

Zusammenfassung der Dissertation

zum Thema: „Quantum-Kinetic Modeling of Electron Release in Low-Energy Surface Collisions of Atoms and Molecules“

vorgelegt von

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In this work we present a theoretical description of electron release in the collision of atomic and molecular projectiles with metallic and especially dielectric surfaces. The associated electron yield, the secondary electron emission coefficient, is an important input parameter for numerical simulations of dielectric barrier discharges and other bounded low-temperature gas discharges. The available reference data for emission coefficients is, however, very sparse and often uncertain, especially for molecular projectiles. With the present work we aim to contribute to the filling of these gaps by providing a flexible and easy-to-use model that allows for a convenient calculation of the emission coefficient and related quantities for a wide range of projectile-surface systems and the most dominant reaction channels.

In particular, we concentrate on the de-excitation of diatomic molecules using the example of the dominant metastable state of the nitrogen molecule, $N_2(^3\Sigma_u^+)$. The latter can de-excite through a two-step resonant reaction in which it first resonantly captures a surface electron to form the $N_2(^2\Pi_g)$ shape resonance which subsequently decays, either due to its natural lifetime or the molecule-surface interaction, by resonantly emitting an electron. Furthermore, in front of a surface $N_2(^3\Sigma_u^+)$ can also de-excite in an indirect Auger process. The direct Auger de-excitation mechanism, on the other hand, is spin-blocked for $N_2(^3\Sigma_u^+)$. However, since it might be important for other metastable species, we, nevertheless, include it in our description. All three of these de-excitation channels are capable of generating secondary electrons provided that the surface band structure allows for the respective transition. In addition, we also regard the interplay of resonant and Auger neutralization of singly charged positive ions where we explicitly consider the cases of $He^+(^2S_{1/2})$, $Ar^+(^2P_{3/2})$ and $N_2^+(^2\Pi_u)$. Here, however, only the Auger channel can produce secondary electrons while the resonant reaction merely neutralizes the incident ion.

In order to study all of these processes, we construct a semi-empirical effective model of the projectile-surface system which is characterized by only a small number of material parameters. This is achieved by treating electronic states of the surface and the projectile independently within an interaction-free description. The energy bands of the surface, on the one hand, are modeled by a free electron gas inside a square potential well. For the projectile, on the other hand, we restrict our analysis

to only those orbitals that actively participate in the considered surface reactions. As a result, the projectile is reduced to a two- and one-level representation for the de-excitation and neutralization channels, respectively. In addition, for the nitrogen molecule we also have to consider projectile continuum states which we describe by two-center Coulomb waves. In total, for both the projectile and the surface the many-particle details of the system are encapsulated in the effective parameters of our model the most important of which are the ionization energies of the active projectile levels and the edges of the involved energy bands within the surface. We stress that all of our model's parameters can be fixed by either theoretical calculations or experimental measurements. Thus, our description contains no free parameter.

Employing the usual trajectory approximation we then couple the isolated projectile and surface systems by considering the interplay of the various real and image charges within the system. The resulting Hamiltonian embraces the individual sub-reactions of the two-step resonant de-excitation, the Auger de-excitation channels as well as the processes of resonant and Auger neutralization. Due to the omission of passive electrons in our description of the projectile, the Hamiltonian does, however, not account for intra-projectile Coulomb correlations which lead to a displacement of the active projectile levels in the two-step resonant de-excitation process. Moreover, the Hamiltonian does not restrict the two steps of the resonant de-excitation reaction to proceed in sequence and, hence, cannot be used to study the resonant de-excitation mechanism and its interaction with the Auger de-excitation processes. In order to resolve these issues, we employ a set of projection operators together with two auxiliary bosonic levels. As a result, all of the considered de-excitation channels are cast into a single Hamiltonian which, with the help of pseudo-particle operators, is made amenable to diagrammatic techniques.

Since, due to the motion of the projectile, the Hamiltonian emerging from our effective treatment varies in time, we have to analyze its dynamics by means of non-equilibrium methods. For this purpose we employ the non-equilibrium Green function technique in both the Keldysh and the Kadanoff-Baym formulation and conduct a quantum-kinetic simulation of the different reaction channels. For every particular situation we retain the full non-locality of the self-energy expressions and derive results that can be considered exact within the respective perturbation order. At the end of each calculation we then employ a saddle-point, or semi-classical, approximation to obtain equations that allow for a numerical evaluation.

In particular, we treat the isolated subreactions of the two-step resonant de-excitation channel using the Keldysh formulation and an exact diagrammatic representation of the self-energy. Exploiting the strong effect of energy conservation we obtain virtually exact expressions for the occupancies of the bound and continuum projectile levels. The results involve an infinite series of nested double integrals, designated as the (infinite) σ -series, which emerges from an iterative solution of the Dyson equation. Variants of this series operating on different complex functions appear at multiple points within this work and, as we demonstrate, can be approximated by a compact semi-classical representation.

Furthermore, the isolated direct and indirect Auger de-excitation channels are also studied by means of the Keldysh formulation. Here we employ a second-order approximation of the self-energy which is extended by a dressed projectile propagator that is needed to make up for a first-order expansion of the Dyson equations of

the Auger electrons. While our general treatment of the Auger de-excitation channels follows the ideas of other authors, our analysis goes beyond previous works in multiple aspects. For one thing, we study the interplay of direct and indirect Auger de-excitation whereas former investigations were mainly concerned with the latter. Moreover, we neither restrict our analysis to a phenomenological matrix element nor employ the wide-band approximation. In addition, our final representation of the occupancies in terms of the infinite σ -series theoretically allows us to calculate higher order correction terms to the simplified semi-classical results.

The combination of the two Auger de-excitation channels and the resonant de-excitation reaction is then analyzed within the scope of our pseudo-particle Hamiltonian while employing the self-consistent non-crossing approximation for the self-energies. Utilizing the Kadanoff-Baym formulation of the non-equilibrium Green function method and the Langreth-Nordlander projection technique we derive a set of integro-differential quantum-kinetic equations for the various pseudo-particle propagators. By means of the semi-classical approximation this set is then reduced to a flexible and easy-to-use system of rate equations describing the occupations of the different projectile states occurring in the course of the de-excitation reaction.

Finally, for the neutralization channels we employ the Keldysh formulation together with a second-order representation of the Auger self-energy and an exact diagonal form of the resonant tunneling self-energy. Similar to the Auger de-excitation reactions, the secondary electrons are handled by introducing a dressed self-energy and expanding the associated Dyson equation up to first order. As a result, we obtain the occupancies of the projectile level and the Auger electron states in terms of the σ -series.

Following our quantum-kinetic calculation we concretize the transition matrix elements within the framework of our effective model. While our approximation to the wave functions might appear crude, it allows us to retain the full single particle quantum number dependence of the matrix elements which is usually dropped in favor of a phenomenological approximation. However, even for our simplistic wave functions the final equations are so complex that they can only be evaluated efficiently by a combination of tabulation, interpolation and Monte Carlo techniques. In applying the latter we then are able to calculate explicit numerical results for the individual surface reactions and their combination.

In particular, for the de-excitation of $N_2(^3\Sigma_u^+)$ our numerical analysis reveals that on aluminum and tungsten the isolated Auger de-excitation, proceeding via the spin-allowed indirect channel, is rather weak. Specifically, for a kinetic energy of 50 meV and a tungsten surface we calculate a secondary electron emission coefficient of $1.533 \cdot 10^{-3}$ in the parallel and $6.116 \cdot 10^{-3}$ in the perpendicular molecule orientation. Both of these values agree well with experimental estimates.

Moreover, for the isolated two-step resonant de-excitation of $N_2(^3\Sigma_u^+)$ we present numerical results for various dielectric surface materials. Using Al_2O_3 , in particular, we find that the spectrum of the emitted electrons exhibits the expected resonance structure with a strong peak at about 1.8 – 1.9 eV. In addition, concerning the decay of the temporary negative ion our results indicate that the surface-induced process can be neglected for our situation since it is about two orders of magnitude weaker than the natural decay. Focusing exclusively on the latter reaction we calculate the emission coefficient for Al_2O_3 , MgO , SiO_2 and diamond, obtaining values between 0.02 and 0.2 for collision energies ranging from 10^{-5} eV to 1 eV. For thermal

energies the figures are on the order of 10^{-1} and, hence, coincide with the values deduced from kinetic simulations of dielectric barrier discharges taking this particular secondary electron emission process into account.

Regarding the combination of two-step resonant and indirect Auger de-excitation of $\text{N}_2(^3\Sigma_u^+)$ we subsequently consider the particular case of a diamond surface and explicitly demonstrate the validity of the semi-classical approximation for a kinetic energy of 50 meV. Using the same energy we also calculate the rates of electron capture due to the two reactions and find that the resonant tunneling channel clearly dominates the indirect Auger transition. As a result, the combined emission spectrum is almost identical to the resonant spectrum and only shows a slight increase due to the Auger reaction. The latter, thus, merely contributes a few percent to the overall secondary electron emission coefficient which is on the order of 10^{-1} . Finally, the correct inclusion of both de-excitation channels in our theory is demonstrated by investigating two artificial situations for an aluminum surface in which we manually modify the lower conduction band edge in order to control the efficiency of the resonant reaction.

Moving on to the neutralization reactions our numerical results indicate that the isolated Auger neutralization channel is rather weak for $\text{He}^+(^2S_{1/2})$, $\text{Ar}^+(^2P_{3/2})$ and $\text{N}_2^+(^2\Pi_u)$ on all of the considered dielectric surfaces. In particular, at a kinetic energy of 50 meV typical values of the emission coefficient range from $5.67 \cdot 10^{-6}$ for $\text{Ar}^+(^2P_{3/2})$ on CaO to $3.97 \cdot 10^{-3}$ for $\text{He}^+(^2S_{1/2})$ on MgO.

For the resonant neutralization reaction, on the other hand, we observe a particularly high efficiency. Here the associated neutralization probability exhibits values between 0.1 and 1 for $\text{Ar}^+(^2P_{3/2})$ and $\text{N}_2^+(^2\Pi_u)$ on Al_2O_3 , MgO and SiO_2 at kinetic energies between 10^{-4} eV and 1 eV.

Focusing on the neutralization of $\text{He}^+(^2S_{1/2})$, $\text{Ar}^+(^2P_{3/2})$ and $\text{N}_2^+(^2\Pi_u)$ on a diamond surface we then find that for the considered low-energy range the resonant reaction clearly outbalances the Auger channel in terms of the isolated neutralization probabilities. As a result, the efficiency of the Auger channel is reduced even more in the combined two-channel neutralization scheme. This is validated for the particular case of $\text{He}^+(^2S_{1/2})$ at a kinetic energy of 50 meV. Here we observe that the inclusion of the resonant neutralization channel with an overall isolated neutralization probability of 0.13 leads to a reduction of the Auger electron yield by roughly 8%. Hence, we conclude that the Auger neutralization channel can only generate significant numbers of secondary electrons when the resonant neutralization channel is either blocked energetically or exhibits a particularly low neutralization probability.

In total, our numerical results imply that, despite its simplicity, our effective microscopic description seems to capture the essential physics of secondary electron emission due to the considered surface reactions quite well. We stress that the effective nature of our model and the associated small parameter space constitute an invaluable asset. In particular, our model can immediately be applied to arbitrary metallic and dielectric surfaces as long as the associated electronic parameters are known. Moreover, with minor modifications of the matrix elements our model can also be used to study different projectiles. This flexibility is highly advantageous especially in view of the application of our model to charge-transferring processes at plasma walls where a great variety of different projectile-surface material combinations arises.