Conclusions and outlook

This chapter briefly summarizes the work presented in this thesis and the objectives listed in chapter 1 will be evaluated. Diabatic and adiabatic approaches to describe the evolution of hollow atoms on their way towards the surface are discussed and a brief outlook is given.

12.1 Timescales of hollow atom deexcitation

The Classical Overbarrier Model (CBM), extended by Burgdörfer et al.\textsuperscript{169} to account for multiple electron capture by highly charged ions from surfaces, primarily models the initial neutralization of the highly charged ion in front of the surface. In this model, the incoming ion captures electrons from the solid sequentially until it is fully neutralized. This way, a hollow atom is formed. The subsequent decay of the hollow atom neutralization is described in terms of a sequence of intra-atomic Auger transitions by which the inner shell vacancies of the hollow atoms are filled. In terms of this model it is difficult to explain the amount of K-vacancies that can be filled – via KLL Auger transitions – outside the surface. Normal Auger cascades are by far too slow to transfer the electron population from the initially populated orbitals to the projectile’s L-shell.

The data presented in chapters 4, 5, and 6 of this thesis clearly indicate that a significant fraction of up to 25\% of the KLL Auger electrons is emitted while the ions are still on their initial trajectory, i.e. before they are appreciably scattered by collisions with surface atoms. This not necessarily means that the projectiles still are above the surface. In contrast,
the calculations for hollow atoms presented in section 5.3 clearly indicate that even the sharp peaks in the KLL Auger spectra may partly stem from electrons emitted by projectiles which have penetrated into the solid. A careful energy analysis of the Auger spectra allowed the determination of the electronic configurations of the hollow atoms at the moment of KLL Auger decay. This analysis readily showed that the measured KLL Auger electron spectra arise from configurations with the electrons divided over the L and M shells. Moreover it was found that the sharp peaks at the low energy side of the Auger spectra - found to be due to electrons emitted on the *inbound* part of the projectile’s trajectory - arise from configurations with two electrons in the L-shell and the rest in the M-shell. This leads to the conclusion that the projectiles rapidly achieve a significant degree of relaxation, as the electrons are transferred from the initial high $n$ states to the L and M shells of the projectile within a limited timespan. For the energies and angles used in the experiments, this timespan is limited to a few tens of femtoseconds.

As mentioned before, chapters 4 to 6 deal with the *early* stages of the collision process during which the L-shell of the projectiles is still scarcely filled. Chapter 7 extends the discussion towards later stages of the multicharged ion-surface interaction. In that chapter, KLL Auger emission is modeled in terms of a balance between KLL Auger decay rates and L-shell filling rates. Using this model, the timescale and the spatial extension of the *overall* projectile deexcitation are found to be of the order of tens of femtoseconds and a few cubic nanometers respectively.

Moreover it is shown that the filling of the projectile’s L-shell proceeds mainly via two processes. One of these processes is a relatively slow filling by means of LVV Auger transitions. This filling starts as soon as the hollow atom is formed. However, as soon as the projectiles suffer close collisions with target atoms, an additional electron capture channel - denoted as *direct inner shell capture* - becomes available. During such close collisions, strongly bound target core electrons can be transferred directly into the L-shell of the projectile. The localized nature of this kind of side-feeding process is reflected in the linear dependence of the associated filling rate on the velocity (i.e. the collision frequency) of the projectile. However, the efficiency of direct inner shell capture depends on the availability of target core levels (quasi-) resonant with the projectile’s L-shell vacancy levels.

### 12.2 Target effects

In order to investigate the two L-shell filling processes in more detail, experiments were performed using an insulating LiF crystal as target.
At a few nm in front of the surface the ion is neutralized forming a hollow atom. As the projectile approaches the surface, the electron cloud — dynamically screening the ion — shrinks. Finally, as the projectile reaches the solid, the screening charge cloud merges into the solid's conduction band. During its travel, the projectile's L shell vacancies are filled, both by LVV Auger processes and by direct inner shell electron capture. Finally, the K-vacancy is filled by a KLL Auger process.

A comparison of KLL Auger spectra obtained from collisions of hydrogenic N ions on this target with those obtained on Al showed profound differences — especially for low ion velocities — at the low energy side of the spectra. These differences imply that neutralization rates are, for the LiF target, strongly reduced as compared to Al. This reduction is explained by the large binding energy and the immobility of the LiF valence electrons. Consequently, electron capture takes place much closer to the surface. Moreover, the immobility of the LiF valence electrons prohibits efficient multiple capture from a single target lattice site. This on its turn suppresses the formation of hollow atoms for small ion velocities. Nevertheless, KLL Auger electrons are emitted. Those electrons are probably not emitted from fully neutralized projectiles but from hollow ions. In ions, the Auger energies are shifted towards lower values. Such a shift is indeed observed at the low energy side of the spectra. In contrast, fast and grazingly incident projectiles probe a large number of LiF lattice sites. These projectiles may be fully neutralized before Auger emission occurs. For these scattering conditions, direct inner shell electron capture becomes important and the Auger
emission is rapidly shifted towards a situation in which the L-shell is filled up to its maximum before decay occurs. This effect is indeed observed as the Auger spectra show a strong dependence on the projectile velocity. Additional support for this scenario was found using hydrogenic Ne ions as projectiles. For Ne, not the L-shell but the M-shell vacancies are (quasi-) resonant with LiF target levels. Indeed, for fast Ne ions grazingly incident on the LiF target, an efficient filling of the M-shell was observed.

These results clearly indicate that whether or not hollow atoms are formed in front of an insulator surface depends on impact energy and angle of incidence of the projectile and on the electronic structure of both ion and target species. Energetic ions grazingly incident on an insulator can very well be neutralized fully thereby forming a hollow atom (see e.g.\(^{178}\)). However, hollow atom formation following collisions of slow ions incident at large angles is very unlikely. Figures 12.1 and 12.2 summarize the formation of hollow atoms in front of conducting and insulating targets respectively.
12.3 The evolution of hollow atoms

In the staircase version of the classical overbarrier model, the charge $q$ of a highly charged ion approaching a surface is lowered stepwise by capture of a single electron into a high $n$ state of the ion every time the potential barrier between ion and solid is lowered below the Fermi energy of the solid. If one now assumes the high-$n$ states to be stationary, and the projectile charge $q$ to be conserved for a certain time, one obtains the familiar picture as shown in figure 12.3, left panel. In this diabatic regime, the binding energy of the captured electron varies and is shifted up due to the image force of the ion as it approaches the surface.

However, if one assumes the potential curves to behave adiabatically and the effective charge $q$ and effective principal quantum number $n$ as continuously varying quantities, or in other words, one takes the binding energy of the captured electron always at least equal to the target work function, then the charge $q$ and principal quantum number $n$ decrease continuously as the ion approaches the solid. This is shown in figure 12.3, right panel. Within this view, no electron promotion takes place and the effective orbital diameters of captured electrons decrease upon capture of additional ones. The question now arises, which of the two views is applicable for the collision systems studied in this thesis.

Simple timing arguments show that during the first neutralization steps of a highly charged ion of a first-row element no highly excited stationary states can be formed. Even for the lowest projectile velocities the time between capture of two consecutive electrons is of the order of or even less than the classical revolution time of a high-$n$ electron (typically a few femtoseconds). Moreover, the constant binding energy constraint limits the amount of electrons which can be captured in such a state. According to the overbarrier model (see chapter 2), a $q$-fold charged ion captures the first electron at a distance $z_0 \simeq \sqrt{2q/W_\phi}$ in front of a target with work function $W_\phi$. For a $N^{6+}$ ion in front of a $W_\phi = 5$ eV surface, $z_0$ is about 10 Å. On its way towards surface, the charge of the ion will now effectively be lowered according to:

$$ q(z) = \frac{1}{2}(zW_\phi)^2 $$

In this, $q(z)$ can be regarded as the effective charge of the projectile approaching the surface. The principal quantum number $n$ in which an electron is captured can be obtained from the well known expression for the binding energy of this electron (hydrogenic energy plus image shift):

$$ E_b = -\frac{q^2}{2n^2} + \frac{q}{2z_0} $$
By taking the binding energy $E_\phi$ of the electron equal to the work function $W_\phi$ of the target, one obtains the effective principal quantum number $n$:

$$n = \sqrt{\frac{q}{2W_\phi(1 + \frac{q}{2W_\phi})}}$$

In the adiabatic regime, the ions must be slow as compared to the electrons. As this is the case for all collision systems studied in this thesis, it seems reasonable to assume the adiabatic regime to be valid here. So, at every point on the way towards the surface, the projectile’s effective charge $q$ and effective principal quantum number $n$ are continuously lowered such that the potential barrier between projectile and solid is just low enough to allow for electron exchange. This effect is displayed in figure 12.4, right panel. The left panel shows the familiar diabatic picture (see also figure 2.3).

This simple treatment shows that the aforementioned problem of too long (theoretical) times for the projectile deexcitation does not exist if one assumes the adiabatic regime to be valid. In this regime, electrons are not captured into well defined Rydberg states of the ion giving rise to stepwise raining down of electrons by AI proceses. The electrons rather dynamically screen the projectile with increasing density (“shrinking charge cloud”) as it approaches the surface. During the projectile’s approach, the electron
12.4 Hollow-atom probing of surfaces

In the preceding paragraphs, an attempt was made to evaluate the first two objectives listed in chapter 1. The temporal and spatial dimensions of the energy dissipation of highly charged ions interacting with solid surfaces have been mapped out. That is, the processes governing the neutralization and deexcitation of hydrogenic ions of first row elements have been found to act on a time scale of tens of femtoseconds and spatial dimensions of a few nanometers. The second objective was to qualify the nature of the charge exchange processes leading to the projectile neutralization and deexcitation for targets having strongly different electronic properties. A comparison of

![Diabatic and Adiabatic Potential Barriers](image)

**Figure 12.4:** Left panel: Ion-surface potentials for a six-fold charged ion at positions $z = 11$ a.u. (small dots), $z = 15.5$ a.u. (dotted line) and $z = 20$ a.u. (full line). In this diabatic picture the potential barrier between the ion and the solid is lowered according to equation 2.10 of chapter 2 (see also figure 2.3). Right panel: Same as the left panel, now for an ion with effective charge $q(z) = 2, 4$ and 6 for $z = 11, 15.5$ and 20 a.u. respectively. Now the potential barrier remains pinned at the Fermi level of the target ($W_\Phi = 5$ eV).

binding energies do not change in the time-varying ion-surface potential, implying the absence of electron promotion into unoccupied conduction band levels, or into the continuum. At the moment of surface impact there is no “sudden onset” of electron screening but the screening charge cloud merges into the solid’s conduction band. Thus only projectile levels located well below the target’s conduction band maintain their atomic nature and can be filled by Auger processes which lead to sharp peaks in the Auger electron spectra.
KLL Auger spectra obtained from these different targets revealed that the major part of the projectile deexcitation is governed by an intricate interplay of (intra- and inter atomic) Auger processes and (quasi-) resonant electron exchange processes. In this, both target valence electrons and target core electrons are found to play an important role.

Now, the question remains whether highly charged ions are suitable probes of surface structure. Part of the answer to this question has already been given. The KLL Auger spectra presented in this thesis carry fingerprints of the charge exchange mechanisms governing the ion-solid interaction. A detailed study of these spectra therefore yields important information, not only on the neutralization and deexcitation of the impinging ions but also on the electronic structure of the target. A study of the energy loss and charge state distributions of projectiles scattered off the surface – as presented in chapters 9 to 11 – gives important additional information on the nature of the ion-solid interaction. The material presented in this thesis allowed for a rather complete description of the mechanisms governing the interaction of highly charged ions with surfaces. The description is, however, to a large extent still formulated in qualitative terms. Before highly charged ions can be used effectively as sensitive probes of surface structure, many of the mechanisms mentioned above need to be quantified. Such quantification is one of the subjects of present (and future) research.