

Charge Transfer in Atom-Surface Interactions

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Abstract

The link between the electronic structure of the solid target and the electron transfer processes in ion-surface collisions is reviewed, together with a discussion of the theoretical approaches required to treat the different cases. The different behaviors of the electron transfer process for metal or ionic crystal surfaces are presented. The main emphasis of this paper is about finite time effects on the electron transfer process, due to the finite duration of a collision event. It is shown how this can deeply modify the characteristics of the electron transfer process in the case of a metal surface with a projected band gap. A review is then presented of different open problems where finite time effects can be expected and qualitatively influence the electron transfer processes.

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1. Introduction

When an atom approaches the surface of a solid, couplings between the electronic levels of the atom and those of the solid can result in electron jumps between the atom and the surface. This process is quite important in the context of ion(atom)-surface collisional interactions since it determines the charge state of reflected as well as of sputtered particles; it also determines the charge state of a projectile as it hits a surface or penetrates the solid, thus influencing other phenomena such as energy transfer. Collisional charge transfer has thus been the subject of quite a few experimental and theoretical detailed studies in the past years (Los and Geerlings, 1990; Rabalais, 1994; Winter, 2002; Monreal and Flores, 2004). However, there is another domain where charge transfer processes play a significant role. Quite a few excited electronic states localized on an atomic or molecular adsorbate on a surface correspond to the transient capture (or loss) of an electron by the adsorbate; electron transfer is then one of the decay channels of these transient states. Excited states and in particular charge transfer states are often invoked as intermediates in reaction processes at surfaces; indeed excitation of an adsorbate often triggers an internal evolution, involving energy transfer between electrons and heavy particle motions that can lead to the breaking of chemical bonds or the creation of new ones. In this context, electron capture or loss appears both as an important step in reaction mechanisms and as a decay channel limiting the efficiency of excited state-mediated reaction processes (Palmer, 1992).

The present article is not intended to be a comprehensive review of the field of charge transfer at surfaces. It rather concentrates on a theorist view of the process and aims at illustrating what are the physical features that influence the nature of the charge transfer process. More precisely, it will first discuss how the electronic properties of the surface, i.e. its electronic band structure, influence the charge transfer and the choice of the theoretical approach to be used to quantitatively describe the process. It then shows how finite time effects modify this simple first view, leading to the discussion of a few open problems where the qualitative nature of the active charge transfer process can still be discussed.

Different charge transfer processes are possible at surfaces. They are usually classified according to the number of electrons involved in the process (Los and Geerlings, 1990). If only one electron is involved, the electron transfer process is called resonant or quasi-resonant charge transfer. Several electrons can also be involved. If the projectile has a vacancy in one of its inner orbitals, an electron from the solid can be transferred to this inner orbital and the corresponding energy gain is used to excite another electron from the solid, in a process called Auger-electron transfer (Hagstrum, 1954; Lorente and Monreal, 1996; Cazalilla et al., 1998). The energy gain can also be used to excite the electrons in the solid collectively, leading to a plasmon-assisted electron transfer (Lorente and Monreal, 1996; Baragiola and Dukes, 1996). Finally, one can also mention that the direct two-electron transfer from the solid to the projectile has also been evidenced and described (Roncin et al., 2002). In addition to the number of electrons involved, the characteristics of the electronic levels involved in the charge transfer directly influence the qualitative nature of the charge transfer. The electronic levels on the projectile are discrete states localized on the projectile. In contrast the solid can exhibit qualitatively different types of electronic levels: the levels can be delocalized over the crystal and form a continuum of states or they can be discrete states localized on one of the sites of the crystal; more generally, the band structure of the solid target can exhibit very different properties. In addition, when adsorbates are present on the surface, electronic states can possibly be localized on the adsorbates. The present review begins with the description of two examples of one-electron transfer processes on two surfaces with very different electronic band structures: a free-electron metal (Section 2) and an ionic crystal (Section 3). This illustrates how different electronic structures of the solid lead to different qualitative pictures of the electron transfer so that the theoretical description of the charge transfer at surfaces has to involve different approaches. Then it is shown how this simple view has to be modified on metal surfaces due to finite time effects (Section 4) leading to the discussion of several open questions (Section 5).

2. Resonant Charge Transfer (RCT) on a Free-Electron Metal Surface

In a free-electron metal, the electrons interact with the metal via a local potential, constant inside the metal and exhibiting a surface barrier at the metal edge. One-electron transfer from a projectile to a free-electron metal can then be described as the evolution of a single electron in a potential describing its interaction with the projectile-target compound system. Figure 1 presents such a potential for a given projectile-surface distance. The potential is plotted along the z -axis normal to the surface and going through the atom center. One recognizes the potential well inside the metal (negative z) and the atomic potential well localized around the

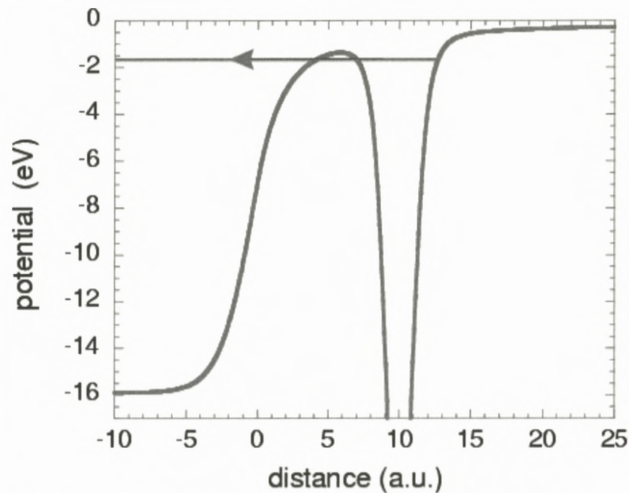


Figure 1. Schematic picture of the potential involved in the electron transfer between an atom and a free-electron metal surface. The potential is shown along an axis perpendicular to the surface and going through the atom center (negative coordinates inside the metal). An atomic level localized inside the atomic potential well is schematized by an horizontal line, together with an arrow representing the electron transfer into the metal.

projectile. An atomic level on the projectile is then degenerate with the continuum of metal states and thus, according to the Fermi golden rule, it becomes quasi-stationary. The atomic level decays by transfer of an electron into the metal states that have the same energy, so that this process is often referred to as Resonant Charge Transfer (RCT). The finite width of the level, inverse of its lifetime, gives the electron transfer rate. Another picture of the same process is to say that the electron can tunnel through the barrier separating the projectile and the surface. The direction of the charge transfer depends on the energy position of the atomic level. Indeed, if the atomic level is above the Fermi level, it is degenerate with an empty continuum (at least at 0 K) and it can decay by transfer of the electron into the metal. In contrast, if the atomic level is below the Fermi level, it is degenerate with a fully occupied continuum and no electron can be transferred into the metal. However, one can repeat the argument with electrons replaced by holes and conclude that, in that case, electron transfer occurs from the metal to the projectile. For a finite temperature, the metal states are neither fully occupied nor fully empty and RCT can occur in both directions, proportionally to the relative weight of empty and occupied states.

To describe the evolution of an atom colliding with a metal surface, one can use a semi-classical approximation, treating the heavy particle motion classically while the electron evolution is treated quantumly. Such an approach is valid for not

too slow projectiles. From the above discussion, one can conclude that the energy and the width of the atomic level are the key parameters to describe the RCT process for a fixed ion-surface distance. Relying on the adiabatic approximation, one can assume that this also holds in the case of an atom colliding with a metal surface (Los and Geerlings, 1990; Geerlings et al., 1986). One can then describe the evolution of the charge state of the projectile in front of a free-electron metal via a rate equation, such as for example:

$$\frac{dP}{dt} = -\Gamma_{\text{loss}}P + \Gamma_{\text{capt}}(1 - P), \quad (1)$$

for the case of two charge states (positive ion and neutral). P is the population of the neutral state of the projectile, Γ_{loss} and Γ_{capt} are the electron loss and capture rates, as determined in a fixed projectile situation. This rate equation makes the implicit assumption that the electron transfer rates are the same in a static situation (fixed projectile-surface distance) and in the course of a collision. As for the energy and width of atomic levels in front of a free-electron metal surface, there exist nowadays a few different parameter-free approaches to compute them. They consist in looking for quasi-stationary states in a 3D-potential using complex scaling (Nordlander and Tully, 1988), coupled angular modes (Teillet-Billy and Gauyacq, 1990), stabilization (Martin and Politis, 1996; Deutscher et al., 1997), close-coupling (Merino et al., 1986; Kürpick et al., 1997; Bahrim and Thumm, 2002), wave-packet propagation (Ermoshin and Kazansky, 1996; Borisov et al., 1999a; Chakraborty et al., 2004). When applied to the same problem, these methods yield the same results. It has also been shown recently that charge transfer rates can be extracted from DFT studies on the projectile-metal system (Niedfeldt et al., 2004). Used with the adiabatic rate equation approach (Equation 1), this yields a quite satisfying account of the charge state of atoms scattered from a free-electron metal surface (Borisov et al., 1992, 1996a; Maazouz et al., 1997; Hill et al., 2000). In particular, a quite satisfying account of experimental results is obtained in the grazing angle scattering geometry, which selects atoms reflected from a defect-free area of the surface. As an example, Figure 2 shows the results for Na^+ ion neutralization in grazing angle collisions with an Al(111) surface (experimental and theoretical results from Borisov et al., 1996a). It presents the ion neutralization probability as a function of the collision velocity parallel to the surface for three different perpendicular velocities. The strong dependence of the charge state as a function of the parallel velocity is due to the so-called “parallel velocity effect” (Van Wunnick et al., 1983): the projectile level and the metal states are defined in two different Galilean reference frames, in fast motion one with respect to the other; the transformation from the metal frame to the projectile frame modifies the energy distribution of the metal electrons, strongly

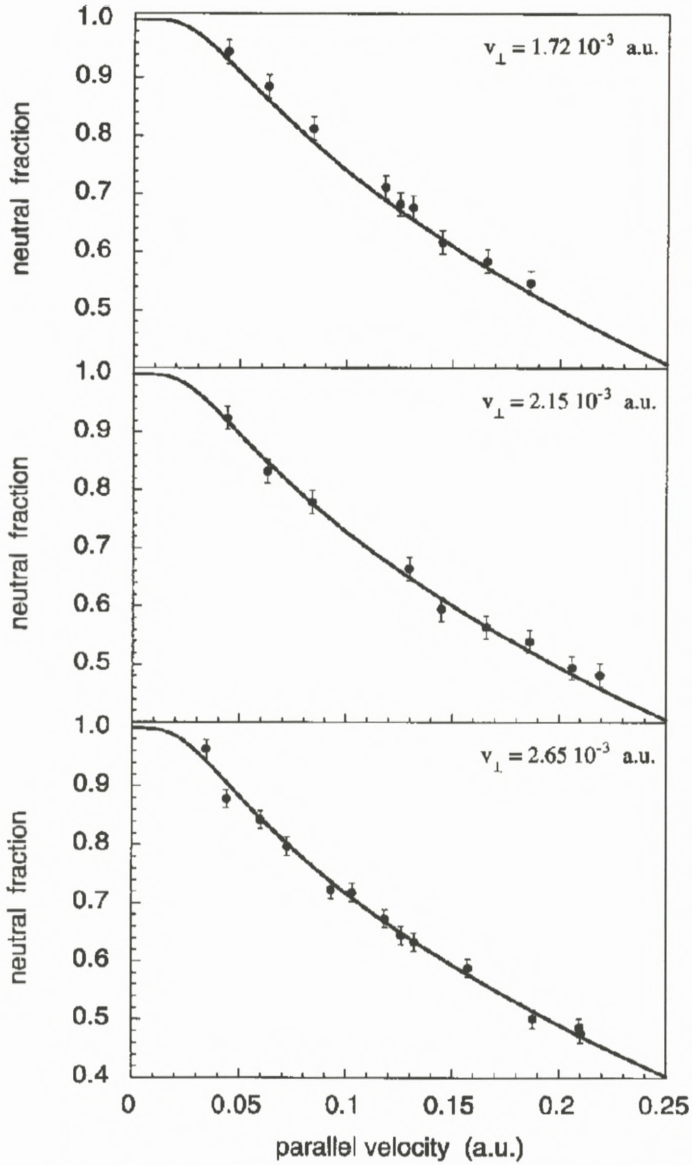


Figure 2. Neutralization probability of Na^+ ions scattering at grazing angle from an Al(111) surface. The probability is shown as a function of the collision velocity parallel to the surface for three different perpendicular velocities. Collision velocities are given in atomic units. Symbols: experimental results and lines: theoretical results (from Borisov et al., 1996a).

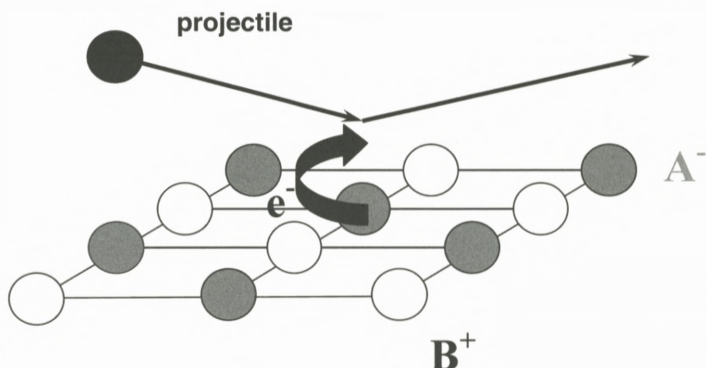


Figure 3. Schematic picture of the electron capture process during a collision on an ionic crystal surface. White spheres: B^+ cation sites; gray spheres: A^- anion sites of the crystal (only the surface plane of the crystal is represented). The projectile (dark sphere) is moving along a classical trajectory (symbolized by the two straight arrows) that hits the crystal on an anion site. Electron capture results from the binary collision between the projectile and the anion site.

influencing the direction of the charge transfer (see a detailed discussion in Van Wunnick et al., 1983; Winter, 2002). So, qualitatively and quantitatively, RCT on a free-electron metal appears to be well understood, it corresponds to irreversible transitions between discrete states of the projectile and the continuum of metal states and the time dependence of the RCT along the collision can be efficiently described via an adiabatic rate equation.

3. Electron Capture from an Ionic Crystal

Experimental studies of electron capture in grazing angle scattering of a projectile from an ionic crystal surface revealed extremely large negative ion formation probabilities, much larger than those observed on a metal surface (Auth et al., 1995; Winter, 2000). The theoretical description of the electron transfer process in this system (Borisov et al., 1996b; Borisov and Sidis, 1997) is completely different from the one discussed in the previous section. It involves binary collisions between the projectile and the anion sites of the crystal, where the valence band electrons are localized and can be captured from. The geometry of the collision when the projectile hits an anion site, A^- , of an A^-B^+ ionic crystal is sketched in Figure 3. The binding energy of the electron in the valence band in e.g. a LiF crystal is very large (around 14 eV) and much larger than the electron affinity of a typical projectile. This feature could *a priori* hinder an electron transfer between the valence band and the projectile. However, analysis of the energies of the initial state (neutral projectile and complete crystal) and of the final state (ionic projectile

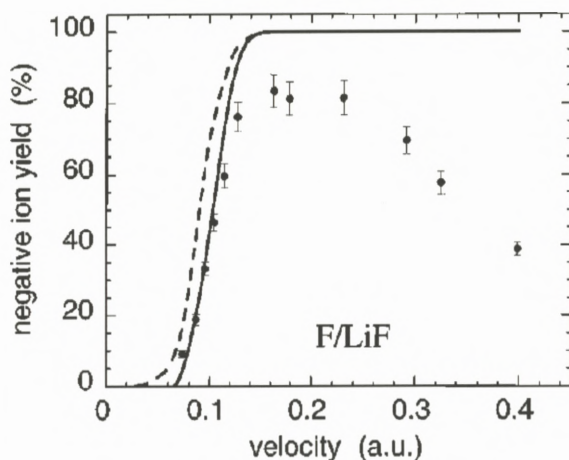


Figure 4. Negative ion yield for grazing angle scattering of F atoms on a LiF(100) surface as a function of the collision velocity parallel to the surface (in atomic units). Symbols: experimental points from Auth et al. (1995) for an incidence angle of 1° with respect to the surface plane. Theoretical results from Borisov et al. (1997) for two incidence angles: 1° and 2.5° : full and dashed lines, respectively. Figure reprinted with permission from Borisov and Sidis, *Phys Rev B* **56**, 10628. Copyright 1977 by the American Institute of Physics.

and one hole in an anion site of the crystal) shows that the energy defect of the electron transfer is greatly reduced by a Coulomb term arising from the interaction between the localized hole in the crystal and the ionic projectile (Borisov et al., 1996b). This “energy confluence” of the initial and final states can lead to an efficient transfer during the binary collision between the projectile and a crystal anion. After the negative ion is formed, its destruction by electron loss has to occur via electron transfer into the conduction band of the crystal or into vacuum, which are not in energetic resonance with the projectile affinity level. Hence, electron loss has to involve a dynamical process. For this reason, the electron loss process can be expected to be weak for low collision velocities. These two features, efficient capture and inefficient loss, make the negative ion formation highly probable on an ionic crystal. In addition, in the case of grazing angle collisions, since the electron transfer process is well localized around an anion site, the projectile can interact successively with different anion sites, leading to a cumulative electron capture process and to a very large negative ion probability in the scattered beam. Figure 4 (from Borisov and Sidis, 1997) presents the negative ion formation probability for F atoms incident on a LiF(100) surface at grazing incidence. The experimental negative ion yield (Auth et al., 1995) is very high, reaching 80% at maximum. The theoretical study (Borisov and Sidis, 1997) involved the determination of the energies and couplings of the states active in the charge transfer by a quantum

chemistry approach of the projectile-crystal system, one can say that it describes an atom-atom binary collision in presence of the field created by the ionic crystal. The quantum chemistry approach yields adiabatic states, eigen-functions of the electronic Hamiltonian, from which diabatic states, better suited for the dynamics treatment, are extracted. The theoretical negative ion yield (Borisov and Sidis, 1997) is seen to rise very rapidly above threshold, quickly reaching 100%. This fast increase above threshold is due to both the collision energy dependence of the electron capture in the binary collision and to the increase of the number of active sites in this grazing angle collision. The theoretical study only included the effect of capture in the binary collision and did not introduce any process for electron loss in the subsequent binary collisions; this explains the saturation of the theoretical negative ion yield at large velocities, different from the decrease of the experimental yield. Though, the threshold region, where electron loss can be thought to be weak, is well reproduced by the theoretical results.

4. Dynamical Effects in the RCT between a Projectile and a Metal Surface

The two situations depicted in the previous sections are qualitatively well understood and nowadays efficient quantitative treatments are available. The electronic structures of the two surfaces are quite different, leading to quite different descriptions of the electron transfer. Besides the existence of a continuum of states in the metal case, a key difference appears to be the reaction of the surface to electron capture: after an electron capture from a metal, the surface is still the same, i.e. one assumes a perfect instantaneous relaxation of the metal, whereas after an electron capture from an ionic crystal, a hole is present at the surface for a while. This leads to a different qualitative nature of the electron transfer and consequently, to the need to resort to different theoretical approaches for treating the charge transfer process. It is shown below on the example of RCT on a metal surface that the situation is not always that simple and that the connection between the surface electronic band structure and the characteristics of the charge transfer is not always straightforward. Non-adiabatic effects associated with the finite time duration of a collision event can appear that deeply affect the charge transfer process. These will be illustrated in the case of the RCT process on a metal surface, treated in a wave-packet propagation (WPP) approach (see Borisov et al., 1999a, for a detailed presentation of the WPP method).

4.1. WAVE-PACKET PROPAGATION APPROACH OF THE RCT PROCESS

The RCT process on a metal surface is a one-electron process and thus, one can treat it as the evolution of a single electron inside a potential representing the

electron interaction with the projectile and the metal surface (see Figure 1). The wave-packet propagation approach of this problem consists of solving the time-dependent Schrödinger equation for the active electron:

$$i \frac{d\Psi(\vec{r}, t)}{dt} = H\Psi(\vec{r}, t) = (T + V)\Psi(\vec{r}, t), \quad (2)$$

where $\Psi(\vec{r}, t)$ is the active electron wave function defined on a 3-dimensional grid of spatial points. T is the electron kinetic energy operator and V is the interaction potential of the electron with the atom+surface system. V is usually modeled as the sum of three terms: $V_{e\text{-atom}}$, the electron interaction with the core of the projectile, $V_{e\text{-metal}}$ the electron-metal surface interaction and $\Delta V_{e\text{-metal}}$, the modification of $V_{e\text{-metal}}$ due to the presence of the projectile. Various kinds of model and pseudo-potentials are available for $V_{e\text{-atom}}$, coming from earlier atomic physics studies. For $V_{e\text{-metal}}$, different modelings of the electron-surface interaction are available. A first description, taken from Jennings et al. (1988), corresponds to a free-electron metal: the electron is free i.e. the $V_{e\text{-metal}}$ potential is constant inside the metal and $V_{e\text{-metal}}$ smoothly joins an image potential outside the metal. This is typically the representation that was used in the theoretical studies on free-electron metal surfaces mentioned in Section 2. Below, results obtained with the model potential introduced by Chulkov et al. (1999) are also presented. Inside the metal, this potential is oscillating with the crystal periodicity perpendicular to the surface and it is constant in the direction parallel to the surface; it smoothly joins an image potential outside the surface. This potential is very efficient in representing the characteristics of the surface electronic band structure for electron motion perpendicular to the surface. Indeed, the modulation of the potential perpendicular to the surface opens a band gap for the electron motion in this direction, i.e. a surface-projected band gap. Surface states and/or image states can then exist on such a surface (Desjonquères and Spanjaard, 1993). $\Delta V_{e\text{-metal}}$ is introduced only in the case of a charged projectile core, it is then simply taken as the interaction between the active electron and the image of the ion core.

The wave function of the active electron $\Psi(\vec{r}, t)$ is obtained from the time-dependent Schrödinger equation by time propagation, starting with an initial wave function Φ_0 . Two different calculations can be performed: (i) a static calculation, in which the projectile is kept at a fixed distance from the surface and (ii) a dynamical one where the projectile is moving with respect to the surface along a classical trajectory. In both cases, the propagation is started with Φ_0 equal to the wave function of a bound state of the free projectile. In case (i), one can obtain from the survival amplitude of the system the energy and width of the projectile states interacting with the metal surface, one can also get the wave function of the quasi-stationary states. Energies and widths of the states can be

used afterwards in an adiabatic rate equation approach (Equation 1) to treat the collision dynamics. In case (ii), one directly follows the collision dynamics and obtains the final charge state after the collision. The time propagation is performed over successive infinitesimal time steps, using a split operator approximation that allows using an appropriate propagator for each term in the Hamiltonian (see Borisov et al., 1999a, for details). In the case of an atom interacting with a metal surface with translational invariance parallel to the surface, the system is invariant by rotation around the z -axis perpendicular to the surface and going through the atom center. Using cylindrical coordinates (z, ρ, ϕ) around the symmetry axis, the full 3D-problem can then be reduced to a 2D-problem, with the ϕ -part of the wave function being factored out (see Borisov et al., 1999a, for details on the propagation scheme in this case).

4.2. EFFECT OF THE METAL ELECTRONIC STRUCTURE ON THE RCT – STATIC CASE

The presence of a surface-projected band gap can be expected to deeply affect the RCT in certain cases. This is illustrated in Figure 5, which presents the surface projected band structure of a free-electron metal and that of the Cu(111) surface. Figure 5 presents the energy of the metal states as a function of $k_{//}$, the electron momentum parallel to the surface. On a free-electron metal, the energy of the states varies quadratically with $k_{//}$. All energies are possible above the bottom of the conduction band. As seen in Section 2, the RCT process corresponds to the transfer of an electron between a projectile state and metal states of the same energy. On a free-electron metal, a projectile state with an energy as indicated in Figure 5 is degenerate with a whole set of $k_{//}$ states, starting at $k_{//} = 0$. In contrast, for Cu(111), a projectile state with the same energy is only degenerate with a surface state of a given finite $k_{//}$ and with a series of states of the conduction band corresponding to finite values of $k_{//}$. The metal states that can actively contribute to the RCT process are then different in the two situations and as shown below, this deeply influences the efficiency of the electron transfer in the two cases.

Figure 6 presents the wave function of the lowest lying quasi-stationary state localized on the Cs adsorbate in the Cs/Cu system. Figure 6 shows the squared modulus of the state wave function, i.e. the electron density in a plane perpendicular to the surface and containing the symmetry z -axis that goes through the atom center. The right panel of Figure 6 presents the results obtained in the free electron case and the left panel the case of the Cu(111) surface. In the case of the free-electron metal, one recognizes the Cs resonance localized around the Cs-center and a flux of electron leaving the Cs atom and going into the metal around the surface normal. This flux corresponds to the RCT process in which the electron is transferred from the Cs into the metal. As illustrated in Figure 1, the RCT can

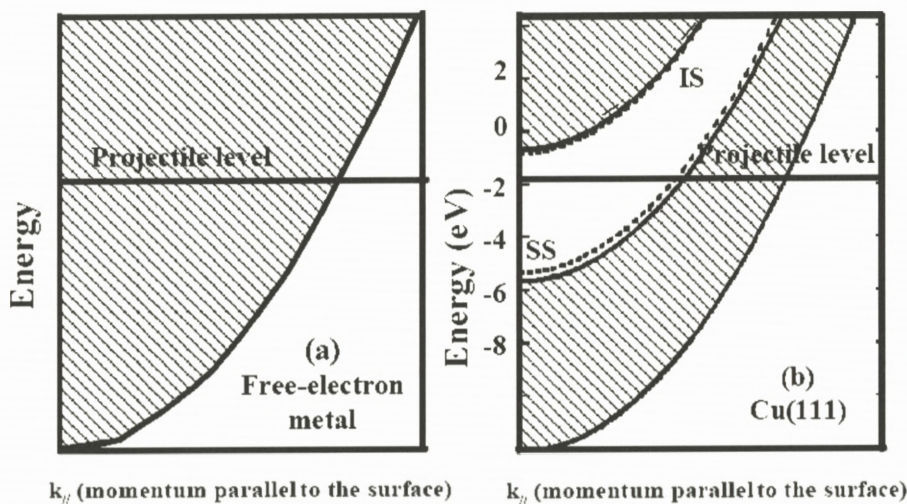


Figure 5. Schematic projected band structure of a metal. (a) Free-electron metal and (b) Cu(111) surface. The energy of the levels are presented as a function of k_{\parallel} the component of the electron momentum parallel to the surface. The shaded areas represent the valence and conduction bands of the system. In addition, in the Cu(111) case, the surface state (SS) and first image state (IS) that appear in the surface projected band gap are represented by dashed lines. The horizontal line is used for the discussion of the electron transfer process between a projectile and the metal surface: it represents the energy of the projectile level and thus allows to determine which are the metal states degenerate with the projectile level.

be viewed as the electron tunneling through the potential barrier that separates the atom and the metal. The thickness of this barrier is minimal along the surface normal and thus tunneling occurs preferentially along this direction, as seen in the right panel of Figure 6. Tunneling along the surface normal populates metal states around $k_{\parallel} = 0$ in the band structure shown in Figure 5a. In the case of a Cu(111) surface, the situation is quite different. One can see in Figure 5b that there is not any metal state degenerate with the adsorbate state around $k_{\parallel} = 0$; i.e. the states that are the most efficient for RCT on a free electron metal are missing in the Cu(111) case. In the left panel of Figure 6, there is only an evanescent wave in the area around the symmetry axis. The electron flux associated to RCT into Cu bulk states appears at a finite angle from the surface normal, this angle corresponds to the metal states that are degenerate with the adsorbate state which have the smallest k_{\parallel} value, i.e. it corresponds to tunneling along a direction that is the closest possible to the surface normal that is compatible with the electronic band structure. Tunneling at a finite angle is associated with a broader barrier to travel through and as a consequence the RCT rate is much smaller in the Cu(111) case (notice in the right panel how fast the electron flux is decreasing as it moves

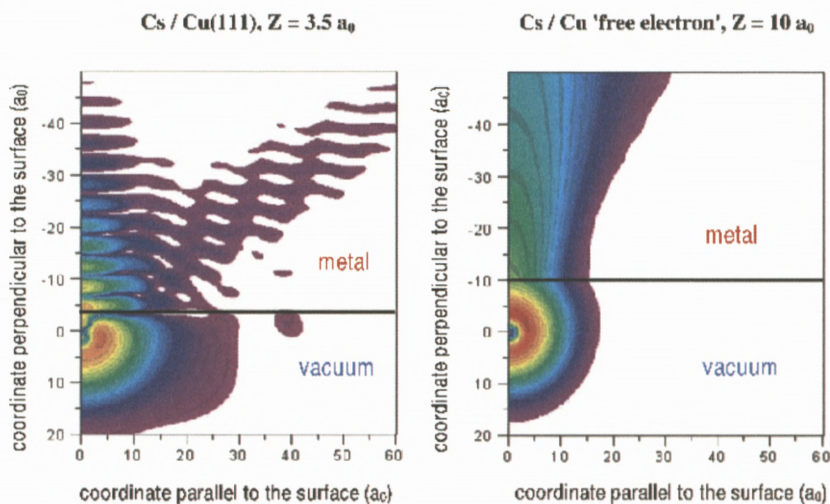


Figure 6. Logarithm of the squared modulus of the electron wave function (electron density) for the quasi-stationary state located on the Cs adsorbate on a Cu surface. Only a cut of the density in a plane perpendicular to the surface and going through the surface is presented. The system symmetry axis is along the vertical coordinate and the metal is on the negative coordinate side. The atom is at the origin of coordinates. Right panel: free-electron metal surface with a Cs atom located at $10 a_0$ from the surface. Left panel: Cu(111) surface, with a Cs adsorbate at $3.5 a_0$ from the surface.

away from the surface normal). RCT into the Cu(111) surface state continuum is also possible though in this case it appears to be very weak and not visible with Figure 6 scale. Quantitative studies (Borisov et al., 1999b) show that the RCT rate amounts to 900 meV on a free-electron metal and to 7 meV on Cu(111), revealing a two orders of magnitude decrease due to the effect of the electronic band structure. Note that the RCT rates are often given in units of energy, so that the rate is directly equal to the level width, a width of 1 eV corresponds to a lifetime of 0.66 fs. Usually, the RCT process is thought to be more efficient than the other charge transfer processes since it implies one-electron transition terms. In the Cs/Cu(111) case, since RCT is much weakened, one should also consider multi-electron transition terms. A theoretical study of the contribution of electron-electron interactions to electron loss by the Cs adsorbate (the excited electron interacts with the metal electrons, leading to its transfer into the metal and to the excitation of the metal electrons) yields a multi-electron transfer rate of 14.5 meV. This is larger than the RCT rate on Cu(111), but, as expected, much smaller than the RCT rate on a free-electron metal (Borisov et al., 2001). In total, this leads to a very long lifetime, 28 fs, for the excited Cs adsorbate state on Cu(111). The Cs localized state has been studied in detail using time-

resolved 2-photon-photoemission experiments. These experiments also revealed a very long-lived transient state (Bauer et al., 1997, 1999; Ogawa et al., 1999). The long lifetime allows the Cs-localized state to be involved as an intermediate in a photo-desorption process (Petek et al., 2000). Theoretical results and experimental data are found to agree quantitatively, in particular once the Cs desorption motion is taken into account (Gauyacq and Kazansky, 2005).

Thus, in this static case (adsorbate on a metal), the electronic band structure of the metal surface is found to deeply affect the charge transfer, leading to a quasi-blocking of the RCT process in the case of a surface-projected band gap. Similar results have been found in other static systems exhibiting the same situation (excited state inside a surface-projected band gap) like other alkali/noble metal systems (Borisov et al., 2002) or core-excited Ar on a Cu surface (Gauyacq and Borisov, 2004). In all these systems, the states that can *a priori* be thought to be the most efficient ones for electron tunneling between the metal and the adsorbate are missing, leading to a severe drop of the RCT rate as compared to what happens on a free-electron metal surface.

4.3. EFFECT OF THE METAL ELECTRONIC STRUCTURE ON THE RCT – DYNAMICAL CASE

If instead of considering an adsorbate/metal system, one considers an atom colliding on a surface, one could, *a priori*, expect similar effects of the surface band structure to appear, i.e. one could expect very different results for collisions on a free-electron metal and on a metal surface exhibiting a surface-projected band gap. This idea is based on the supposed validity of the adiabatic rate equation (Equation 1), i.e. on the assumption that the charge transfer rate during a collision is the same as the charge transfer rate for a static atom-surface system. Below, it is shown how non-adiabatic effects can modify the dynamical case and make it look different from the static case.

Recently a joint experimental-theoretical study has been devoted to the Li^+ ion neutralization by collision with an Ag(100) surface (Canario et al., 2005). Figure 7 presents the energy and width of the Li(2s) atomic level interacting with an Ag surface, either Ag(100) or a free-electron metal model. On a free-electron metal, the energy of the 2s level is seen to increase as the atom approaches the surface and to cross the Fermi energy at a distance, Z_X . The RCT process then leads to electron capture for $Z > Z_X$ and to electron loss by the projectile for $Z < Z_X$. The level width (the RCT rate) increases quasi-exponentially as the projectile approaches the surface. The situation appears different in the case of an Ag(100) surface. Though the level width appears only slightly affected by the surface band structure, the energy of the Li(2s) is much different. The Ag(100) surface exhibits a surface-projected band gap between -2.89 eV and $+2.21$ eV (with respect to

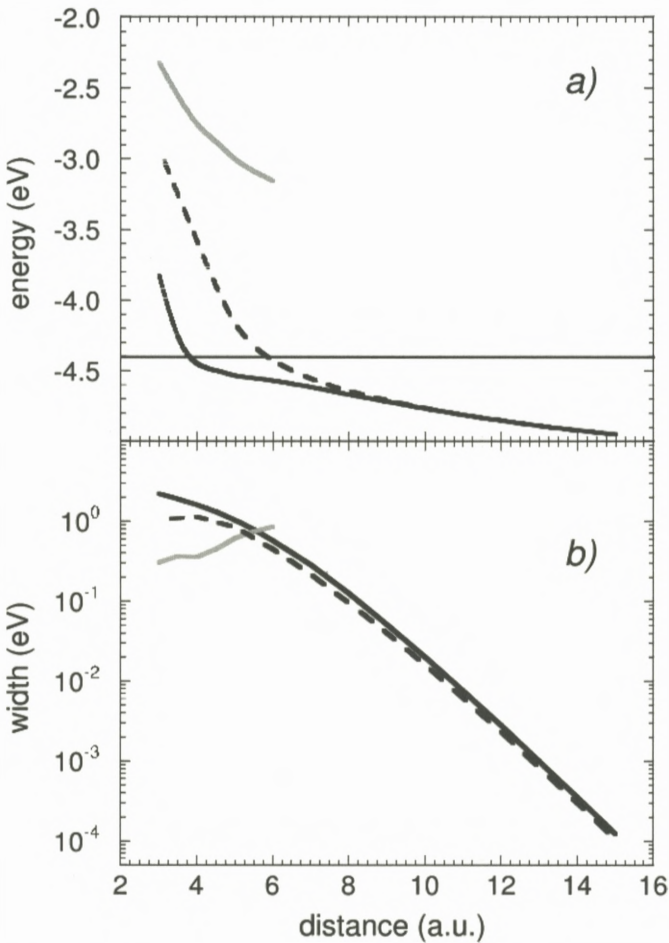


Figure 7. Energy (a) and width (b) of the adiabatic quasi-stationary states involved in the neutralization of Li^+ ions on a Ag surface as a function of the Li-surface distance. Dashed line: state correlated to Li(2s) at infinite separation in front of a free-electron metal surface. Full black line: state correlated to Li(2s) at infinite separation in front of Ag(100). Full gray line: state correlated to the surface state resonance (from Canario et al., 2005).

vacuum), leading to a surface state resonance located at -3.19 eV. The interaction between the Li(2s) state and the 2D-surface state resonance continuum results in a state splitting off the bottom of the 2D-continuum, with which the Li(2s) level exhibits an avoided crossing as a function of Z , the Li-surface distance. As a consequence, on Ag(100), at small Z , the energy of the Li(2s) state appears much different from the free-electron case. The range of Z distances where Li^+ neutralization can occur is much broader on Ag(100) and, in an adiabatic view,

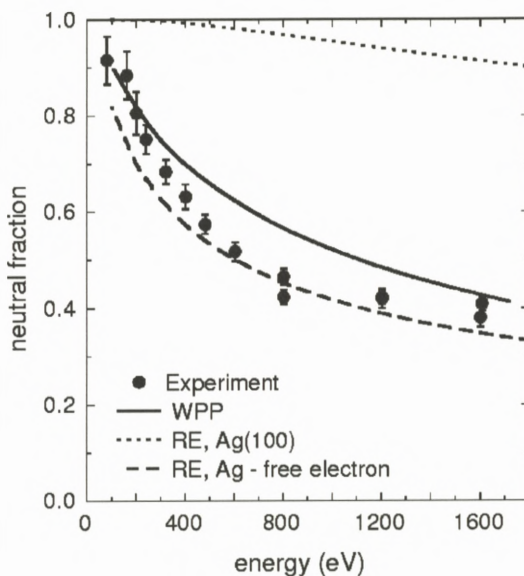


Figure 8. Neutralization probability of Li^+ ions colliding on a $\text{Ag}(100)$ surface. Symbols: experimental results as a function of the collision energy. Dotted line: theoretical results using a rate equation approach with the adiabatic $\text{Ag}(100)$ description. Dashed line: theoretical results using a rate equation approach with a free-electron metal description. Full line: dynamical WPP results (from Canario et al., 2005).

one would then expect a much more efficient Li^+ neutralization on $\text{Ag}(100)$ than on a free electron metal surface.

Figure 8 presents the neutralization probability as a function of the ion collision energy. It shows the experimental results together with three different theoretical results. First, two theoretical results are obtained using the adiabatic rate equation (Equation 1) together with the energy and width obtained in the static study, for the $\text{Ag}(100)$ or free-electron case. As discussed above, in this adiabatic approximation, the neutralization is much more efficient in the $\text{Ag}(100)$ case. A third theoretical result is obtained using the dynamical WPP approach, i.e. with all the non-adiabatic aspects of the electron transfer taken into account. The dynamical WPP result appears rather far away from the adiabatic rate equation result for $\text{Ag}(100)$ revealing strong non-adiabatic effects in this system. It also appears that the dynamical WPP result is in quite good agreement with the experimental results, confirming the validity of the present approach. The first conclusion is then that non-adiabatic effects are important and that one cannot deduce the collisional behavior of the system from the knowledge of the static system. One can link this with the existence of an avoided crossing between two quasi-stationary states in

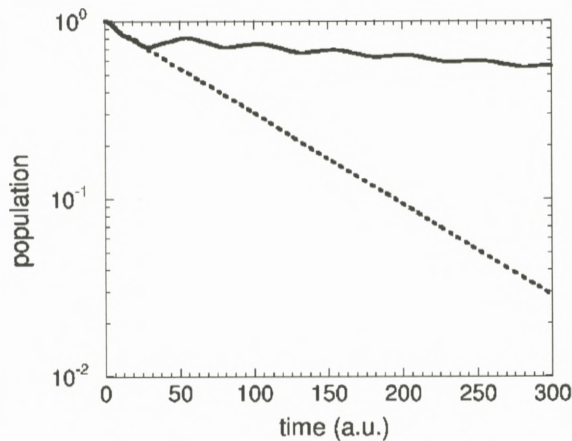


Figure 9. Survival probability as a function of time (in atomic units) for an H^- ion located at $10 a_0$ from a metal surface. Dashed line: free-electron metal surface. Full line: Cu(111) surface (from Borisov et al., 1999a).

this system (see Figure 7), which should play a role at large enough velocities. However, one can also notice that the non-adiabatic effects tend to bring the Ag(100) results very close to those of a free-electron metal, i.e. that non-adiabatic effects seem to erase the effect of the Ag(100) electronic band structure.

Qualitatively, this disappearance of the band structure effect can appear surprising, though it can be understood by looking at earlier results on H^- ions interacting with a Cu(111) surface (Borisov et al., 1999a). The H^- ion level is inside the Cu(111) surface-projected band gap and similarly to the Cs/Cu(111) case, the H^- ion RCT rate is much smaller on a Cu(111) surface than on a free-electron metal surface. Figure 9 presents the survival probability of the H^- ion level at a fixed ion-surface distance from two different surfaces: a free-electron metal and Cu(111). The ion survival probability is computed with the WPP approach as outlined in Section 4.1. On the free-electron metal surface, the ion survival probability is seen to decrease exponentially with time; this further confirms the discussion in Section 2: the ion level is degenerate with a continuum and following the Fermi Golden Rule, its population decreases exponentially with time, the lifetime being the inverse of the RCT rate. On Cu(111) at late times, the population is also seen to decrease exponentially, though with a smaller slope; the slope difference between the two cases is the signature of the projected band gap effect that partially blocks the RCT on Cu(111). However, on Cu(111), the very early decay of the ion level is identical to that on a free-electron metal. This can be understood in the following way: at the beginning of the propagation, the electron wave packet is around the projectile. The electron wave packet starts to

tunnel through the barrier separating the projectile and the metal, this step is the same on the two surfaces and favors the area around the surface normal. On the free-electron metal surface, the electron wave packet spreads into the bulk. On Cu(111), as the electron wave packet penetrates into the metal, it feels the periodicity of the potential that is responsible for the band structure; more precisely, the electron wave packet is partly reflected at each atomic plane inside the metal and the interference created by these multiple reflections generates the projected band gap, i.e. prevents the electron from propagating into the metal along the surface normal. These interferences are visible in Figure 9 as the small undulations in the ion survival probability, in the Cu(111) case. After many reflections, the electron wave packet “fully knows” about the band structure and the RCT process stabilizes at a very slow rate, signature of the projected band gap effect. This discussion leads to the understanding of the Li/Ag case: if the collision is fast, i.e. if the collision time is short, the effect of the band structure does not have enough time to set in during the collision and the surface behaves as a free-electron metal surface.

This result has a few direct consequences for charge transfer studies. It illustrates that electron transfer at low and high collision velocities can be qualitatively different. The change of behavior of the RCT process as a function of the collision velocity formed the basis of the interpretation of experimental charge transfer studies on Ag(111) as a function of collision energy (Guillemot and Esaulov, 1999). For grazing angle scattering on Cu(111) surfaces (Hecht et al., 2000), the collision energy for the motion perpendicular to the surface is in the eV range and experimental and theoretical studies showed that the RCT process is deeply influenced by the Cu(111) band structure, in particular a clear signature of the role played by the surface state is present. At higher velocities, like those discussed above on the Li/Ag system, the effect of the band structure is basically absent (note that the energy scale in Figure 8 is in the keV range, showing that, in this system, the critical velocity where non-adiabatic effects appear is low).

5. Open Questions

Sections 2 and 3 have presented results on two different kinds of collisional systems where the electronic structure of the solid target is directly influencing the characteristics of the electron transfer process. Though, the last section detailed an example where the effect of the electronic structure of the solid on the charge transfer disappears when the collision time is short enough. This feature can look surprising at first sight, however, it is rather easily understood in terms of the minimum time required for the active electron to probe the structure of the solid. In addition, it brings in quite a few questions on various systems, in which it

is not obvious at first sight which are the solid characteristics that are actually influencing the charge transfer. Some of these systems are reviewed below.

5.1. BULK ELECTRONIC STRUCTURE EFFECTS

Theoretical studies of the RCT using a free-electron description of the metal surface have been used successfully for non-free-electron metals; possibly, the finite collision velocity was the reason for their success. We can then wonder about other solids like semi-conductors or semi-metals (graphite). Can a finite time effect remove the effect of a semi-conductor band gap? Though a few theoretical studies have been reported for collisions on Si surfaces (García et al., 2006; Lorente et al., 1997), the author is not aware of a work specifically addressing this point. Similarly, graphite is expected to present some specific features for charge transfer linked with the very small density of states around the Fermi level. This feature has been invoked (Tsumori et al., 1997) to interpret the large negative ion yields on graphite or diamond: the low density of states around the Fermi level should reduce the efficiency of re-neutralization of the negative ions formed close to the surface. Here again, one can wonder how such an effect would survive in fast enough collisions and what would be the critical velocity for the switch between the two behaviors.

5.2. CORRELATION EFFECTS

The approaches to electron transfer discussed above rely on a one-electron description of the process. However, there are a large number of electrons in a solid and they can possibly lead to many body effects in the charge transfer process. Various theoretical approaches have been developed to include many body effects (Brako and Newns, 1985; Nakanishi et al., 1987; Langreth and Nordlander, 1991; Marston et al., 1993; Shao et al., 1994; García et al., 1995; Merino and Marston, 1998). The effect due to correlation on the projectile (existence of equivalent electrons or of different levels on the projectile) is significant and in the rate equation approach, it can be handled simply by introducing several charge states and/or electronic levels in the rate equations. In the case of degenerate atomic levels, this leads to extra statistical factors, bringing an unbalance between capture and loss processes (see e.g. a discussion in Zimny, 1990; Langreth and Nordlander, 1991; Gauyacq et al., 2000). Correlation inside the metal is more delicate to handle. In many cases, it does not seem to play an important role (Ustaze et al., 1998). However, in the case of a degenerate impurity interacting with a metal surface, many-body effects have been shown to lead to the appearance of a peak in the density of states close to the Fermi energy, the so-called Kondo peak. Such a peak has been observed by scanning tunneling spectroscopy (Madhavan et al., 1998).

It has been proposed to play a role in the case of collisional charge transfer (Shao et al., 1995, 1996). Indeed, an atom approaching a metal would generate a Kondo peak in the density of states; the transient population of the Kondo peak during the collision time would then influence the final outcome of the electron transfer process. However, the Kondo peak is a narrow structure which needs time to appear and the question arises whether in a finite time collision, such a peak could be generated and influence the collision. Theoretical discussions of the conditions for its appearance in a collision have been presented (Shao et al., 1996; Merino and Marston, 1998), but it has not been observed experimentally yet.

A projectile can have different electronic levels that could participate at the same time in the charge transfer process. This brings some correlation effects. For example, a positive ion can capture electrons in different levels, but once it has captured an electron on a given level, this blocks the capture on the other levels. This effect is automatically introduced in a rate equation approach by adding a population term for each level. There has been a few experimental and theoretical studies of neutralization of alkali projectiles on metal surface partially covered by alkali adsorbates, which showed that neutralization could occur both toward the ground state and toward the lowest lying excited states (Behringer et al., 1996a, 1996b; Brenten et al., 1991; Goryunov, 1998). In this case, the electron was transferred between the projectile and the target and no transition between projectile states was invoked. However, when several states are close in energy, one can expect transitions between these states to be induced by the motion of the projectile. Such transitions are linked to a non-adiabatic behavior of the collisional system. This happens for example in the case of Rydberg atoms approaching a metal surface. Rydberg states are very close in energy one from the other and can be easily mixed by the interaction with the surface. Recently, a new method has been proposed to measure the ionization distance of a Rydberg atom approaching a metal surface (Hill et al., 2000; Dunning et al., 2003). It makes use of an external electric field that can repel the ions from the surface once they are formed by ionization. Because of the presence of an external electric field, the Rydberg atoms incident on the surface are in fact in Stark states and can thus be polarized in two directions: toward the surface or away from it. A striking result of these experiments was that Stark hybrid states polarized toward the surface appear to ionize at the same distance as Stark hybrids polarized away from it (Dunning et al., 2003). This is at variance with what can be expected from static theoretical studies of the Rydberg-metal system (Nordlander, 1996), which showed drastic variations of the RCT rate as a function of polarization. In addition, these static calculations revealed the existence of many avoided crossings between Rydberg states that could induce inter-Rydberg transitions. A dynamical theoretical study of this system revealed important inter-Rydberg transitions and

allowed to account for the apparent absence of polarization effect: it is simply due to the inter-Rydberg mixing induced by the interaction with the surface and the field (Sjakste et al., 2006). In the Rydberg state case, non-adiabatic transitions between projectile states are then able to qualitatively change the outcome of a given ionization experiment. This result points at the possible importance of intra-projectile transitions induced by the collision motion; these can deeply modify the electron transfer process from the usual picture in which transitions only occur between the projectile and the target.

5.3. SURFACES WITH ADSORBATES

The case of adsorbates present on the surface also brings some interesting questions. The effect of adsorbates on the charge transfer has often been split into two (Gauyacq and Borisov, 1998): a non-local effect associated with the change of surface work-function due to the adsorbate and local effects due to the local modifications of the potentials and couplings in the vicinity of the adsorbate. Several theoretical studies of the local perturbations on the RCT have been reported (Nordlander and Lang, 1991; Borisov et al., 1996c) that confirmed their importance, an adsorbate being able to perturb the charge transfer in a large area surrounding it (Borisov and Gauyacq, 2000). Studies including both local and non-local effects on the RCT brought detailed accounts (Goryunov et al., 1998) of experimental studies in back scattering geometry (Weare and Yarmoff, 1996) that allows selecting the impact atom, adsorbate or substrate, on the surface. Similar studies of other charge transfer processes also brought experimental evidence of charge transfer probabilities depending on the impact point on the surface (Brongersma et al., 1994). Scattering from a surface partly covered with adsorbates leads to another interesting effect if the electron active in the transfer can be temporarily captured by the adsorbate. One then has a three-body problem, the active electron making transitions between the projectile, the adsorbate and the substrate. Different time scales for the different transfer processes between the three bodies lead to quite different electron transfer behaviors. In the case of a long-lived state localized on the adsorbate, as for example for Cs adsorbates on Cu(111), a theoretical study has shown that multiple jumps of the electron between the projectile and the adsorbate are possible, leading to interferences (Sjakste et al., 2004). The charge transfer between the projectile and the surface then has the properties of charge transfer between atoms slightly perturbed by the surface environment; in particular, the irreversibility of the charge transfer with a metal surface has partly disappeared. In contrast, if the adsorbate localized state is very short-lived, like in the case of alkali adsorbates on a free-electron metal, the adsorbate-localized state appears more like a sub-structure of the metal continuum than as a meaningful intermediate in the charge transfer. As an extreme

situation, theoretical calculations in the case of H^- ions approaching an Al surface with Li adsorbates on it (Sjakste et al., 2003), revealed a very striking situation. In the static picture (fixed hydrogen projectile) there exists an avoided crossing between the H^- state and a state localized on the Li adsorbate. However, when the H^- ion approaches the surface, the active electron is not transferred to the adsorbate; the electron dynamics is always non-adiabatic in the avoided crossing region even at very low collision energy and it is as if the system was ignoring the existence of a state localized on the adsorbate. This feature should have important consequences. It means that, in general, one cannot rely on static calculations, like e.g. those performed in quantum chemistry, to predict what will happen in a collision process: the presence of an avoided crossing points at the possibility of an electron transfer process which finally turns out not to exist. Said in other words, a feature in the electronic structure of the surface (in the present case, a state localized on the adsorbate) is not playing a role in a collision. This makes it analogous to the point discussed in Section 4.3 and had to be linked with the very short lifetime of the adsorbate-localized state.

More generally defects at surfaces should influence the charge transfer process characteristics. Besides the case of adatoms or adsorbates outlined above, this effect has not been much investigated. Indeed this is not an easy problem to study in a controlled way. It could play a significant role in the case of sputtering events where one expects the surface target to be locally perturbed by the impacting particle (see articles by Wucher and Urbassek in this volume). Recently, this problem has been investigated experimentally at the individual collision level and a significant effect of the collision-induced deformation of the lattice on the charge transfer has been reported (Maazouz et al., 2003). Steps at surfaces could also influence the charge transfer process at surfaces. Very few studies have been performed on the effect of steps on the surface. Experimental evidence was reported for the enhancement of the H^- ion formation in collisions on Al surfaces in the presence of steps (Wyputta et al., 1991) and this was interpreted in Makhmetov et al. (1996) as a consequence of the asymmetry of the perturbations induced by the steps up and steps down in the so-called “parallel-velocity effect” (see Section 2). More recently, a theoretical study of charge transfer on vicinal metal surfaces also concluded on the different effect of the steps up and steps down on the charge transfer (Obreshkov and Thumm, 2006). Though, the case of a vicinal surface might be different from the case of individual steps on a surface, because of the extra periodicity brought by the vicinal surface that influences the surface located electronic states and can thus influence the charge transfer.

5.4. FINITE SIZE EFFECTS

A finite size (nano-structured) target can also be thought to lead to a specific behavior of the electron transfer processes. For example, in a thin film, the metal states are quantised for the motion perpendicular to the surface and the 3D-continuum of metal states becomes a set of 2D-continua. Theoretical studies of the static situation (a fixed atom in front of a thin metal film) revealed strong differences with the corresponding situation with a semi-infinite metal (Borisov and Winter, 1996; Thumm et al., 2000; Usman et al., 2001). The width of an atomic level was found to exhibit sharp variations as a function of the atom-surface distance, when the atomic level crosses one of the metal quantised levels, i.e. at the opening/closing of a 2D-continuum as a channel for electron transfer. The existence of sharp steps is connected with the 2-dimensional nature of the metal continua. This situation bears some resemblance with the case of a metal with a surface-projected band gap and 2D-surface and image states. The 2D-nature of the metal continua is also expected to lead to some specificities for the so-called “parallel velocity effect” (Yan et al., 1977), similarly to what has been observed for Cu(111) surfaces (Hecht et al., 2000). No detailed experimental studies have been reported on these systems. However, one can expect finite time effects to play a role in such systems (Usman et al., 2001). An electron will need some time to fully “know about” the quantisation in the thin film. Typically, the electron has to perform at least a back and forth trip across the film to know about its finite size. If the collision is fast, then quantisation inside the film does not play a role and the electron transfer occurs as on a semi-infinite metal. The conditions for the observation of finite size effects on charge transfer during a collision on a thin film have been discussed (Usman et al., 2001), based on a theoretical study using a dynamical wave packet propagation approach (Section 4.1). A detailed experimental study on such a system is still missing but would certainly bring a lot of information on finite size and finite time effects and their interplay.

A more extreme situation for finite size effects is provided by metal clusters adsorbed on a surface. Electron transfer between a projectile and a supported cluster is an appealing system to study, both for its expected peculiarities and for its links with catalysis. Recently two experimental studies (Liu et al., 2004; Canario and Esaulov, 2006) were devoted to such a system: alkali ion neutralization by collision on Au and Ag clusters adsorbed on TiO_2 . A strong enhancement of the neutralization probability was observed when going from the semi-infinite metal to clusters and as the size of the clusters decreases. This has been interpreted as an effect of the presence of quantised states inside the cluster or equivalently to the transition of the target electronic states from a metal continuum to quantised discrete states (Liu et al., 2004; Canario and Esaulov, 2006). Similarly to the case

of thin films discussed above, this effect should be dependent on the collision velocity. Another interesting question arises in the case of supported clusters (actually it also arises in the case of atomic or molecular adsorbates). Upon adsorption, the Ag and Au clusters reach charge equilibrium with the substrate and may become negatively charged due to an electron capture from the substrate. What happens when an electron from the cluster is captured by the projectile: is the cluster/substrate charge equilibrium immediately restored, i.e. are electrons flowing between the cluster and the substrate extremely rapidly? Or does the cluster charge remain unbalanced for a while? These two behaviors remind of the difference between the two systems discussed in Sections 2 and 3, metal and ionic crystal targets. Depending on the rate of electron transfer between the cluster and the substrate, different descriptions of the projectile-cluster charge transfer should be chosen. This choice is again *a priori* dependent on the collision velocity. A detailed theoretical study of electron transfer during a collision with a supported cluster with all its finite size and finite time effects is still to be developed.

6. Conclusions

The collisional electron transfer process links discrete atomic levels of the projectile to the electronic states of the solid. Since electron transfer is very sensitive to the characteristics of the electronic structure of the solid, it can be seen as a probe of the various electronic structures that can exist in solids. Indeed, the nature of the electron transfer process is quite different if one considers delocalized continuum states like in a metal or electronic states localized on certain sites of the solid like in an ionic crystal. For one-electron transition for example, one can expect irreversible bound state-continuum transitions in one case and reversible transitions like in atom-atom collisions in the other. These different behaviors are clearly evidenced in a series of electron transfer problems, for which efficient theoretical schemes could be developed. The present review focuses on an effect that modifies the simple view seen above and that can even eliminate the effect of some characteristics in the solid electronic structure: a collision event only lasts for a finite amount of time and this introduces finite time effects on the electron transfer. This can be related to the time-energy uncertainty relation. When viewed on a short time scale, a system cannot exhibit all the characteristics of its electronic structure and this can deeply influence the electron transfer process. There is a series of collisional systems where one can expect finite time effects to play a role and where they have not yet been observed or fully discussed. These involve for example surfaces with narrow band gaps or quasi-band gaps, with adsorbates, with thin films or with nano-structures adsorbed on them.

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