamiltonian to be a priori fixed, either by experiment or by quantum-chemical calculations, there is no free parameter in the kinetic equations which can be a posteriori adjusted to experimental data concerning the surface collision itself.

VI. NUMERICAL RESULTS

In this section we present numerical results based on the semi-classical equations of Sec. V. We consider the particular case of a diamond surface and restrict our investigations to normal incident with a molecular kinetic energy of 50 meV. The turning point of the molecule’s trajectory is then 4.4 Bohr radii. As in our previous work 27,28 we treat only the two principal orientations of the metastable N$_2$(3Σ$_u^+$) molecule: molecular axis perpendicular to the surface and molecule axis parallel to the surface. Furthermore, we omit the surface induced decay channel by setting $\Gamma_1(t) = \Gamma_A$. As our previous investigations showed, this is an excellent approximation.

The numerics necessary to calculate within the semi-empirical model the Auger matrix element $V_{\varepsilon_q}$ has been
the molecule along a distance of 0.025 \(a_B\). For \(\tilde{\sigma}_{\tilde{k}q}\) the fall-off is even more drastic. The behavior for shifted anti-diagonals as well as for parallel orientation is very similar and hence not shown here. Altogether, we can conclude that with respect to the macroscopic motion of the molecule the functions \(\tilde{\sigma}_{\tilde{k}}\) and \(\tilde{\sigma}_{\tilde{k}q}\) are indeed sufficiently peaked on the time diagonal. Thus, the semi-classical approximation is valid in our case.

We now turn to the occupancies of the molecular pseudo-particle states, that is, the probabilities with which the molecular configurations involved in the de-excitation process appear in the course of the scattering event. The time dependent occupancy of the ground state \(n_g\), the metastable state \(n_\ast\), and negative ion state \(n_{\ast\ast}\) can be calculated from Eqs. (40), (42), and (43), respectively. The results are depicted in a semi-logarithmic plot in Fig. 5.

Inspection of the curves in Fig. 5 reveals that even close to the surface the occupancy of the negative ion state is rather low. Hence, the metastable projectile is almost immediately converted into a ground state molecule and thus stays mostly neutral during the whole collision. In Fig. 5 this fact is recognizable at the crossing point of the \(n_\ast\) and \(n_g\) curves which occurs at approximately half filling of both levels. The low occupancy of the negative ion state is caused by the high efficiency of the natural decay channel\(^{28}\) and not by the Auger channel destroying the metastable molecule, which is the generating species of the negative ion. In fact, it is the other way around and in order to substantiate this claim, we investigate below the relative efficiency of the RCT and Auger channel by considering the respective reaction rates. Before we do that let us note however that due the neutrality of the projectile along most of its path it would not gain much kinetic energy in front of a charged surface. We expect therefore the semi-classical approximation and hence the rate equations to be also valid in case the de-excitation occurred in front of a negatively charged plasma wall.

Figure 6 shows the rates of resonant electron capture \(\Gamma_0\) and Auger de-excitation \(\Gamma_A\). For both channels the rates are highest at the molecule’s turning point (approximately 4.4 \(a_B\)) which is the point of smallest molecule-surface separation and strongest molecule-surface interaction. When the molecule-surface distance is increased, the rates decrease exponentially. The RCT channel’s rate is about two orders of magnitude higher than the Auger channel’s rate. Consequently, the RCT channel captures surface electrons much more efficiently than the Auger channel. In fact, the RCT channel is so effective in capturing electrons that it under-runs the Auger channel by destroying its starting basis, the metastable state. As a result, in the combined two-channel system the Auger channel’s performance is significantly diminished as compared to the isolated Auger reaction.

This conclusion may be verified by considering the term in the rate equations which is responsible for the production of the ground state molecule by an Auger de-
The combined occupation of the reaction channels. The latter can be obtained by setting \( \bar{\rho}_A \equiv 0 \) or \( \bar{\rho}_1 \equiv 0 \). As can be seen, the isolated RCT spectra exhibit a strong peak at about 1.5 eV and slowly drop off for higher energies. The isolated Auger spectra, on the other hand, monotonously increase until approximately 2.8 eV and then immediately fall off. The low energy cut-off of all curves is due to the trapping of the emitted electron in the image potential close to the surface when its perpendicular energy is too low. The combined spectra almost equal the respective isolated RCT spectra. Only in the range from 1.5 eV to 2.5 eV are the combined spectra slightly increased with respect to the RCT curves. This minor enlargement is due to the Auger channel and supports our previous finding that the RCT channel dominates the Auger channel.

The combined spectra in Fig. 7 are different from the simple addition of the isolated spectra. This behavior is caused by the unified treatment of the RCT and Auger reaction channels. The effect would be even more pronounced for molecular species forming stable negative ions. Here the resonant electron emission would be almost completely blocked as the surface induced decay is always very weak. The resonant electron capture, however, would be still very efficient in destroying the initial species. Consequently, the spectrum of the emitted electron would resemble the Auger spectrum in shape but would be strongly decreased in magnitude.

The secondary electron emission coefficients are given by the area beneath the curves in Fig. 7 and are summarized in Table 1. In accordance with our previous observations the emission coefficients are not changed significantly by the inclusion of the Auger channel. A similar result was found by Stracke et al.\(^{(25)}\) for \( N_2(3\Sigma^+_u) \) de-exciting at a tungsten surface. Their experimental measurements imply that only about 10% of the secondary electron emission coefficient is made up by the Auger channel.

excitation. It is given by (see Eqs. 33c and 40)

\[
\Gamma_A(t) n_+(t) = \Gamma_A(t) n_+^{(A)}(t) n_+^{(0)}(t). \tag{49}
\]

Here the factor \( n_+^{(0)}(t) \) is only present in the combined two-channel system but not in the isolated Auger system. Without explicit proof but based on numerical observations we note that the term \( n_+^{(0)}(t) \) is almost identical to the combined occupation \( n_+^t \) depicted in Fig. 5. Hence, in the combined system the Auger channel’s ground state production term \( \bar{\rho}_A \) is strongly suppressed already in the incoming branch of the trajectory.

Finally, we turn to the energy spectrum of the emitted electron. Figure 7 depicts the emission spectrum at \( t = \infty \) for the combined two-channel reaction as well as for the isolated reaction channels. The latter can be obtained by setting in \( \bar{\rho}_A \equiv 0 \) or \( \bar{\rho}_1 \equiv 0 \). As can be seen, the isolated RCT spectra exhibit a strong peak at about 1.5 eV and slowly drop off for higher energies. The isolated Auger spectra, on the other hand, monotonously increase until approximately 2.8 eV and then immediately fall off. The low energy cut-off of all curves is due to the trapping of the emitted electron in the image potential close to the surface when its perpendicular energy is too low. The combined spectra almost equal the respective isolated RCT spectra. Only in the range from 1.5 eV to 2.5 eV are the combined spectra slightly increased with respect to the RCT curves. This minor
ties with which the molecular configurations contributing pseudo-particles a set of rate equations for the probabili-

ties integrals in the self-energies we finally derived from the energies and a saddle-point approximation for the time self-consistent non-crossing approximation for the self-diagrammatic quantum-kinetic calculation. Using the particle operators, could then be made amenable to a gle model Hamiltonian which, with the help of pseudo-

ing and the Auger channel could be cast into a sin-

gular bosons. As a result, both the resonant tunnel-

how this can be done with projection operators and aux-

liary bosons. By construction, the semi-empirical model is not restricted to a partic-

ular projectile-target combination. Having applications of the model to charge-transferring processes at plasma walls in mind, where a great variety of different projectile-
target combinations occurs, we consider this as a real advan-
tage. Another advantage is that the semi-empirical model separates the many-body theoretical description of the non-interacting projectile and target from the quantum-kinetic treatment of the scattering process. The former is simply encapsulated in the parameters of the model Hamiltonian and the latter is performed by Green functions. This is particularly advantageous in cases where the surface scattering event is studied primarily because of its connection to the physics of quantum-

impurities.

For the semi-empirical model to work a method was re-

quired to assign and control the energies of the two-level system in accordance to the reaction channels, that is, to have the two-level system describing all three molecular configurations involved in the de-excitation process: the metastable \( \Sigma\_u^+ \) molecule, the negative ion \( \Sigma\_g^- \), and the molecular ground state \( \Sigma\_g^+ \). We showed how this can be done with projection operators and auxiliary bosons. As a result, both the resonant tunnel-

ing and the Auger channel could be cast into a single model Hamiltonian which, with the help of pseudo-

particle operators, could then be made amenable to a diagrammatic quantum-kinetic calculation. Using the self-consistent non-crossing approximation for the self-

energies and a saddle-point approximation for the time integrals in the self-energies we finally derived from the Dyson equations for the propagators of the molecular pseudo-particles a set of rate equations for the probabili-

ties with which the molecular configurations contributing to the de-excitation process can be found in the course of the scattering event. Without the Auger channel, the system of rate equations reduces to the one postulated by us before on intuitive grounds for the RCT channel alone. The present work justifies therefore this reasoning a posteriori.

For the particular case of a diamond surface we veri-

fied the validity of the semi-classical approximation and investigated for a collision energy of 50 meV the inter-

play of the resonant tunneling and the Auger channel. In particular, we analyzed the temporal evolution of the probabilities with which the projectile is to be found in the \( \Sigma\_u^+ \) state, \( \Sigma\_g^- \), or the \( \Sigma\_g^+ \) state and explicitly calculated the rates for electron capture due respectively to tunneling and Auger de-excitation. We also obtained the spectrum of the emitted electron and the secondary electron emission coefficient \( \gamma \) which are the two quantities of main importance for the modeling of gas discharges. Our results indicate for a diamond sur-

face and a kinetic energy of 50 meV the resonant tunnel-

ing channel clearly dominating the Auger channel. The contribution of the Auger channel to the secondary electron emission coefficient lies only in the range of a few percent. The overall \( \gamma \) coefficient is on the order of \( 10^{-1} \) in agreement with what has to be typically assumed to make kinetic simulations of dielectric barrier discharges reproduce the properties of the discharge.

With minor modifications the semi-empirical model and its quantum-kinetic handling leading to the easy to use set of rate equations can be adopted to other plasma-

relevant charge-transferring surface collisions as well. At least for low-energy collisions, where the projectile veloc-

ities are low enough to allow for a reduction of the full double-time kinetic equations to a set of simple rate equations, we can thus hope to replace the rules of the thumb which are often needed to characterize secondary electron emission due to neutral and charged heavy plasma species hitting the plasma wall by plausible quantitative estimates.

|       | \( \gamma\_u^+ \) | \( \gamma\_g^- \) |
|-------|-----------------|-----------------|
| RCT   | 0.16685         | 0.15873         |
| Auger | 0.02760         | 0.04921         |
| RCT & Auger | 0.16754 | 0.16335 |

TABLE I: Secondary electron emission coefficients in parallel (\( \gamma\_u^+ \)) and perpendicular (\( \gamma\_g^- \)) orientation at a kinetic energy of 50 meV.

VII. CONCLUSIONS

We constructed in this work a semi-empirical gen-

eralized Anderson-Newns model for secondary electron emission due to de-excitation of metastable \( \Sigma\_u^+ \) molecules at dielectric surfaces. The model treats Auger de-excitation and the two-step resonant charge transfer process, where the \( \Sigma\_g^- \) ion acts as a relay state, on an equal footing. It reduces the molecular projectile to a two-level system representing the molecular orbitals which change their occupancies during the reaction and treats the surface as a simple step potential confining the electrons of the solid. By construction, the semi-empirical model is not restricted to a partic-

ular projectile-target combination. Having applications of the model to charge-transferring processes at plasma walls in mind, where a great variety of different projectile-
target combinations occurs, we consider this as a real advan-
tage. Another advantage is that the semi-empirical model separates the many-body theoretical description of the non-interacting projectile and target from the quantum-kinetic treatment of the scattering process. The former is simply encapsulated in the parameters of the model Hamiltonian and the latter is performed by Green functions. This is particularly advantageous in cases where the surface scattering event is studied primarily because of its connection to the physics of quantum-

impurities.

For the semi-empirical model to work a method was re-

quired to assign and control the energies of the two-level system in accordance to the reaction channels, that is, to have the two-level system describing all three molecular configurations involved in the de-excitation process: the metastable \( \Sigma\_u^+ \) molecule, the negative ion \( \Sigma\_g^- \), and the molecular ground state \( \Sigma\_g^+ \). We showed how this can be done with projection operators and auxiliary bosons. As a result, both the resonant tunnel-

ing and the Auger channel could be cast into a single model Hamiltonian which, with the help of pseudo-

particle operators, could then be made amenable to a diagrammatic quantum-kinetic calculation. Using the self-consistent non-crossing approximation for the self-

energies and a saddle-point approximation for the time integrals in the self-energies we finally derived from the Dyson equations for the propagators of the molecular pseudo-particles a set of rate equations for the probabili-

ties with which the molecular configurations contributing to the de-excitation process can be found in the course of the scattering event. Without the Auger channel, the system of rate equations reduces to the one postulated by us before on intuitive grounds for the RCT channel alone. The present work justifies therefore this reasoning a posteriori.

For the particular case of a diamond surface we veri-

fied the validity of the semi-classical approximation and investigated for a collision energy of 50 meV the inter-

play of the resonant tunneling and the Auger channel. In particular, we analyzed the temporal evolution of the probabilities with which the projectile is to be found in the \( \Sigma\_u^+ \) state, \( \Sigma\_g^- \), or the \( \Sigma\_g^+ \) state and explicitly calculated the rates for electron capture due respectively to tunneling and Auger de-excitation. We also obtained the spectrum of the emitted electron and the secondary electron emission coefficient \( \gamma \) which are the two quantities of main importance for the modeling of gas discharges. Our results indicate for a diamond sur-

face and a kinetic energy of 50 meV the resonant tunnel-

ing channel clearly dominating the Auger channel. The contribution of the Auger channel to the secondary electron emission coefficient lies only in the range of a few percent. The overall \( \gamma \) coefficient is on the order of \( 10^{-1} \) in agreement with what has to be typically assumed to make kinetic simulations of dielectric barrier discharges reproduce the properties of the discharge.

With minor modifications the semi-empirical model and its quantum-kinetic handling leading to the easy to use set of rate equations can be adopted to other plasma-

relevant charge-transferring surface collisions as well. At least for low-energy collisions, where the projectile veloc-

ities are low enough to allow for a reduction of the full double-time kinetic equations to a set of simple rate equations, we can thus hope to replace the rules of the thumb which are often needed to characterize secondary electron emission due to neutral and charged heavy plasma species hitting the plasma wall by plausible quantitative estimates.

Acknowledgments

Johannes Marbach was funded by the federal state of Mecklenburg-Western Pomerania through a postgraduate scholarship. In addition this work was supported by the Deutsche Forschungsgemeinschaft through the Transregional Collaborative Research Center SFB/TRR24.

Appendix A: Langreth-Wilkins rules

The Langreth-Wilkins rules are a powerful tool for the analytic continuation of propagators defined on a complex time contour onto the real time axis. Their explicit form depends on the initial definition of the Green functions. Unfortunately, there is no common agreement about the usage of \( i \) factors. Moreover, rules published in
the past sometimes contained typographic errors\cite{17,19}. Due to these reasons we list the explicit form of the Langreth-Wilkins rules used in this work. The rules can be derived in the standard way\cite{17,18} using however the definitions\cite{17,19} for the Green functions. In the following $F$ and $B$ denote fermion and boson propagators, respectively.

To analytically continue the boson-like fermion-antifermion pair

$$B(t,t') = F_1(t,t') F_2(t',t),$$

we utilize

$$B^>(t,t') = iF^<(t,t') F^<_2(t',t),$$
$$B^<(t,t') = iF^<(t,t') F^<_2(t',t),$$
$$B^R(t,t') = i\left[ F^<_1(t,t') F^>_2(t',t) + F^R_1(t,t') F^<_2(t',t) \right],$$
$$B^A(t,t') = i\left[ F^<_1(t,t') F^<_2(t',t) + F^A_1(t,t') F^<_2(t',t) \right].$$

For the fermion-like fermion-boson pair

$$F(t,t') = F_1(t,t') B_1(t,t'),$$

the following rules hold

$$F^>(t,t') = -iF^<_1(t,t') B^<_1(t,t'),$$
$$F^<(t,t') = -iF^<_1(t,t') B^<_1(t,t'),$$
$$F^R(t,t') = -i\left[ F^<_1(t,t') B^<_1(t,t') + F^R_1(t,t') B^<_1(t,t') \right],$$
$$F^A(t,t') = -i\left[ F^<_1(t,t') B^<_1(t,t') + F^A_1(t,t') B^<_1(t,t') \right].$$

The boson-like boson-boson pair

$$B(t,t') = B_1(t,t') B_2(t',t),$$

can be analytically continued by

$$B^>(t,t') = -iB^<_1(t,t') B^<_2(t',t),$$
$$B^<(t,t') = -iB^<_1(t,t') B^<_2(t',t),$$
$$B^R(t,t') = -i\left[ B^R_1(t,t') B^<_2(t',t) + B^<_1(t,t') B^R_2(t',t) \right],$$
$$B^A(t,t') = -i\left[ B^A_1(t,t') B^<_2(t',t) + B^<_1(t,t') B^A_2(t',t) \right].$$

Finally, to analytically continue the boson-like boson-antiboson pair

$$B(t,t') = B_1(t,t') B_2(t',t),$$

we use

$$B^>(t,t') = -iB^<_1(t,t') B^<_2(t',t),$$
$$B^<(t,t') = -iB^<_1(t,t') B^<_2(t',t),$$
$$B^R(t,t') = -i\left[ B^<_1(t,t') B^A_2(t',t) + B^R_1(t,t') B^<_2(t',t) \right],$$
$$B^A(t,t') = -i\left[ B^<_1(t,t') B^A_2(t',t) + B^A_1(t,t') B^<_2(t',t) \right].$$

Furthermore, for the analytic continuation of the contour integrals within the Dyson equations we also need to project terms of the form

$$D(t,t') = \int dt_1 D_1(t,t_1) D_2(t_1,t'),$$

where $D$, $D_1$ and $D_2$ are either fermion-like or boson-like. This can be accomplished by the rules

$$D^>(t,t') = \int_{-\infty}^{\infty} dt_1 \left[ D^R_1(t,t_1) D^<_2(t_1,t') + D^<_1(t,t_1) D^>_2(t_1,t') \right],$$
$$D^<(t,t') = \int_{-\infty}^{\infty} dt_1 \left[ D^R_1(t,t_1) D^<_2(t_1,t') + D^<_1(t,t_1) D^>_2(t_1,t') \right],$$
$$D^R(t,t') = \int_{-\infty}^{\infty} dt_1 \left[ D^R_1(t,t_1) D^R_2(t_1,t') + D^R_1(t,t_1) D^R_2(t_1,t') \right],$$
$$D^A(t,t') = \int_{-\infty}^{\infty} dt_1 \left[ D^A_1(t,t_1) D^A_2(t_1,t') + D^A_1(t,t_1) D^A_2(t_1,t') \right].$$

**Appendix B: Dyson equations**

In this appendix we summarize the Dyson equations for the analytic pieces of the molecular Green functions $G_-$, $B_+$, and $B_-$ as obtained by an application of the Langreth-Wilkins rules of appendix\cite{18} to the self-energies shown in Fig. 3.

The lesser Green functions satisfy
\(\left(\frac{i}{\hbar} \frac{\partial}{\partial t} - \frac{\varepsilon_-(t)}{\hbar}\right) G^<(t, t') = \int_{-\infty}^{t'} dt_1 \left[ \sigma^R_k(t, t_1) B^R_k(t, t_1) G^<(t_1, t') + \sigma^R_k(t, t_1) B^<_k(t, t_1) G^>(t_1, t') + \sigma^R_q(t, t_1) B^R_q(t, t_1) G^<(t_1, t') + \sigma^R_q(t, t_1) B^<_q(t, t_1) G^>(t_1, t') \right] \) \hspace{1cm} (B1a)

\(\int_{-\infty}^{t'} dt_1 \left[ \sigma^>_k(t, t_1) B^>_k(t, t_1) G^A(t_1, t') + \sigma^>_q(t, t_1) B^>_q(t, t_1) G^>(t_1, t') \right] \),

\(\left(\frac{i}{\hbar} \frac{\partial}{\partial t} - \frac{\varepsilon_+(t)}{\hbar}\right) G^<(t, t') = \int_{-\infty}^{t'} dt_1 \left[ \sigma^R_k(t, t_1) B^R_k(t, t_1) G^<(t_1, t') + \sigma^A_k(t, t_1) G^>(t_1, t_1) B^>_k(t, t_1) + \sigma^R_q(t, t_1) B^R_q(t, t_1) G^<(t_1, t') + \sigma^A_q(t, t_1) G^>(t_1, t_1) B^>_q(t, t_1) \right] \) \hspace{1cm} (B1b)

\(\int_{-\infty}^{t'} dt_1 \left[ \sigma^>_k(t, t_1) B^>_k(t, t_1) G^A(t_1, t') + \sigma^>_q(t, t_1) B^>_q(t, t_1) G^>(t_1, t') \right] \),

\(\left(\frac{i}{\hbar} \frac{\partial}{\partial t} - \frac{\varepsilon_g(t)}{\hbar}\right) B^R_g(t, t') = \delta(t - t') + \int_{t'}^{t} dt_1 \left[ \sigma^R_k(t, t_1) B^R_k(t, t_1) G^R(t_1, t') + \sigma^R_k(t, t_1) B^<_k(t, t_1) G^R(t_1, t') + i\sigma^R_k(t, t_1) B^>_k(t_1, t') + i\sigma^R_q(t, t_1) B^>_q(t_1, t') \right] \) \hspace{1cm} (B1d)

\(\int_{-\infty}^{t'} dt_1 \left[ \sigma^A_k(t, t_1) G^R(t_1, t_1) B^A_k(t, t_1) + \sigma^R_k(t, t_1) B^<_k(t, t_1) G^R(t_1, t') + i\sigma^R_k(t, t_1) B^>_k(t_1, t') + i\sigma^R_q(t, t_1) B^>_q(t_1, t') \right] \),

\(\left(\frac{i}{\hbar} \frac{\partial}{\partial t} - \frac{\varepsilon_g(t)}{\hbar}\right) B^R_g(t, t') = \delta(t - t') + \int_{t'}^{t} dt_1 \left[ \sigma^A_q(t, t_1) G^R(t_1, t_1) B^A_q(t, t_1) + \sigma^R_q(t, t_1) B^<_q(t, t_1) G^R(t_1, t') + i\sigma^R_q(t, t_1) B^>_q(t_1, t') + i\sigma^R_k(t, t_1) B^>_k(t_1, t') \right] \) \hspace{1cm} (B1e)

\(\int_{-\infty}^{t'} dt_1 \left[ \sigma^A_k(t, t_1) G^R(t_1, t_1) B^A_k(t, t_1) + \sigma^R_k(t, t_1) B^<_k(t, t_1) G^R(t_1, t') + i\sigma^R_k(t, t_1) B^>_k(t_1, t') + i\sigma^R_q(t, t_1) B^>_q(t_1, t') \right] \).

The greater and advanced Green function can be obtained from the definitions \[19\] and the symmetry relations \[20\].

\[1\] H.-P. Winter and J. Burgdörfer, eds., \textit{Slow heavy-particle induced electron emission from solid surface} (Springer-Verlag, Berlin Heidelberg, 2007).

\[2\] J. W. Rabalais, ed., \textit{Low energy ion-surface interaction} (Wiley and Sons, New York, 1994).

\[3\] X. He and J. A. Yarmoff, Phys. Rev. Lett. \textbf{105}, 176806 (2010).

\[4\] J. Merino and J. B. Marston, Phys. Rev. B \textbf{58}, 6982 (1998).

\[5\] H. Shao, D. C. Langreth, and P. Nordlander, Phys. Rev. B \textbf{49}, 13929 (1994).

\[6\] A. C. Hewson, ed., \textit{The Kondo problem to heavy fermions} (Cambridge University Press, Cambridge, 1993).

\[7\] H. Grabert and M. H. Devoret, eds., \textit{Single charge tun-
nelling: Coulomb blockade phenomena in nanostructures
(Plenum Press, New York, 1992).

8 M. A. Lieberman and A. J. Lichtenberg, Principles of plasma discharges and materials processing (Wiley-Interscience, New York, 2005).

9 R. Brandenburg, V. A. Maiorov, Y. B. Golubovskii, H.-E. Wagner, J. Behnke, and J. F. Behnke, J. Phys. D: Appl. Phys 38, 2187 (2005).

10 F. Massines, S. P., N. Gherardi, C. Khamphan, and A. Riccard, Surface and Coatings Technology 174-175, 8 (2003).

11 K. H. Becker, K. H. Schoenbach, and J. G. Eden, J. Phys. D: Appl. Phys 39, R55 (2006).

12 K. J. Snowdon, R. Hentschke, A. Närnmann, W. Heiland, E. Mühlting, and W. Eckstein, Nucl. Instr. Meth. Phys. Res. B 23, 309 (1987).

13 R. Zimny, Z. L. Miskovic, N. N. Nedeljkovic, and L. D. Nedeljkovic, Surface Science 255, 135 (1991).

14 A. V. Onufriev and J. B. Marston, Phys. Rev. B 53, 13340 (1996).

15 C. A. Keller, A. C. Lavery, and B. H. Cooper, Phys. Rev. B 58, 10959 (1998).

16 N. Lorente, M. A. Cazalilla, J. P. Gauyacq, D. Teillet-Billy, and P. M. Echenique, Surface Science 411, L888 (1998).

17 M. A. Vicente Alvarez, V. H. Ponce, and E. C. Goldberg, Phys. Rev. B 57, 14919 (1998).

18 E. C. Goldberg, R. Monreal, F. Flores, H. H. Brongersma, and P. Bauer, Surface Science 440, L875 (1999).

19 R. T. Pepino and G. G. Kleiman, Solid State Commun. 124, 317 (2002).

20 N. P. Wang, E. A. García, R. Monreal, F. Flores, E. C. Goldberg, H. H. Brongersma, and P. Bauer, Phys. Rev. A 64, 012901 (2001).

21 E. A. García, N. P. Wang, R. C. Monreal, and E. C. Goldberg, Phys. Rev. B 67, 205426 (2003).

22 W. Heiland, in Low energy ion-surface interaction, edited by J. W. Rabalais (Wiley and Sons, New York, 1994), p. 313.

23 U. Imke, K. J. Snowdon, and W. Heiland, Phys. Rev. B 34, 48 (1986).

24 U. Imke, K. J. Snowdon, and W. Heiland, Phys. Rev. B 34, 41 (1986).

25 P. Stracke, F. Wiegershaus, S. Krischok, and V. Kempter, Surface Science 396, 212 (1998).

26 N. Lorente, D. Teillet-Billy, and J. P. Gauyacq, Surface Science 432, 155 (1999).

27 J. Marbach, F. X. Bronold, and H. Fehske, Phys. Rev. B 84, 085443 (2011).

28 J. Marbach, F. X. Bronold, and H. Fehske, Eur. Phys. J. D 66, 106 (2012).

29 P. Coleman, Phys. Rev. B 29, 3035 (1984).

30 N. S. Wingreen and Y. Meir, Phys. Rev. B 49, 11040 (1994).

31 D. C. Langreth and P. Nordlander, Phys. Rev. B 43, 2541 (1991).

32 R. Aguado and D. C. Langreth, Phys. Rev. B 67, 245307 (2003).

33 C. M. Dutta and P. Nordlander, Prog. Surf. Science 67, 155 (2001).

34 J. B. Marston, D. R. Andersson, E. R. Behringer, B. H. Cooper, C. A. DiRubio, G. A. Kimmel, and C. Richardson, Phys. Rev. B 48, 7809 (1993).

35 D. C. Langreth and J. W. Wilkins, Phys. Rev. B 6, 3189 (1972).

36 U. Kaldor, J. Chem. Phys. 81, 2406 (1984).

37 M. Honigmann, R. J. Buenker, and H. P. Liebermann, J. Chem. Phys. 125, 234304 (2006).

38 P. Kürpick and U. Thumm, Phys. Rev. A 54, 1487 (1996).

39 G. Carmona and J. L. Cardoso, Rev. Mex. Fis. Suppl. 48, 010000 (2002).

40 H. D. Hagstrum, Phys. Rev. 96, 325 (1954).

41 H. D. Hagstrum, Phys. Rev. 122, 83 (1961).

42 G. Katz and R. Kosloff, J. Chem. Phys. 103, 9475 (1995).

43 H. Haug and A.-P. Jauho, Quantum kinetics in transport and optics of semiconductors (Springer-Verlag, Berlin, 1996).