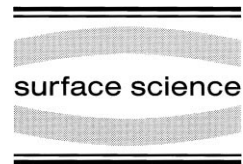




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Auger neutralization and de-excitation of helium at an aluminium surface: a unified treatment

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Abstract

The neutralization rate of He^+ and the de-excitation rates of excited He atoms in front of an Al surface are computed. This is achieved by evaluating the transition of electronic eigenstates of the He^+-Al system to the He^+ core hole while producing surface excitations. These surface excitations are computed in a self-consistent way. The present work accounts for the full many-body excitation of the metal surface as well as the hybridization of the He–Al orbitals. This hybridization leads to a new qualitative picture of the Auger processes in which the neutralization and de-excitation processes are mixed. © 1998 Elsevier Science B.V. All rights reserved.

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Electron transfer between atomic particles and a metal surface is a very important and much studied process in atom–surface interaction systems both because it determines the charge equilibrium at the interface and because it can initiate a variety of other processes by triggering an internal evolution in the colliding particles [1,2]. Charge transfer between a slow singly charged positive ion and a metal surface is usually classified as resonant transfer (RT) if it involves one metal electron, or as an Auger transition if more than one electron plays an active role in the neutralization process with the possibility of electron emission [3–5]. The available theoretical treatments of resonant

transfer processes lead to quantitative agreement with experiment [6,7]. However, even if the Auger processes are a priori very important for the neutralization of systems presenting a core hole [1–3,8], their multielectron character makes them difficult to handle. Early treatments had to introduce very restrictive approximations such as the use of much simplified electron wavefunctions [9–13], the neglect of the electron–electron interaction screening [14] or the inclusion of phenomenological screening [9,13,15] rendering the quantitative treatment of Auger neutralization still an open problem.

In the Auger neutralization process, a metal electron fills in the core hole of the incident ion and the energy associated with this capture is used

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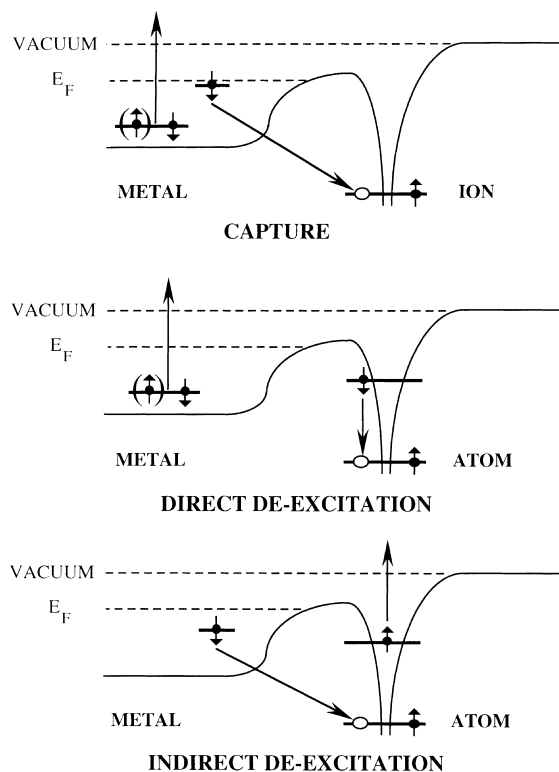


Fig. 1. Scheme of the Auger processes at a metal surface.

to excite the metal electrons (Fig. 1). This process can also be pictured as the relaxation of an independent-electron system when the electron–electron interaction is switched on. Because of the core hole, the initial system is in an excited state, which de-excites when energy can be transferred from the neutralizing electron to the rest of the electronic system.

In the present work, we develop a quantitative treatment of the Auger neutralization process which introduces both a self-consistent screening of the electron–electron interaction via a self-consistent representation of the metal surface [16–20] and a full three-dimensional non-perturbative treatment of the modification of the metal wavefunctions by the ion presence. The first aspect has been shown [18,19] to be very important for a quantitative description of the Auger processes. The second aspect corresponds to the intuitive idea that, owing to the attraction by the ion core, the metal electron wavefunctions are distorted in such

a way that the probability that one electron can be found in the ion vicinity is increased. This distortion, or equivalently the hybridization of the atomic and metallic states, should then lead to an increase of the Auger process. An earlier study of this distortion, performed with a one-dimensional approximation, concluded that there was a very large effect [21,22].

The present approach leads to an important change in the qualitative view of the Auger neutralization process. Indeed, consideration of perturbed metal wavefunctions contains the adiabatic assumption that the system's time evolution is slow enough to have fully hybridized electron states. Auger neutralization and direct Auger de-excitation processes differ in that the electron which goes into the atomic core level comes from the metal or from the atom; in both cases, the metal surface is excited (Fig. 1). In a treatment with unperturbed wavefunctions, the separation between metal and atom electrons, and thus between the neutralization and direct de-excitation processes, is straightforward, but it becomes much less obvious when the initial states are the one-electron eigenstates of the ion–metal surface system. Two different situations are then encountered: (i) there exists an atomic level degenerate with the metal electronic band. The use of hybridized electron wavefunctions assumes that the projectile ion has been neutralized via RT. The Auger process computed with the perturbed metal electron wavefunctions then contains the Auger de-excitation of the atomic state, or (ii) there is not any atomic level degenerate with the metal electronic band, then there is no real atomic level that can play the role of a relay state in the process and one computes the perturbed Auger neutralization process.

The neutralization of He^+ on Al surfaces is the usual example of Auger neutralization because the filled states of the Al surface are not resonant with any He state, thus preventing any RT mechanism. The Auger neutralization rate is calculated by convoluting the energy and momentum distribution associated with the transition from the initial metal electron to the final atomic electron with the probability of exciting either a surface electron–hole pair or a surface plasmon [18,19].

The neutralization probability is given by [18,19]:

$$\begin{aligned} \Gamma = & 2 \sum_{\mathbf{k}} \int_0^{\infty} d\omega \int d^2q_{\parallel} \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dz'' \frac{1}{q_{\parallel}^2} \\ & \times [-\text{Im} \chi(q_{\parallel}, \omega, z', z'')] \langle s | e^{-q_{\parallel}|z-z'|} e^{iq_{\parallel} \cdot \mathbf{r}_{\parallel}} | \mathbf{k} \rangle \\ & \times \langle \mathbf{k} | e^{-q_{\parallel}|z-z''|} e^{-iq_{\parallel} \cdot \mathbf{r}_{\parallel}} | s \rangle \delta(\omega - (E_{\mathbf{k}} - E_s)) \quad (1) \end{aligned}$$

where $|s\rangle$ is the final atomic state, and $|\mathbf{k}\rangle$ is the initial metal state. In order to have a realistic behavior of the He^+ –Al one-electron wavefunctions we have used the singlet model potential given in Ref. [23], and for the Al surface, we have used the potential (LDA description + image potential) given by Jennings et al. [24] where the image plane–jellium edge distance is $1.0a_0$. In particular, we obtain the same RT properties of the He–Al system as published in Refs. [25,26]. The $\langle \mathbf{r} | \mathbf{k} \rangle$ wavefunctions are calculated by solving Schrödinger’s equation in the potential of the ion, the surface and the ion image, with a truncated expansion of the wavefunction over spherical harmonics centered on the ion, in a way analogous to the coupled angular mode method [27]. Hence, we are using a non-perturbative method to solve the one-electron Schrödinger equation for a model potential which is not self-consistent. This model potential recovers the asymptotic image limit at large distances, where it is more accurate. The sum over $|\mathbf{k}\rangle$ runs over the occupied metal states which can be written as a sum over the electron energy E and a sum over the angular modes for the electron. The latter contains a sum over M , the projection of the electron angular momentum on the atomic axis normal to the surface, which is a good quantum number in the present problem.

The surface response function, χ , has been calculated for a slab of jellium ($r_s = 2.0a_0$) [28] following the work by Eguluz [29]. This self-consistent response function provides us with a many-body description of the surface in this way accounting for realistic electron–hole pairs and surface plasmons [30,31]. Our results are the same for slab widths of 30 and $60a_0$, so that no difference with a semi-infinite system is expected.

Let us define $\Gamma(E)$, the probability per unit time and unit energy that an electron, with initial energy

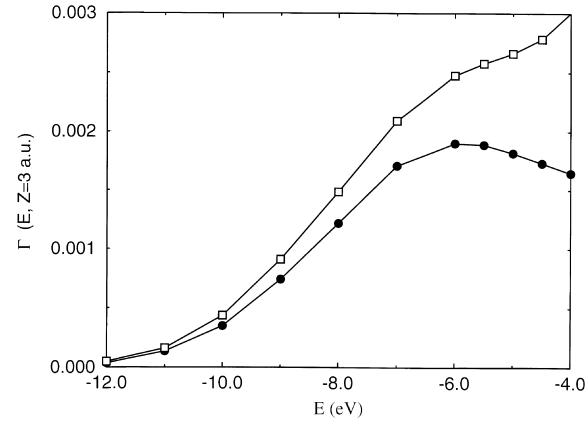


Fig. 2. Neutralization rate $\Gamma(E, Z)$ versus E , the neutralizing electron energy in eV for an He^+ ion fixed at $3a_0$ from the image plane. The line with open squares is the calculation with the eigenstates of the He^+ –Al system for the $|\mathbf{k}\rangle$ states, and the line with filled circles is the calculation with the eigenstates of the clean Al surface.

E , ends up in the $|s\rangle$ core state of the He^+ ion, when the ion is located at a distance Z from the metal image plane. The integral of $\Gamma(E)$ over the occupied energies yields the Auger rate Γ .

Fig. 2 shows the effect of the ion potential on the neutralization probability $\Gamma(E)$ as a function of E , the neutralizing electron energy, for an ion–surface distance $Z = 3a_0$. The line with open squares is the calculation using the eigenstates of the He^+ –Al system for the $|\mathbf{k}\rangle$ states, and the line with filled circles is the calculation using the eigenstates of the unperturbed Al surface. As the electrons approach the bottom of the band, the two calculations coincide owing to the prevailing effect of the metal potential over the ionic one. Conversely, the difference increases markedly as the electron approaches the Fermi level. Above -6 eV, the ion perturbation changes the behavior of $\Gamma(E)$ compared with that in the unperturbed case. This is the effect of the tail of the $n=2$ manifold of the He atom. This is more clearly seen in Fig. 3, which extends the electron energies up to -1.5 eV, in the region of unoccupied metal states. In Fig. 3 we present the $M=0$ component of $\Gamma(E)$ for four different ion–surface distances. The most striking feature of this figure is the high-energy structure. For the ion at $11a_0$ from the image plane, two peaks are perfectly resolved. This

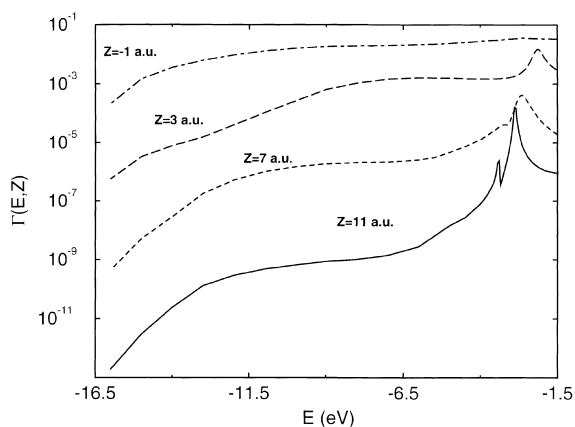


Fig. 3. $M=0$ component of the neutralization rate $\Gamma(E,Z)$ for four different ion-surface distances when the eigenstates of the He^+ -Al system are used in the Auger calculation. The neutralizing electron energy is extended above the Fermi level in order to reach the $n=2$ resonant levels of the He atom. Distances are measured from the surface image plane.

structure can be unambiguously identified by fitting the double structure with (the background is neglected):

$$\Gamma(E) = \left| \frac{p_1}{E - E_1 + iA_1/2} + \frac{p_2}{E - E_2 + iA_2/2} \right|^2$$

where p_1 and p_2 are the only fitting parameters. They correspond to two interacting Breit-Wigner resonances, namely the 2^1S and $2^1\text{P}(M=0)$ resonant levels of He interacting with the Al surface, the widths and energies of which (A_1 , A_2 , E_1 , E_2) are given in Refs. [25,26].

The surface strongly mixes the two levels, making it impossible to resolve the two peaks for distances, Z , smaller than $7a_0$ [25,26]. The correct $1/4Z$ behavior of the level shift is obtained here. A self-consistent LDA calculation would not be able to reproduce the correct image interaction at the surface. Thus, we are led to solve Schrödinger's equation for a non-self-consistent potential of the He^+ -Al system which is a minor inconvenience since self-consistent DFT treatments [32,33] of the perturbed wavefunctions for calculations of bulk Auger filling of core states give a 15% deviation from the orthogonalized plane wave calculation [16,17] to which our present calculation converges in bulk [18,19].

The present study with perturbed metal wavefunctions assumes that metal electrons have enough time to adjust to the presence of the ion, i.e. to relax toward the eigenstates of the He^+ -Al system before the Auger process takes place. This electron relaxation corresponds to an RT process and should require a similar time. In the energy range discussed, the relaxation time can be estimated from the He ($n=2$) RT rate. Since this RT process is much faster than the Auger neutralization to the He ground state, the use of hybridized orbitals is well justified for the computation of this Auger rate, obtained as the energy integral of $\Gamma(E)$ below the Fermi level.

When one considers metal electron energies, E , above the Fermi energy, in the vicinity of an atomic level, the Auger rate $\Gamma(E)$ is dominated by the atomic level contribution. The present calculation can be used to extract this atomic contribution, i.e. the Auger de-excitation rate from $\Gamma(E)$. For the He ($n=2$) levels, one has to integrate over the peak of $\Gamma(E)$ because it corresponds to the contribution of the atomic electron to the core hole filling. Since the peak structure is well reproduced by the two Breit-Wigner resonances, we need only to integrate one of the Breit-Wigner peaks over the energy. We can thus obtain the part of the $\Gamma(E)$ function that corresponds to the direct Auger de-excitation process (Fig. 1). It must be stressed that the Auger neutralization and de-excitation rates are obtained within the same approach from the same $\Gamma(E)$ rate; however, since they correspond to different initial states, the neutralization and de-excitation rates are obtained from the integration of the different regions of the $\Gamma(E)$ function. The above calculation provides us with the first direct Auger de-excitation calculation of the singlet atom in which the atom states have been adapted to the presence of the metal surface. At this point, one must realize that this de-excitation rate corresponds to the case where the RT has already occurred. It will be relevant to situations where, even after the RT, there is still an atomic population on the He ($n=2$) levels. This is, for example, the case of fast grazing collisions [34].

In Fig. 4 we present the global results of this work. In filled circles we have the neutralization

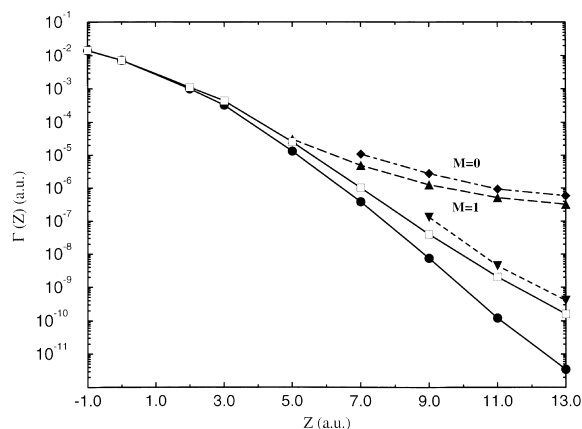


Fig. 4. Transition probabilities per unit time, Γ , in atomic units, versus ion-surface distance, Z , measured from the image plane. In filled circles, we have the neutralization probabilities for He^+ ions assuming that the metal electron states did not have time to relax to the presence of the ion. \square , the Auger neutralization results when perturbed wavefunctions are used. We present the results for the de-excitation of He in the following states: \blacklozenge , $2^1\text{P}(M=0)$; \blacktriangle , $2^1\text{P}(|M|=1)$; \blacktriangledown , 2^1S .

rate for He^+ ions as a function of the distance Z between the ion and the aluminum image plane, assuming that the metal electron states did not have time to relax to the presence of the ion. As open squares we plot the Auger neutralization rate when hybridized wavefunctions are used. The effect of the presence of the ion is quite important at large distances (almost two orders of magnitude at $Z=13a_0$) and decreases as the ion approaches the surface. With the present results introduced into a semiclassical rate equation, we can obtain the effective neutralization or freezing distance. For a 2 keV ion incident at 0.5° from the surface plane, typical of grazing collisions [34], the freezing distance is located around $1.5a_0$ from the image plane. It should be noted that the present effective neutralization distance is larger than that obtained previously in first-principle calculations [18,19], which was $-0.5a_0$, and in better agreement with the available experimental estimates for this distance, obtained from emitted-electron energy spectra ($3.5a_0$ for various substrates [3]) or ion beam deviation ($3a_0$ for the Al surface [34]). In an earlier study [21], the effect of the presence of the ion on the Auger neutralization rate had been found to be more important than in the present

study. This difference is attributed to the one-dimensional surface-ion barrier used in Ref. [21]. In the present treatment the use of unperturbed wavefunctions gives a freezing distance of $1.2a_0$, while the perturbed wavefunction calculation shifts the freezing distance $0.3a_0$ outwards. This small shift justifies the use of unperturbed wavefunctions in order-of-magnitude calculations. The difference with the result of Refs. [18,19] comes from the very compact hydrogen-like wavefunction used for the He 1s electron in those references.

Finally, as filled upward triangles we present the results for the de-excitation of $2^1\text{P}(|M|=1)$ levels of helium and as filled diamonds, the de-excitation rate for the $2^1\text{P}(M=0)$ level. The present treatment is qualitatively different from previous calculations [20,35] because of the self-consistent description of the surface response and the modification of the atom wavefunctions by the metal presence. Quantitatively, the differences in the wavefunctions can be illustrated on the case of the 2^1S level (downward triangles). With the use of unperturbed wavefunctions, the 2^1S level decay rate vanishes [35]. However, the perturbation of the atomic states by the metal leads to a spherical-symmetry breaking effect and to a de-excitation rate which is actually bigger than the He^+ neutralization rate at the same distance. At small distances, the strong mixing of the hybridized wavefunctions for the $M=0$ states impedes assigning free-atom levels to the Auger de-excitation results.

As also discussed in the literature [36] indirect Auger de-excitation (Fig. 1) may be dominant at short distances. This is supported by our calculation which shows that around $Z=5a_0$, the 2^1P de-excitation rate merges with the Auger neutralization rate. At these distances capture of a metal electron by the core hole becomes more likely than the de-excitation of the atomic electron, assuming that the response of the metal surface is not very different in the direct de-excitation and neutralization processes, the main difference comes from the origin of the electron filling in the core hole. Thus the indirect Auger de-excitation mechanism may become more important than the direct Auger de-excitation process calculated here.

In this Letter, we have presented parameter-free calculations of Auger processes. We have shown

that, in the He⁺–Al system, the effect of the ion perturbation on the metal states has to be taken into account. It leads to a significant increase of the Auger neutralization rate at large ion–surface distances. The introduction in the Auger treatment of hybridized ion–metal electron states results in the mixing of the Auger neutralization and de-excitation processes. This allows us to perform the first calculation of Auger de-excitation rates in which the effect of the metal surface is included in the distortion of the atomic states. Accurate results for the de-excitation of $n=2$ excited atoms are obtained, and in particular, we calculate and show that the probability of direct de-excitation of the metastable He (2^1S) is not zero due to the distortion of the atom wavefunctions by the interaction with the metal surface.

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