Charge Transfer Processes in Atom-Surface Collisions

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Charge transfer processes in atom-surface collisions

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Abstract

Theoretical methods for describing charge transfer processes in atom-surface collisions will be reviewed. Special emphasis will be on the resonant tunneling mechanism, which normally is expected to be the dominant decay mechanism of excited states near metal surfaces. Recent theoretical calculations have shown that the lifetimes for excited atomic states near metal surfaces can be much longer than what previously has been believed. This finding has important consequences for the interpretation and modeling of charge transfer processes in atom-surface scattering events. In particular, it means that excitations in a desorbing species formed at the time of impact or near the surface may survive the passage through the surface region.

In the region close to the surface, it is important to describe the hybridization between the atomic and the surface levels as well as effects of impurities on the local electronic structure. It is shown that such effects can be particularly strong when alkali atoms are coadsorbed on the surface. At finite alkali coverage, the energies of atomic levels will appear corrugated along the surface. It is shown that this effect can drastically influence the probability for a charge exchange process in an atom-surface scattering event.

A dynamical theory for describing ion/atom-surface charge exchange processes that takes into account the low tunneling rates as well as non-image-like level shifts and lateral corrugations of the surface potential at small atom-surface separations is presented. The results are applied to recent experimental sputtering, desorption and ion-surface neutralization data. Good agreement between experiments and theoretical predictions is found indicating that the theoretical model is accurate.

Introduction

Charge transfer processes play an important role in surface science. Many surface reactions such as dissociation and sticking are believed to depend crucially on the probability for an electron to transfer from the surface into excited atomic or molecular levels, (Sjøvoll et al., 1987) and (Norskov et al., 1979).

Electron transfer processes also play a very important role in quenching certain dynamical responses that could be induced by electronic transitions. One example of this is stimulated desorption, (Tolk et al., 1978) and (Madey, 1986). The stimulated desorption process can occur if an atom is electronically excited into an antibonding state sufficiently longlived to enable the atom to acquire enough kinetic energy to leave the surface, (Menzel and Gomer, 1964), (Redhead, 1964) and (Feibelman and Knotek, 1978). In the same way, photochemistry at surfaces depends on the enhanced reactivity of electronically excited species and the time the photon induced excitation survives, (Ho, 1988).

The occurrence of charge transfer at surfaces can also be used to probe important microscopic features of the surface. For instance, in the Scanning Tunneling Microscope, (STM), both the electronic and geometrical structure of the surface is probed by measuring the tunneling current between an external tip and the surface as a function of lateral position and voltage, (Hamers et al., 1986) and (Wolkow and Avouris, 1988). The state selective study of desorbing or sputtered particles can in principle reveal the same type of information but also provide details of the electronic structure of the surface not accessible with STM, (Wunnik et al., 1983).

The purpose of the present paper is to review some theoretical descriptions of charge transfer processes between atoms and surfaces. The starting point for charge transfer models is an accurate calculation of the tunneling rates between atomic levels and the surface.

Early calculations of tunneling rates between atoms and surfaces have found that the atom-surface electron transition rates can be very large so that charge transfer can occur at large distances from surfaces, (Remy, 1970,1978) and (Gadzuk, 1967). In this region the metal surfaces can be assumed to be uniform since the lateral corrugation of...
the electronic structure of a metal surface decays exponentially away from the surface. The charge transfer dynamics between atoms and perfectly uniform surfaces can therefore be modeled using relatively straightforward 1-dimensional models.

In some recent calculations, (Nordlander and Tully, 1988) and (Nordlander and Tully, 1989a), it has been shown that charge transfer processes involving atoms moving at energies around 1 eV are only possible relatively close to the surface (1-10 a.u.). At such small distances the neglect of lateral corrugation of the surface electronic structure is not appropriate. In addition, the shift and broadening of atomic levels will no longer be simply image-like, but can be influenced by hybridization with the surface states. It will also be shown in the present paper that atomic level shifts and broadenings at these short distances can be strongly affected by chemisorbed impurities. Theoretical calculations of the shift and broadening of the lowest hydrogen atomic levels as function of perpendicular distance outside a potassium atom chemisorbed on a metal surface will be presented and compared with the corresponding situation outside a clean metal surface. The results show that the adsorbate levels can be strongly corrugated along the surface when chemisorbed alkalis are present.

The proper modelling of charge transfer processes between atoms and corrugated surfaces represents a very complicated problem where the charge transfer along the various possible trajectories of the atom outside the surface must be considered and averaged.

In order to investigate the qualitative aspects of a lateral corrugation of energy levels a simple extension of the earlier one-dimensional charge transfer theories to include surface corrugation will be presented. An application of this model to some recent experiments will be presented. It will be shown that a consistent explanation of several experimental observations can be given using the calculated energy shifts and tunneling rates.

Theory

In this section the theoretical background necessary to describe charge transfer processes between atoms and solids will be reviewed. Section I contains a description of how the surface electron potential can be calculated. In section II, the present method for calculating the shifts and widths of atomic levels is presented. In section III, it will be demonstrated how the calculated shifts and level widths can be combined with a dynamical theory to calculate the probabilities of observing excited atoms and ions emerging from surfaces.

I. Electron potential outside surfaces.

In the next subsections, it will be shown how the surface potential can be calculated using density functional methods. In the first subsection, a clean metal surface will be considered and in the second subsection an alkali-covered surface will be treated.

1a. Clean metal surfaces. In the following we will assume a one-electron description of the surface and atomic electrons. Atomic units will be used throughout the text except when otherwise indicated. The coordinate system will be cylindrical with the positive z-axis oriented towards vacuum. The coordinate origin, z=0, corresponds to the actual location of the surface. The radial coordinate \( \rho \) refers to a surface normal through the atom. Upper case letters will be used to describe the coordinates of the atom and lower case letters refer to the electron coordinates.

Atomic levels shift and broaden in the vicinity of a metal surface. The origin of these effects are changes in the electron potential around an atom due to the presence of a surface. The basic features of the shifts and broadenings can be understood from a simple classical electrostatic model where the metal is assumed to be perfectly conducting. In order to introduce some basic concepts, the discussion will start with the properties of the classical surface potential. After this initial discussion, a more realistic metal surface description will be invoked. To begin the discussion, a neutral atom is placed outside the surface. We are interested in how the various neutral levels will shift in the vicinity of the surface. The atom can be considered as a positive core and one electron. If the atom is placed at a distance \( Z \) outside the perfectly conducting metal surface the total potential for the electron located at \((\rho, z)\) is

\[
V^{\text{eff}}(\rho, z; Z) = -\frac{1}{4z} + \frac{1}{\sqrt{\rho^2 + (z + Z)^2}} + V^A(\rho, z; Z).
\]

The first part of this expression represents the image interaction between the electron and its image. The second part describes the repulsive interaction of the electron with the image of the positive atom core. \( V^A \) is the interaction between the electron and the rest of the atom and \( \vec{r} \) denotes the coordinates of the electron with respect to the atom. We note that if the electron is close to the atom, the total surface induced electron potential is repulsive. The atomic levels will thus shift upwards. This means that it will be easier to ionize an atom close to the surface. In fig. 1a we plot the various contributions to the electron potential. From fig. 1a, it is also obvious why the atomic states will broaden. The surface potential is attractive and an electron in the atom can tunnel into the surface or vice versa.

For a negative atomic state, the situation is somewhat different. The electron potential for an atomic affinity level takes the form

\[
V^{\text{eff}}(\rho, z; Z) = -\frac{1}{4z} + V^A(\rho, z; Z),
\]

where \( V^A \) is the interaction between the electron and the neutral atomic core. Electrons in negative ion states thus feel a different electron potential since the electron-core image repulsion is absent. Affinity levels of an atom tend to shift downwards near the surface. Since there is no repulsive electron-core image potential in this case, affinity levels can be expected to be broader than ionization levels.
Charge transfer processes in atom surface collisions

A real surface is not perfectly conducting and the induced image charges will be distributed in a thin layer close to the surface. In addition, for small electron-surface separations the electron will not be separated from its exchange correlation hole and the potential will saturate to a finite value. In order to describe this process we invoke the jellium model of the surface, (Lang and Kohn, 1970). The jellium approximation amounts to treating the conduction electron in the solid as an electron gas. The positive background in the solid is smeared out into a constant attractive potential. The surface is modeled by abruptly truncating the potential at z=0. The jellium model is entirely specified by the valence electron density and the corresponding $r_s$ describing the average distance between the electrons.

In the jellium model, the different terms in the expression for the surface potential in Eq.(1) are modified. The total potential for the electron at coordinates $(\rho, z)$ in the presence of an atom at distance $Z$ from the surface can be written as

$$V^{\text{ef}}(\rho, z; Z) = V_0^p(z) + \Delta V^A_0(\rho, z; Z) + \Delta V^A(\rho, z; Z).$$

The first part of the potential describes the bare electron-surface interaction. This potential can be calculated within the non-local density functional scheme. In the present case we have adopted the weighted density approximation, (Gunnarsson and Jones, 1980) and (Ossicini et al., 1986). This particular many-body approach describes both the image interaction and the potential in the bulk. For large $Z$, $V_0^p \to \frac{1}{4z_{im}}$, where $z_{im}$ is the image plane defined as the first moment of the charge distribution induced by an external electric field. The $\Delta V^A(\rho, z; Z)$ term describes how the bare surface electron potential is modified when an adsorbate is present. For large $Z$ this term approaches $\frac{1}{\sqrt{\rho^2 + (z+Z-2z_{im})^2}}$. For intermediate distances this term is estimated using a linear response approach. The electron charge induced by an external perturbation is distributed in a thin layer around the surface. The thickness of this layer depends on the $r_s$ of the metal and has been calculated within the local density approximation, (Lang and Kohn, 1970) We assume that the image charge distribution can be written as

$$\sigma(\rho', z', Z) = \frac{1}{\sqrt{\Delta}} e^{-\frac{(\rho')^2}{\Delta}} \sigma_0(\rho', Z - z_{im}),$$

where $\sigma_0$ is the radial surface charge electron density in the presence of a unit positive charge located at a distance $Z - z_{im}$ from a perfectly conducting metal. Using this ansatz for $\sigma$, the change in the electrostatic potential as well as the induced exchange correlation potential can be calculated using Poisson’s equation and a proper exchange correlation functional.

In Fig. 1b, we show the electron potential for an adsorbate outside a jellium surface modeled using the present many-body approach. It can be seen that the density functional potential is much more smoothly varying than the result from classical electrostatics in fig. 1a. The classical potential diverges at the origin while the proper potential saturates at the bulk value. In order to properly describe the interaction between the atom and the surface, it is important to use an accurate description of the surface potential, (Nordlander and Tully, 1990)

In this paper various neutral excited states of hydrogen and alkali atoms will be studied. For hydrogen, the atomic potential, $V^A = \frac{1}{\rho}$ will be used and for the alkali atoms a pseudopotential, (Bardsley, 1974) will be employed in Eq.(3).
Alkali covered surfaces. Alkali coadsorption on metal surfaces can dramatically increase the catalytic activity of transition metal surfaces. This phenomenon, referred to as catalytic promotion, has been the subject of numerous experimental and theoretical treatments. The origin of this effect is not well understood. Hamann et al have proposed that this effect is induced by global changes in the density of states, (Feibelman and Hamann, 1984). An alternative explanation has been given by (Lang et al., 1985), who point out that strong electrostatic fields will be induced in the vicinity of chemisorbed alkali atoms. Such fields may shift the levels of chemisorbed atoms and thus alter their reactivity.

Coadsorption of alkali atoms on metal surfaces is often used as a means of changing the work function of a metal. In the context of understanding the charge transfer dynamics, it is important to investigate the microscopic interaction between atoms and alkali covered surfaces.

In order to model such a system calculations of the shift and broadening of atomic levels will be performed for H levels outside a K chemisorbed on jellium. Due to the low symmetry of this system, the H will be placed along the surface normal through the chemisorbed impurity. The chemisorbed K is modeled using a K pseudopotential and a negative image charge located at $Z_K$.

The chemisorption distance $Z_K$ of K on Al jellium is $4 \text{ a.u.}$ The K induced potential is added to the expression (3) for the potential $V^{eff}$. In fig. 2, a contour plot of the K induced potential is shown outside the surface.

It is clear that both the shifts of atomic level and the tunneling rates will be influenced by such impurities. In the next section a calculation of these quantities will be presented.

II. Calculations of the shifts and broadening of atomic levels near surfaces.

The presence of the surface opens up the possibilities for resonant tunneling between the atom and the solid. The atomic levels become resonances. This fact complicates the description of the atomic levels significantly. In order to calculate the level shifts and broadenings the Schrodinger equation for the electrons must be solved

$$[-\nabla^2 + V^{eff}(\rho, z; Z)]\psi = \epsilon \psi.$$  

under the proper boundary conditions. Resonances satisfy the so-called Siegert boundary conditions:

$$\Psi(r) \rightarrow e^{i(k_\rho r + k_z z)} \phi(r)$$  

where $k_\rho$ is positive. The energy is related to the complex wavenumber, $k$ through $\epsilon = -\frac{1}{2}(k_\rho + i k_z)^2$. The energy thus becomes complex, $\epsilon = \epsilon_R - i \epsilon_I$. The real part of the energy $\epsilon_R$ describes the energy of the level and the imaginary part, $\epsilon_I$ describes the width of the resonance.

It can be seen that these boundary conditions diverge at infinity. This is the case because the number of electrons has to be conserved. The time evolution of the resonance state is

$$|\Psi(r, t)|^2 = e^{-2\epsilon_I t} |\Psi(r, 0)|^2$$  

At infinite time the integral over all space of this expression has to be finite. A convenient solution to the Schrodinger equation is provided by the so-called complex scaling method, (Reinhardt, 1982) and (Junker, 1982). The idea here is to introduce a complex variable substitution in the radial coordinate $r$,

$$r \rightarrow e^{\theta} r.$$  

Upon this variable transformation the resonance boundary condition is changed to

$$\Psi(r) \rightarrow e^{i(k_\rho \cos \theta + k_z \sin \theta)} (k_\rho \cos \theta - k_z \sin \theta) r.$$

If $\theta$ is chosen larger than $\arctan \frac{\epsilon_I}{\epsilon_R}$ this boundary condition goes to zero for large $r$. This means that the resulting Hamiltonian can be diagonalized using an integrable basis. The advantage of simpler boundary conditions is at the expense of having to invert a complex nonhermitian Hamiltonian. This lengthens the computation time somewhat but is not a serious problem. The wave functions are expanded in a finite basis set consisting of generalized Laguerre polynomials. The Hamiltonian is then diagonalized. The accuracy of the calculations can be checked by investigating the dependence of the calculated eigenvalues on the parameter $\theta$. For a complete set of basis functions there should be no $\theta$ dependence provided $\theta > \arctan \frac{\epsilon_I}{\epsilon_R}$.

In fig. 3 we show how the lowest excited H levels shift and broaden with distance from an Al surface($r_z=2$). All
Charge transfer processes in atom surface collisions

Figure 3: Calculated energy shifts (a) and widths (b) of the lowest excited hydrogen states as a function of distance outside an Aluminium surface. Atomic units are used. The dotted lines refer to the H(n=2), m=0 state. The dashed-dotted line is the H(n=2), m=1 state. The solid lines refer to H(n=3), m=0 states, and the dashed lines are the two H(n=3), m=1 states.

Levels shift upwards and become broader with decreasing atom-surface separation. We note that the degeneracy of the n=2 and n=3 states is lifted. The n=2 states are initially four-fold degenerate. When the atom feels the surface potential atomic states similar to the Stark states are formed. These states are denoted \( \psi_{2}^* = \psi_{2s} + \psi_{2p} \), \( \psi_{2}^* = \psi_{2s} - \psi_{2p} \), and \( \psi_{2}^* = \psi_{2s} - \psi_{2p} \), and oriented away, along and towards the surface respectively. As the atom comes closer to the surface, the atomic wavefunction will contain an increasing amount of surface and bulk states.

The different levels show a complicated behaviour with distance. The state oriented towards the surface increases its energy fastest due to the overlap with the surface electrons and eventually crosses the two other states. We note that the different states have very different lifetimes. The widths of the 6s and 4d levels show considerable structure around Z=16 a.u. This is due to hybridization. The spatial extent of the \( \psi_{6s} \) and \( \psi_{4d} \) wave functions is different and consequently these levels will shift differently with distance. For Z=16 a.u., the energies of these states are relatively close and the states can hybridize relatively easily. It can be seen that the state that derives from the atomic 4d levels actually becomes narrower with decreasing atom-surface separation. The variation of the width with distance is obviously non-exponential. Similar effects show up for all alkali atoms, (Nordlander and Tully, 1990).

In Fig. 4, we show how the lowest excited levels of rubidium shift and broaden with distance on an Al surface. The shifts are qualitatively similar to those obtained for hydrogen. The lifetimes behave very differently, however. The widths of the 6s and 4d levels show considerable structure around Z=16 a.u. This is due to hybridization. The spatial extent of the \( \psi_{6s} \) and \( \psi_{4d} \) wave functions is different and consequently these levels will shift differently with distance. For Z=16 a.u., the energies of these states are relatively close and the states can hybridize relatively easily. It can be seen that the state that derives from the atomic 4d levels actually becomes narrower with decreasing atom-surface separation. The variation of the width with distance is obviously non-exponential. Similar effects show up for all alkali atoms, (Nordlander and Tully, 1990).

In Fig. 5, we compare the calculated shifts as a function of distance for H(n=2) and H(n=3) states outside a clean Al and outside a potassium atom chemisorbed on Al. It can be seen that in the latter case the hydrogen levels shift downwards toward the surface. We also note that the splits between the different n=2 and n=3 states are strongly increased. These effects are induced by the strong dipole field induced by the K. Such large downshift of atomic levels near chemisorbed impurities means that charge transfer
is facilitated. This effect will be further discussed in the applications section.

In fig. 6, we show a comparison of the widths of the H(n=2) and H(n=3) states outside a clean Al and outside a K chemisorbed on Al. It can be seen that the widths of the hydrogen levels increase when potassium is present on the surface. This is due to the lowering of the surface potential barrier between the atom and the metal surface, (see fig. 1). When modeling charge transfer processes between atoms and alkali covered surfaces, both the alkali induced shifts of the atomic levels as well as the alkali induced changes of the widths must be included.

III. Dynamical theory for charge transfer.

Surface scattering experiments involve the motion of atoms. The probability for charge transfer will thus depend on the velocity, tunneling rates and the relative position between occupied and unoccupied levels of the surface and the atom. In this section it will be shown how the results of the previous sections can be combined with the assumptions of an atomic trajectory outside the surface to calculate the charge state of an atom. In the first subsection, the standard theory for charge exchange outside perfectly smooth surfaces will be reviewed. In the second subsection it will be shown how a lateral corrugation can affect the charge transfer dynamics.

IIIa. Adsorbate outside a uniform surface. There exist a large number of theoretical treatments of charge transfer processes in atom-surface collisions. For a recent review see (Newns, 1989). One distinguishes between the so-called probability models, (Overbosch, 1980) where the classical rate equation is integrated along atomic trajectories and the so-called amplitude models where the process is described quantum mechanically. The latter method is more accurate and since the probability models can be derived from the amplitude models we will discuss only this model.

The standard theory for charge transfer involves the solution of the time-dependent Anderson Hamiltonian. This
Charge transfer processes in atom surface collisions

was first done in this context by (Blandin et al., 1976). Subsequent applications of this method to a variety of dynamical processes have established the usefulness of this formalism, (Tully, 1977), (Norskov and Lundqvist, 1979), (Brako and Newns, 1981), and (Lang, 1983). The Hamiltonian has the form

\[ H = \epsilon_a(t)n_a + \sum_k V_{ak}c_k^\dagger c_k + \sum_k V_{ak}c_k^\dagger c_a + \text{h.c.}, \]  

(10)

where h.c. is the hermitian conjugate. In this Hamiltonian, \( |a\) represents an atomic level, \( |k\) represent the metal electrons and \( V_{ak}\) is the coupling between the atom and the metal. The time dependence arises from the motion of the atom. Both the energy of the atomic level and the strength of the atom-substrate coupling will thus be time-dependent. The time dependence is entirely specified by the assumptions of an atomic trajectory.

The time dependent Anderson Hamiltonian can be solved using the equations of motion for the operators \( c_a\) and \( c_k\):

\[ i\frac{d}{dt}c_a(t) = [c_a(t), H(t)] \]
\[ i\frac{d}{dt}c_k(t) = [c_k(t), H(t)]. \]  

(11)

The initial population \((t=0)\) of the corresponding states is \( n_a = n_a^0 \) and \( n_k = f(\epsilon_k, T) \) where \( f\) is the Fermi-Dirac distribution

\[ f(\epsilon, T) = \frac{1}{1 + e^{(\epsilon - \mu)/kT}}. \]  

(12)

The solution for the occupation \((t=0)\) of the corresponding states is

\[ \langle n_a(0) \rangle = \langle n_a(0) \rangle e^{-\Delta(t)} \]  

\[ \times \int_{\Delta(t)}^{\infty} d\epsilon \epsilon^{-1} f(\epsilon, T) e^{-\epsilon(t)} \]  

\[ = \int_{\epsilon_{\text{min}}}^{\infty} d\epsilon f(\epsilon, T) e^{-\epsilon(t)} e^{-\epsilon\Delta(t)}. \]  

(13)

We have introduced here the quantities \( \Delta \) and \( \chi \) which are related to the hopping matrix element \( V_{ak} \) through

\[ \Delta(t) = 2\pi \sum_k |V_{ak}|^2 \delta(\epsilon_a(t) - \epsilon_k) \]  

(14)

and

\[ \chi(t) = \int_{\Delta(t)}^{\infty} dt_1 \Delta(t_1). \]  

(15)

The quantity \( \Delta \) is the width of the level \(|a\rangle\). The quantity \( \langle n_a(0) \rangle > e^{-\Delta(0)} \) can be given a simple interpretation by noting that

\[ e^{-\Delta(0)} = \prod_{t>0} [1 - \Delta(t)'\delta(t')]. \]  

(16)

Since \( \Delta(t)' \) describes the tunneling rate per unit time out of \(|a\rangle \) the first term in Eq.(13) describes the survival rate of an electron initially in \(|a\rangle \).

The \( dc \) integration can be performed analytically in Eq. (13), using

\[ \int_{-\infty}^{\infty} d\epsilon f(\epsilon, T) e^{i\epsilon x} = \pi e^{ix\beta} \frac{e^{i\beta x}}{\beta \sinh \frac{\beta x}{2}}, \]  

(17)

If we assume a constant velocity of the atom and a position \( Z_0 \) of the atom at \( t=0 \), the time integrations can be converted to distance integrals weighted by the perpendicular velocity \( v_\perp \). The resulting expression reads

\[ < n_a(0) > = < n_a(Z_0) > e^{-\chi(Z_0)} + \frac{1}{2} \left[ 1 - e^{-\chi(Z_0)} \right] \]  

\[ + \frac{1}{2v_\perp} \int_{Z_0}^{\infty} dZ_1 \sqrt{\Delta(Z_1)} e^{-\chi(Z_1)/2} \Gamma(Z_1). \]  

(18)

\[ \Gamma(Z_1) = \frac{1}{v_\perp} \int_{Z_0}^{\infty} dZ_2 \sqrt{\Delta(Z_2)} e^{-\chi(Z_2)/2} \times \sinh \left( \frac{\Delta(Z_2) - \Delta(Z_1)}{\beta \sinh \frac{\beta}{2}} \right). \]  

(19)

we have here introduced the quantity \( \Lambda \) defined by

\[ \Lambda(Z) = \int_{Z}^{\infty} \frac{dZ_1}{v_\perp} \int_{\epsilon_a(Z_1) - \epsilon_F}^{\epsilon_a(Z)} e^{i\beta x}. \]  

(20)

The function \( \Gamma \) describes the charge transfer dynamics involved when the atomic level crosses the Fermi energy of the metal. We note that the integration over \( Z_1 \) in Eq.(19) involves a function that will oscillate rapidly with \( Z_2 \). The \( \sinh \) term in the denominator tends to cut off contributions where \( Z_2 - Z_1 \) is large.

For large temperatures and low velocities the integration of \( Z_2 \) can be performed analytically and the so-called semi-classical approximation for resonant charge transfer results:

\[ < n_a(\infty) > = < n_a(Z_0) > e^{-\chi(Z_0)} \]  

\[ + \int_{Z_0}^{\infty} dZ f(\epsilon_a(Z), T) \frac{\Delta(Z)}{v_\perp} e^{-\chi(Z)}. \]  

(21)

This expression has a simple interpretation. The first term describes the memory of the initial configuration at \( Z_0 \). The position \( Z_0 \) can be chosen arbitrary along the trajectory of the atom as long as the charge states at \( Z_0 \) and the trajectory evolution, \( Z(t) \) out of \( Z_0 \) is known. \( f(\epsilon_a(Z), T) \) describes the availability of metal electrons of energy \( \epsilon_a \), the ratio \( \frac{\Delta(Z)}{v_\perp} \) describes the tunneling probability per unit distance. The exponential term describes the survival probability of an electron in \(|a\rangle \) during the atomic motion out from the surface. The integrand in Eq. (21) is often sharply peaked around a certain \( Z \). This distance is often referred to as the distance of formation of the excited state or the "freezing distance", (Overbosch et al., 1980).

In order to make the physics more transparent we neglect the memory term and assume exponentially varying level widths, \( \Delta(Z) = \Delta_0 e^{-\alpha Z} \). The \( \chi \) integral can then be performed analytically. The resulting expression reads

\[ \chi(Z) = \frac{\Delta_0 e^{-\alpha Z}}{v_\perp \alpha}. \]  

(22)
For $T=0$, Eq. (21) can be integrated analytically. We assume that at a distance $Z_c$, the level $\epsilon_a(Z_c) = \epsilon_F$. We first consider the probability of observing a positive ion desorbing from the surface. For an ionization level, $\epsilon_a(Z)$ shifts upwards towards the surface. The integral in Eq. (21) is between $Z_c$ and $\infty$. The resulting expression is

$$P^+ = 1 - <n_a(\infty)> = e^{-\frac{\Delta E_2}{\hbar\omega}}$$

(23)

For a negative ion state $\epsilon_a$ shifts down close to the surface and the integral in Eq. (21) is between $Z_0$ and $Z_c$. The resulting expression reads,

$$P^- = <n_a(\infty)> = e^{-\frac{\Delta E_1}{\hbar\omega}}$$

(24)

These formulas show that the probabilities for observing positive or negative ions emerging from the surface will depend on the tunneling probabilities at the position where the levels cross the Fermi energy. Such Landau-Zener type formulas were first derived by (Hagstrum, 1975), and can be used for a qualitative estimate of ion yields as a function of the velocity and $Z_c$. However, they are often too crude for a quantitative interpretation of experimental data as will be discussed in the applications section.

IIIb. Adsorbate outside a corrugated surface. The proper consideration of such effects would involve numerical simulations using realistic trajectories and integrating Eq. (13) along the possible trajectories. In the last section however it was shown that the charge transfer dynamics were strongly influenced by the possibilities of tunneling between the metal Fermi energy and the adsorbate levels. In this section we will investigate how the assumption of a lateral corrugation of $E_a$ can modify the charge transfer dynamics in atom-surface collisions. The formalism is on a qualitative level. The lateral corrugation is assumed to come from chemisorbed impurities or defects such as described in the theory subsection II. In principle, the corrugation due to the lattice can also be treated but is expected to be negligible for metals.

The starting point for our discussion is Eq. (13). This equation is valid provided the proper time dependence of $\epsilon_a$ and $V_{ab}$ is taken into account. In the presence of a lateral corrugation we can make the ansatz

$$E_a(Z(t), p(t)) = \epsilon_a(Z(t)) + \epsilon_1 e^{-\gamma Z(t)} cos(2\pi X(t)/a)$$

(25)

where $X(t)$ denotes the lateral coordinate along the surface. If we assume a linear motion of the atom, $X$ can be expressed in terms of $Z$ through $X = \frac{\alpha}{v_1} Z + X_0$ and the ansatz for $\epsilon_a$ can be written as

$$\epsilon_a(Z, \rho) = \epsilon_a^0(Z) + \epsilon_1^0 e^{-\gamma Z} cos(\kappa Z + \phi),$$

(26)

where $\phi$ represents the lateral position of the atom when $Z = Z_0$. Eq. (18) can now be used to calculate $<n_a(\infty)>$.

First this ansatz is inserted in the expression for $\Lambda$, Eq. (20):

$$\Lambda(Z_2, \phi) - \Lambda(Z_1, \phi) = \Lambda^0(Z_2) - \Lambda^0(Z_1) + \Lambda^1(Z_1, Z_2, \phi)$$

(27)

where $\Lambda^0$ refers to the situation without the corrugation. The $dZ$ integration can be performed analytically and we obtain

$$\Lambda(Z_2, \phi) - \Lambda(Z_1, \phi) = \Lambda^0(Z_2) - \Lambda^0(Z_1) + \Lambda^1(Z_1, Z_2, \phi)$$

(28)

We have here introduced the quantities $\beta = \frac{\gamma}{\sqrt{\kappa^2 + \eta^2}}$ and

$$g(Z) = \frac{\epsilon_1 e^{-\gamma Z}}{v_1 \sqrt{\kappa^2 + \eta^2}}$$

(30)

The expressions will later be averaged over the phase $\phi$ so any constant term adding $\phi$ such as $\beta$ can be neglected. Using the addition theorems for trigonometric functions we can write

$$\Lambda^1(Z_1, Z_2, \phi) = \sqrt{a^2(Z_1, Z_2) + b^2(Z_1, Z_2)}$$

$$\times \sin(\phi + \phi(Z_1, Z_2))$$

(31)

$$a(Z_1, Z_2) = g(Z_1) \sin(KZ_1 + \phi - \beta) - g(Z_2) \sin(KZ_2 + \phi - \beta).$$

(29)

$$b(Z_1, Z_2) = g(Z_1) \cos(KZ_1 - \beta) - g(Z_2) \cos(KZ_2 - \beta).$$

(32)

$$\gamma(Z_1, Z_2) = \arctan \frac{b(Z_1, Z_2)}{a(Z_1, Z_2)}$$

(33)

Because of the $\phi$ averaging we can neglect $\gamma$ in eq. (31). Eq. (28) is now inserted into Eq. (19). The phase $\phi$ only enters in the sine term in the numerator. The phase averaging can thus be performed directly on this term. We define

$$I(Z_1, Z_2) = \int_0^{2\pi} \frac{d\phi}{2\pi}$$

$$\times \sin[\Lambda^0(Z_2) - \Lambda^0(Z_1) + \Lambda^1(Z_1, Z_2, \phi)]$$

(34)

The sine term in this expression can be expanded and we obtain

$$I(Z_1, Z_2) = \sin[\Lambda^0(Z_2) - \Lambda^0(Z_1)]$$

$$\times \int_0^{2\pi} \frac{d\phi}{2\pi}$$

$$\sin[\Lambda^1(Z_1, Z_2, \phi)]$$

$$\times \int_0^{2\pi} \frac{d\phi}{2\pi}$$

$$\sin[\Lambda^1(Z_1, Z_2, \phi)]$$

(35)
Charge transfer processes in atom surface collisions

If the expressions (31) for \( \Lambda^1 \) are inserted here, we obtain

\[
I(Z_1, Z_2) = \sin[\Lambda^0(Z_2) - \Lambda^0(Z_1)] \\
\times J_0(\sqrt{a^2(Z_1, Z_2) + b^2(Z_1, Z_2)}),
\]

where \( J_0 \) is the cylindrical Bessel function of zeroth order. This expression for \( I(Z_1, Z_2) \) should be substituted for the sine term in Eq. (19). As we pointed out earlier the \( dZ_2 \) integration will only contribute for \( Z_1 \approx Z_2 \). In this limit the argument of \( J_0 \) can be expanded:

\[
\sqrt{a^2(Z_1, Z_2) + b^2(Z_1, Z_2)} \rightarrow \frac{\epsilon^2}{v} (Z_2 - Z_1).
\]

We can now clearly see the effect of the lateral corrugation on the charge transfer rates. The effect of \( J_0 \) on the \( Z_2 \) integration in Eq. (19) is to restrict the integration further to small \( Z_2 - Z_1 \). This effect is similar to cut off of the \( Z_2 \) integration induced by sineh term in the denominator of Eq. (19). Qualitatively the effects of a lateral corrugation on the charge transfer process is thus the same as that of an increased temperature. A comparison between the localization induced by a finite temperature and the \( J_0 \) term show that the lateral corrugation of \( \epsilon^2 \) can be accounted for by renormalizing the temperature. It is possible to define an effective temperature

\[
T^{eff}(Z) = \min\left[\frac{1}{kT}, \frac{2}{\epsilon^2(Z)}\right],
\]

This definition is not a functional identity but gives rise to the proper effect in charge transfer. It can be seen that the effective temperature is independent of the periodicity of the corrugation. This result is true to lowest order in the hopping matrix element as long as the thickness of the atomic beam is larger than the spacing between the coadsorbed alkali atoms.

The semiclassical approximation can now be invoked and the resulting expression is

\[
< n_a(\infty) > = < n_a(Z_0) > e^{-\chi(Z_0)} \\
+ \int_{Z_0}^{\infty} dZ f(\epsilon_a(Z), T^{eff}(Z)) \Delta(Z) \frac{\epsilon^2}{v} e^{-\chi(Z)}.
\]

The temperature used in Eq. (39) has nothing to do with the real surface temperature. It is simply a manifestation of the fact that the crossing distances for an atomic level will depend on a lateral coordinate. Resonance conditions \( \epsilon_F = \epsilon_a \) will depend on the lateral position on the surface. This is illustrated in fig 7, which qualitatively describes how an atomic level shifts close to an impurity and outside the clean metal surface, as was discussed in theory subsection II. The crossing distances will be very different in these two situations. In an atom-surface scattering experiment, the lateral positions of the trajectories will be distributed randomly along the surface. The corresponding energy level variations and crossing distances will therefore be distributed over a region between the two limits indicated in fig. 7. The same effect would occur if the Fermi electrons were highly excited. Charge transfer can then occur over a relatively broad region of distances. In principle, this effect could be empirically reproduced by the assumption of a local work function in the vicinity of the chemisorbed alkalis and the clean metal work function outside these regions. The proposed method for including a lateral corrugation is more physically correct, however, since the work function is a macroscopic property and electrons on a metal will distribute themselves so that the Fermi energy remains constant along the surface.

Figure 7: Schematic picture of the variation of a atomic affinity level, \( \mid \alpha \rangle \), near a chemisorbed alkali impurity(A) and on a clean surface(B). For simplicity a triangular DOS is assumed. The occupied metal part of the DOS is shaded. In the upper part of the figure, (a), the trajectories are defined. In the middle part, (b), the density of states of the adsorbate surface system is indicated. The atomic levelshift along the trajectories A and B is schematically indicated. The distances where the atomic level cross the Fermi energy are indicated with \( z^A \) and \( z^B \) for the A and B trajectory respectively. In the lower part, (c), the effect of a high electron temperature on the different crossing distances between the atomic state and populated metal states is schematically indicated.
Applications

In the following section, the applications of the charge transfer formalism developed in the theory section to stimulated desorption, ion-surface neutralisation and sputtering experiments will be discussed.

I. Stimulated Desorption.

Stimulated desorption experiments such as Electron Stimulated Desorption (ESD) and Photon Stimulated Desorption (PSD) are known to provide very detailed microscopic information about the bonds and binding geometry of adsorbed species. (Tolk et al., 1978). In particular the Electron Stimulated Desorption Ion Angular Distribution, (ESDIAD) technique, (Madey, 1986) has extensively been used to probe the structure of various adsorbate/substrate systems. Very recently it has been demonstrated that this method also can provide information about the survival and formation of excited adsorbate species, (A.L. Johnson et al. 1988).

The detection of excited atoms in stimulated desorption provides a particularly interesting means of studying charge transfer reactions between atoms and surfaces since the initial state of the desorbing species can be studied separately and therefore be relatively well characterized.

In recent ESD experiments, (P.D. Johnson et al., 1988) and (P.D. Johnson et al., to be published), the desorption of hydrogen from alkali promoted Ni and Pt surfaces was studied as function of alkali coverage. The formation of H\((n=2)\) and H\((n=3)\) was detected from the Lyman-\(\alpha\) and Lyman-\(\beta\) radiation emitted from the desorbing particles. It was found that the formation of H\((n=2)\) and H\((n=3)\) increases monotonically with alkali coverage even for work functions as high as 5 eV. The onsets for the formation of H\((n=2)\) and H\((n=3)\) occur over a much broader regions of work functions and for much larger work functions than what would be expected for desorption from a clean metal surface. On a clean metal surface, the H levels shift relatively uniformly upwards. The threshold for H\((n=2)\) formation would here be expected to be relatively narrow and located at a work function of around 1 eV. The threshold for H\((n=3)\) formation would be expected to lie at even lower work functions. From the results in the theory section, it is obvious that if the desorbing H originates from the vicinity of the coadsorbed alkali atoms, the charge transfer dynamics will be modified. Since in this region, the atomic levels are downshifted and the splittings and broadenings calculated in theory subsection IIb can be used in the model. Since the hydrogens move normal to the surface they will not experience any lateral corrugation and the charge transfer formalism developed in theory subsection IIIa should be used.

The desorbing H will be assumed to have an initial velocity of 1 eV. The bond length between H and K is taken as 4 a.u. corresponding to the free KH molecule bond length. These assumptions are realistic and the results of the calculation do not depend sensitively on these parameters.

The study of excited state formation in desorption is in principle complicated by the electron correlation effects within the desorbing atoms. The intra-atomic correlation, \(U\), can prevent the electron tunneling into a state if other excited atomic states are occupied. An exact treatment of the time-dependent Anderson Hamiltonian including such effects is relatively complicated. For the work functions in the present experiment, such problems are avoided, however. The downward shifts of the H\((n=3)\) excited state are insufficient to allow tunneling from the metal into these states. The occurrence of any H\((n=3)\) excited state would therefore arise purely from the memory term. Only the most longlived of the H\((n=3)\) states, \(\psi_3^{-}\), can survive the passage out from the surface. With the above trajectory parameters, this state has a survival probability of 25% if formed initially. The remaining H\((n=3)\) states decay immediately if formed near the surface. The \(\psi_3^{-}\) state is longlived and only contributes to the H\((n=2)\) yield through the memory term. The survival probability for this state is 60%. For the description of the formation of the remaining H\((n=2)\) states, we note that the \(\psi_2^\pm\) level and the \(\psi_2^0\) level have such short lifetimes that they will be populated immediately if their energy is below the Fermi level near the surface. These levels can therefore effectively be treated as a threelfold degenerate \(\psi_2^0\) level. The width of this level is so large that the memory term for this state can be neglected. The \(\psi_2^0\) and \(\psi_2^+\) states are the only states that can be formed by resonant tunneling from the metal. Since all other excited states except \(\psi_2^-\) and \(\psi_2^0\) will decay in the vicinity of the surface, the yield of positive ions, \(P^+\), desorbing from the surface will be determined by the probability of formation of \(\psi_2^0\) and \(\psi_2^+\). Since desorption can only occur from a KH surface complex, the total yield of desorbing particles will be proportional to the alkali coverage, \(\Theta_K\). The resulting expressions for the populations of the H\((n=2)\) and H\((n=3)\) states are:

\[
\begin{align*}
n_3^{-}(\infty)_{\phi} &= k\Theta_K P_{3}^{\infty} \exp(-\chi_3^{-}(Z_0)) \\
n_2^{-}(\infty)_{\phi} &= k\Theta_K P_{2}^{\infty} \exp(-\chi_2^{-}(Z_0)) \\
n_2^{0}(\infty)_{\phi} &= [k\Theta_K - n_3^{-}(\infty) - n_2^{-}(\infty)] \\
&\times \int_{Z_0}^{\infty} dZ f(e_{0}(Z), T) \frac{\Delta(Z)}{\psi_2^0(Z)} \exp(-\chi_2^{0}(Z)) \\
P_{\phi}^+ &= k\Theta_K - n_2^{+}(\infty)_{\phi} - n_3^{-}(\infty)_{\phi}
\end{align*}
\]
Charge transfer processes in atom surface collisions

Figure 8: Calculated (Eq. 40) yield of Lyman-α (solid line), Lyman-β (dashed line) and H⁺ (dotted line) as function of work function for H desorbing from a K covered Pt surface. The recent experimental data (P.D. Johnson et al., to be published) for Lyman-α (plus signs) and Lyman-β (filled circles) are also indicated.

The relation between work function and alkali coverage has been measured, (P.D. Johnson et al., to be published), T is the surface temperature (300K). Δ(Z), ε(Z) and χ(Z) are calculated for the different states respectively. We assume that all states are populated initially with equal probability, P.

These expressions can readily be evaluated as function of alkali coverage. The results of the calculation are shown in fig. 8 along with the experimentally determined points.

It can be seen that the agreement between theory and experiment is excellent. Both the H(n=2) and H(n=3) intensity increases linearly at small coverages (large work functions). This is due to the memory terms for the respective states. We also note that the yield of H(n=3) is much lower than the yield of H(n=2). This is due to the differences in lifetimes between the levels. At a work function of around 5 eV, the intensity of H(n=2) starts to increase more rapidly. This is due to the possibilities of formation of H(n=2) at smaller work functions. At a work function of around 3.5 eV, the slope of the work function versus coverage relation decreases, leading to a correspondingly larger increase in alkali coverage. This leads to a more rapid increase of the yield of excited H. We have here neglected the proposed increase in bond length between adsorbed alkali atoms and the metal surface below this work function, (Lamble et al., 1988). A proper inclusion of such an effect would result in a slightly larger slope of the H(n=3) intensity curve for work functions below 3.5 eV, since the survival probability for an excited state is larger the further out from the surface the atom starts.

The decrease in the total ion yield for work functions smaller than 4.5 eV is in good agreement with the findings in the previous study, (Lanzilotto et al., 1988). The reason for this behavior is the efficient formation of H(n=2) for low work functions. This process could not occur on the clean metal surface since the H levels would be image shifted towards the vacuum level.

II. Ion-surface scattering.

Perhaps the most direct method of probing the microscopic details of atom-surface charge transfer is provided by ion-surface scattering techniques. Here the atom(ion) is sent in with well-controlled energy and directions towards...
the surface. The detection can be performed under different angles. Depending on the perpendicular velocity and the relative difference between various atomic energy levels and the Fermi level, detailed information about the surface electronic structure can be obtained. In atom-surface scattering, the lateral corrugation of the surface potential and its effect on the atomic energy levels of the scattered atom will be sampled either through a grazing trajectory or through the finite thickness of the atomic beam. In this section, two recent experiments will be discussed and interpreted using the methods developed in theory subsection IIIb.

In a recent experiment (Geerlings et al., 1987) the neutralization of Li+, K+, and Cs+ ions in surface collision was studied as a function of work function. In the experiment, alkali ions were directed towards a cesiated W(110) surface and the fraction of ions leaving the surface under low angle was measured as a function of Cs coverage. The experimental data is indicated by the symbols in fig. 9. The data refers to different kinetic circumstances. The scattering angles \( \beta \) (angle between outgoing atom trajectory and the surface normal) and ion kinetic energies \( E_{\text{kin}} \) are for Cs, \( (\beta = 85^\circ, E_{\text{kin}} = 100\text{eV}) \) for K, \( (\beta = 80^\circ, E_{\text{kin}} = 1000\text{eV}) \) and for Li, \( (\beta = 80^\circ, E_{\text{kin}} = 400\text{eV}) \).

The experiment was interpreted using Eq. (23) and assuming that the ionisation potential, \( I_0 \) follows the image force. The resulting expression gives for the fraction of ions as a function of work function \( \phi \),

\[
P(\phi) = \exp\left[-\frac{\Delta_0}{a_0} \exp\left(\frac{-\alpha}{4(I - \phi)}\right)\right].
\]

The width parameters \( \Delta_0, a_0, \alpha \) were taken from an earlier calculation (Remy, 1978). The velocity parameters are the same as in the experiment. The results are shown in fig. 9 for Li (dotted line), K (dashed line) and Cs (dash-dotted line). It can be seen that the calculated \( P \) as function of \( \phi \) behaves essentially like a step function around the ionisation energy of the respective atom. The agreement between the calculated and measured ion fraction is very poor. In particular, this is the case for K, where the simple theory predicts no neutral for work functions above the ionisation energy 3.9 eV, but the experiment reveals neutralisation of K for all finite Cs coverages.

We note that in the high work function region, \( P \) increases almost linearly for both K and Li. Since the work function shifts here are linear in Cs coverage this fact suggests that the neutralisation correlates directly with Cs coverage rather than indirectly through the work function.

In order to analyse this data properly we invoke Eq. (39). This expression contains three unknown quantities, \( \Delta_0, a_0(Z_0) \), and \( T^{\text{eff}}(Z) \). In principle \( T^{\text{eff}} \) depends on the distance \( Z \). This dependence will be neglected and \( T^{\text{eff}} \) will be treated as a free parameter.

From the calculations in theory subsection II, we know that the relevant atomic levels will be downshifted in the neighborhood of a chemisorbed alkali atom. Associated with each chemisorbed alkali atom there is thus a volume of influence such that if the scattered ion would pass close to the coadsorbed alkali the ion will be neutralised.

We now make the assumption that if the ion passes through a volume \( a_0^2(Z_0) \) surrounding the alkali atom it will be neutralized. Until realistic calculations of the lateral corrugation of \( e_0 \) have been performed we will treat \( Z_0 \) and \( a_0 \) as free parameters to be determined by a best fit to the experiments. \( a_0^2 \) will be referred to as the area of influence of the coadsorbed alkali atom.

The memory term in the following refers to the atomic state at the surface. If the ion passes sufficiently close to a coadsorbed alkali atom the ion will be neutralised otherwise it remains an ion. As the atom recedes from the surface it can either reionize, neutralize or remain neutralised. The dynamics of this processes is entirely contained in the second term of Eq. (39). The contribution of the memory term will thus depend on linearly on the alkali coverage.

With these three parameters, the resulting expression for the occupation of the ionisation level is

\[
< n_0(\infty) > = \min(\theta_0, \frac{q_0^2}{a_0^2}, 1)e^{-\chi(Z_0)} + \int_{Z_0}^{Z_0} dz f(e_0(Z), T^{\text{eff}}(Z) \chi(z)) e^{-\chi(z)}
\]

In this expression \( a_0^2 \) is the side of the bare surface unit cell, \( \Delta(Z) \) and \( \chi(Z) \) are the calculated widths and corresponding survival integral and \( e_0(Z) \) is the calculated ionisation energy. \( v_1 \) is obtained from the kinetic conditions in the experiment. The results turn out to be insensitive to whether \( v_1 \) is taken as constant or is allowed to vary according to the image force.

The experiments are performed under very different kinetic conditions. The Cs data refer to very low perpendicular velocities. The memory term will therefore not contribute and the calculated results are entirely insensitive to \( Z_0 \) and \( a_0 \). \( T^{\text{eff}} \) can therefore be determined directly from a comparison between the calculated data and the experimental results. The best fit is provided by \( T^{\text{eff}} = 1500\text{K} \). This value might seem low in view of the rather large corrugations depicted in fig. 5, but due to the low velocity the charge transfer from cesium occurs for rather large distances from the surface (15 a.u.). Here the lateral effect of coadsorbed alkalis are relatively small.

For K and Li, the perpendicular velocities are comparatively large and also the memory term will influence the calculated \( P = 1 - < n_0(\infty) > \).

The remaining parameters are now extracted from a comparison with the experimental data. A best fit yields \( Z_0 = 9 \text{ a.u.} \) and \( a_0 = 22 \text{ a.u.} \). The rather large value for \( a_0 \) can be expected in this experiment due to the geometry.
The desorbing atoms move at almost grazing incidence and the lateral size of the chemisorbed impurities could therefore be enhanced.

Using Eq. (43), and the above parameters, the ionisation fractions $P$ are calculated for different work functions. The work function coverage relations that are needed in the evaluation of the memory term have been measured independently, (Desplat and Papageorgopoulos, 1980). The results are shown with solid lines in fig. 9. It can be seen that the overall agreement is very good. The sensitivity of the calculated values to $Z_0$ and $T^{eff}$ is small. The most important parameter is $a_f$ describing the area of influence of the chemisorbed alkali atom in the case where memory is present. We note that $a_f$ in principle should depend on the type of ion that is studied. The ionisation potential for Li is 5.4 eV but for K, the ionisation potential is 4.3 eV. This means that the effective size, $a_f$, of the chemisorbed Cs should be taken larger for Li scattering than for K scattering. This would improve the agreement between the calculated and experimental $P$ for potassium further. However, in view of the qualitative nature of the model, no further attempts on improving the agreement between the theory and the experiment are performed.

The previous experiments were all performed under almost grazing conditions between the scattered ion and the surface. In a very recent series of experiments the neutralisation of potassium and lithium against cesiated Cu(110) surface have been studied under different types of geometry, (Kimmel et al., 1989). The ionic fraction of the scattered particles was studied both as a function of scattered angle, energy and as function of work function. With the help of sophisticated ion trajectory programs the authors were able to discriminate between charge transfer processes along different ion-surface trajectories.

In fig. 10, the results for the ionic fraction $P$ as a function of work function is plotted. The substrate is here cesiated Cu(110). The experiment was performed at 45 degrees scattering angle and for kinetic energies of 100 eV, 400 eV and 1000 eV. It can be seen that the experimental results are rather insensitive to the kinetic energy. Since the scattering angle is much smaller in this experiment it is reasonable to assume a slightly smaller $a_f$. A best fit of Eq. (43) to the experimental data gives $a_f$=18 a.u. The other parameters are as for the above discussed W(110) experiments, i.e. $T^{eff}$=1500K and $Z_0$=9 a.u. The different curves in fig. 10 are the results of a calculation using Eq. (43) for the different kinetic energies used in the experiment.

These applications have shown that Eq. (39) accurately describes charge transfer reactions in alkali-ion neutralisation experiments. The functional form for the neutralization rates provided by Eq. (39) contained three parameters. The values of the parameters obtained by a fit to the experimental data are entirely reasonable as demonstrated in theory section II. A crucial step in obtaining this agreement was the finding of weak broadening for the alkali states, and could not have been obtained using the previous short levels, (Remy, 1978).

![Figure 10: Comparison of calculated and experimental ionisation fraction of K ions specularly scattered at 45 degrees incident angle against a cesiated Cu(110) surface. The open symbols are the experimentally determined values for different kinetic energies of the K ions, (Kimmel et al., 1989): Open boxes refer to 100 eV, open circles refer to 400 eV and the open triangles refer to 1000 eV kinetic energy of the ion. The lines refer to the calculations using Eq. (43) for the different kinetic energies. 100 eV (solid line), 400 eV (dashed line) and 1000 eV (dotted line)](image)
One of the key factors behind the success of this approach was the use of accurate atomic level shifts and widths. These properties were calculated self-consistently at close atom-surface separations and properly extrapolated into the vacuum region.

The velocity distribution of excited sputtered atoms can be measured by studying the doppler shift of laser induced fluorescence of the atomic metastable levels, (Yu et al., 1982) and (Huzinsky et al., 1983) and contain important information about the charge transfer dynamics. The velocity distribution of the total yield of sputtered particles in a collision cascade after a high energy ion impact is broad and can be described by the Thompson distribution function, (Sigmund, 1969).

\[ f(V) = \frac{V^3}{(V^2 + V_0^2)^{3/2}} \] (44)

In this equation \( V^* \) is normally of the order 1eV to 10eV. If the excited atomic levels can decay, only the fastest excited atoms will survive the passage through the surface and the excited atoms will be distributed according to the high energy tail of Eq. (44). If resonant deexcitation of the atomic states is prohibited the velocity distribution of excited atoms will be broad and described by the Thompson formula.

In a recent series of experiments, (Wurtz et al., 1988), the velocity distribution of excited neutral metal atoms from clean and adsorbate covered surfaces have been measured using laser techniques.

In table 1, the results of the experiment is summarized. The observed velocity distributions have been fitted to the Thompson formula and the parameters \( V^* \) resulting from a best fit are listed. The work function of the clean metal as well as the energy of the excited atomic state is also listed.

In the interpretation of all data it will be assumed that the only deexcitation mechanism present is resonant deexcitation. Since the sputtered particles derive from inside the surface we will assume that the transition rates are so high that whether tunneling events occur or not is entirely determined by the relative positions of the atomic levels and the Fermi energy in the vicinity of the surface.

We note that with the exception of Ca, all excited atomic states lie above the Fermi energy and could in principle de-excite resonantly. From the bare atomic picture one would thus expect high velocity distributions in all cases except for calcium. The experiment however only shows high velocity distributions for the beryllium triplet and for chromium. Beryllium provides a particularly interesting case since the singlet shows a broad velocity distribution while the triplet only desorbs with very high velocities.

An interpretation assuming resonant deexcitation as the only possible decay channel thus indicates a downshift of the atomic levels close to the surface. This is quite unexpected since the conventional image potential shifts the levels upwards close to the surface.

From the different behaviour of the two beryllium levels we can estimate the downshift to be of the order 1 to 2 eV.
Charge transfer processes in atom surface collisions

![Schematic picture of the valence-electron, (sp), and d-electron density of states of a transition metal. The valence electrons are characterised by the parabolic band and the d-band is the semi-elliptical line. The position of the d-band is as for Cr. the position of the atomic level, (gas-phase value), is indicated with |a >.]

In the near-surface region, atomic level shifts can be non-image-like. In addition, it was demonstrated that both the shifts and broadening of atomic levels can be influenced by coadsorbed impurities. Using a simple extension of the time dependent Anderson model, it was shown that the effects of a lateral corrugation of atomic energy levels can be incorporated into the standard model for charge exchange in atom-surface scattering.

The formalism for calculating tunneling rates is presently extended to treat more complicated atom-surface systems. The formation of negative ions in atom-surface scattering experiments is one such example. The interaction of ions with halogen-covered surfaces is also of interest since halogen atoms are known to poison certain transition metal catalysts. The calculation of energy shifts and broadening of molecular levels is another problem that has a large number of applications.

The finding of almost degenerate levels with very different widths makes it important to extend the dynamical theory for charge transfer processes to the finite U limit. Such a method is presently being developed and will be presented elsewhere.

The finding of low rates for resonant tunneling between atoms and metal surfaces makes it important to consider other forms of charge transfer processes such as Auger decay. Auger processes are known to be a dominant decay channel for excited states very close to the surface. As of this date, the author is not aware of any accurate density functional calculation of the Auger transition matrix elements for atoms near metal surfaces. An interesting question in the context of the present finding of relatively low probabilities for resonant electron tunneling is to find out at what distance from the surface the probability for Auger decay starts to dominate over the probability for a resonant tunneling event.

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Discussion with Reviewers

W. Heiland: At what distances in the case of alkali adsorption will the tunneling event leading to ionisation or neutralisation occur.

Author: This will depend on the velocity of the particle. For normal velocities of around 1 eV kinetic energy it typically will happen at 5 a.u. from the alkali atom, i.e. 10 a.u. outside the surface.

W. Heiland: How does the alkali effect compare for the jellium case (Al) and for a transition metal case (Cr)?
Charge transfer processes in atom surface collisions

**Author:** I would expect the effect of alkali coadsorption to be much stronger on a transition metal than on jellium, due to the overestimated screening properties of a free electron metal such as aluminium jellium.

C. Humphreys: Your theoretical model for sputtering and desorption from the surfaces of metals and oxides assumes a jellium material with atomically smooth surfaces. However it is known experimentally that surface structure, surface steps and kink sites play an important role in sputtering and desorption. Which result of your theory do you expect to be largely independent of the surface structure of real crystals and which results may need modifying.

**Author:** The influence of steps and anomalies in the surface structure will have a similar influence on the shifts and broadening of atomic levels as impurity absorption. I would say that none of the results that I have presented would apply. It would however be a relatively simple task to calculate the influence of such defects on the resonance energies using the methods presented in the present paper.

**P. Kruijt:** A generally used method to increase the ion yield in SIMS, is to adsorb some oxygen on the surface. Can this dramatic effect be explained with the surface potential theory you present here, or do we have to take into account effects like oxidation of the surface and subsequent sputtering of excited molecules or maybe chemical desorption of the ions.

**Author:** At low coverages, the effects of electronegative adsorbates on the surface potential is the opposite of the effect of the alkali atoms, i.e. the ionisation levels of desorbing ions will be shifted upwards. This will certainly increase the ion yield dramatically and lead to the observed effect. Oxygen do however interact very strongly with metals and in addition to the induced dipole fields there are changes in the bandstructure which cannot be described with the present approach.

**J. Los:** In the derivation of the charge transfer dynamics outside a corrugated surface the author starts with the ansatz Eq. (25) in which it is expressed that \( \epsilon_a \) is periodically varying in the lateral direction. The amplitude of the corrugation is exponentially decreasing with the atom-surface distance \( Z \). In the subsequent theoretical evaluation of \( \langle n_a(\infty) \rangle \), however, only the variation of \( \epsilon_a \) as a function of the lateral position is taken into account, not the slope of \( \epsilon_a \). From gas phase collision theory we have learned that the transition probability will depend on the velocity component normal to the crossing seam. This would imply that \( v_\perp \) is not the relevant factor, but the component of \( v \) normal to the curve of constant \( \epsilon_a \). Experimental proof for this viewpoint is obtained from the experiment of (Geerlings et al., 1987). In fig. 3 of that reference, measurements are shown of the ion fractions of Cs scattered from a W(110) surface as function of Cs coverage. Experiments were performed with a fixed angle of incidence and with exit angles of 80 and 85 degrees. Note that \( v_\parallel \) is differing by a factor of two for these scatter angles. The primary beam energies were 100 eV and 400 eV; the velocity \( v \) of the particles in these two sets differ by a factor of two. Although there is some scatter in the data, it is quite clear that the ion fraction does not depend on the exit angle, that is not on \( v_\perp \). However, the curves show a shift as function of primary energy. From their model, assuming that the velocity normal to the seam is the relevant velocity, the authors could reproduce the shift of the ion fraction as function of velocity.

**Author:** I definitely agree that for an individual trajectory, the crucial parameter for the charge transfer is the velocity normal to the seam. This effect is completely taken into account by the ansatz Eq. (25). When this ansatz is inserted into the expression for \( \Lambda \), Eq. (20), the actual time development of \( \epsilon_a \) with respect to the Fermi energy will depend on the corrugation amplitude and lateral position on the surface where the particle impinge. A stationary phase analysis for an individual trajectory would indeed show that the velocity normal to the seam is the crucial velocity. Even after the averaging over the phase \( \phi \) is performed, the result for \( P \) depend on \( \eta \). It is only the "local time" approximation Eq. (37) is performed, that the \( \eta \) dependence vanishes and Eq. (39) results. In actual numerical tests I have found that at room temperature and for perpendicular kinetic energies of less than 10 eV, the semiclassical approximation, Eq. (39) with the effective temperature given by Eq. (38) accurately reproduces the exact results obtained using Eqs. (36) and (19).

With respect to the statement about the influence of the incoming kinetic energy and scattering angle dependence of the neutralisation yield, I can only point out that both the experiment and the theory give very small changes in the neutralisation rates. This can for instance be seen from the calculated curves in fig. 10. Here Eq. (43) has been used for ion kinetic energies from 100 eV to 1000 eV. If a more accurate treatment would be desired Eq. (36) should be used for the sine term in the expression Eq. (19).

In view of the other approximations pertaining to the structure of the substrate etc, this effort would appear wasted.

**J. Los:** In fig. 6 of the manuscript the widths of the \( H(n=2) \) and \( H(n=3) \) states outside clean and outside chemisorbed K on Al are compared. Although the different states are not behaving identically, a first approximation to the effects of potassium coadsorption would be that the curves representing the level widths are shifted outwards a distance of 3 or 4 a.u. This shift occurs at distances of about 10 to 15 a.u. At closer distances the widths for clean and potassium covered surfaces are merging. It looks the jellium edge is bulging outwards at the place of the alkali atom over a distance of 3 or 4 a.u. Could the author comment on the underlying physics of this effect? Is there any prediction for the width along lines not going through the center of the adsorbed atom?

**Author:** Although not of quantitative accuracy, the WKB approximation can be used for simple estimates of the tunneling rates. The tunneling rates are basically determined here by the length of the potential barrier separating the classical turning points of the surface potential for...
the energy of the atomic state. When an alkali atom is chemisorbed it induces an outward "bulge" in the surface potential. This effect leads to smaller barriers and its effect is roughly equivalent to an actual deformation of the jellium barrier. This is, however, not true for the induced shifts of the energy levels.

For the non-symmetrical case one must bear in mind that the tunneling rate is determined by the area of the smallest classical barrier separating the atomic state from a metal state. At off-symmetry positions there would appear several possible tunneling paths and one would have to average over those in some systematic way. At present I do not know how to perform this average in a simple fashion.

**J. Los:** Figure 2 (and related curves for the crossing seam in the work of Geerlings et al., 1987 which are based on a much simpler model) indicate that in scattering experiments but also in electron stimulated desorption and sputtering multiple crossings will occur. Could the author comment on the influence of these multiple crossings on the final charge state, and the eventual occurrence of interferences.

**Author:** The effects of multiple crossings are included in the present formalism but their effect on the charge exchange is washed out during the phase averaging as discussed above. For individual trajectories there are oscillations of the proposed type in the occupation of the ionisation level versus atom-surface separation.

Such oscillations could possibly be seen experimentally if the ion beam somehow was focused or channeled towards a small point at the surface so that all ions would enter the charge transfer region at the same lateral position. By varying the perpendicular velocity of the ions, so that the time of the interaction changes, I would expect oscillations in the ionic fraction to occur.

**R.H. Ritchie:** In your theoretical analysis of the capture of an electron from the valence band of a solid into a bound state on the moving ion, do you allow for capture accompanied by the creation of electron-hole pairs or plasmons in the solid?

**Author:** No, I am strictly working within a one-electron description of the tunneling process. Such a many body effect is not described within the present formalism.

**R.H. Ritchie:** You represent the self-energy of an electron interacting with a metallic surface as a local quantity. How important is it to employ a non-local self-energy, i.e., how much error do you estimate that the local approximation will cause in your theory?

**Author:** In the calculations that are presented in the present paper, I have exclusively used the non-local density functional theory for the surface potentials. A comparison with the standard local density shows that at distances larger than 6 a.u. from the jellium edge, the non-local theory gives about 50% more longlived atomic states.