

## DISSERTATION

## Classical and Quantum Simulations of Ion-Surface Interaction

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## 1 Introduction

During the last decades, the interaction of charged particles with solids has evolved to a broad field of research [1], in part due to its importance for technical applications such as controlled surface modifications on the nanoscale, development of improved data storage devices etc. Fundamental research has been stimulated by the variety of interesting and often surprising findings. Observation of unusually high spin polarization of electrons emitted from magnetized iron after impact of  $N^{6+}$  ions [2], hillock formation on insulator targets after impact of slow highly charged ions [3], or the linear dependence of the stopping power on the velocity of an antiproton penetrating through LiF [4] which makes LiF to look like a metal in this context, are only a few examples. A detailed theoretical description of the different aspects of ion-surface interaction is important to understand the underlying physical processes.



Figure 1.1: Ion-surface interaction scenario, schematically (cf. text).

Before outlining the specific questions addressed in the present work, we briefly summarize the commonly accepted scenario of ion-surface interaction: The impact of an ion on a surface initiates a complex chain of electron transfer and emission processes, target excitations and subsequent decay processes (Fig. 1.1). Depending on the target material, the projectile charge, its kinetic energy, and the scattering geometry, certain processes will dominate over others making them accessible to experimental studies. For example, the above-surface part of the ion-surface interaction is efficiently probed by scattering of highly charged ions (HCI) under a grazing angle of incidence. The ion trajectory is then reflected above the topmost atomic layer due to surface channeling without penetrating into the bulk. From the high-energy spectrum of emitted electrons information about the mechanism of potential emission which is governed by the potential energy brought into the collision by the HCI, is obtained. The low-energy part of the emission spectrum consists, in addition, of electrons produced by other emission processes. One of them is kinetic emission due to binary collisions of the projectile with the surface electrons. Another source of electron emission is the production of secondary electrons in the target. They are excited by inelastic collisions of primary electrons originating from potential and kinetic emission with electrons of the target.

An HCI approaching a surface polarizes the target electronic system, leading to the formation of an image charge in the target (Fig. 1.1). This induced charge of opposite sign accelerates the ion towards the surface setting a lower limit to the kinetic impact energy. With decreasing ion-surface distance the potential barrier separating the projectile from the surface is lowered. When the potential saddle falls below the highest energy level of occupied target electron states, classical electron transfer over the barrier from the target into the HCI becomes possible. Compared to this classical process, tunneling of electrons through the potential barrier is negligible, so that electron transfer above the surface can be well described by a classical theory, the Classical Over the Barrier (COB) model [5]. It describes the evolution of the electron occupation of the projectile levels. At the early stage of the neutralization sequence, highly excited Rydberg states are populated forming a so-called "hollow atom". Subsequently, deexcitation via Auger processes sets in. In addition, the projectile levels are shifted upwards in energy. When they reach the vacuum level, their electrons are emitted with very low energies. As Auger processes are too slow to assure complete deexcitation of the hollow atom before impact on the surface, the projectile ion is typically far from its ground state when hitting the surface.

The capture of electrons leads to electronic excitations of the surface. In metals these excitations can be effectively dissipated among the conduction band electrons due to the short relaxation time. In insulator targets surface holes are produced charging up the surface which may lead to desorption of target atoms and ions. In addition to this so-called "potential sputtering" the deposition of potential energy on insulators by slow HCI can cause the formation of nano-hillocks on the surface [6].

HCI penetrating the solid still carry a considerable amount of potential energy leading to the formation of a "hollow atom of  $2^{nd}$  generation" and to further electron

exchange and emission processes as well as bulk excitations. Eventually, the ion is slowed down and stopped in the solid by inelastic processes. The stopping process due to target excitation is a field of interest on its own. The detailed knowledge of the energy deposition in the target along the projectile path is important for technical and medical applications. For example, in cancer treatment particle beams are used to destroy tumor cells by deposition of energy. The detailed knowledge of the stopping power (energy loss per distance traveled) as a function of the projectile kinetic energy is important to optimize the efficiency of such a treatment where the bulk of the particle energy should be deposited at the position of the tumor. This is approximately the case for proton projectiles. While for photons the amount of deposited energy decreases exponentially with increasing penetration depth, the energy deposition of protons shows a sharp peak at a certain penetration depth. As the position of this so-called Bragg peak depends on the projectile energy protons can be efficiently used for controlled energy deposition.

For positively charged ions electron transfer can influence the deceleration of the projectile. In the case of an antiproton projectile, the deposition of energy is exclusively caused by the Coulomb interaction with the electronic system of the target without bound state formation. The electronic excitation spectrum of the target can therefore be directly probed by studying the stopping power of antiprotons.

Although ion-surface interactions have been studied both experimentally and theoretically during the last decades, there are still many open questions to be answered. In the present work we will address some of them focusing on interesting aspects of ion collisions with both insulator and metal targets.

The theoretical study of ion-surface collisions is a challenging task due to the large number of coupled degrees of freedom involved. In addition, one has to deal with many-body systems far from equilibrium, so that many theories commonly used in (equilibrium) solid state physics are not applicable. In the description of ion-surface interactions elements from solid state physics, atomic physics, and quantum chemistry enter, leading to new physical concepts. Ab initio quantum calculations are still restricted to singly charged projectiles for computational reasons. For problems where the translational symmetry of the crystal lattice is broken due to an external perturbing charge, the embedded cluster approach has proven to be a successful tool [7]. There, the solid is approximated by a cluster of atoms of finite size. This allows for a full ab initio calculation where the Schrödinger equation is solved for all N electrons involved. We adopt this method for two interesting physical questions. One of them concerns the interaction of antiprotons and protons with LiF. In a recent experiment [4] it was found that LiF appears to act like a metal target at least as far as the stopping power of the (anti)proton going through LiF is considered. Due to the large band gap of LiF one would expect a clear deviation from metallic behavior for low kinetic energies of the projectiles. However, while

such deviations have recently been found for protons with energies below about 4 keV [8, 9], they have not yet been found for antiprotons. Motivated by this surprising finding we have studied the local deformation of the LiF band structure by the external charge which turns out to be rather dramatic (see section 2.3). We can provide a new upper bound for the projectile energy below which a deviation from metallic behavior can be expected. For proton projectiles the obtained threshold energy for non-metallic behavior agrees well with experimental data. The threshold energy for antiproton projectiles is reduced by more than an order of magnitude in comparison to previous estimates. So far, experiments with antiprotons have only been performed with kinetic energies at least in the keV range being far above the threshold energy found in the present work. However, in the near future, intense beams of very low-energy antiprotons should become available, e.g. at FAIR (Facility for Antiproton and Ion Research) [10], a new accelerator facility currently built at the GSI Darmstadt, Germany.

The second phenomenon investigated using ab initio methods is the formation of trions (two holes binding an excited electron) on an LiF surface. The results of an experiment by Khemliche *et al.* [11] where  $Ne^+$  ions were scattered from an LiF surface, lead to the hypothesis that the interaction with the projectile causes the formation of trions in the surface. As the existence of such a trion which corresponds to a bound state within the band gap of the insulator was highly speculative, we have studied excited states of the charged LiF surface using quantum chemistry methods. We confirm that trions in fact constitute bound electronic states in the LiF surface and calculate their binding energy and excitation energy (see section 2.2). The corresponding energies derived from the experiment agree well with our results. Trion formation can only serve as an efficient energy loss channel in ion-surface scattering if trions are rather compact quasi-molecules with the two holes being located at close proximity to each other. We have therefore calculated the pair correlation function of the two holes. We obtain a next-to nearest neighbor configuration of the holes showing that the requirement of close proximity is fulfilled.

The interaction of a solid with highly charged ions requires a classical treatment, or more precisely, a hybrid classical-quantum description where quantities such as charge transfer rates, decay rates, density of states etc. determined from quantum calculations enter classical simulations of projectile trajectories. This is successfully employed in the investigation of electron transfer and emission during the impact of multiply and highly charged ions on metal and insulator surfaces. In the present work an extended version of the COB model first developed for metal targets [5] is used to simulate the impact of N<sup>6+</sup> ions on a magnetized iron surface. Motivated by experiments on the same target where a surprisingly high spin polarization of emitted electrons was found, we investigate spin dependent electron transfer and emission processes (section 3.2) supporting the interpretation of the experimental findings. The COB model was extended to insulator targets [12] for projectile charge states  $Q \leq 10$  where the cylindrical symmetry is broken and the surface can be charged up due to holes left behind by electrons resonantly transferred to the projectile. In this work, we extend the method to charge states  $Q \leq 36$ . The main question addressed in the simulation of the impact of HCI on an LIF surface will be the existence (or the lack thereof) of the so-called trampoline effect. This idea of an ion being reflected well above the surface due to the repulsive Coulomb field of the holes in the surface was first put forward by Briand *et al.* [13] and has been subject of many discussions since. If ions could be trampoline reflected without hitting the surface they could be used for controlled surface modifications avoiding damage of the crystal structure due to the impact of the ion. However, it was shown [12] that for  $Q \leq 10$  the possibility of such an effect can be ruled out as the image acceleration of the ion overcomes the repulsive force of the holes. For higher charge states, the phenomenon is investigated in the present work (section 3.1). Our results show that also for Q > 10 trampoline reflection is absent.

## 2 Ion Induced Excitations in LiF

In this chapter we will focus on electronic excitations in an LiF target caused by an ion impinging on or traveling through the ionic crystal. The study of one specific type of perturbation or excitation as opposed to a complete simulation of the whole interaction process (see chapter 3) allows for full ab initio calculations. In the following, we will briefly review the methods of quantum chemistry which we apply to the investigation of trion formation in an LiF surface as well as of the influence of proton and antiproton projectiles on the LiF band structure.

### 2.1 Methods of Quantum Chemistry

To determine the electronic structure of a molecular system the stationary Schrödinger equation  $\hat{H}\Psi = E\Psi$  for N electrons of the system is solved employing the variational principle where E is the total energy of the system and  $\hat{H}$  is the Nelectron Hamiltonian in the Born-Oppenheimer approximation,

$$\hat{H} = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} - \sum_{i}^{N} \sum_{\alpha}^{n} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i < j}^{N} \frac{1}{r_{ij}} + \sum_{\alpha < \beta}^{n} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}}.$$
(2.1)

 $Z_{\alpha}$  are the nuclear charges,  $r_{i\alpha}$  denotes the distance between electron *i* and nucleus  $\alpha$ ,  $r_{ij}$  is the distance between electron *i* and electron *j*, and  $R_{\alpha\beta}$  is the distance between nucleus  $\alpha$  and nucleus  $\beta$ . The solution  $\Psi(\mathbf{x_1}, ..., \mathbf{x_N}; \mathbf{R_1}, ..., \mathbf{R_n})$  of the Schrödinger equation depends on the electron coordinates  $\mathbf{x_i}$  which include all spatial and spin degrees of freedom. As within the Born-Oppenheimer approximation the *n* nuclei are considered to be fixed at their positions, their coordinates  $\mathbf{R_j}$  only enter the calculation as parameters. For our calculations we use the quantum chemistry code COLUMBUS [14]. Through the use of different forms of trial functions for the electronic wavefunction one can distinguish several levels of accuracy of quantum chemistry calculations implemented in this code. Especially in large molecular systems the gain of accuracy is always accompanied by a considerable increase of computational costs and time. Hence, the adequate method applicable to a given physical problem must be chosen carefully in view of both an appropriate accuracy level and computational feasibility.

All methods used for electronic structure calculations are based on the *Self Consistent Field* (SCF) method, also called the *Hartree Fock* (HF) method (for a de-

tailed description see e.g. [15, 16]). There, employing the one-electron approximation [16] the N-electron Schrödinger equation is separated into a system of effective one-electron equations where each electron is assumed to move in the average potential of all other electrons. Within this approximation the N-electron solution  $\Psi(\mathbf{x_1},...,\mathbf{x_N})$  can be written as a product of one-electron wavefunctions. More precisely, a Slater determinant of these wavefunctions is used so that the required asymmetry of the total wavefunction according to Pauli's principle is accounted for. The replacement of the instantaneous mutual repulsive interaction of all electrons by an average potential leads to the neglect of correlation effects. Especially for the investigation of excited states it is important to go beyond the HF level to include electron correlation. This is achieved by using a linear combination of configuration state functions (CSFs) as a model for the solution of the N-electron Schrödinger equation instead of only one single Slater determinant. Every CSF is again an N-electron Slater determinant with different distributions of the electrons over the molecular orbitals (MOs) of the system. In a *Configuration Interaction* (CI) calculation the model wavefunction is built up by exciting one or more electrons from the ground state configuration to unoccupied MOs [15, 16]. The expansion coefficients of the linear combination of these CSFs are subsequently optimized to minimize the total energy of the system. We will use a different, but conceptually similar method in this work, a Multi Configuration Self Consistent Field (MCSCF) approach which is more effective within the given computational resources. It will be presented in more detail in the following subsection.

#### 2.1.1 Multi configuration self consistent field method

In an MCSCF calculation the N-electron wavefunction  $\Psi(\mathbf{x}_1, ..., \mathbf{x}_N)$  is expressed as a linear combination of different configuration state functions  $\Phi_l$ ,

$$\Psi = \sum_{l} \alpha_l \Phi_l, \tag{2.2}$$

where every  $\Phi_l$  is an *N*-electron Slater determinant which corresponds to a certain distribution of the *N* electrons over the molecular orbitals (MOs)  $\phi_j$  of the system. The weighting of the different configurations is given by the coefficients  $\alpha_l$ . Every molecular orbital is expanded in a finite Gaussian basis set,

$$\phi_j = \sum_i \beta_{ij} \chi_i. \tag{2.3}$$

During the MCSCF calculation the coefficients  $\alpha_l$  and  $\beta_{ij}$  are optimized simultaneously. Through the superposition of many configuration state functions correlation effects are taken into account. The conceptual difference to CI calculations is that in CI the MOs are fixed, taken from the result of the preceding SCF calculation, while in MCSCF both the CSFs and the orbitals are varied. Therefore, fewer CSFs may be needed to achieve very accurate results compared to a CI. The MCSCF method allows for the calculation of the ground state and several excited states at the same time. If this is the case a state averaged MCSCF calculation is performed, i.e. the CSF expansion coefficients  $\alpha_l$  are optimized separately for each state while the  $\beta_{ij}$ are determined such that the total energy averaged over all states is minimized.

A very efficient MCSCF method commonly used is the so-called *Complete Active* Space Self Consistent Field (CASSCF) method which is also employed in the present work. There, all occupied and unoccupied MOs are divided into active and inactive orbitals. The inactive occupied orbitals are kept doubly occupied in all CSFs during the calculation, the unoccupied inactive orbitals, also called virtual orbitals, are kept empty. The remaining MOs form the active space among which the active electrons are distributed forming the different CSFs. The physical motivation for the devision into different types of orbitals is that the inner shell (inactive) electrons are deeply bound to the nuclei. They occupy molecular orbitals very similar to the atomic orbitals of the free atoms. The overlap of the wavefunctions of inner shell electrons with those of adjacent crystal atoms is very small. As opposed to that, valence electrons are more weakly bound forming molecular orbitals with larger overlap of the wavefunctions. Valence electrons therefore contribute to bonding and chemical reactions. Usually, the active space thus consists of the MOs of the valence electrons and low lying unoccupied MOs.

For very large molecular systems it is often necessary to restrict the active space or the selection of CSFs further in order to make the calculation computational feasible. In LiF the valence electron MOs are formed by the F 2p states and the lowest unoccupied MOs by the Li 2s states. Therefore, all F 1s, 2s and Li 1sorbitals are kept doubly occupied. If necessary, the total number of possible CSFs can be reduced further by allowing only single excitations from the occupied orbitals which are then termed *restricted active space* (RAS) orbitals, or by allowing only single excitations into unoccupied MOs, then termed *auxiliary orbitals* (AUX). In our calculations it turned out that for the systems treated in our work, the use of at most three AUX orbitals assures the inclusion of the most probable configurations.

The computational feasibility of a quantum chemistry calculation on an LiF cluster depends on two further aspects. The higher the symmetry of the problem, the higher the efficiency of the calculation. For the studies of trion energies (section 2.2) the MCSCF is performed in the  $C_{2v}$  symmetry (for an application-oriented introduction in group theory see e.g. [15]). Due to the breaking of the translational symmetry of the crystal lattice by the external charge, the calculations with antiprotons or protons inside the cluster (section 2.3) are performed partly without symmetry (or, in terms of group theory, in  $C_1$  symmetry). The second aspect influencing the accuracy and computing time of the calculation is the choice of an appropriate set of basis functions  $\chi_i$ . It must be carefully chosen in view of both computational and physical considerations. For example, for the study of atomatom collisions such as Li-F it is important to include long ranging diffuse Gaussian basis functions in the fluorine basis set in order to describe the large-distance interaction between F and Li accurately. However, for our purposes this aspect is less important so that the use of even small basis sets leads to reliable results which has been verified by convergence tests on small clusters.

For small systems the results of an MCSCF can be used as reference configurations forming, instead of only one HF Slater determinant, the basis for a CI. This *Multi-Reference Configuration Interaction* (MR-CI) calculations are, however, not manageable for the problems addressed in this work.

## 2.2 Excitation Energy and Pair Correlation Function of Trions near an LiF Surface

Within the framework of quantum chemistry we will now investigate one particular type of target excitation caused by the interaction of charged particles with insulator surfaces. This interaction may lead, in addition to single-hole creation, to the formation of excitation complexes involving more than two quasi-particles such as an electron-bihole complex or trion. It consists of one electron excited from the valence band bound to two holes (Fig. 2.1). The interest in trions has recently been stimulated by interesting findings in ion-surface scattering experiments on LiF [11]. The existence of a trion and other similar excitonic states was first suggested by



Figure 2.1: Formation of a trion on an LiF surface, schematically.

Lampert [17] in 1958. The subsequent studies of trions during the next decades were focused, both experimentally and theoretically, on semiconductors [18–26]. To our knowledge, the first experimental evidence for a trionic state in LiF was found only recently by Khemliche *et al.* [11] who studied the neutralization of Ne<sup>+</sup> ions during grazing incidence on a lithium fluoride surface. They measured the energy loss and final charge state of the projectile in coincidence with the energy spectrum of emitted electrons. For neutral final states ( $Ne^0$ ) together with the emission of one electron they identified Auger neutralization as the underlying neutralization channel. This process is characterized by the capture of one F 2p electron from the surface into a low lying projectile state while a second F 2p electron is emitted. Surprisingly, they also observed neutral final states unaccompanied by electron emission ruling out Auger neutralization. As resonant electron transfer can be ruled out as neutralization channel due to a mismatch of the electronic levels involved, the detection of the neutral Ne<sup>0</sup> final states without electron emission was explained by an Auger-like capture and excitation process where the transfer energy does not suffice to excite the valence electron above the vacuum level. Instead, a hole and an electron-hole pair are created forming a trion which constitutes a bound state within the band gap of LiF. From the measured projectile energy loss the trion excitation energy relative to the ground state of the singly charged surface was

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estimated to about 12.6 eV and the mean binding energy relative to the ground state of the doubly charged system to  $3.5 \pm 1$  eV which was confirmed in a later experiment using F<sup>+</sup> projectiles [27].

Earlier theoretical studies of trions in semiconductors were based on a three-body Hamiltonian for two holes and one electron using effective masses for the particles and dielectric constants [18–23, 28]. The corresponding Schrödinger equation was either solved numerically [18–21] or simplified by restricting configuration space to lower dimensions [28] or by fixing positions of the holes [22, 23] thereby imposing a Born-Oppenheimer approximation. Three-body bound states in LiF have been studied by Shibata et al. [29] applying the Faddeev equation, however, only within a one-dimensional model where only one lithium and two adjacent fluorine ions are considered. The two holes are fixed to the fluorine sites and the electron to the lithium site. To our knowledge, ab initio calculations for trions in LiF are not yet available. So far only excitonic excitations in the *neutral* system have been treated on the ab initio level. The excitation energy of an exciton corresponds to the energy of an electron that has been excited to the conduction band reduced by the attractive electron-hole interaction. The latter is taken into account by the Bethe-Salpeter equation (BSE) [30]. With this method, Wang et al. [31] obtained for LiF a bulk exciton at 12.7 eV and a surface exciton at 9.2 eV [32, 33] above the ground-state energy.

In the present work we perform ab initio calculations for trionic excitations in the singly charged system. We calculate the excitations in a finite-size  $F_m^-Li_n^+$  cluster embedded into a matrix of point charges that represent the remainder of the infinitely extended surface and bulk. For such a finite system we employ a quantumchemistry approach. In our calculations the Schrödinger equation for all electrons (up to 204) of all atoms in the cluster is solved self-consistently. Excitation energies are calculated as the total-energy difference between ground and excited states. As Hartree Fock (HF) calculations neglect correlations while trions represent strongly correlated particle-hole complexes, it is important to go beyond the HF level. Using the MCSCF method we systematically study clusters of increasing size up to 13 fluorine and 37 lithium ions to assess possible finite-size errors.

#### 2.2.1 Theoretical model

For the MCSCF the molecular orbitals are expanded in the Gaussian basis set of Schäfer *et al.* [34]. For the fluorine three *s*-type and two *p*-type Gaussians are used while lithium orbitals are expanded in two *s*-type functions. The choice of this basis constitutes a compromise between accuracy and computational feasibility, the limit of which is rapidly reached with increasing number of active ions in the cluster. For a small cluster we checked that increasing the basis size changes the resulting trion excitation energies by less than 0.5 eV. For the simultaneous calculation of the ground state and several excited states, a state averaged MCSCF is performed.



Figure 2.2: Representation of the LiF surface by embedded clusters of increasing size. Clusters studied in the present work are depicted.

We investigate seven different clusters (Fig. 2.2) where the total systems including the ions and all point charges consist of  $7 \times 7 \times 4$  lattice sites for clusters with 4 to 12 fluorine ions while the  $F_{13}L_{137}$  cluster is embedded in a  $9 \times 9 \times 4$  lattice. Every  $F^$ is surrounded by Li<sup>+</sup> ions to avoid artificial distortion of the electron density [35] and all sites not occupied by ions are filled with point charges ensuring the proper inclusion of the Madelung potential [7]. This embedded cluster approach has been successfully used in studies on ionic crystals (see [7] and references therein).

In an MCSCF calculation, the different CSFs are generated by exciting one or several electron-hole pairs, i.e. one or several electrons in excited orbitals outside the ground-state configuration. For reasons of computational limitation we only allow excitations of valence electrons (from F 2p-like MOs) to the energetically lowest unoccupied orbitals (Li 2s-like MOs). Most of the MCSCF calculations are performed in the  $A_1$  symmetry of the  $C_{2v}$  symmetry group which has the highest symmetry and thus should contain the lowest lying excitation energy. Within this symmetry a wavefunction remains unchanged under the symmetry operations, rotation by 180°, reflection at the x - z-plane, and reflection at the y - z-plane where z denotes the direction of the surface normal. For consistency checks additional calculations in the  $B_1, B_2$ , and  $A_2$  symmetries were performed. We restrict the active space, i.e. the active orbitals to and from which excitations are allowed, further by including only F 2p-like MOs of  $A_1$  symmetry and the three lowest  $A_1$ Li 2s-like MOs. Although these constraints may seem rather restrictive, up to 113 CFSs of the most probable configurations are taken into account. A comparison with excitation energies calculated using a larger active space which can be handled

for small clusters, show that the results do not change significantly. We observe differences in the 500 meV range which is well within the overall accuracy level ( $\approx 1$  eV) we aim for.



Representing the continuous band structure by a finite cluster leads to a discretization of the band (Fig. 2.3). The density of discrete levels increases with increasing cluster size. The continuous band structure can be recovered by assigning each discrete level a finite (typically) Gaussian width. Trionic excitations near the surface should feature a narrow band signifying the dispersion relation for propagation in the surface plane. The present calculation for a finite cluster reproduces the energetically lowest trion state corresponding to the k = 0 ( $\Gamma$ ) point of the band which determines the threshold for the energy loss channel. The determination of the trionic state is schematically illustrated in Fig. 2.4. Within the singly charged sector (q = 1), excited states are determined from configurations that contain already one hole. The lowest total energy (ground state) results from configurations with the (first) hole at the top of the valence band (Fig. 2.4b) corresponding to the hole with k = 0 ( $\Gamma$  point) while excited states correspond to a distribution of the hole in lower lying valence band states (holes with finite k). The trionic state corresponds to the lowest particle-hole excitation starting from this (q = 1) onehole ground state. Note that the ordering in the total energy diagram (Fig. 2.4a) is inverted relative to the single particle (hole) energy level diagram (Fig. 2.4b).

As mentioned above, there will be additional excited trion states of higher energy or, in the limit of an infinitely extended crystal, a dispersive band of trion states. We limit our studies to the energetically lowest trion state as the calculations of the first excited state are already computationally very demanding.



Figure 2.4: a) Energy diagram of the total energies determined from MCSCF calculations.  $E_{tot,g}(q = 1)$  and  $E'_{tot,g}(q = 1)$  are the lowest and highest "ground states" of the singly charged cluster, respectively,  $E_{tot,trion}(q = 1)$  is the trion state, and  $E_{tot,g}(q = 2)$  is the ground state of the doubly charged cluster. b) Single-particle energy level diagram. Relative energies used in Table 2.1 are also shown.

#### 2.2.2 Trion energies and pair correlation functions

#### Trion energy

We present in the following excitation energies, binding energies, and wavefunctions for trions which are excited states in the band gap of the surface with asymptotic charge state q = 1. It is instructive to compare these excitations to those in other charge sectors (Fig. 2.5) for which ab initio calculations are available.

Excitonic states in the neutral sector q = 0 are well investigated, both experimentally and theoretically. In electron energy loss spectroscopy (EELS) thresholds for the excitation energy  $E_{exc}$  relative to the neutral ground state were found at  $E_{exc} = 9.7 \text{ eV} [36]$  and approximately 9 eV [37]. From other EELS studies dominant excitation energies of 10.4 eV [38] and 10.3 eV [39] were obtained (threshold energies were not published in these cases) in agreement with Ref. [36] and [37] where the loss peaks were found at 10.65 eV and 10.2 eV, respectively. From energy loss spectroscopy of low energy protons [40] an excitation energy of about 10.15 eV can be derived with a threshold at about 9 eV while electron-stimulated desorption (ESD) experiments yield a threshold for the excitation of surface excitons of  $9.1 \pm 0.6 \text{ eV} [41]$ . For excitations in the neutral sector also accurate theoretical



Figure 2.5: Excitations in the band gap of LiF for different charge states of the cluster (i.e. surface), schematically (VB: valence band, CB: conduction band).

calculations are available. Numerical solutions of the Bethe-Salpeter equation yield for bulk excitons  $E_{exc} = 12.6 \text{ eV} [18]$ , for excitons near the surface with the electronic wavefunction confined to the surface layer  $E_{exc} = 12.3 \text{ eV} [31]$ . When the wavefunction is allowed to extend several Angstroms into the vacuum by adding Gaussian orbitals centered above the surface the exciton energy is reduced to  $E_{exc} \approx 9.2 \text{ eV} [32]$ .

We have calculated the energy of neutral excitons for clusters of different sizes to compare it with these data. This allows us to determine an upper bound for the systematic error of our method which is better suited for the q = 1 than for the q = 0 sector. Unlike excitons, i.e. an electron-hole pair configuration with the hole localized near an F in the surface layer and the electronic cloud reaching out into vacuum, trions in the charge q = 1 sector are expected to be more strongly confined to the surface. For a collinear geometry with the electron in between the two holes in analogy to the  $H_2^+$  molecule (see below) the trionic wavefunctions should be localized in the surface. [We do not include in these calculations additional orbitals on virtual sites above the surface.] Consequently, our MCSCF result giving an excitation energy of  $E_{exc} = 10.75$  eV for a large cluster ( $F_{13}Li_{37}$ ) in the q = 0 sector should be compared with the BSE result for surface-confined excitons. We obtain satisfactory agreement on the 10 % level. We note parenthetically that such a basis set would fail to represent excitations in the q = -1 sector (Fig. 2.5) such as image states weakly bound and de-localized above the surface.

The excitation energy of trions is defined as the total energy difference between the ground state and the excited state of the singly charged cluster. Since in ionsurface scattering experiments the excitation is "broad band", i.e. not spectrally selective, the "first" hole can be generated anywhere in the valence band. Accordingly, the minimum excitation energy is given by the energy difference of the trion

	experiment	$\mathrm{F}_{13}\mathrm{Li}_{37}$	error interval
min. $E_{trion}$ [eV]	12.6	10.45	10.12 - 11.55
$max. E_{trion} [eV]$		12.08	11.71 - 12.99
$2^{nd} E_{ioniz} [eV]$		14.79	14.32 - 16.90
$E_{bind}$ [eV]	$3.5{\pm}1$	2.24	1.56 - 3.52

Table 2.1: Calculation results in comparison to experimental estimates [11]: minimum  $(min. E_{trion})$  and maximum trion excitation energy  $(max. E_{trion})$ , ionization energy of the charged cluster  $(2^{nd} E_{ioniz})$ , and binding energy  $(E_{bind})$  defined as the difference between  $max. E_{trion}$  and  $2^{nd} E_{ioniz}$ . The error interval includes calculation results from smaller clusters.

state and the state with the initial hole at the "bottom of the valence band" (see Fig. 2.4). The maximum excitation energy corresponds to the hole at the top of the valence band or, equivalently, to the ground state of the q = 1 ionic system. Results for excitation energies and binding energies are displayed in Table 2.1. The maximum excitation energy obtained from the MCSCF calculations is 12.08 eV for the largest cluster. Results for smaller clusters give an error interval from 11.71 eV to 12.99 eV. The excitation energy derived from experiment was 12.6 eV [11] in good agreement with the present results.

Among the energies for the different clusters, we found systematically slightly lower values for  $F_5$ -based clusters with a fluorine in the center ( $F_5Li_{17}$ ,  $F_9Li_{25}$ , and  $F_{13}Li_{37}$ ) compared to  $F_4$ -based clusters with a lithium in the center ( $F_4Li_{13}$ ,  $F_5Li_{14}$ ,  $F_9Li_{25}^*$ , and  $F_{12}Li_{33}$ ). This can be understood in view of the symmetry of the system. For the trion state two holes have to be distributed over the fluorine sites. The configuration of one hole in the center and the wavefunction of the second hole symmetrically distributed over surrounding fluorine sites is a configuration of higher symmetry in the finite cluster and thus energetically more favorable than a distribution where none of the holes is located in the center of symmetry. This leads to slightly higher trion energies in  $F_4$ -based clusters than in  $F_5$ -based clusters.

The trion binding energy is given by the energy difference to the ground state of the doubly charged (q = 2, two-hole) system. Unlike for the excitation energy, for the binding energy a correction for a finite-size cluster calculation is more important and should be included. For the q = 2 ground state the three charges should have reached asymptotic distances. Within our calculation only the electron can be regarded as infinitely distant in this case. Due to the finite cluster size possible values for the distance  $R_{hh}$  between the residual two holes lie between 5.4 a.u. and 21.5 a.u. (in the  $F_{13}Li_{37}$  cluster) where the spatial distribution of the MOs occupied by the holes indicates a largest possible separation of the holes, i.e.  $R_{hh} = 21.5$  a.u. for the  $F_{13}Li_{37}$  cluster. We therefore subtract the screened hole-hole interaction,  $(\epsilon(\omega)R_{hh})^{-1}$ , from the trion energy where  $\epsilon(\omega)$  is the the dielectric constant. As a

first-order estimate the optical value for LiF [42],  $\epsilon(\omega) = 1.96$ , can be used. For an improved estimate we take into account the dependence of  $\epsilon(\omega)$  on the ratio of the hole-hole distance to the mean hole velocity  $\langle v_h \rangle$  with  $\langle v_h \rangle = 0.22$  a.u. being the mean velocity in LiF. The ratio  $R_{hh}/\langle v_h \rangle \approx 98$  in the F<sub>13</sub>Li<sub>37</sub> cluster corresponds to an  $\epsilon(\omega) \approx 2.7$  according to the dielectric response function calculated by Hägg et al. [43]. We note parenthetically that there, the response function was determined for the perturbation by an external charge above the surface. However, as the induced potential for charges below but very close to the surface is very similar to the latter case |44| we expect the obtained value for  $\epsilon(\omega)$  to be a good approximation. We therefore use  $\epsilon(\omega) \approx 2.7$  to calculate the trion binding energy (Table 2.1). We determine an "error bar" of the present excitation and binding energies (Table 2.1) from the (non-monotonic) fluctuations of the results with cluster size where for every cluster the  $R_{hh}$  dependent dielectric constant was used. To determine the binding energy of a trion, the ground state energy of the doubly charged cluster was calculated to obtain the second ionization energy of the LiF cluster (see Fig. 2.4). The latter may be affected by the uncertainty in the groundstate determination: as we use state averaged MCSCF, the average total energy of all states is minimized during the calculation. As a consequence, the ground state energy of the singly charged cluster obtained in our calculations is slightly higher than the result would be in the case of a one-state calculation. To be consistent, all possible nearly degenerate "ground states" of the doubly charged cluster should be calculated. If there are  $n \neq 2p$ -like MOs considered in the calculation, there are n different possibilities for the location of one hole (in the singly charged cluster) while for two holes in the doubly charged cluster already  $n^2$  different configurations are possible for the "ground state". The simultaneous optimization of 16 states in the case of  $F_4Li_{13}$  and of 121 states in the case of  $F_{13}Li_{37}$  would be necessary which goes beyond our present capabilities. We therefore calculate only the lowest, "real" ground state of the doubly charged cluster. To get an estimate for the shift of the ground state energy when all "ground states" are considered in the MCSCF calculation, we have studied the effect on the doubly charged  $F_4Li_{13}$  cluster where, for computational reasons, we restricted the number of active states to 14. The energy difference compared to the one-state calculation was below 0.3 eV. For all clusters, the second ionization energy determined from MCSCF calculations exceeds the trion excitation energy so that the trion state is, indeed, a bound state. We obtain a trion binding energy  $E_{bind}$  of about 2.24 eV with an error interval due to finite-cluster size corrections ranging from 1.56 eV to 3.52 eV. This is consistent with the estimated energy of  $3.5 \pm 1$  eV found in experiment [11, 27].

#### **Trion** wavefunction

We present now results for the "wavefunction" of the trion, more precisely, for the pair correlation function for its two holes. We evaluate the joint probability distribution function  $\rho\left(\vec{r}_{1}^{(h)}, \vec{r}_{2}^{(h)}\right)$  of the two holes. Fixing the first hole at the central F site,  $\rho\left(0, \vec{r}_{2}^{(h)}\right)$  gives the pair correlation function or conditional probability for finding the second hole of the bound complex at  $\vec{r}_{2}$  when one hole resides at the central F site of the cluster. This quantity is, apart from conceptual aspects, also of interest for the collisional interaction process: the excitation of a trion during the impact of positive ions on an LiF surface can only be an efficient charge exchange and energy loss channel when the trionic state is well localized so that a sufficient overlap of the corresponding wavefunctions can occur during the short interaction time window.

To determine the pair correlation function we calculate the two-hole wavefunction  $\Psi^{(h)}(\mathbf{r_1}, \mathbf{r_2})$  which is given, after tracing out of all other degrees of freedom, by the superposition of different two-hole Slater determinants,

$$\Psi^{(h)} = \sum_{l} \alpha_l \Phi_l^{(h)} \tag{2.4}$$

where  $\Psi^{(h)}$  depends on  $\mathbf{r_1}$  and  $\mathbf{r_2}$  which include all spatial and spin coordinates of the holes. The difference to Eq. 2.2 is that the Slater determinants  $\Phi_l^{(h)}$  include only the two molecular orbitals  $\phi_{j_1,l}$  and  $\phi_{j_2,l}$  of the holes:

$$\Phi_{l}^{(h)} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{j_{1},l}(\mathbf{r_{1}}) & \phi_{j_{1},l}(\mathbf{r_{2}}) \\ \phi_{j_{2},l}(\mathbf{r_{1}}) & \phi_{j_{2},l}(\mathbf{r_{2}}) \end{vmatrix}.$$
(2.5)

For a given spin orientation of the holes,  $|\Psi^{(h)}(\vec{r_1},\vec{r_2})|^2$  gives, up to a normalization constant, the probability for finding one hole at the point  $\vec{r_1}$  and the other hole at  $\vec{r}_2$ . A typical result for the pair distribution function  $\rho(0, \vec{r}_2) = \left|\Psi^{(h)}(\vec{r}_1 = 0, \vec{r}_2)\right|^2$ in the surface plane  $(z_2 = 0)$  is shown in Fig. 2.6 for an F<sub>13</sub> cluster. The probability density has  $A_1$  (i.e. the highest) symmetry as expected for the lowest excited state. It shows very pronounced maxima at the next-to-nearest neighbor fluorine sites while the probability to find the second hole at a nearest neighbor F is smaller by an order of magnitude and even smaller at a  $3^{rd}$  nearest neighbor F site. This can be understood in view of the position of the excited electron which is located near a lithium. It is therefore energetically favorable for the holes to be located at two sites adjacent to the electron which are next-to-nearest F sites. In other words, the electron-bihole complex forms a collinear three-center "quasi molecule". Note the *p*-orbital character of the four main peaks with a clearly visible nodal plane through the exact position of the fluorine lattice sites. As expected, we find a correlation hole, i.e. zero probability to find the second hole at the exact location of the first hole (x = y = z = 0).

The "radial" probability distribution  $|\Psi^{(h)}(|\vec{r_1} - \vec{r_2}|)|^2$  corresponding to Fig. 2.6 is plotted in Fig. 2.7. The expectation value for  $|\vec{r_1} - \vec{r_2}|$  is 7.62 a.u. coinciding with twice the lattice constant of LiF (distance between an F and an adjacent Li



Figure 2.6: Pair correlation function (conditional probability distribution) for one hole when the second hole is fixed at  $x_1 = y_1 = z_1 = 0$ , cut through the  $z_2 = 0$  plane for an  $F_{13}Li_{37}$  cluster. The position of the 13 fluorides is also marked ( $\times$ ).

Figure 2.7: Radial probability distribution  $|\Psi^{(h)}(|\vec{r_1} - \vec{r_2}|)|^2$  where  $\vec{r_1} = 0$ , and  $z_2 = 0$ .

atom) a = 3.8 a.u. Due to the *p* character of the hole orbital (see Fig. 2.6) the distribution shows a double peak at the corresponding distance. The dip within the double peak originates from the nodal planes of the orbitals, however, smeared out somewhat by the spherical average. Our results confirm the conclusion drawn from experiment [11] that the two holes of a trion are located in close proximity to each other.

In comparing the trion problem (excitation of the charged cluster) with the exciton problem (excitation of the neutral cluster), the question arises if a trion configuration is possible with the excited electron protruding into vacuum as is the case for surface excitons. There, the inclusion of basis sets in the vacuum allowing the electron wavefunction to be centered above the surface leads to a 25% reduction of the excitation energy [32, 33]. Due to the stronger attraction of the electron to the two holes of the trion we expect electron states in the vacuum to be of minor importance for trion energies. Due to computational reasons basis functions centered outside the cluster surface have therefore been not included in most of our calculations. However, in order to clarify if such a configuration may be energetically more favorable than the surface confined trion, we have performed test calculations on the  $F_9Li_{25}$  cluster. The set of basis functions was extended by three s and one p Gaussian including a diffuse s orbital for every virtual lattice site in the vacuum, centered above the five central fluorine ions at z = 1.9 a.u. and z = 3.8a.u. The use of a larger basis set or a larger cluster would go beyond the present abilities of the code. MCSCF calculations on the charged cluster yield, in fact, a trion configuration where the electron wavefunction has dominant contributions from MOs built up by the vacuum basis functions. The excitation energy as well as the binding energy of this trion are, however, comparable to the collinear case within the accuracy level of the method and appear not to lead to a significant lowering of the energy. Of interest is the spatial distribution of this configuration. As opposed to the typical collinear alignment of a three-body Coulomb complex, the angle between the three charges is considerably smaller than  $180^{\circ}$ . As in the collinear case the holes tend to occupy next-to-nearest fluorine sites. For a more detailed study of such trion configurations convergence tests on cluster size, basis set size as well as on active configuration space are necessary which are not feasible at this moment.

#### 2.2.3 Relation to the three-body Coulomb problem

The trion is a bound state of the three-body Coulomb system embedded in the solid environment. It is now instructive to compare this state with other Coulomb three-body systems in vacuum as well as states in lower-dimensional confined space.

One key input parameter for such a comparison are the effective masses of the holes,  $m_h^*$ , and the electron,  $m_e^*$  which represent, to first order, the coupling of the quasi-particles to the periodic potential of the solid. The effective masses were determined from band structure calculations of LiF [45] using the relation  $1/m^* = \partial^2 E(k)/\partial k^2$  (in atomic units) where E(k) is the band energy as a function of the wave vector k. The three valence bands and the lowest conduction bands of LiF are shown in Fig. 2.8 together with the parabolic fits near the  $\Gamma$  point to determine the curvature of E(k). As there are three valence bands, two of which are degenerate at the  $\Gamma$  point, a mean value for the effective mass of the hole was calculated via  $\frac{1}{m_h^*} = \frac{1}{3} \left( \frac{1}{m_1^*} + \frac{2}{m_2^*} \right)$  where  $m_2^*$  and  $m_1^*$  are the effective masses in the degenerate and in the non-degenerate valence bands, respectively. We find the effective masses for electrons and holes to be  $m_e^* = 0.948m_e$  and  $m_h^* = 2.227m_e$  with  $m_e$  being the mass of a free electron.

The two holes are the "heavy" particles, the electron is the "light" particle. This suggests an analogy to the one-electron molecular ion, e.g.  $H_2^+$ . The binding energy defined as the difference between the minimum energy at the equilibrium distance



Figure 2.8: Band structure of LiF. Shown are the valence bands and the lowest conduction bands (solid lines). Fits to parabolae near the  $\Gamma$  point (dashed, dotted and dashed-dotted lines) give the effective masses (see text).

of the nuclei  $(R_{min} = 2.00 \text{ a.u.})$  and the asymptotic energy of  $H_2^+$  amounts to 2.79 eV. The  $H_2^+$  ion corresponds to a limiting case of three interacting charges where two of them can be regarded as infinitely heavy compared to the third, light particle, so that the reduced mass of the system  $\mu \approx 1$  in units of the light mass. This is clearly very different from the present system of two holes with  $m_h^* = 2.227 m_e$  binding an electron with  $m_e^* = 0.948m_e$ . The corresponding reduced mass of  $\mu = 0.54$  (in units of  $m_e^*$ ) is much closer to that of the opposite limit of three particles with equal mass which is given by the charged positronium ion  $Ps^+$   $(e^+e^-e^+)$  with  $\mu = 1/3$ . Another three-body system in-between these limiting cases is the muonic molecule  $pp\mu^{-}$  with a reduced mass of  $\mu = 0.812$  (in units of  $m_{\mu}$ ). The total energy of these three-body systems scaled by the factor  $1/m_1$  where  $m_1$  is the mass of the light particle, shows an approximately linear dependence on the reduced mass of the system (Fig. 2.9). It is now instructive to relate our present result for trions to this "universal" binding energy scaling. To do so, we have to take into consideration corrections due to the solid state environment. To first order, this three-body Coulomb problem is embedded in a dielectric medium with a dielectric constant for which we take again the value  $\epsilon(\omega) \approx 2.7$  as obtained in Sec. 2.2.2. The Coulomb interaction between two charges  $Q_1$  and  $Q_2$  will be screened by a factor  $1/\epsilon$ :

$$\frac{Q_1 Q_2}{r_{1,2}} \to \frac{Q_1 Q_2}{\epsilon r_{1,2}} \tag{2.6}$$

where  $r_{1,2}$  is the distance between the two charges. The effect of screening manifests itself in a shift of the energy curve towards lower (absolute) energies and a reduced binding energy. For a comparison with the scaled binding energy of the three-body



Figure 2.9: Total scaled energy of the three-body systems  $H_2^+$ ,  $pp\mu^-$ ,  $Ps^+$  [46] and a trion as a function of the reduced mass of the system in units of the light mass.

Coulomb problem in vacuum, we have to remove the screening by multiplying the scaled trion energy by  $\epsilon$ . This corresponds to a trion in vacuum, i.e. a free three-body system of  $\mu = 0.54$ . The resulting energy ( $E \approx -0.35$  a.u.) is now close to the "universal" curve of the free three-body systems.

Within the framework of a three-body Coulomb problem in a screening environment, Thilagam [28] derived an analytical expression for the binding energy of a trion in a two-dimensional electron system in order to provide an order of magnitude estimate. His description is based on a three-body Hamiltonian of the two holes and the bound electron where the three charges are assumed to form a line. In this model the effect of the periodic crystal potential is included only through the effective masses of electrons and holes. The charges are thus treated as free particles (with effective masses) moving in a dielectric medium. Thilagam's expression for the trion binding energy reads:

$$E_{bind} = \left(\frac{s^2 + 4s + 2}{s^2 + 6s + 3} \cdot \frac{9}{4} - 1\right) s \frac{M_R R_H}{\epsilon^2 m_e}.$$
 (2.7)

Here,  $s = m_h^*/m_e^*$ ,  $M_R = m_e^*m_h^*/(m_e^* + m_h^*)$  is the reduced effective mass, and  $R_H$  denotes the Rydberg constant. As the hole-hole distance is not described in Ref. [28], we have here used the optical limit of the dielectric constant,  $\epsilon = 1.96$  for LiF. Remarkably, Eq. 2.7 predicts a binding energy close to the present results  $(E_{bind} = 3.78 \text{ eV})$ . The surprisingly good agreement should be taken with caution given the simplicity of the model, in particular the neglect of the crystal potential.

## 2.3 Perturbation of the LiF Band Structure by Antiprotons and Protons

We will now turn to electronic excitations in the bulk initiated by antiprotons and protons moving through an LiF crystal.

Fast light ions traveling through solids lose energy predominantly to the electronic system of the target by exciting and ionizing electrons. The resulting slowing down process of the projectiles is characterized by the stopping power -dE/ds, the energy loss per distance traveled. For very slow projectile ions, in addition to the just described electronic stopping, nuclear stopping becomes important. This slowing down process is caused by binary collisions of the projectile with the target atomic nuclei. While swift ions move through the solid approximately along a straight line, the trajectory of very slow ions is deflected by scattering at target nuclei.

By measurements of the stopping power in the energy regime where electronic stopping is dominant, the response of the target electrons to external perturbations can be probed. The detailed knowledge of the stopping power is, apart from its fundamental interest, important for technical applications such as ion-beam analysis in material science or radiotherapy in cancer treatment using ion-beams. There, the stopping power must be known very accurately to ensure that the projectile deposits most of its energy in the tumor cells while the surrounding tissue should suffer, in the ideal case, no damage.



Figure 2.10: Excitation of electrons in metals and insulators, schematically.

Already in the first half of the last century, Lindhard [47] provided a theory for the stopping power for ions in a free electron gas. Within this free-electron gas (FEG) approximation as well as within other models [48] the stopping power at low energies is approximately proportional to the projectile velocity. The model is only valid if the condition  $m_e v_e v > E_g$  is fulfilled [49] where  $m_e$  is the electron mass and  $v_e$  is the electron velocity. The quantity  $m_e v_e v = \Delta E$  corresponds to the average energy transfer following from energy and momentum conservation in a binary collision of the ion with a target electron. In metals, the projectile can lose an arbitrary small amount of energy  $\Delta E \rightarrow 0$  by exciting electrons from the Fermi edge to unoccupied states in the conduction band (Fig. 2.10). To excite an electron from the valence band in an insulator the transfered energy must exceed the band gap  $E_g$  of the material (Fig. 2.10). Consequently, a clear deviation for insulator targets from the velocity proportionality of the stopping power is expected below a certain energy threshold when the possible energy loss becomes comparable to the band gap. In stopping power calculations where the energy condition  $m_e v_e v > E_q$ was taken into account [50], a deviation from  $-dE/ds \propto v$  in targets with energy gap for energies below  $500E_g$  was found. Although the calculations were done for a Ne target where  $E_q = 16.7$  eV, we assume the threshold for an LiF target to be of the same order of magnitude. For LiF where the band gap is about 14 eV, this estimate would yield a threshold of 7 keV. Recently, Møller et al. [4] have measured the stopping power of protons and antiprotons in LiF at projectile energies down to 2 keV and 4 keV, respectively. Surprisingly, no deviation from metallic behavior even for very low energies was found. In another recent experiment by Draxler et al. [8] the stopping cross section for protons in thin LiF films was studied in backscattering geometry for projectile energies down to 700 eV and later down to 65 eV [9]. A deviation from velocity proportionality of the stopping power was found for proton energies below about 4 keV.

This interesting finding motivated us to investigate the influence of protons and antiprotons on the band structure of LiF. Due to the strong perturbation by the external charges, deviations of the band structure and consequently of the band gap from the ground state situation are expected. First studies on this account have been made by Eder *et al.* [51] who measured the stopping cross section of protons and deuterons in LiF down to 2 keV projectile energies where no threshold for a deviation from the velocity proportional regime could be found. Ab initio calculations for the system H-F<sup>-</sup> showed a decrease of the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) with decreasing distance between the nuclei.

In this work, we study the dependence of the band gap on the position of the projectile in LiF in detail using ab initio calculations on the SCF and MCSCF level to include correlation effects. We employ again the embedded cluster approach. For our study we used bulk clusters of different sizes up to  $F_{19}Li_{44}$  (Fig. 2.11).

#### 2.3.1 SCF calculations for the perturbed band gap

As a starting point, SCF calculations were performed on the  $F_{19}Li_{44}$ ,  $F_{17}Li_{42}$ , and  $F_{13}Li_{38}$  clusters for a discrete grid of projectile positions within the marked area in (Fig. 2.12) of the LiF unit cell. Again, the quantum chemistry code COLUMBUS



Figure 2.11: Bulk clusters used in the present work.

was used for the calculations employing the restricted Hartree-Fock approximation where the electrons are distributed over the MOs in pairs of opposite spin. For the SCF calculations the Gaussian basis set of Schäfer *et al.* [34] was used ((7s, 3p)/[3s2p] for F, (6s)/[2s] for Li)<sup>1</sup>. For the proton projectile we used a ccpVDZ basis ((4s, 1p)/[2s, 1p]) with diffuse functions (1s, 1p). Here, cc-p stands for "correlation consistent polarized" and VDZ for "valence double-zeta" [16] indicating that the basis functions for the valence electrons consist of two basis functions of different angular momentum l per atomic orbital. This allows the electron density to adjust its spatial extent to the particular molecular environment.

As the presence of the projectile breaks the symmetry of the cluster the calculations were first performed without any point-group symmetry (or equivalently, in

<sup>&</sup>lt;sup>1</sup> The quantum chemistry notation (7s, 3p)/[3s2p] reads as follows: this basis set consists of three *s*-type and two *p*-type (contracted) functions which are built up by linear combinations of seven *s*-type and three *p*-type (primitive) Gauss functions, respectively.



Figure 2.12: Unit cell of LiF. The gray shaded volume indicates the range of projectile positions used in the calculations.

the  $C_1$  symmetry). As inspection of the results revealed that the most interesting positions of the antiproton where the band gap reaches a minimum, lie on the connection line between a fluorine and an adjacent lithium, the  $C_{2v}$  symmetry could be used for all further calculations by varying the position of  $\bar{p}$  along the connection line between the central  $F^-$  of the cluster (Fig. 2.11) and the next Li<sup>+</sup> along the z-axis. Due to convergence problems at the  $F_{19}Li_{44}$  cluster in the region of  $z_{\bar{p}} < 0.9$ a.u. which coincides with the distance of minimum band gap, we present SCFresults of the  $F_{13}Li_{38}$  cluster in Fig. 2.13. We show the density of states (DOS) for different positions of the projectile. Here, the results for the band gap  $E_q$  for all projectile positions used have already converged in cluster size, the difference between results for the  $F_{19}Li_{44}$  and the  $F_{13}Li_{38}$  cluster lying below 0.1 eV. The DOS was obtained by broadening the SCF-energy levels by Gauss functions with a standard deviation of 0.01 a.u. For comparison, the DOS for the unperturbed cluster is also shown in Fig. 2.13. As is well known [52], the SCF calculation clearly overestimates the band gap defined as the total energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO). We obtain  $E_q = 15.34$  eV compared to the literature value of about 14 eV [53].

The presence of an antiproton in the LiF cluster influences the band gap drastically (Fig. 2.13a). For all positions of  $\bar{p}$  within the unit cell,  $E_g$  is reduced compared to the neutral cluster due to a "leaking out" of a few occupied states in the energy range of the neutral band gap (Fig. 2.13b). With decreasing distance of  $\bar{p}$  to the fluorine site the band gap decreases reaching a minimum at a distance of about 0.54 a.u. to the F<sup>-</sup> ion on the connection line between the fluorine and the adjacent lithium (Fig. 2.14). The energy gap between LUMO and HOMO is lowered to only  $E_{g,min} = 2.35$  eV.If we assume a threshold at about 500 times the minimum excitation energy this will bring the threshold for non-metallic behavior of the stopping power below 1 keV explaining the experimental observation of velocity-proportional stopping power for antiproton energies above 2 keV.

For a proton projectile the situation is similar but by far not as dramatic as in the antiproton case. The gap is close to the neutral value (Fig. 2.14) where now the minimum band gap appears for the proton being at the exact position of a lithium



Figure 2.13: SCF results for the density of states for the F<sub>13</sub>Li<sub>38</sub> cluster for different positions of the projectile along the connection line between F<sup>-</sup> and Li<sup>+</sup>.
a) Antiproton projectile, b) unperturbed cluster, c) proton projectile.

 $(E_{g,min} = 14.66 \text{ eV})$ . Apart from their opposite charges, the main difference between the p and  $\bar{p}$  projectile is the ability of the proton to form molecular orbitals with the target ions and capture electrons. For the stopping power this charge exchange constitutes an additional channel of energy loss as opposed to  $\bar{p}$  projectiles where the



Figure 2.14: Dependence of the SCF-band gap  $E_g$  on the position of the projectile along the connection line between F<sup>-</sup> and Li<sup>+</sup> for the F<sub>13</sub>Li<sub>38</sub> cluster. The result for the unperturbed neutral cluster is also shown. Lines are to guide the eye.

target electrons are perturbed by the repulsive field of the negative charge brought into the crystal. This also manifests itself in a different form of  $E_{a}$ -reduction. While for a  $\bar{p}$  projectile, both valence and conduction band are shifted upwards in energy, the energy shift of the bands is towards lower energies in case of a proton projectile. This is not surprising given the composition of the valence and conduction band of LiF. The valence band is given by the F 2p-like MOs. Bringing an antiproton close to an  $F^-$  therefore strongly perturbs the valence band. In the limiting case of merging the  $\bar{p}$  with an F<sup>-</sup>, i.e. bringing them on top of each other, the negative nuclear charge of  $\bar{p}$  reduces the (positive) nuclear charge of F<sup>-</sup> by one. This unified atom limit is equivalent to replacing  $F^-$  by the isoelectronic equivalent of an  $O^{2-}$ . As this ion in vacuum environment has an unbound electron it is not surprising that the HOMO of LiF is considerably shifted towards the vacuum level due to the presence of an antiproton. By contrast, a proton at the exact position of an  $F^$ corresponds to replacing  $F^-$  by a neutral Ne atom with all electrons well bound. In this case, the valence band is shifted to lower energies (Fig. 2.13c) in analogy to an outer electron deeper bound in  $Ne^0$  than in  $F^-$ .

The conduction band of LiF is composed of Li 2s-like orbitals. Bringing an antiproton at the exact position of a Li<sup>+</sup> corresponds to a reduction of the nuclear charge of the ion by one yielding a neutral He so that no dramatic influence on the conduction band by a  $\bar{p}$ , apart from a constant shift to higher energies, is expected. The upward shift can be understood in terms of the increased energy needed to excite an electron in He than in Li<sup>+</sup>. Less energy is necessary to excite an electron

in  $Be^{2+}$  which corresponds to the limiting case of merging a Li<sup>+</sup> with a proton. The conduction band is therefore shifted towards lower energies compared to the unperturbed solid (Fig. 2.13c).

The detailed dependence of the SCF-band gap on the position of the projectiles is shown in (Fig. 2.14).

#### 2.3.2 Excitation energies of the perturbed cluster determined by MCSCF calculations

In SCF calculations where correlation effects are neglected, the band gap of LiF is clearly overestimated. To include correlation, we go beyond the HF-level using the multi-configuration self consistent field method. We perform state averaged MC-SCF calculations for different positions of the projectiles in the cluster calculating the ground state and the first excited state. From the difference of the respective total energies we obtain excitation energies  $E_{exc}$  corresponding to the minimum energy necessary to excite an electron from the valence to the conduction band in analogy to the band gap  $E_g$  in an SCF calculation. Our results will therefore provide a threshold for electron excitation when a proton or antiproton is present in LiF.

For computational reasons, the MCSCF is performed on the smaller cluster  $F_5Li_{22}$ . It is difficult to estimate a systematic error due to cluster size as an MC-SCF for a larger cluster is not feasible. Comparing SCF results for the band gap for clusters of different sizes using the same basis set yields a difference in  $E_g$  of about 0.6 eV between the value for the  $F_5Li_{22}$  and the  $F_{13}Li_{38}$ . Comparing the SCF results for different clusters for an antiproton projectile shows that there, the deviation of the  $F_5$ -value with respect to the  $F_{13}$ -value is smaller for several positions of the projectile, especially at close distance of the  $\bar{p}$  to the F<sup>-</sup>, i.e. the most interesting range. We therefore expect the systematic error due to cluster size effects to lie in the  $10^{-1}$  eV range. The (comparably) small number of active ions in the  $F_5Li_{22}$  cluster allows for the use of a larger basis set. For a convergence test of the basis set we have compared again SCF band gaps, now for the F<sub>5</sub>Li<sub>22</sub> cluster, using different basis sets of increasing size. The optimal choice for a basis set is required to be small enough to allow for computationally demanding calculations and large enough to be converged in the size of the basis set. For the  $F^-$  ions the so obtained basis set is a cc-pVDZ (9s, 4p, 1d)/[3s, 2p, 1d] with additional diffuse functions (1s, 1p), for the Li<sup>+</sup> ions it is the (7s/[3s]) basis set of Schäfer *et al.* [34], and for the proton projectile it is again the cc-pVDZ basis ((4s, 1p)/[2s, 1p]) with diffuse functions (1s, 1p) already used for the SCF calculations. The difference in  $E_q$  when a larger basis set is used is about  $10^{-1}$  eV.

The MCSCF calculations are performed in  $A_1$  symmetry, the highest symmetry within the  $C_{2v}$  symmetry group, as the states of lowest energy are expected to have highest symmetry. For all calculations the F 1s-, F 2s-, and Li 1s-like MOs are kept doubly occupied. The active space is divided into a restricted active space (RAS) from which only single excitations are allowed and a complete active space (CAS) where also double excitations are possible. All F 2p-like MOs of A<sub>1</sub> symmetry are in the CAS while all F 2p-like MOs of other symmetries are in the RAS. For the auxiliary orbitals (AUX), i.e. MOs where electrons can be excited to, the lowest three  $A_1$  MOs are used for calculations with a  $\bar{p}$  projectile. This configuration space containing all MOs corresponding to the valence band of LiF is already well converged with respect to the size of the active space. For the p projectile calculations, only one MO in the AUX was used due to convergence problems in calculations when using a larger AUX. This leads to a systematic error in the MCSCF results for proton projectiles which we estimate to < 1 eV from variations of the auxiliary space in calculations on a smaller cluster.

The MCSCF results for the (threshold) excitation energies  $E_{exc}$  are shown in Fig. 2.15. For comparison, the excitation threshold for the neutral cluster is also



Figure 2.15: Dependence of the (MCSCF) excitation energy  $E_{exc} = \Delta E$  on the position of the antiproton and the proton along the connection line between F<sup>-</sup> and Li<sup>+</sup>. The result for the neutral cluster is also shown. Lines are to guide the eye.

shown corresponding to the excitation of an exciton. As in the SCF results, the strong perturbation of the crystal band structure due to the presence of an antiproton becomes obvious, even more so than in the calculated SCF band gaps. The absolute values for  $E_{exc}$  are overall smaller than the SCF values (Fig. 2.14). In addition, the shape of the curve has changed. Whereas in the MCSCF results for  $\bar{p}$  projectiles the energy threshold increases monotonically with increasing distance

from the fluorine, a minimum could be found in the SCF results. This emphasizes the importance of including correlation effects, i.e. going beyond the HF level.

The extremely low excitation thresholds for distances z to the F<sup>-</sup> below 2 a.u. (down to 0.44 eV) can be understood when we take a closer look at the dominant configurations contributing to the ground state and the first excited state. Surprisingly, we found that already in the state of lowest energy the F 2*p*-like MOs are not all doubly occupied as one would expect for the ground state. Instead, one of these MOs (the highest in energy) is only singly occupied and so is the lowest Li 2*s*-like orbital. As the adjacent state higher in energy has a similar dominant configuration where just another F 2*p* MO is singly occupied, the two states of lowest energy are nearly degenerate. The excitation energy from the lowest to the next state is consequently very small.

Comparing the perturbation caused by the  $\bar{p}$  at the F<sup>-</sup> site again with the unified atom limit of an O<sup>2-</sup> ion, the single MO occupations in the ground state become more clear. A free O<sup>2-</sup> ion is unstable such that the outermost electron would be unbound. It is therefore not surprising that within an ionic crystal, this outermost electron is excited to the conduction band. The ground state consequently has a singly occupied HOMO. For a consistency check we have performed the MCSCF calculation also in an O<sub>1</sub>F<sub>4</sub>Li<sub>22</sub> cluster, i.e. we have replaced the central F in the F<sub>5</sub>Li<sub>22</sub> cluster by an oxygen atom and run the calculation with the same number of electrons as before. As expected, the results were exactly the same as in the F<sub>5</sub> cluster when the antiproton position is on top of the central F.

The promotion of the outermost electron to a higher orbital at close distances between the  $\bar{p}$  and an  $F^-$  is similar to the Fano-Lichten effect [54]. It describes the promotion of electrons to higher atomic levels in ion-atom collisions due to the coupling of quasi-molecular orbitals formed at close distances of the collision partners. As our calculations are performed in the adiabatic approximation, dynamical effects leading to diabatic promotion are not accounted for. Our results for the threshold energy therefore represent a static limit providing an upper bound for  $E_{exc}$ . Dynamical effects such as transitions due to avoided crossings of the potential energy surfaces may lead to an additional decrease of this threshold.

For z > 2 a.u., the antiproton is near to the Li<sup>+</sup> site and the dominant configuration of the energetically lowest state is given again by the typical ground state configuration with a doubly occupied HOMO of F 2*p*-character. The excitation thresholds increase with increasing z reaching a maximum of  $E_{exc} = 6.42$  eV at the  $\bar{p}$  position on top of an Li<sup>+</sup>. This limit is equivalent to replacing the Li<sup>+</sup> by He<sup>0</sup> having two well bound electrons in the ground state.

The proton curve (Fig. 2.15) is found close to the excitation energy of the unperturbed cluster with a similar shape as in the SCF results. However, the difference between the smallest threshold energy ( $E_{exc} = 10.18 \text{ eV}$ ) and the largest ( $E_{exc} = 13.91 \text{ eV}$ ) is about twice as large as in the latter. Interesting is the minimum at about 2.4 a.u. lying below the the excitation energy of the neutral cluster. As this distance coincides with the typical spatial extension of an F 2p orbital, this dip may originate from a large overlap of the F<sup>-</sup> and H wavefunctions for this particular geometry. The configurations in the ground state of the cluster perturbed by a proton are for all p positions dominated by the usual distribution of the valence electrons over the F 2p-like orbitals with a doubly occupied HOMO. This is not surprising given the limits of a Be<sup>2+</sup> and Ne<sup>0</sup> for proton positions on top of the Li<sup>+</sup> and of the F<sup>-</sup>, respectively, which both have only well bound electrons.

For an antiproton projectile, our results imply a drastic reduction for the expected threshold in the antiproton kinetic energy below which a deviation from metallic behavior in the stopping power should occur. Estimating the threshold to  $500E_g$  yields about 220 eV only, i.e. more than a magnitude smaller than previously expected. Experiments with much lower antiproton energies than used before are therefore needed to find a deviation from metallic behavior.

For proton projectiles, the estimated threshold lies at about 4.5 - 5.5 keV where we have considered the systematic uncertainty of  $\sim 1 \text{ eV}$  in the MCSCF calculations for proton projectiles due to restrictions in the active space (AUX). Although experiments measuring the stopping power of protons penetrating through LiF foils have been performed down to about 2 keV kinetic energy, no clear deviation from a linear v-dependence was found [4, 51, 55] where the data, however, cannot be well fitted by a linear curve. Especially the data points for kinetic energies  $E_{kin} < 4$ keV typically lie below the straight line fitted to the results which may be a first indication of a deviation from metallic behavior. In stopping power experiments using backscattering geometry [8] a deviation from a linear v-dependence was found for proton energies below about 4 keV in good agreement with our estimate for the threshold energy. A deviation from metallic behavior was also found for grazing scattering of protons at an LiF surface with kinetic energies down to 300 eV [56]. The onset of the deviation approximately coincides with our predicted threshold. However, detailed calculations for a surface cluster (as opposed to bulk clusters studied in this work) are necessary for a direct comparison between theory and this surface-sensitive experiment.
# 3 Scattering of Highly Charged lons at Insulator and Metal Surfaces

After detailed descriptions of particular target excitations in the previous chapter, we will now study the complex scenario of an ion impinging on a surface including the dynamics of the ion as well as of the electrons of the system.

During the last decades more and more details of ion-surface interaction have been identified forming the following generally accepted physical picture (for details see e.g. Ref. [12]): When an ion approaches a solid surface the potential barrier separating the ion from the surface is lowered while the electronic levels of the ion are shifted upwards in energy due to the image potential (image shift). This potential originates from the response of the surface electrons to the external perturbation of the ion. Consequently, at a certain critical distance  $d_c$  resonant electron transfer from the surface to the projectile and back (if there are unoccupied states available) sets in. The classically allowed transitions are well described by the Classical-Over-the-Barrier (COB) model developed for metal targets by Burgdörfer *et al.* in 1991 [5]. It was later extended to insulator surfaces [12] and has been successfully used since in many studies.

The model is based on a set of rate equations describing the electron population dynamics of the *n*-shells of the approaching ion. First, highly excited Rydberg states get populated leading to the formation of a "hollow atom". The subsequent deexcitation process of the ion is governed by a variety of electron exchange- and emission processes (Fig. 3.1). A dominant deexcitation channel above the surface is autoionization (AI) while close to the surface, inter-atomic Auger processes become increasingly important. These are Auger capture (AC) which involves two surface electrons, one of them being emitted and the other one captured by the projectile, and Auger deexcitation (AD). Here, one surface and one projectile electron interact with each other leading to the population of a low lying projectile level and to the emission of the other electron. Due to the image shift high electronic projectile states are promoted to the vacuum level so that electrons in these levels are "peeled off" at the surface with very low kinetic energies. Electrons from deeply bound states in the target can, in principle, tunnel through the barrier feeding inner shells



Figure 3.1: Electron transfer processes during the approach of an ion to a solid surface: resonant capture (RC), resonant loss (RL), Autoionization (AI), Auger capture (AC), Auger deexcitation (AD), direct inner feeding (DF), and promotion to continuum states.

of the projectile (DF). However, this process is very unlikely compared to the other neutralization- and deexcitation processes.

If the projectile penetrates the solid target a "hollow atom" forms again, subsequently decaying by further electron exchange- and emission processes. For the present studies of the "trampoline" effect in front of an LiF surface and of the spin polarization of electrons emitted during grazing incidence scattering of ions at an iron surface, we focus on the above-surface part of the trajectory including, however, the region directly close to the surface.

The original form of the rate equations of the COB model reads [5]:

$$v_{z} \frac{d}{dR_{z}} P_{n}(R_{z}) = I_{n}^{C}(R_{z}) - I_{n}^{L}(R_{z})P_{n}(R_{z}) + \frac{1}{2} \sum_{n' > n} A_{n',n} P_{n'}^{2}(R_{z}) - P_{n}^{2}(R_{z}) \sum_{n' < n} A_{n,n'}.$$
(3.1)

They describe the evolution of the electron population  $P_n$  of the  $n^{th}$  shell of the ion as a function of the distance  $R_z$  to the surface where  $I_n^C(R_z)$  and  $I_n^L(R_z)$  are the current of (resonantly) captured and lost electrons, respectively. The terms containing  $A_{n,n'}$  describe autoionization, i.e. intra-atomic Auger decay from shell nto n'. On the left hand side of Eq. 3.1  $v_z$  denotes the velocity of the ion perpendicular to the surface determined by Newton's equation of motion

$$\frac{d}{dR_z}v_z(R_z) = \frac{1}{mv_z}\frac{d}{dR_z}V_p(R_z).$$
(3.2)

Here, m is the projectile mass and  $V_p(R_z)$  is the self-image potential of the projectile which governs the acceleration of the ion towards the surface [5].

Although the above described scenario applies to both metal and insulator targets, there are fundamental differences between the interaction of ions with metals and insulators. While the valence electrons in an ionic crystal such as LiF are localized near the anionic sites of the crystal, the quasi-free electrons in a metal are de-localized so that they cannot be ascribed to certain atoms. A metal surface can thus be approximated by the jellium model assuming a uniformly distributed electron gas embedded in a constant positive background. The problem of ion-surface collision has then cylindrical symmetry allowing for simple estimates of captureand loss rates [5].

In an insulator such as LiF, this symmetry is broken by the lattice structure. Capture and loss rates therefore not only depend on the distance  $R_z$  of the projectile to the surface but also on the position of the ion in the x - y-plane. In addition, surface electrons in LiF are not "readily" available as in a metal so that if an electron has been captured from a certain F<sup>-</sup>, the probability for capturing a further electron from the same site is considerably reduced. An appropriate method to determine capture and loss rates for resonant electron transfer during the approach of ions to an LiF surface is to perform Classical Trajectory Monte Carlo (CTMC) simulations for the electron to be captured or lost [12, 57], see section 3.1. From the results of the CTMC capture and loss rates can be extracted. This determination of the transfer rates is rather time consuming where the computing time rapidly increases with the projectile charge as thousands of electron trajectories must be calculated for any projectile charge state, any distance to the surface, any position in x - y-direction, and any number of holes already present in the surface. Therefore, in previous studies [12, 57] the projectile charge was limited to  $Q \leq 10$ . In this work we extent this range to  $Q \leq 18$  to study the impact of  $\operatorname{Ar}^{Q+}$  projectiles on LiF. We study the systematic dependence of the rates on Q and  $R_z$  and determine fit functions for these rates so that an extension of ion-surface calculations to higher charge states is possible avoiding the tedious computation of transfer rates by CTMC in advance (section 3.1).

The neutralization sequence of the ion in front of the surface is again calculated employing the CTMC method. Along the trajectory different electron transfer processes occur according to their transition rates. The population numbers  $P_n$  of all *n*-shells are frequently updated. In the case of an insulator target, also the hole population in the surface must be updated. Through averaging over thousands of calculated ion trajectories the physical quantities of interest can be obtained such as the number of emitted electrons per projectile, the probability for reflection without hitting the surface (trampoline effect), the spin polarization of emitted electrons, etc. In the following sections we will apply the COB model to the interaction of ions with LiF and Fe thereby addressing very different physical questions but both depending crucially on the electron dynamics during the interaction.

# 3.1 Scattering of HCI at an LiF Surface

In metals, the short relaxation times (in the order of the inverse plasmon frequency  $\tau \approx \omega_p^{-1}$ ) justify the approximation of a quasi-instantaneous refill of holes as well as removal of excess charges entering the conduction band through loss processes. This fundamental assumption of the rate-equation approach is clearly not valid for insulators where the population dynamics of the projectile and the target F<sup>-</sup> ions are highly correlated. Therefore, for an insulator target such as LiF, instead of Eq. 3.1, the Liouville master equation is used [12] where the problem of ion-LiF interaction is formulated in terms of a joint phase-space probability density ensuring the proper inclusion of many-point correlations. In the following, we will briefly review the methods of this approach (for details see [12]).

# 3.1.1 Liouville master equation for multielectron dynamics

The joint phase-space probability density  $\rho(t, \vec{R}, \vec{R}, \{P^{(p)}\}, \{P^{(F)}\})$  depends on the time t, the phase-space coordinates  $(\vec{R}, \vec{R})$  of the projectile ion, and on the electron/hole population distributions  $\{P^{(p)}\}$  and  $\{P^{(F)}\}$  of the projectile and  $F^-$  ions, respectively. These are strings of integer numbers representing the occupation of different n shells in the projectile and of localized holes on different target fluorine sites in the target,

$$\{P^{(p)}\} = \{P_1^{(p)}, \dots, P_{n_{max}}^{(p)}, P_I\},\tag{3.3}$$

and

$$\{P^{(F)}\} = \{P^{(F)}_{(0,0,0)}, P^{(F)}_{(1,1,0)}, \dots, P^{(F)}_{\vec{a}}\}.$$
(3.4)

In Eq. 3.3  $n_{max}$  is the highest n shell considered determined by the critical shell  $n_c$  into which the first electron is captured. Ionized electrons are also kept track of during the calculation in terms of the occupation number  $P_I$  of continuum states. In Eq. 3.4 the subscript  $\vec{a}$  denotes the fluorine sites with the components (i, j, k)in the x-, y-, and z-direction along the edges of the cubic unit cell with lattice constant d. The surface plane is given by z = 0. For clarity, we will use the notation  $\vec{a} = (i, j) =: (i, j, k = 0)$  for surface fluorine sites. The choice of lattice sites  $\vec{a} = (i, j)$  (see Fig. 3.2) considered in the calculation for capture and loss processes depends on the projectile charge Q. The higher the charge state the stronger is the attractive force acting on the surface electrons. Thus, with increasing Q electron capture from more distant fluorine sites becomes increasingly important. For example, a  $Ne^{10+}$  projectile captures electrons from the (0,0) and (1,1) zones (see Fig. 3.2) while in the case of an  $Ar^{18+}$  projectile, a few electrons (about 5%) are also captured from the (2,0) site. The  $P_{\vec{a}}^{(F)}$  refer to the occupation of 2p states of the  $F^-$  in the surface. The contribution of deeper bound states to over-barrier processes is negligible. Of course, the occupation number for a given projectile n



Figure 3.2: Crystal zones used in the calculations relative to the impact point in (0,0).

shell is restricted to at most  $2n^2$  electrons. At most 6 (2p) holes are possible per fluorine.

As in the original work on the COB model [5], projectile levels are distinguished solely by their principle quantum number n avoiding a separation into subshells with different angular momentum l. This approximation is justified by the averaging character of the Monte Carlo approach as well as by the stability of the transition rates against changes in the subshell configurations.

The Liouville master equation for the motion of  $\rho$  is given by

$$\left[\frac{\partial}{\partial t} + \dot{\vec{R}} \cdot \vec{\nabla}_{\vec{R}} - \frac{1}{M} (\vec{\nabla}_{\vec{R}} V_p) \cdot \vec{\nabla}_{\dot{\vec{R}}}\right] \rho = \Re \rho.$$
(3.5)

Here,  $V_p$  is the effective projectile potential determining the projectile motion which will be discussed in the next section.  $\Re$  is a "relaxation" (collision) operator describing changes of  $\rho$  due to the different capture and loss processes and hole hopping.

The physical assumptions and approximations entering the Liouville master equation will be reviewed in the following section.

# 3.1.2 Effective potentials

The electron transfer dynamics and the motion of the projectile are governed by an effective potential which includes the collective screening of external charges by the surface electrons as well as polarization of the active fluorine.

The effective potential  $V_p$  determining the projectile motion according to Eq. 3.5 includes contributions from the interaction of the ion with the surface in its ground state,  $V_p^g$ , with the positive holes in the surface,  $V_p^h$ , as well as with its self image,  $V_p^{SI}$ , which is a consequence of the polarization of the surface induced by the

approaching ion:

$$V_p = V_p^g + V p^h + V_p^{SI}.$$
 (3.6)

All contributions to  $V_p$  depend on the position of the ion and on the occupation numbers of the projectile,  $\{P^{(p)}\}$ . In addition,  $V_p^h$  is determined by the hole population  $\{P^{(F)}\}$  of the fluorine ions. Due to the overall charge neutrality of the surface in the ground state,  $V_p^g$  is only short ranged while the long range potential is dominated by the Coulomb interaction with the holes and polarization effects. In the case of an insulator target, Coulomb interaction is reduced due to the collective screening of the target electrons which enters the expressions for the corresponding potential through a screening factor

$$\chi = \frac{\epsilon - 1}{\epsilon + 1} \tag{3.7}$$

where  $\epsilon = \epsilon(\omega)$  is the frequency dependent dielectric function of the material. In accordance with the fixed-ion approximation (FIA) we here use the static limit  $\epsilon(\omega = 0) \approx 9.1$  for LiF. For metals,  $\chi = 1$ .

During the CTMC performed to determine transition rates for resonant electron transfer between the surface and the projectile, the trajectory of one "active" electron is followed. Its motion is determined by the effective one-electron potential  $V_e$  including the interaction with the target,  $V_{te}$ , with the projectile,  $V_{pe}$ , and with the image of the projectile,  $V_{pe}^{I}$ :

$$V_e = V_{te} + V_{pe} + V_{pe}^I.$$
 (3.8)

This potential depends on the electron position  $\vec{r}$ , the ion position  $\vec{R}$  and on the internal states of the projectile and the surface, i.e. on  $\{P^{(p)}\}$  and  $\{P^{(F)}\}$ . The target potential  $V_{te}$  includes the interaction of the active electron with the active fluorine, its interaction with the crystal environment as well as the screened Coulomb potential of the holes and the other (passive)  $F^-$  sites. The crystal potential includes the Coulomb interaction with the lattice ions as well as correlation effects due to the redistribution of the target electrons upon removal of a surface electron and due to screening of the positive holes.

For the CTMC one further potential not entering the Liouville master equation must be introduced to avoid artificial attraction of the active electron to surrounding  $Li^+$  sites. The negative singularities at the lithium sites in the classical picture lead to an un-physically high probability for the electron to end up there. In a quantum mechanical calculation the orthogonality of the valence electron states to the core states reduces this probability. To overcome this deficiency of a classical one-electron description, a "blocking" potential around the Li ions is introduced to reduce the available phase-space of the electron (for details see [12]).

# 3.1.3 Electron transfer processes

#### Resonant one-electron capture and loss

Two important contributions to the relaxation operator  $\Re$  entering Eq. 3.5 are the electron transfer rates for resonant capture and loss over the barrier. Loss rates are typically lower than capture rates by about an order of magnitude due to a larger available phase space within the projectile than at a target fluorine site. As a full quantum calculation of resonant transfer rates for an LiF target and projectile charges  $Q \gg 1$  is still computationally not feasible, the rates are determined using CTMC calculations for an ensemble of electron trajectories represented by the phase-space distribution  $\rho_e$ . A classical approach is also justified by the high quantum numbers n of final states in the projectile where electrons are primarily captured into.

The electron dynamics are determined by the Hamilton-Liouville equation

$$\frac{\partial \rho_e}{\partial t} = \{H, \rho_e\},\tag{3.9}$$

where H is the Hamiltonian including the one-electron potential  $V_e$  described in the previous section. Using FIA, we calculate the time evolution of the electron motion solving Eq. 3.9 for fixed positions  $\vec{R}$  of the projectile as well as for fixed configurations of the projectile,  $\{P^{(p)}\}$ , and fixed numbers of holes,  $\{P^{(F)}\}$ , in the surface. Therefore, these quantities enter Eq. 3.9 as parameters.

The initial distribution  $\rho_{e,i}$  for the time propagation of Eq. 3.9 is given for the first captured electron by the density of states (DOS) of LiF [53]. After the first capture the band structure of LiF is disturbed due to the positive hole. As no detailed data of the perturbed DOS are available the initial distribution of states for further capture and loss (i.e. projectile states) have been approximated in Ref. [12] by a narrow rectangular distribution function with a relative width  $\delta E_i/E_i = 0.1$  a.u. We adopt this choice for our work. For small distances  $R_z$  where the valence band of LiF lies above the barrier, the ensemble of initial conditions is molecular in character.

The Hamilton-Liouville equation (Eq. 3.9) is solved numerically by propagating a finite sample of phase-space points in small time steps  $\Delta t$ . After each time step the total force acting on the active electron is calculated. If the projection of the force onto the connecting line between electron and projectile exceeds the projected force onto the electron-fluorine line, the electron is stronger attracted to the projectile than to "its" active fluorine and the electron is counted as captured. The reverse applies to electrons lost back to the surface. The time dependent transfer probability is then given by

$$P^{(\alpha)}(t) = \frac{N_{\alpha}(t)}{N_{traj}}$$
(3.10)

where the label  $\alpha$  stands either for capture ( $\alpha = c$ ) or loss ( $\alpha = l$ ).  $N_{traj}$  is the total number of propagated trajectories and  $N_{\alpha}(t)$  is the number of trajectories of electrons captured (lost) during the time interval [0, t]. The resulting time evolution of the transition probabilities can be well fitted by the functional form

$$P^{(\alpha)}(t) = P^{\alpha}_{max}(1 - e^{-\gamma^{\alpha}t}).$$
(3.11)

The parameter  $P_{max}$  constitutes an upper limit of the transfer probability. It is typically lower than unity implying that even if the electron is energetically above the barrier, it will not necessarily be captured eventually. As the energy hypersurface of the classical electron contains regular islands disconnected from the saddle of the potential barrier, electrons can be transferred to and trapped in this part of the phase space.

The transition rates  $\Gamma^{\alpha}$  entering the relaxation operator  $\mathfrak{R}$  in Eq. 3.5 are determined from the slope of  $P^{(\alpha)}(t)$  at  $t \to 0$ ,

$$\lim_{t \to 0} \frac{d}{dt} P^{(\alpha)}(t) = P^{\alpha}(t) \Gamma^{\alpha}$$
(3.12)

where  $\Gamma^{\alpha} = \gamma^{\alpha} P_{max}^{\alpha}$ . The justification for the use of the initial slope is based on the fact that if capture/loss occurs it happens very fast, i.e. within the time period where the curve representing Eq. 3.11 has a linear slope. The rates  $\Gamma^{\alpha}$  are functions of the ion position with respect to the active fluorine. By averaging over the x and y coordinates of every included unit cell, this can by reduced to a dependence on the parameters  $R_z$  and on the different zones labeled by  $\vec{a}$  (see Fig. 3.2). In addition, the rates depend on the number of holes and on the projectile configuration. The latter can be represented by one parameter, the effective projectile charge  $Q_{eff}$ . It is given by

$$Q_{eff}(R_z, \{P^{(p)}\}) = Z - \sum_{n:r_n < R_z} P_n^{(p)}$$
(3.13)

where Z is the nuclear charge of the projectile and the shell radius  $r_n$  is approximately given by  $r_n = n^2/q_n$ . Here,  $q_n$  is the effective charge felt by an electron sitting in shell n which we determine according to Slater's rules [58]. The capture and loss rates are tabulated in dependence on the following parameters:  $R_z$ ,  $Q_{eff}$ ,  $\vec{a}$ , and  $\{P^{(F)}\}$ . To include many-electron effects in the effective rates for resonant capture and loss entering the relaxation operator  $\Re$  in Eq. 3.5, the energy shift of the target and projectile states due to many-hole interactions is taken into account in the resonance condition. The latter is given by the conservation of the total energy of the active electron during the transfer process, i.e. initial and final states of the captured/lost electron have the same energy. In addition, capture and loss probabilities are not only determined by the one-electron rates  $\Gamma^{\alpha}$  but also depend on the multiplicity of the initial-state population and the number of available final states. This many-body feature is also incorporated in the determination of effective transfer rates by the inclusion of multiplicity and blocking factors as in the collision term in a quantum Boltzmann equation:

$$\Gamma^{c}(\vec{R}, \Delta P_{n} = 1, \Delta P_{\vec{a}}^{(F)} = -1) = (6 - P_{\vec{a}}^{(F)})(1 - \frac{P_{n}}{2n^{2}})\Gamma_{1}^{c}(Q_{eff}, R_{z}, P_{\vec{a}}^{(F)})$$
(3.14)

and

$$\Gamma^{l}(\vec{R}, \Delta P_{n} = -1, \Delta P_{\vec{a}}^{(F)} = +1) = P_{n} \frac{P_{\vec{a}}^{(F)}}{6} \Gamma^{l}_{1}(Q_{eff}, R_{z}, P_{\vec{a}}^{(F)}).$$
(3.15)

Here, n and  $\vec{a}$  label the active projectile shell and fluorine, respectively.

### Electron promotion to continuum states

During the approach of the projectile ion to the surface the electronic energy levels are shifted due to the interaction with the LiF surface. As a consequence, high nlevels will be eventually promoted to the continuum and electrons populating these levels will be ionized (thereby increasing the occupation number  $\{P_I\}$  (Eq. 3.3)). These electrons are emitted with very low energies,  $E \rightarrow 0$ , so that most of them do not penetrate into the solid. The threshold of continuum states is therefore identified with the vacuum level instead of the bottom of the conduction band of LiF lying about 2 eV above the vacuum threshold. Electron promotion from high-n states to the continuum can also happen due to filling of inner shells of the hollow atom. These deeper bound shells reduce the effective charge felt by the outer electron which is consequently more weakly bound or even ionized.

### Auger processes

In addition to the one-electron transfer processes already mentioned, relaxation of the projectile occurs via Auger processes where two electrons interact with each other leading for both to transitions to other states. For large ion-surface distances  $R_z$ , the dominating Auger channel is autoionization (AI), i.e. intra-atomic Auger decay. Here, one of two projectile electrons preferentially occupying the same *n* shell populates a lower lying level *n'* while the other one is ionized. For the transition of two *s* electrons from shell *n* with  $P_n^{(p)} = 2$  to an *s* state of an empty shell *n'* the autoionization rate  $\Gamma_{AI}$  can be expressed as [5]

$$\Gamma_{AI}(ns^2 \to n's) = \frac{5.06 \cdot 10^{-3} \text{a.u.}}{\Delta n^{3.46}},$$
(3.16)

with  $\Delta n = n - n'$ . If more electrons are present in the initial and final shell, multiplicity factors for the *n* shell population and blocking factors according to final shell occupation must be introduced. The multiplicity factors  $M^{AI}$  assure that the Auger rates increase with increasing number of electrons in the initial shell n while the blocking factors  $B^{AI}$  account for a reduction of the rate if final states on the n' shell are already populated. In particular,  $B^{AI} = 0$  for the initial condition  $n' = 2n'^2$  so that the transition to a fully occupied level is prohibited according to Pauli blocking. The AI rate for any occupation number of n and n' then reads

$$\Gamma^{AI}(\vec{R}, \Delta P_n = -2, \Delta P_{n'} = +1, \Delta P_I = +1) = M^{AI}(P_n)B^{AI}(P_{n'})\Gamma_1^{AI}(s^2 \to n's)$$
(3.17)

For the multiplicity and blocking factors we adopt the choice of Ref. [12],

$$M^{AI}(P_n) = \frac{P_n(P_n - 1)}{2}$$
(3.18)

which is simply the standard binomial expression, and

$$B^{AI}(P_{n'}) = C_{n'}(1 - \frac{P_{n'}}{2n'^2})^2$$
(3.19)

with  $C_{n'} = 0.38$  for n' = 1 and  $C_{n'} = 1$  else. This factor originates from the fact that Eq. 3.16 is used not only for s transitions but also for initial and final states with  $l \neq 0$  which is an appropriate approximation for higher-n levels including several l > 0 states. However, the first shell consists of only two s states so that the KLL Auger transition rate is reduced. The choice of Eq. 3.19 was motivated by the comparison of AI rates with quantum calculations [12].

For small distances interatomic Auger processes involving target electrons such as Auger deexcitation (AD) and Auger capture (AC) become more important. Below a certain "sharing" distance  $D_s$  projectile and target electrons are even shared like in a molecule so that AD and AC rates will become comparable to AI rates. The sharing distance is reached when the active projectile and target levels meet the resonance condition. For small distances  $D = \left| d\vec{a} - \vec{R} \right|$  we therefore obtain [12, 59]

$$\Gamma^{AC}(D \le D_s, \Delta P_{\vec{a}}^{(F)} = -2, \Delta P_{n'} = +1, \Delta P_I = +1) = M^{AC}(P_{\vec{a}}^{(F)})B^{AI}(P_{n'})\Gamma_1^{AI}(s^2 \to n's), \quad (3.20)$$

$$\Gamma^{AD}(D \le D_s, \Delta P_{\vec{a}}^{(F)} = -1, \Delta P_n = -1, \Delta P_{n'} = +1, \Delta P_I = +1) = M^{AD}(P_{\vec{a}}^{(F)})B^{AI}(P_{n'})\Gamma_1^{AI}(s^2 \to n's), \quad (3.21)$$

where  $M^{AC}$  and  $M^{AD}$  are given by the number of electron pairs available in the initial configuration,

$$M^{AC} = \frac{(6 - P_{\vec{a}}^{(F)})(5 - P_{\vec{a}}^{(F)})}{2}, \qquad (3.22)$$

$$M^{AD} = P_n(6 - P_{\vec{a}}^{(F)}). \tag{3.23}$$

For distances larger than the sharing distance AD rates approximately decrease as  $D^{-3}$  while AC rates show an exponential decay corresponding to the exponential tail of electron density leaking out of the surface. We therefore get [12, 59]

$$\Gamma^{AC}(D > D_s) = \rho(D - D_s) \frac{D_s}{D} \Gamma^{AC}(D = D_s), \qquad (3.24)$$

$$\Gamma^{AD}(D > D_s) = \frac{1}{2} [(\frac{D_s}{D})^3 + \rho(D)] \Gamma^{AD}(D = D_s), \qquad (3.25)$$

where  $\rho(D) = \exp[-2\sqrt{-2E_{i0}^F}(D-D_s)]$  with the orbital energy  $E_{i0}^F$  of an F<sup>-</sup> in the crystal. We note that these transition rates correspond to an order of magnitude estimate [12, 59]. To be more precise, they represent an upper bound for AD and AC rates. This in turn justifies their application in our study of the trampoline effect: Both AN and AD increase the difference between the number of holes in the surface and electrons in the projectile by 1. Accordingly, the Coulomb repulsion felt by the projectile due to the positive holes increases and decelerates the ion supporting a possible trampoline effect. We therefore investigate the trampoline effect under most favorable conditions (we also use the smallest projectile velocity possible) implying that if we do not find trampoline reflected trajectories in our simulations, the detection of a trampoline effect under "real" (experimental) conditions can be ruled out.

We note here that, in principle, radiative decay constitutes an additional decay channel of the highly excited hollow atom. For projectiles up to about Z = 18 (Ar) this channel is negligible compared to AI. For Z > 32 Auger and radiative decay rates become comparable so that the latter should be included in a full description of the relaxation process of the ion. However, the neglect of this channel again increases the chances for trampoline reflection as it conserves the charge state of the ion while AI reduces Q by one increasing the repulsion by the holes. Therefore, radiative decay is neglected for all Z thereby favoring trampoline reflection even more.

### 3.1.4 Hole mobility

An important effect of the many-body nature of ion-insulator collisions is given by the dynamics of the positive holes in the surface. In previous studies, hole hopping was modeled as an unbiased, force-free random walk where the hopping time and rate are determined from the band structure of LiF in the following way: The valence band of LiF is approximated by the tight-binding relation

$$E(k) = E_0 - \beta \cos(kd\sqrt{2}) \tag{3.26}$$

where k is the wave number,  $\beta$  is the band half-width ( $\beta = 1.75$  eV for LiF), and d = 3.8 a.u. is the lattice constant. A hole velocity can then be obtained using  $v_h = -\frac{dE(k)}{dk}$ . The hole hopping rate to any one of the 12 next-neighbor F sites is estimated as

$$\Gamma_{hop} = \frac{1}{12t_{hop}} \tag{3.27}$$

with the average hopping time  $t_{hop} = d\sqrt{2}/v_h$ . For surface holes, the factor 1/12 is changed to 1/8 according to 8 next-neighbor F sites . The absolute value for  $v_h$  lies in the range between  $v_h^{cold} \approx 0.1$  a.u. for a "cold" hole near the top of the valence band and  $v_h^{hot} \approx 0.3$  a.u. for a "hot" hole in the band center. The mean velocity is  $\langle v_h \rangle = 0.22$  a.u.

The model of a force-free hole mobility is certainly a crude approximation for the dynamics of a hole in the surface given the fact that Coulomb forces originating from the projectile and the other holes act on the "active" hole. In the present work we therefore include the interaction with the other holes and the projectile in the description of the hole dynamics. The total force acting on hole  $h_i$  is given by

$$\vec{F_h} = (\chi - 1) \frac{Q_{eff} Q_{h_j}}{(\vec{r_{h_j}} - \vec{R})^2} \hat{n}_{h_j R} - \sum_{i \neq j} \frac{1}{\epsilon} \frac{Q_{h_i} Q_{h_j}}{(\vec{r_{h_i}} - \vec{r_{h_j}})^2} \hat{n}_{h_i h_j}.$$
(3.28)

Here, the first term describes the screened interaction with the projectile where  $Q_{h_i}$  is the charge of the hole ( $Q_{h_i} = 1$  for a single hole,  $Q_{h_i} = 2$  for a double hole on the same F<sup>-</sup> site, etc.),  $\vec{r}_{h_j}$  denotes the position of the hole, and  $\hat{n}_{h_iR}$  is the unit vector along the connection line between hole  $h_j$  and the projectile. The second term in Eq. 3.28 gives the repulsive force due to the other holes where  $\hat{n}_{h_ih_j}$  is the unit vector along the connection line between hole  $h_i$  and hole  $h_j$ .

To determine the change of hole velocity due to  $\vec{F_h}$ , we first extend Eq. 3.26 representing a one-dimensional chain of fluorine ions to three dimensions. As the valence band is formed by the F 2*p*-like orbitals (with only negligible contributions from lithium electrons) we use a tight-binding dispersion relation on the fluorine sublattice:

$$E(k) = E_0 - \frac{\beta}{3} \left[ \cos\left(k_1 d\sqrt{2}\right) + \cos\left(k_2 d\sqrt{2}\right) + \cos\left(k_3 d\sqrt{2}\right) \right].$$
(3.29)

For the fluorine sublattice we choose a coordinate system aligned along those lines in the crystal connecting next-neighbor fluorine ions at a distance of  $d\sqrt{2}$ .  $k_1$ ,  $k_2$ , and  $k_3$  are therefore not identical to the components of the wave vector  $\vec{k}$  along the edges of the cubic unit cell but are the  $\vec{k}$  components along the [011], [101], and [110] directions of the crystal, respectively (see Fig. 3.3). We will refer to this coordinate system as "sublattice coordinate system" in the following and will denote vectors in this coordinate system by the subscript "sub". The coordinate system



Figure 3.3: Coordinate system (x, y, z) with pairwise orthogonal axes along the cube edges of the unit cell and coordinate system of the fluorine sublattice  $(k_1, k_2, k_3)$  used in the tight binding relation (see text).

with the axes along the cube edges of the unit cell will be referred to as "unit cell coordinate system" in the following.

The hole velocity in the valence band (without inclusion of the external force) is given by

$$\vec{v}_{h,sub} = -\vec{\nabla}_{k,sub} E(k_{sub}) = \frac{\beta}{3} d\sqrt{2} \begin{pmatrix} \sin(k_1 d\sqrt{2}) \\ \sin(k_2 d\sqrt{2}) \\ \sin(k_3 d\sqrt{2}) \end{pmatrix}.$$
 (3.30)

After transformation of the three force components from unit cell coordinates to sublattice coordinates,  $(F_{h,x}, F_{h,y}, F_{h,z}) \rightarrow (F_{h,1}, F_{h,2}, F_{h,3})$ , we obtain the new components of the wave vector which change during the time interval dt as:

$$k_i \to k_i + \Delta k_i = k_i + F_{h,i}dt \tag{3.31}$$

where i = 1, 2, 3. With this wave vector, the hole velocity is calculated according to Eq. 3.30 and subsequently transformed back to unit cell coordinates.

Taking into account the force acting on the holes leads to a site-dependent rate instead of a hopping rate uniformly distributed among the 12 fluorine neighbors of the hole. Eq. 3.27 is therefore modified by weighting the hopping rate from the initial site to a neighboring site (x, y, z) by the projection  $\bar{v}_{(x,y,z)}$  of the hole velocity  $\vec{v}_h$  onto the connection line between the hole and (x, y, z). The site dependent hopping rate is then given by

$$\Gamma_{hop}(x, y, z) = \frac{1}{t_{hop}} \frac{\bar{v}_{(x,y,z)}}{\bar{v}_{tot}}$$
(3.32)

where  $\bar{v}_{tot} = \sum \bar{v}_{(x,y,z)}$  is the sum of all (positive) projections running over the neighboring fluorine sites.

One might now intuitively assume that the holes diffuse faster if the external force is taken into account compared to the unbiased random walk model. However, in addition to external forces, further restrictions to the hole mobility arise from the crystal environment. Rather than a permanent increase of velocity due to the acceleration like for a free particle, the hole velocity shows oscillatory behavior originating from the cosine shape of the band structure and the sine-dependent hole velocity (Eq. 3.30). The hole velocity may thus become negative so that the hole may move towards the repulsive force. This, on the first glance strange, phenomenon is well known for electrons in solids. These "Bloch oscillations" have been already predicted by Bloch in 1929 [60], who showed that an electron moving in a periodic potential and exposed to an external field, is oscillating in space. A direct experimental measurement was performed (only about ten years ago) by Lyssenko *et al.* on semiconductor super-lattices [61]. In analogy to the electronic Bloch oscillations, the diffusion of the holes is considerably slower than expected for "free" holes (not embedded in a crystal) pushed by an external force.

## 3.1.5 The neutralization sequence

With the electron transition- and hole hopping rates described above included in the Liouville master equation (Eq. 3.5), the neutralization of a highly charged ion (HCI) is simulated employing the Monte Carlo method. As we want to study the occurrence of a trampoline effect we let the projectiles incident vertically on the surface. The lower the projectile velocity, the higher are the chances for trampoline reflection. We therefore set the asymptotic velocity of the ion to zero,  $v_p(R_z \rightarrow \infty) = 0$ . Of course, this limit cannot be achieved in any experiment. Consequently, if the trampoline effect is not observed in our studies of trampoline reflection under most favorable conditions, the observation of this effect in experiment can be ruled out.

The calculation of the trajectory of the HCI starts beyond the critical distance  $d_c$  for the onset of over-barrier transfer, e.g. at  $R_z = 25$  a.u. for an Ar<sup>18+</sup> projectile. Due to the image acceleration the ion has experienced on its way to this point it starts from there with about  $v_p \approx 0.009$  a.u. The ion is propagated in small time steps  $\Delta t$ . In every step the conditions for the different electron transfer processes are checked. If a transition is energetically allowed, the corresponding transfer rate is determined and the process happens with a certain probability according to this rate.

It is important to clearly distinguish between a reflection of the projectile due to a close binary collision with the surface and a trampoline reflection due to the repulsion of the positive charge-up of the surface where the ion is supposed to turn around without close contact with the surface (see Fig. 3.4). A trampoline-reflected trajectory (i) keeps its high charge to a large extent ( $Q_{final} \approx Q_{initial}/2$ ) and (ii) has its turning point at least a few a.u. above the surface. We choose  $R_z \geq 2$  a.u.



Figure 3.4: Projectile velocity as a function of the distance to the surface for different trajectories, schematically. Trampoline reflection occurs if v becomes positive at  $R_z > 2.5$  a.u.

as operational criterion as the typical spatial extension of the electron density of an  $F^-$  ion is about 2.5 a.u. Consequently, an ion reaching such a close distance to the surface can already form a quasi-molecule with surface atoms. If ions reach this distance, no trampoline reflection has occurred.

# 3.1.6 Results for Ar<sup>18+</sup> projectiles

In Fig. 3.5 the evolution of the ion velocity is displayed as a function of the ionsurface distance. The negative sign of the velocity indicates movement towards the surface. Up to the point of first capture at about  $R_z = 20$  a.u. (Fig. 3.5) the ion is further accelerated due to the attractive potential of its image charge. With the onset of resonant capture the reduced image force due to the lower ion charge as well as the repulsion by the holes created in the surface lead to a decrease of acceleration. At about 6 a.u. above the surface the repulsion overcomes the image acceleration and the ion is slowed down. However, the repulsion is not strong enough to force the ion to reverse its course towards the surface, i.e., the velocity does not go to zero and change to positive values. A trampoline effect is clearly not happening, none of the propagated trajectories is reflected above 2 a.u. from the surface. If we suppress hole mobility (Fig. 3.5), all trajectories are reflected, however, with the turning point being at 2.1 a.u. Therefore, even without hole mobility trampoline reflection does not occur.

To understand the evolution of the trajectory better we take a closer look at the electronic dynamics during the ion approach. At about  $R_z = 20$  a.u. resonant



Figure 3.5: MC simulation results for 1000 trajectories of Ar<sup>18+</sup> ions approaching an LiF surface. Upper panel: ion velocity as a function of the ion-surface distance. Lower panel: evolution of the charge state of the ion and the production of holes and emitted electrons during the approach.

capture of target electrons into projectile levels sets in starting with n = 13 and subsequently followed by n < 13 (see Fig. 3.6). Before the *n*-shells reach a population of typically 3 - 4 electrons, they are again depleted due to Auger decay or promotion to the vacuum level. Resonant loss back to the surface only starts at about 11 a.u. above the surface when already enough holes have been produced in the target, so that the corresponding multiplicity factor in  $\Gamma^l$  assures an efficient loss rate. Although the charge state of the Ar<sup>18+</sup> projectile decreases monotonically to Q = 0 at about 7.5 a.u. above the surface, relaxation of the hollow atom has not yet been completed at 2 a.u. The shell population statistics show on the



Figure 3.6: Evolution of the shell population numbers during the approach of Ar<sup>18+</sup> ions to an LiF surface.

average 0.65 electrons in the K-shell, 2.1 electrons in the L-shell and 2.7 electrons in the M-shell as well as considerable contributions from higher shells up to n = 9 (Fig. 3.6). The ion is therefore, despite its slow velocity, far from its ground state when it hits the surface.

During the approach of the ion, on the average 65 holes are produced in the surface where up to half of them get filled again by RL. The majority of the holes are single holes, i.e. only one electron has been captured from the corresponding  $F^-$  site. Starting at  $R_z \sim 12$  a.u. some doubly charged holes are produced (two electrons captured from the same fluorine) and at smaller distances there are even a few holes with charges up to five holes at one  $F^-$ , however, with negligible frequency. A typical distribution of the trajectories of surface holes is shown in Fig. 3.7 for the first eight holes produced. The projection of their paths onto the x - y plane at the surface shows that they are typically spread within an area of  $x, y = \pm 10$ lattice sites. From the projection onto the x - z-plane we observe a maximum penetration depth of the holes into the bulk of about 35 a.u. For comparison, we also show typical hole paths for calculations where the force acting on the holes is neglected. No clear difference to the former case is observed as the force acting on a hole does not push it in a certain direction, but leads to an oscillating behavior of the hole velocity due to the band structure (see subsection 3.1.4). The effect of the force acting on the holes cancels when averaging over a large ensemble of ion trajectories, so that the mean velocity as a function of the ion-surface distance remains practically the same as for an unbiased random walk model of hole hopping.



Figure 3.7: Sample of hole trajectories during the approach of an Ar<sup>18+</sup> ion on LiF. Shown are the first eight holes produced (different colors). a) Hole hopping according to a driven random walk (present model), b) the force due to the projectile and other holes is neglected. Upper panels: projection onto the x - y-plane, lower panels: projection onto the x - z-plane.

The  $R_z - v$  curves for calculations with and without inclusion of the force in the hole hopping model practically lie on top of each other (they cannot be distinguished in Fig. 3.5) where differences of at most 0.1% between the two simulations were found.

The dominant deexcitation process during the approach of the ion is autoionization producing on the average about 24 emitted electrons until the simulation is stopped. Also AD plays an important role leading to the emission of about 16 electrons. Level promotion happens to take place at a slower rate than Auger decay producing about eight electrons. This is a consequence of the slow ion velocity.

#### a) driven random walk

#### b) unbiased random walk

For velocities typically used in the experiment, the electron levels are promoted much faster due to the faster approach to the surface, so that there is typically not enough time to deplete the *n*-shell via AI before the electrons are peeled off. The least important electron transfer process is AC producing only 3-4 electrons on the average.

# **3.1.7** Neutralization of ions with Q > 18

Since the resonant capture and loss rates depend on four parameters (see Sec. 3.1.3) their calculation for all higher charge states is very time consuming. To bypass this tedious procedure we have studied the available data for  $Q \leq 18$  searching for (positive definite) analytic functions allowing the extrapolation of the dependence of the quantities  $P_{max}$  and  $\gamma$  on  $R_z$  and  $Q_{eff}$  for given impact zones  $\vec{a}$  and number of holes  $n_e$  to higher charge states. Functional forms could be found depending on at most three free parameters for given  $\vec{a}$  and  $n_e$ . They are described in detail in Appendix A.

Using the fitted capture and loss rates in the simulation leads to typical deviations of the ion velocity from the original calculations below 1%, values up to about 12% are only found at distances lower than 2.5 a.u. (Fig. 3.8). However, if trampoline reflection occurs the ion hardly reaches such close distances, so that these deviations are irrelevant in the present context. Using the fitted rates leads to lower average velocities compared to the original calculation for  $R_z < 3$  a.u. thereby increasing the chances for trampoline reflection. The agreement with other properties such as charge state evolution, number of autoionized electrons, etc., are also in very good agreement with original results (taking the rates obtained from the CTMC calculations). A typical comparison is shown in Fig. 3.8 for an Ar<sup>18+</sup> projectile.



Figure 3.8: Comparison of simulation results for Ar<sup>18+</sup> projectiles when resonant transfer rates are determined by CTMC calculations (solid lines) or these data are fitted by analytic functions (dashed lines), see text.

For the investigation of the impact of ions on LiF with charge states Q > 18 we now use the functional forms determined by the fit to the tabulated data for  $Q \leq 18$ . Of course, the validity of this extension is still limited due to several reasons. Up to this point, the surface zones  $\vec{a}$  involved were limited to the central and the three next nearest unit cells (Fig. 3.2) which was by far enough for calculations with  $Q \leq 18$ . There, all electrons are captured from within the nearest three zones where only about 5% of the holes are produced in the outer (2,0) zone. However, at some point the projectile charge will be high enough to efficiently capture electrons from more distant fluorine ions. We have therefore systematically studied the production of holes for projectiles with increasing charge state (and atomic number Z). Capture from zone (2,2) starts with a Ti<sup>22+</sup> projectile increasing its occurrence with increasing Z. We conclude that our simulations are reliable up to at least  $Kr^{36+}$  projectiles where about 17% of the holes are captured from the outermost zone (2,2). Comparison with lower charge states shows that capture from an outer zone only starts when more than about 20% of the holes have been produced in the next inner zone. We therefore expect only negligible contributions to hole production from zones not included in our calculations.

Another limitation is the restriction to capture of valence electrons. This may, however, constitute only a minor problem as even for very high initial charge states it is unlikely that all six valence electrons of one fluorine are captured before the holes have a chance to diffuse away. In addition, the rate for capture in the presence of a multiple hole is considerably reduced compared to capture from an adjacent zone with fewer holes. For example, if there are three holes at the active fluorine, the capture rate for a further electron from this site is reduced by a factor of about  $10^{-4}$  compared to the capture rate from the  $F^-$ . A complete depletion of valence electrons in a certain area seems therefore only possible if hole mobility is completely suppressed. We found that up to charge states of at least Q = 36 our simulations are not affected by the restrictions to valence electrons as even  $\mathrm{Kr}^{36+}$ ions produce at most five holes per fluorine site.

Results of the MC simulation for  $\mathrm{Kr}^{36+}$  ions approaching an LiF surface under normal incidence are depicted in Fig. 3.9. Starting asymptotically with zero velocity the ion is first accelerated by its image charge. Resonant capture into the n = 25shell sets in at  $R_z = 35$  a.u. while effective loss starts much later at about  $R_z = 9$ a.u. Due to partial neutralization of the projectile the acceleration decreases during the approach until near  $R_z = 5$  a.u. the ion is slowed down by the repulsion of the positive holes in the surface. Again, 100% of the calculated trajectories reach the  $R_z = 2$  a.u. limit ruling out a trampoline effect. For comparison, we also show the evolution of the velocity when the hole mobility is suppressed in the simulation. Although in this case all trajectories are reflected, the turning point is even here too close at the surface ( $R_{z,min} = 2.25$  a.u.) to speak of a clear trampoline effect. When the initial (asymptotic) velocity is increased to v = 0.01 a.u. again 100% of the projectiles arrive at  $R_z = 2$  a.u.



Figure 3.9: Monte Carlo simulation results for 1000 trajectories of Kr<sup>36+</sup> ions approaching an LiF surface. Upper panel: projectile velocity as a function of the distance to the surface (blue curve). For comparison, the calculation results when hole mobility is suppressed are also shown. Lower panel: evolution of the charge state of the ion and the production of holes and emitted electrons during the approach.

During the approach of  $Kr^{36+}$  ions 138 holes are produced on the average about 30% of which are filled again by resonant loss. The majority represent single holes while the production of double holes at a given site sets in at a distance of only 16 a.u. from the surface. There are also a few triple holes produced (on average about 7 per ion) and even fewer holes with charge state  $Q_h = 4$  and  $Q_h = 5$ . Although  $Kr^{36+}$  is neutralized below  $R_z = 15$  a.u. they are far from equilibrium when they reach the distance  $R_z = 2$  a.u. The average occupation number of the K-shell is 0.4 while there are about 1 electron in the L-shell, 1.7 in the M-shell, and about 2.3

electrons in n = 4. All other electrons are distributed over higher *n*-states up to n = 14 where all shells with n > 5 have reached their maximum population already, so that their occupation numbers  $P_n$  are decreasing again. During the approach to the surface, all *n* shells are populated with at most 4 to 7 electrons before depletion due to Auger processes or promotion sets in.

Of course, the situation would change if radiative decay was taken into account becoming for Z = 36 as important as AI. The transition rate for radiative decay  $\Gamma_{n,n'}^{rad}$  is proportional to  $\omega_{n,n'}^3$  where  $\omega_{n,n'} = E_n - E_{n'}$  (in atomic units) is the energy difference between the states n and n'. Therefore, as opposed to autoionization, in radiative transitions the probabilities for direct decay from high-n to very low-nshells are typically higher compared to decay rates to next lower levels. Consequently, the inclusion of this additional deexcitation channel would speed up the relaxation process of the hollow atom considerably so that the projectile may be closer to its ground state when hitting the surface. The inclusion of radiative decay would therefore further suppress a trampoline effect.



Figure 3.10: Dependence of the above-surface electron emission yield (for  $R_z > 2$  a.u.) on the charge state Q for bare nuclei with Q = Z (blue symbols) and  $Kr^{Q+}$  ions (red symbols).

When radiative decay is neglected the dominant electron emission channels are autoionization and Auger deexcitation where for  $Kr^{36+}$ , as opposed to the  $Ar^{18+}$  projectile, the importance of AD is comparable to that of AI (Fig. 3.9). Level promotion and AC produce, by comparison, only a few electrons per ion.

We have systematically studied bare nuclei between  $Ne^{10+}$  and  $Kr^{36+}$  finding no indication for a trampoline effect. If we take a look at the number of (above surface) emitted electrons, a nearly linear dependence of the electron yield on the charge

state can be found (Fig. 3.10) where Q = Z for the bare nuclei. Again, inclusion of radiative decay would alter the picture, i.e. fewer electrons would be emitted above the surface as the charge state is conserved in radiative decay. However, the emitted energetic photons in turn would lead to emission of photo- and secondary electrons from the surface making up for at least part of the smaller electron emission yield.

Also the yield for fixed Z but different charge states  $(Kr^{Q+})$  shows an approximately linear dependence where the number of emitted electrons increases with Z (or equivalently with the projectile mass) for fixed Q. This originates from the dependence of the image acceleration on the projectile mass. If two ions of different mass but with the same charge state start at an asymptotic distance  $R_z \to \infty$  with the same initial velocity, the light particle is more efficiently accelerated than the heavy projectile. Consequently, the latter approaches the surface with lower speed thereby having more time to emit electrons via AI. Comparison of the emission processes for  $Ar^{18+}$  and  $Kr^{18+}$ , indeed, shows that the difference in the total electron emission yield originates predominantly from the higher AI yield for the Kr projectile.

In summary, we found that a trampoline effect can be ruled out for charge states up to Q = 36 although increasing the charge leads to the production of more holes in the surface and, consequently, to a stronger repulsion of the projectile. However, as the charge states of an ion are restricted to  $Q \leq Z$  going to higher charge states implies going to higher atomic numbers, or equivalently, increasing the ion mass. The heavier the projectile, the stronger the repulsive force necessary to repel the ion prior to impact is. As our calculations show, the repulsion by the surface holes is not strong enough to stop the ions, the nuclei are simply too heavy to allow for a trampoline reflection. While the number of produced holes in our calculations is roughly proportional to the number of (above-surface) emitted electrons and. equivalently, scales approximately linearly with the charge state, the mass of the nuclei increases stronger than linearly with increasing atomic number. The conditions for a trampoline effect thus become more unfavorable with increasing Z. Moreover, with increasing Z radiative decay which is not included in our model becomes increasingly important. As radiative decay would speed up the deexcitation of the projectile its inclusion would further reduce the chances for trampoline reflection. We consequently predict that also for heavier projectiles such as  $Xe^{Q+}$ or  $U^{Q+}$  no trampoline effect will occur.

# 3.2 Spin Polarization of Electrons Emitted during Impact of N<sup>6+</sup> Ions on Magnetized Iron

Due to the variety of technical applications such as hard discs, spintronics, etc., magnetized materials are of considerable interest in the electronics industry. A detailed understanding of the properties of magnetized surfaces is thus sought for to optimize these applications. In the last decades, different experimental techniques have been developed to probe spin effects in magnetized materials. Two examples are photoemission [62, 63] and secondary electron spectroscopy [64]. However, the penetration depths involved limits their ability to selectively probe the surface. The use of ions as projectiles and grazing scattering geometries promises to drastically increase the surface sensitivity. Information on the surface spin properties can be obtained from emitted electrons (electron capture spectroscopy using low charge states). While D<sup>+</sup> ions were used in first experiments [65, 66], most experiments have been performed with He<sup>+</sup> projectiles [67, 68] as the underlying charge transfer processes are well understood.

Spectroscopy of magnetized surfaces using highly charged ions (HCI) has emerged only recently [2, 69]. The interpretation of experimental results is a challenging task due to the multitude of charge transfer processes involved. In order to gain insight into the dependence of the electron spin on the different transfer processes involved, we simulate the complete in- and outgoing trajectory of an N<sup>6+</sup> ion scattering from a magnetized Fe surface under a grazing angle of incidence. As opposed to the previous section where only potential emission (PE) governed by the potential energy of the projectile was taken into account, additional sources of electron emission are included. These are the production of secondary electrons (SE) in the target as well as kinetic emission (KE) due to binary collisions of the projectile with the electron gas at the surface.

In order to interpret experimental emission data which include all three contributions, we use the same parameters (projectile kinetic energy, charge state, angle of incidence, etc.) as in the experiment by Pfandzelter *et al.* [2] where the electron emission spectrum together with the mean polarization of the emitted electrons was measured. 150 keV N<sup>Q+</sup> ions ( $Q \leq 6$ ) were scattered off a magnetized Fe(001) surface. Because of the grazing angle of incidence ( $\Phi = 1.5^{\circ}$ ) the ions were reflected due to surface channeling [1], the point of closest approach being at about 0.5 a.u. above the topmost atomic layer. As the jellium edge, i.e. the border between the electron gas of the solid and the vacuum (Fig. 3.11), lies about half a lattice constant above the first atomic layer, part of the projectile trajectory goes through the electron gas. It is therefore important to include KE and SE in the model as they contribute to the electron emission spectrum.



Figure 3.11: The jellium edge lies about half a lattice constant above the topmost atomic layer,  $z_{jell} \sim a/2$ . The image plain  $z_{im}$  is also shown, schematically.

# 3.2.1 Projectile trajectory

In our Monte Carlo simulation, the calculation of the projectile trajectory begins beyond the critical distance  $d_c$ . As we are dealing with a metal surface, the interaction of the ion with the target has cylindrical symmetry and therefore only depends on the velocity component perpendicular to the surface which will be denoted by vin the following. The evolution of the trajectory, i.e. the ion-surface distance  $R_z(t)$ as a function of time, is calculated in discrete time steps of  $\Delta t = 0.1$  a.u. In every time step the distance is reduced by  $\Delta z = v\Delta t$  (and analogously increased on the outgoing trajectory). At large distances, the projectile trajectory is governed by the image force  $F_{image} = Q^2/4R_z^2$  which we suppress for  $R_z < z_{im}$  by including the factor  $(e^{2(-R_z-z_{im}+2)}+1)^{-1}$  in the latter expression to avoid unphysical (divergent) behavior below  $z_{im}$ .

At close vicinity to the surface, due to the grazing angle of incidence, the shadow cone overlap of the repulsive target core potentials leads to suppression of surface penetration. The effective atomic potential governing this channeling,  $V_{planar}$ , is given by the "planar" averaged atomic potentials and its derivative  $F_{ZBL}$  can be written as [1]

$$F_{ZBL} = 2\pi n_a Z_P Z_T \sum_i c_i \exp(-d_i z/a_s)$$
(3.33)

with  $\sum c_i = 1$ . Here,  $n_a$  is the atomic density of the surface,  $Z_P$  and  $Z_T$  are the projectile and target atomic number, respectively. For the set of parameters  $c_i$  and  $d_i$  and the screening length  $a_s$  we use the values of the Ziegler-Biersack-Littmark (ZBL) potential (see Ref. [1]). The point of closest approach of the ion is defined by the condition

$$E_{\perp} = V_{planar} \tag{3.34}$$

where  $E_{\perp}$  is the kinetic energy of the ion perpendicular to the surface. Fig. 3.12 illustrates this condition for the maximum value of  $E_{\perp}$  occurring in our simulation. The point of closest approach is approximately 0.4 a.u. above the first atomic layer in accordance with our simulation.



Figure 3.12: Illustration of the energy condition for the point of closest approach (Eq. 3.34): at the turning point of the trajectory the normal kinetic energy of the ion,  $E_{\perp,max}$ , matches the repulsive potential governing surface channeling (solid line).

# 3.2.2 Potential emission

Electrons emitted above the surface originate in part from potential emission. Although a metal target is very different in nature from an insulator such as LiF studied above, the physics of the scenario is very similar and the method employed will be the same as in the preceding section.

The interaction starts with the resonant capture of conduction band electrons where the critical distance  $d_c$  is now considerably larger than for an LiF target due to the smaller work function. On the other hand, the saddle of the potential barrier is higher in energy for metals than for insulators as the positive contribution of the image potential to the total potential is reduced for insulators by the dielectric response function  $\chi < 1$ . However, the effect of the smaller work function in metals overcomes the effect of the higher saddle so that electron capture sets in earlier than for an LiF target.

Due to the access to unoccupied states between the Fermi edge and the vacuum level, resonant loss back to the surface plays a more important role than in insulators where the band gap suppresses this channel. This also allows for an additional loss channel, an Auger transition to the conduction band (denoted by  $A_{cond}$  in the following), also called dielectronic loss [1, 5].  $A_{cond}$  corresponds to an AI process where the energy transferred to the emitted electron does not suffice to raise it above the vacuum level. Instead, it fills a state in the unoccupied part of the conduction band (Fig. 3.13). Due to the short distance at the point of closest approach, AC and AD processes involving deeper bound target electrons may become important. We have therefore also included Auger transitions from the Fe 3s and 3p levels in our calculations (Fig. 3.13). However, compared to the conduction electrons these states are very localized so that the overlap with projectile states is too small to find a significant contribution of this channel to the emission spectrum. The role of direct inner feeding (DF) also implemented in the simulation is similarly negligible. In the case of an iron target and nitrogen projectile DF is energetically only possible



Figure 3.13: Auger process to the conduction band and Auger processes involving inner target levels, schematically.

for transitions from the target 3p and 3s states into the L-shell of the projectile (see Fig. 3.14). This restricts the process to a short time window ( $\sim 10^{-16}$  s) in which the transition may occur. For this short time window the transition rates are too small to efficiently enable direct inner feeding.



Figure 3.14: Energy condition for direct inner feeding (DF). Solid lines: projectile energy levels for n > 1, dashed lines: binding energies of the Fe 3p and 3s level. At the intersection points DF is energetically allowed.

According to the rate equations (Eq. 3.1) of the COB model the occupation numbers  $P_n$  of all  $n \leq n_c$  projectile levels are updated after every time step  $\Delta t$  in the simulation. We have extended the form of the original rate equations by adding other sources of electron transfer mentioned above,

$$v_{z}\frac{d}{dR_{z}}P_{n} = I_{n}^{C}(R_{z}) - I_{n}^{L}(R_{z})P_{n} + A_{n}^{AC}(R_{z}) - I_{n}^{promo}(R_{z}) + I_{n}^{DF}(R_{z}) + \frac{1}{2}\sum_{n'>n} \left(A_{n',n}^{AI}P_{n'}^{2} + A_{n',n}^{AD}(R_{z})P_{n'} + A_{n',n}^{A_{cond}}P_{n'}^{2}\right)$$
(3.35)  
$$-\sum \left(A_{n'}^{AI}P_{n'}^{2}(R_{z}) + A_{n',n}^{AD}(R_{z})P_{z} + A_{n',n}^{A_{cond}}P_{n'}^{2}\right)$$
(3.36)

$$-\sum_{n' < n} \left( A_{n,n'}^{AI} P_n^2(R_z) + A_{n,n'}^{AD}(R_z) P_n + A_{n,n'}^{A_{cond}} P_n^2 \right) \quad (3.36)$$

where we have suppressed the dependence of  $P_n$  on  $R_z$  for clarity and used the notation analogously to Eq. 3.1. Both valence and inner shell processes are included in the rates  $A_{n,n'}^{AD}(R_z)$  and  $A_{n,n'}^{AC}(R_z)$ . Depending on the transition (not) occurring during the time step  $\Delta t$ , the population in shell n is increased by one electron, decreased by one or two electrons or remains constant.

The emission energies of the electrons as well as the conditions deciding whether a certain transition process is energetically allowed or forbidden are determined by the energies of the projectile levels. An important point is therefore the calculation of the binding energy of an electron sitting in shell n. In order to get an estimate for this binding energy we start out with the formula for a hydrogen-like ion

$$E_n = -\frac{Q_{eff}^2}{2n^2}$$
(3.37)

where  $Q_{eff}$  is given by the projectile core charge Z reduced by Slater screening by inner shell electrons [70].  $E_n$  is influenced by the presence of the surface which we take into account by shifting the energy levels due to screening and image charge effects. When the ion reaches the surface the core charge is screened by electrons of the metal electron gas so that projectile electrons experience a reduced Coulomb field of the positive core. This field is a function of the effective ion charge  $Q_{eff}$ , the electron-ion distance r, the distance  $R_z$  to the topmost atomic layer and the screening radius of the target electron gas [71]. The latter is given in Thomas-Fermi approximation by  $a_{TF} = 0.641r_s(z)^{1/2}$  where  $r_s$  is the Wigner-Seitz radius determined by the electron density. The  $r_s$  value for Fe according to the FEG model is  $r_s = 2.12$  determined by the density of the two 4s electrons of iron. However, as the six 3d electrons also contribute to the conduction band, we use  $r_s = 1.335$  a.u. For an electron bound at the distance of the *n*th projectile orbit radius  $\langle r \rangle_n$  this leads to the following self consistency relation for the (hydrogenic) orbitals [71]:

$$\frac{n^2}{Q_{eff}a_{TF}(z)} = (x+x^2) e^{-x}$$
(3.38)

where  $x = \langle r \rangle_n / a_{TF}(z)$ . The solution of this relation determines a stability limit for which the electron still remains bound to the projectile. For the calculation of the electronic energy levels this effect gives additional terms to the binding energy including screening effects giving [71]

$$E_n = -\frac{Q_{eff}^2}{2n^2} \cdot \left[ (1+x) \cdot e^{-x} \right]^2 + (Q_{eff} - 1) \cdot e^{-x} \cdot \frac{1}{a_{TF}(z)}.$$
 (3.39)

For large ion-surface distances, the response of the target electrons to the external perturbation of the approaching ion is described by the image potential which is given in the adiabatic approximation by [1, 5]

$$E_{image} = \frac{Q_{eff} - \frac{1}{2}}{2R}.$$
 (3.40)

For  $R_z \gg 0$  the hydrogenic energy levels are therefore shifted to higher energies by the contribution  $E_{image}$ . The expression for the image potential in Eq. 3.40 is valid for ion-surface distances large compared to the dynamic screening length  $\lambda_D = v_F/\omega_s$  where  $v_F$  and  $\omega_s$  are the Fermi velocity of the electron gas and the surface plasma frequency, respectively. As we simulate not only the approach of the ion but also processes taking place close to the surface, we suppress the divergence for  $R_z \to 0$  by extending Eq. 3.40 using a truncation function [12],  $f = [10^5 + (2R_1 + 1.2)^5]^{-1/5}$ , with  $R_1 = \max\{R_z, z_{im}\}$ , chosen such that  $-Q_{eff}^2/2n^2 + E_{image}$ falls below the value of Eq. 3.39 at close ion-surface distance. This allows for a smooth transition of  $E_n$  at intermediate distances from the large-distant limit to Eq. 3.39 by taking into account only the dominant contribution to the energy shift in our calculation.

Binding energies below the jellium edge are determined by density functional theory (DFT) calculations using a DFT code for an infinite jellium [72]. The electron binding energies for an ion embedded in the electron gas of the target are calculated. They indicate that only the K-shell and two L-shell electrons remain bound to the projectile below the surface. We therefore determine binding energies for all possible populations of these four bound states. We obtain K-shell energies depending predominantly on the filling of the K-shell (see Fig. 3.15). All configurations with one K-shell hole have similar energies  $E_1$  (maximum difference 0.05 a.u.) and the same is obtained for configurations with a filled K-shell (maximum difference 0.1 a.u.). For computational reasons we therefore use the mean value for  $E_1$  in each case.  $E_2$  is similar for all configurations so that we use again the mean value. The calculated energies are implemented as the asymptotic limit  $z \to 0$  in our simulation. This assures a smooth transition of the energy curves between the correct asymptotic values (Fig. 3.16).

The energy distribution of PE electrons as a function of the ion-surface distance measured from the first atomic layer is shown in Fig. 3.17. Electron emission sets in at about 23 a.u. above the topmost atomic layer after resonant capture has started into the critical shell  $n_c = 7$ . These low energy electrons are emitted via promotion



Figure 3.16: Energy levels for n > 1 as a function of their distance z to the first atomic layer. Left: for fixed population  $P_1 = 1$ ,  $P_2 = 2$ ,  $P_n = 0$  for n > 2. Right: with charge exchange processes (initial state of the N<sup>6+</sup> projectile:  $P_1 = 1$ ,  $P_n = 0$  for n > 1): due to discrete changes of the projectile charge and occupation numbers of the different levels caused by electron transitions, the energy levels also show discrete jumps.

to vacuum and high n AI. Image (screening) shift leads to electron emission due to promotion from all projectile levels down to n = 3 during the approach of the ion. Below a distance of about 5 a.u. promotion stops as the M-shell has reached the vacuum level. Consequently, also autoionization from n > 2 ceases at the



Figure 3.17: Energy distribution of PE electrons as a function of the ion-surface distance at which the emission takes place (see text). The dotted line indicates the jellium edge.

same distance. While promoted electrons dominate the very-low energy spectrum (E < 10 eV) with 66% of the emitted electrons, AI strongly dominates for energies 10 eV < E < 150 eV with up to 99% of the total yield. In this energy range all other processes are negligible. However, for R < 3 a.u. AC is energetically possible into the L-shell emitting electrons with very low energies below the jellium edge (Fig. 3.17).

With decreasing initial n shell AI emission energies increase. The features seen in Fig. 3.17 at about 70 eV and 350 eV correspond to emission of L- and K-Auger electrons, respectively. The evolution of the distribution of the K-Auger (AI, AC, AD) electrons during the approach reflects the decrease of emission energies with decreasing distance originating from the projectile level shift. The K-Auger electron distribution for distances larger than about 3 a.u. from the topmost layer is predominantly given by AI electrons (about 87%). Near the jellium edge AC and AD become increasingly important and emit about 82% of the K-Auger electrons for  $R_z < 3$  a.u. K-Auger electrons emitted from the projectile via AI or AD show a broad energy distribution (270 – 450 eV) due to the momentum contribution from the fast projectile where for the emission process itself, we have assumed an emission angle uniformly distributed over  $2\pi$ . Auger electrons emitted from the surface due to AC or AD have a much narrower distribution with an energy width below 10 eV and can be well distinguished in Fig. 3.17.

### Spin dependence of charge exchange processes

The average spin polarization  $\mathcal{P}$  of emitted electrons is defined for a given emission energy by

$$\mathcal{P} = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} \tag{3.41}$$

where  $N_{\uparrow(\downarrow)}$  is the number of spin-up (down) electrons.  $\mathcal{P}$  depends on the type of transfer processes each electron has undergone prior to emission. While the initial polarization of N<sup>6+</sup> is zero, i.e. the spin of the 1s electron in the N<sup>6+</sup> ion is chosen randomly, the target polarization is given by the polarized spin density of states (SDOS) of Fe (Fig. 3.18). Magnetized materials are characterized by a difference



in the number of spin-up  $(\uparrow)$  and spin-down  $(\downarrow)$  electrons where spin up (majority)

means parallel and spin down (minority) means antiparallel to the direction of magnetization. The minority states are shifted upwards in energy with respect to the majority states by the exchange splitting  $\Delta$  (see Fig. 3.18b in comparison to the paramagnetic case in Fig. 3.18a). This leads to an excess of occupied spin-up states and consequently to a positive mean polarization of the electrons.

The present SDOS for iron was determined by DFT calculations by Hatcher [73] using the all-electron full-potential linearized augmented plane wave (FLAPW) method [74]. Further SDOS data for regions above the surface in dependence on the distance to the topmost atomic layer have also been provided recently by Hatcher [75]. This z-dependent SDOS was used for our calculations as the projectile ion does not penetrate into the bulk.

The initial condition for the spin of resonantly captured electrons is given by the SDOS at the energy satisfying the resonance condition. RC sets in as soon as the potential barrier falls below the Fermi edge. The first electrons captured into projectile levels and subsequently emitted due to level promotion with very low energies will consequently have a similar polarization as the SDOS around the Fermi edge. For later capture as well as for AD and AC, electrons from the whole conduction band contribute so that the involved electrons on average have the mean polarization of the conduction band. Of course, this does not apply for electrons captured from inner shell target levels via DF, AD or AN as these electrons are unpolarized.

The polarization of autoionized electrons depends on their initial state level n. If they originate from high levels close to  $n_c$  they have been captured in the early neutralization process and hence reflect the polarization around the Fermi edge. On the other hand, late low-n transitions are expected to reflect the average target polarization, especially the high-energy KLL Auger electrons. For loss processes back to the conduction band (RI and  $A_{cond}$ ) the SDOS of the unoccupied part of the conduction band determines which electrons are preferably lost. As there is an access of unoccupied spin-down states, minority electrons have a greater change to find an available final state.

# 3.2.3 Secondary electrons

In our work, electron transport is treated in the framework of the classical transport theory (CTT [76]) for open systems in which the electronic dynamics is represented by a classical phase-space distribution  $f(\mathbf{r}, \dot{\mathbf{r}}, t)$  whose evolution is determined by test-particle discretization, i.e. by solving the corresponding Langevin equation for representative trajectories ( $i = 1, ..., N_E$ )

$$\ddot{\vec{r}}_{i} = -\vec{\nabla}V(\vec{r}_{i}, t) + \vec{F}_{stoc}(\vec{r}_{i}, \dot{\vec{r}}_{i}, t), \qquad (3.42)$$

where  $N_E$  is the number of particles in the ensemble. The ensemble is propagated employing the CTMC technique. The stochastic forces,  $\vec{F}_{stoc}$ , entering Eq. 3.42



Figure 3.19: Electron transport near the surface, schematically. The primary electron is denoted by  $e_p$  and escaping secondaries by  $e_s$ . The intensely yellow area near the surface indicates the region where inelastic surface excitations dominate over bulk excitations.

are derived from the collision kernels of the associated Liouville master equation, determined either from independent ab initio quantum calculations or independent experimental data. Collision processes governing the input  $(\vec{F}_{stoc})$  are treated as Poissonian stochastic processes and will be discussed below in more detail. Conservative forces in Eq. 3.42 (i.e.  $-\nabla V(\vec{r_i})$ ) will be neglected in the following but could be included straightforwardly if needed. Two points are worth mentioning: as the stochastic forces and their underlying collision kernels are derivable from (mostly) quantum (linear) response functions, the resulting transport theory corresponds to a hybrid classical-quantum treatment [77] despite its purely classical appearance. In fact, in the limit  $V(\vec{r_i}) = 0$ , the treatment is equivalent to a quantum-kinetic (Boltzmann) equation since classical-quantum correspondence holds for impulsively perturbed free-particle propagation in line with Ehrenfest's theorem. Secondly, the present simulation treats the entire collision cascade. Accordingly, the number of particles in the ensemble,  $N_E$ , is not constant but increases during the evolution as inelastic scattering generates secondary electrons whose trajectories are followed as well. Correlation effects between primary and secondary electrons are neglected. The spin degree of freedom is accounted for by following two subensembles of electrons with spin up and spin down which would remain decoupled in the absence of spin-dependent interactions. Spin-flip processes treated below lead to an exchange of populations among the subensembles.

Momentum-, energy- and spin exchange are simulated by a sequence of elastic and inelastic scattering events (Fig. 3.19). While inelastic scattering is accompanied



Figure 3.20: Collision channels included in our simulation. a) Elastic scattering: only momentum is transferred according to the deflection angle  $\theta$ . b) inelastic scattering: the scattering electron with energy  $E_p$  suffers an energy loss  $\omega$  which is transferred to an electron of the conduction band with energy  $E_s$ . The primed quantities indicate the final energies of the electrons.

by a certain energy loss, an elastically scattered electron is assumed to retain its energy and only momentum is transferred in the collision (Fig. 3.20). Electrons are elastically scattered at the screened Coulomb potential of the atomic cores in the solid approximated by a muffin-tin potential. Inelastic scattering proceeds by excitations of the electronic system of the solid. The negative electron charge brought into the medium constitutes a strong perturbation to the electron gas of the solid. The target electrons react by collective excitations (i.e. plasmons), particlehole pair creation, or by driving inter-band transitions. If the energy transfer suffices to raise the excited electron into an unbound state, the trajectory of this secondary electron is followed. Electrons dissipate their energy continuously until they are stopped in the bulk or escape into the vacuum. We assume that all plasmon excitations eventually decay into electron-hole pairs thereby creating secondary electrons. Alternative relaxation channels via emission of phonons or photons are neglected. While this approximation overestimates the total electron emission, we expect this error to be of minor importance as plasmon decay into electron-hole pairs happens on a femto-second time scale thereby dominating over the other decay channels which typically happen on a pico-second or even larger time scale. A possible spin dependence of plasmon decay will be discussed below.

Due to the breaking of symmetry at the solid-vacuum interface, additional excitation channels open in the vicinity of the surface. These surface excitations are dominant close to the surface (indicated by the intensely yellow area in Fig. 3.19) while bulk excitations dominate a few a.u. below.

The stochastic force entering Eq. 3.42 is described as a sequence of impulsive
momentum transfers  $\vec{p}_{i,\alpha}$ ,

$$\vec{F}_{stoc}(t) = \sum_{i,\alpha} \delta(t - t_i^{(\alpha)}) \Delta \vec{p}_{i,\alpha}, \qquad (3.43)$$

where the index  $\alpha$  labels the different channels for collision processes (elastic, inelastic etc., see below) while the index *i* refers to different collisions of the same channel. The mean free path (MFP) between two collisions,  $\lambda_{\alpha}$ , determines the time interval between two collisions

$$\langle t_{i+1}^{(\alpha)} - t_i^{(\alpha)} \rangle = \lambda_\alpha(E_e)/v_e \tag{3.44}$$

where  $E_e$  and  $v_e$  are the energy and velocity along the trajectory. The MFP is related to the collision kernel  $P_{\alpha}$  (or differential scattering cross section) for each channel as

$$\lambda_{\alpha}^{-1} = \int d^3(\Delta p) P_{\alpha}(\Delta \vec{p}, E_e, s)$$
(3.45)

which may depend on the electron energy, the spin s, and, possibly, other variables as well. In Eq. 3.45 the integral extends over all allowed momentum transfers consistent with energy and momentum conservation as well as the Pauli principle of maximal single occupancy of any initial and final spin orbital accessible by a momentum transfer  $\Delta \vec{p}$ . The inverse MFP (Eq. 3.45) is the zeroth moment of  $P_{\alpha}$ . The probability for a stochastic momentum transfer  $\Delta \vec{p}_{\alpha}$  is given by the (normalized) kernel  $P_{\alpha}$ . Accordingly,  $\langle \Delta \vec{p}_{\alpha} \rangle$  gives the first moment of  $P_{\alpha}$ . Straggling and fluctuations reflect higher moments. The total mean free path  $\lambda_{tot}$  is determined by the cross sections of the different scattering processes,

$$\lambda_{tot}^{-1} = \sum_{\alpha} \lambda_{\alpha}^{-1}, \qquad (3.46)$$

and  $\lambda_{\alpha}^{-1}/\lambda_{tot}^{-1}$  is the probability for the process  $\alpha$  to happen. The detailed models for calculating the different  $\lambda_{\alpha}$  are presented in the following sections.

#### Spin polarized density of states

One key ingredient of our simulation is the magnetized band structure. The occupied states determine the initial conditions for the spin-polarized subensembles of secondary electrons as the density of occupied states constitutes, up to a normalization factor, the distribution of electron energies in the conduction band. In addition, the probability for a certain spin direction is given by the relative fraction of states of this spin at the given energy. The bulk SDOS (Fig. 3.18b) is used for excitations in the bulk while the SDOS of the first atomic layer (Fig. 3.18c) is used for secondary electrons generated by surface excitations. Moreover, the unoccupied states play a key role as accessible final states in inelastic scattering processes. Electrons excited from the conduction band reflect the SDOS so that secondary electrons emitted after impact of an unpolarized electron beam show a positive polarization. For very low electron energies (< 15 eV) this effect is additionally enhanced by so-called Stoner excitations [78, 79], a consequence of the excess of minority spin states in the unoccupied part of the conduction band (see below).

## **Elastic scattering**

An electron traveling through a solid medium is elastically scattered off the screened core potentials of the lattice atoms. The elastic ( $\alpha = e$ ) mean free path (EMFP)  $\lambda_e$ between subsequent elastic scattering events depends on the atomic density  $\rho$  of the solid and the total elastic scattering cross section  $\sigma_e$  and is given by  $\lambda_e = 1/(\rho\sigma_e)$ . The momentum transfer in an elastic scattering process depends on the scattering angle  $\theta$  which is determined by the collision kernel for elastic scattering, i.e. the differential cross section  $d\sigma_e/d\Omega$ . As we study spin-dependent processes in our work, we calculate elastic cross sections using the Dirac equation which includes the possibility of spin-flip during scattering by means of a so-called spin-flip scattering amplitude  $g(\theta)$ . The differential cross section is then expressed in terms of two scattering amplitudes f and g:

$$\frac{d\sigma_e}{d\Omega} = |f(\theta)|^2 + |g(\theta)|^2 \tag{3.47}$$

where  $f(\theta)$  is the direct scattering amplitude. The nonrelativistic limit corresponds to g = 0 describing an electron whose spin direction is conserved during the scattering event. The ratio  $|g|^2/(|f|^2 + |g|^2)$  determines the probability for spin-flip during the scattering process. The scattering amplitudes are independent of the azimuthal angle  $\phi$  due to the spherical symmetry of the scattering potential.

For the calculation of differential and total elastic cross sections we use the ELSEPA (Elastic Scattering of Electrons and Positrons by Atoms) code of Salvat *et al.* [80]. The Dirac equation for elastic scattering of an electron by a static central potential V(r) approximated by a muffin-tin model potential is solved by partialwave analysis. Electron densities are taken from multi-configuration self consistent Dirac-Fock calculations. The high level of accuracy for differential cross sections for atoms cannot be reached in the solid environment, in particular for energies below  $\sim 10^2$  eV. However, integral cross sections determining  $\lambda_e$  should be sufficiently reliable. We have compared the obtained EMFP with calculations using an atomic potential (Fig. 3.21). The EMFP modeled by a muffin-tin potential is larger than for an atomic potential which is a consequence of the different *r*-dependences of the potentials used. In the muffin-tin approximation the deflection of trajectories is confined to impact parameters inside a sphere of the muffin-tin radius around the nucleus. The scattering cross section for large partial waves associated with impact parameters outside this sphere is smaller than in the case of a free atom target. This leads to a reduction of the differential cross section for small scattering angles and subsequently of the total cross section in solids compared to free atoms.



Figure 3.21: Elastic mean free path  $\lambda_e$ for solid Fe represented by a muffin-tin potential [80] (solid line) and for atomic Fe (dashed line).

### Inelastic (bulk) scattering

We investigate both surface and bulk scattering processes. Cross section and corresponding inelastic mean free path (IMFP)  $\lambda_{(\alpha=in)}$  in the bulk are calculated from the frequency and momentum dependent dielectric function  $\epsilon(q, \omega)$ . This quantity describes the response of the bulk electrons (plasmon and particle-hole pair excitations, inter- and intra-band transitions) to an external perturbation with frequency  $\omega$  and wave number q (see e.g. [81, 82]). The inverse dielectric function  $\epsilon^{-1}(q, \omega)$ , more precisely, the energy loss function Im  $\{-1/\epsilon(q, \omega)\}$ , is related to the differential inverse mean free path as [83]

$$\frac{d^2 \lambda_{in}^{-1}}{d\omega dq} = \frac{1}{\pi Eq} \operatorname{Im} \left\{ -\frac{1}{\epsilon(q,\omega)} \right\} \Theta \left[ \omega_m(q) - \omega \right].$$
(3.48)

Here,  $\omega$  is the energy loss suffered by an electron with energy E, q is the transferred momentum, and the step function  $\Theta$  assures momentum and energy conservation with  $\omega_m(q) = \min\{v_e^2/2 - E_F, v_eq - q^2/2\}$ .  $v_e$  is the velocity of the scattered electron and  $E_F$  is the Fermi energy. The right hand side represents, up to normalization factors, the collision kernel for inelastic scattering in the bulk. Integration of Eq. 3.48 over q yields the probability for an electron with energy E to lose the energy  $\omega$ . Further integration over all possible energy losses (upper integration limit  $\omega_{max} = E - E_F$ ) gives the inverse inelastic mean free path as a function of the electron energy,  $\lambda_{in}^{-1}(E)$ , which determines the probability for an inelastic scattering event to take place. The angular distribution of the scattered electron follows from [81]

$$\frac{d\lambda_{in}^{-1}}{d\Omega} = \frac{1}{\pi^2} \int_0^\infty \frac{d\omega}{q^2} \sqrt{1 - \frac{\omega}{E}} \operatorname{Im}\left\{-\frac{1}{\epsilon(q,\omega)}\right\} \Theta\left[E - E_F - \omega\right].$$
(3.49)

For a given momentum (q) and energy transfer  $\omega$ , Pauli blocking due to occupied final states should be taken into account in Eq. 3.49. The energy and angular distributions of the secondary electrons excited in an inelastic scattering process directly follow from energy and momentum conservation.

An analytic expression for  $\epsilon(q, \omega)$  was first derived by Lindhard [47] for a free electron gas. It was later modified by Mermin [84] to account for the finite width of the plasmon peak. As an example, Fig. 3.22 shows the loss function Im  $\{-\epsilon(q, \omega)^{-1}\}$ for the jellium-like metal Al where a Mermin function was chosen for the dielectric function. For energies lower than the ionization energy of inner shells, the Mermin dielectric function is determined by the plasmon frequency  $\omega_p = \sqrt{4\pi n}$  and the width  $\gamma$  of the plasmon peak where *n* is the density of the free electron gas. Different contributions to inelastic loss can be distinguished in Fig. 3.22: the electron-hole pair continuum confined to the region between  $\omega = q^2/2 \pm qk_F$  and the plasmon resonance peak starting at the plasmon frequency  $\omega_p$  at q = 0.



Figure 3.22: Momentum and energy dependent loss function  $\operatorname{Im} \{-\epsilon(q,\omega)^{-1}\}$  of a freeelectron gas (Al). The plasmon frequency  $\omega_p$  coincides with the position of the maximum for q = 0. The two lines demarcate the particle-hole continuum.

For transition metals with d-electrons contributing to the conduction band structure (Fe, Au, Ni, etc.) the simple model of a quasi-free electron gas breaks down. The optical data Im  $\{-\epsilon(q=0,\omega)^{-1}\}$  for Fe [42] (see Fig. 3.23) feature a broad structure composed of the plasmon peak and convoluted by inter- and intra-band transitions. Various models have been proposed to calculate  $\epsilon(q,\omega)$  by extrapolation of  $\epsilon(q=0,\omega)$  into the q- $\omega$ -plane (e.g. [85–87]). They have been used to describe inelastic scattering of high-energy electrons. However, some of these models result in a neglect of electron-hole pair excitations for very low energies ( $\omega < 1$ a.u.) where this is the most important loss channel for electron trajectories down to the few-eV regime.

The method of calculating  $\epsilon(q, \omega)$  which we use in our work is very similar to one of those presented in [87]. The starting point is a fit of the optical data  $\text{Im}(-\epsilon(\omega)^{-1})$ by a sum of Drude functions (Fig. 3.23). We then calculate the q and  $\omega$  dependent



Figure 3.23: Optical data of Fe (open circles [42]), overall fit to  $\operatorname{Im}(-\epsilon^{-1}(q=0,\omega))$  (solid line), and fit functions for the individual peaks (dashed lines).

loss function as a sum of several Drude functions

$$\operatorname{Im}\left\{-\frac{1}{\epsilon(q,\omega)}\right\} = \sum_{i} A_{i} \operatorname{Im}\left\{-\frac{1}{\epsilon_{i}(q,\omega)}\right\}$$
(3.50)

for each of which we employ the parameterized form [88]

$$\epsilon_i(q,\omega) = 1 + \frac{\omega_{p,i}^2}{s^2 q^2 + q^4/4 - i\pi\omega s^2 q \Theta(x_1)\Theta(x_2)/2q_F - \omega[\omega + i\gamma_i]}$$
(3.51)

where  $s^2 = 3q_F^2/5$  according to the hydrodynamical model [88].  $\Theta(x_1)$  and  $\Theta(x_2)$ are step functions with arguments  $x_1 = \omega - q^2/2 + q_F q$  and  $x_2 = q^2/2 + q_F q - \omega$ defining the regions of particle-hole pair creation and plasmon excitation in the q- $\omega$ -plane (see Fig. 3.22). For each term the "plasmon" frequency  $\omega_{p,i}$ , width  $\gamma_i$  and weight  $A_i$  are determined by the fit to the optical data at q = 0 and constrained by the Thomas-Reiche-Kuhn sum rule for the generalized oscillator strength

$$\int_{0}^{\infty} d\omega \,\omega \,\mathrm{Im}\left\{-\frac{1}{\epsilon(q,\omega)}\right\} = 2\pi n\,. \tag{3.52}$$

The present method differs from that of Ref. [87] only in the details of the fit function of Eq. 3.51 in which we preserve the distinction between regions of electronhole pair creation and of collective excitations in the q- $\omega$  plane. We find only minor differences in the resulting numerical results for the collision kernel.

### Surface excitations

As the penetration and escape depths of low energy electrons are small, inelastic scattering processes due to surface excitations become increasingly important. They are treated in the framework of the specular-reflection model introduced by Ritchie *et al.* [89]. The surface dielectric function  $\epsilon_s$  can be expressed in terms of the bulk dielectric function  $\epsilon$  as [90]

$$\epsilon_s(Q,\omega,z) = \frac{Q}{\pi} \int dq_z \, \frac{e^{iq_z z}}{(Q^2 + q_z^2)\,\epsilon(q,\omega)} \tag{3.53}$$

where we use the notation  $\vec{q} = (\vec{Q}, q_z)$  with the z axis along the surface normal and with z = 0 located at the surface. For the quasi-free electron contribution we can employ a jellium approximation within which z = 0 corresponds to the jellium edge. In the following, we will extend Eq. 3.53 to d-band metals, the validity of which being an open question. Nevertheless, since our approach has the correct sum rules built into it, integral mean free paths should be reasonably well approximated. If we neglect dispersion along the z axis, i.e.  $\epsilon(q, \omega) \simeq \epsilon(Q, \omega)$ , the surface dielectric function can be approximated by

$$\epsilon_s(Q,\omega,z) \simeq \epsilon(Q,\omega)^{-1} e^{-Q|z|} \tag{3.54}$$

and the inverse surface inelastic mean free path  $\lambda_{(\alpha=s)}^{-1}$  is given by [83]

$$\frac{d^2\lambda_s^{-1}}{dQd\omega} = \frac{2e^{-2Q|z|}}{v_{\parallel}\pi\sqrt{Q^2v_{\parallel}^2 - \left(\omega + \frac{Q^2}{2}\right)^2}} \operatorname{Im}\left\{\frac{\epsilon(Q,\omega) - 1}{\epsilon(Q,\omega) + 1}\right\} \Theta\left[\omega_m(Q) - \omega\right]$$
(3.55)

where  $\omega_m(Q) = \min\{v_{\parallel}^2/2 - E_F, v_{\parallel}Q - Q^2/2\}$  and  $v_{\parallel}$  is the velocity component parallel to the surface. Although Eq. 3.54 was derived for electrons moving parallel to the surface [89] it is a reasonable approximation also for electrons with  $q_z \neq 0$  for the energies and the dielectric properties of the material considered in our work. We verified the validity of Eq. 3.54 by numerical calculations at eight different distances z between the jellium edge and z = -20. For all z the relative error of Eq. 3.54 lies below 10%, only for z = 0 the maximum error is about 20%.  $\lambda_s^{-1}$  has its maximum at the surface and decreases with increasing distance to the jellium edge. The energy dependence of the bulk inelastic MFP  $\lambda_{in}$  and of the surface MFP at z = 0 (Fig. 3.24) clearly indicate that surface inelastic processes dominate over bulk processes near the surface over a wide range of energies. For reasons of computational efficiency for the Monte Carlo simulation, the z dependence resulting from Eq. 3.55 was fitted to the analytic formula  $\lambda_s(z) = \lambda_s(0) \left(1 + a|z|^b\right)$  with energy-dependent parameters a(E) and b(E) which were found to be a = 1.04 - 0.008E and  $b = 2.08 - 0.24\log E$  for  $E > E_{min}$  and a = 0.19 + 0.54E and  $b = 1.96 - \exp\left[-7.8(E - 0.4)\right]$  for  $E < E_{min}$  where  $E_{min} = 1.6$  a.u. (43 eV) corresponds to the minimum in  $\lambda_s$  (see Fig. 3.24).

As the generalized oscillator strength is shifted from the bulk to the surface response function, we incorporate the z dependence into the bulk  $\lambda_{in}$  near the surface such that (i) for large distances from the surface  $\lambda_{in}^{-1}$  asymptotically tends to its bulk value (i.e. Eq. 3.48) and (ii)  $\lambda_{in}^{-1}$  tends to zero at the surface. In [83] it was proposed to include the z dependent factor  $(1 - e^{-2Q|z|})$  in Eq. 3.48 which assures that these two criteria are satisfied. We adopted this choice for our calculations.



Figure 3.24: Bulk  $(\lambda_{in}(-\infty))$ , solid line) and surface  $(\lambda_s(0))$ , dashed line) inelastic mean free paths for Fe, see text.

### Spin effects in electron scattering

Spin-dependent effects can contribute to both inelastic as well as elastic scattering. Spin-dependence of the latter is accounted for by extending Eq. 3.47 [91]:

$$\frac{d\sigma_{e,\uparrow\downarrow}(\theta)}{d\Omega} = (|f(\theta)|^2 + |g(\theta)|^2)[1 \pm S(\theta)]$$
(3.56)

where  $S(\theta)$  is the Sherman function which is a measure for the asymmetry between spin-up and spin-down cross sections. The positive (negative) sign in Eq. 3.56 corresponds to spin  $\uparrow(\downarrow)$ . Measurement of electron polarization in Mott detectors exploits the broad maximum (full width at half maximum in the range of 50° to 100°) of the Sherman function for electron energies of several tens of keV. For the material and energies considered in our work, however,  $S(\theta)$  features very small values over the whole range of scattering angles and renders elastic scattering effectively spin independent. Consequently, spin polarization of low-energy electron beams in magnetized iron is dominated by inelastic scattering events. We treat two processes which are expected to control the polarization of emitted electrons, schematically depicted in Fig. 3.25. The occupation of majority



Figure 3.25: Illustration of spin-dependent scattering processes for the bulk SDOS of Fe. Left panel: A secondary electron with initial energy  $E_i$  is excited to a continuum state of energy  $E_i + \omega$ . On the average, more majority than minority electrons are emitted due to the positive polarization of the occupied states. Right panel: Spin-filter effect due to Stoner excitations controlled by the unoccupied part of the spin densities of states (cf. text).

and minority states in the magnetized SDOS is unbalanced. Spin-up electrons are therefore more likely to be excited and emitted in an inelastic collision (left panel of Fig. 3.25). On average, secondary electrons generated in a collision cascade by primary electrons with energies large compared to  $E_F$  should reflect the mean polarization  $\bar{\mathcal{P}}$  of the target conduction band which in the case of iron is  $\bar{\mathcal{P}} \approx 35\%$ according to the band structure calculations (Fig. 3.18).

The second process is the so-called Stoner excitation (right panel in Fig. 3.25). It results from the unoccupied SDOS which is available for final states of electronelectron scattering processes. An electron with minority spin has access to a larger number of final states in an inelastic collision accompanied by energy loss. Since the number of available final states determines, by way of Fermi's golden rule, the collision probability, the collision rate of minority spin electrons is enhanced relative to that of majority spin electrons. The excess energy is transferred to an electron from the occupied part of the conduction band which is predominantly of majority spin, so that this process appears as inelastic scattering accompanied by a spin-flip of the electron even though no explicitly spin-dependent interactions enter the transition amplitude. As the maxima of the two spin density distributions are separated by the energy  $\Delta \approx 2.5$  eV, a characteristic energy loss of  $\omega \simeq \Delta$  connected to a change of polarization is observed in experiment [92].

The asymmetry between unoccupied spin-up and spin-down states results in a spin-dependent IMFP: minority electrons are scattered more often than majority electrons and, therefore, have a shorter mean free path. The asymmetry between the spin-up and down IMFPs decreases with increasing primary energy due to the decreasing probability of the electron to access a final state below the vacuum level  $E_v = E_F + W$  where W is the work function of the target. If the final state of the scattered electron lies above  $E_v$ , there are as many free final states for majority as for minority electrons. Only below  $E_v$ , a spin dependence of available final states becomes significant. We therefore separate inelastic scattering in collisions with final states above and below  $E_v$ . Accordingly, we split the integration of  $d\lambda_{in}^{-1}/d\omega$ over the possible energy losses  $\omega$  as

$$\lambda_{in}^{-1} = \int_{0}^{E-E_F} \frac{d\lambda_{in}^{-1}}{d\omega} d\omega$$
$$= \int_{0}^{E-E_F-W} \frac{d\lambda_{in}^{-1}}{d\omega} d\omega + \int_{E-E_F-W}^{E-E_F} \frac{d\lambda_{in}^{-1}}{d\omega} d\omega$$
$$= \lambda_{>E_v}^{-1} + \lambda_{(3.57)$$

The first integral corresponds to spin independent scattering processes with final projectile state above the vacuum level while the second integral describes scattering to states with energies  $E_F < E < E_v$ . Up to this point, the latter contribution is also spin independent as the construction of  $\epsilon(q, \omega)$  is based on spin-independent photo-absorption spectra. To account for the magnetization of the target, we calculate the number of unoccupied (ferromagnetic) spin-up  $(N_{\uparrow})$  and spin-down states  $(N_{\downarrow})$  and weight the spin-independent (paramagnetic)  $\lambda_{< E_v}^{-1}$  by the ratio of majority (minority) to paramagnetic states (denoted by  $N_0$  in the following):

$$\lambda_{\langle E_v,\uparrow}^{-1} = \lambda_{\langle E_v}^{-1} \frac{N_{\uparrow}}{N_0}$$
$$\lambda_{\langle E_v,\downarrow}^{-1} = \lambda_{\langle E_v}^{-1} \frac{N_{\downarrow}}{N_0}$$
(3.58)

where  $N_0 = N_{\uparrow} + N_{\downarrow}$ , as the total number of unoccupied states is the same for the para- and the ferromagnetic systems. Using the calculated SDOS for iron (Fig. 3.18) we find the ratios  $N_{\uparrow(\downarrow)}/N_0$  to be 0.172 for spin up and 0.828 for spin down, respectively. The resulting spin-dependent total IMFP (Fig. 3.26) is given by

$$\lambda_{in\uparrow(\downarrow)}^{-1} = \lambda_{>E_v}^{-1} + \lambda_{
(3.59)$$

Increasingly large differences between  $\lambda_{in\uparrow}$  and  $\lambda_{in\downarrow}$  at small energies lead to the spin-filter effect. Experimental data for a spin-dependent IMFP, denoted by  $\lambda_{exp\uparrow(\downarrow)}$  in the following (Ref.[93], also shown in Fig. 3.26), contain largely spin-independent elastic contributions. For a comparison with the present  $\lambda_{in\uparrow(\downarrow)}$  we subtract the



Figure 3.26: Spin-dependent inelastic mean free paths  $\lambda_{in,\uparrow}$  (blue line) and  $\lambda_{in,\downarrow}$  (red dashed line). The asymmetry between  $\lambda_{in,\uparrow}$  and  $\lambda_{in,\downarrow}$  due to Stoner excitations increases with decreasing energy. Experimental results for  $\lambda_{\uparrow(\downarrow)}$  which include elastic scattering (Ref. [93]) are also shown (open triangles: spin-up, open circles: spin-down, lines to guide the eye). Right panel: Comparison with the experimental data after subtraction of estimated elastic contributions.

elastic contribution by setting  $\lambda_{exp\uparrow(\downarrow)}^{-1} = \lambda_{in\uparrow(\downarrow)}^{-1} + \lambda_e^{\prime-1}$  where the prime indicates that the experimental  $\lambda_e^{\prime}$  includes only part of the elastic scattering events due to the scattering geometry. The corrected experimental data are in fair agreement with the calculated asymmetry between  $\lambda_{in\uparrow}$  and  $\lambda_{in\downarrow}$  considering the large uncertainty of the data reduction.

As bulk excitations clearly dominate over surface excitations, we expect the spin dependence to be predominantly governed by inelastic bulk scattering. For computational reasons, a spin-dependent mean free path is only used for bulk excitations in the present work.

### Application to Fe

As a first test of our model, we compare our results for the absolute electron yield resulting from electron scattering at an iron surface with the measured data of Kirschner *et al.* [64] in which unpolarized electron beams were scattered at a magnetized Fe surface. Both the calculated and measured total secondary electron yield (Fig. 3.27) increase with primary electron energy towards a maximum at about 500 - 600 eV. Although a further increase of the primary energy increases the number of secondary electrons in the bulk, the observed electron yield does not increase further. As a result of the larger penetration depth of the primary electron, more secondaries are produced too far inside the solid as to reach the surface during transport. The energy dependence of the simulated yield closely follows the experimental data while exceeding the yield by about 30% which may be a consequence of the limited collection efficiency in the experiment [64].



Figure 3.27: Total secondary electron yield from Fe versus primary electron beam energy. Blue diamonds: experimental results [64], red circles: this work.

For the comparison of our polarization data with the experiment, we focus on the results for primary energies  $E_p$  below 500 eV (Fig. 3.28). Two trends are observed in



Figure 3.28: a) Spin polarization of emitted electrons from a magnetized Fe(110) surface bombarded with 90 eV and 500 eV unpolarized electrons under an impact angle of 50°. Blue dots: experimental results [64]; red dots: present simulation. The dashed lines indicate the simulated polarization neglecting Stoner excitations. b) Same as a) including the additional polarization contribution due to plasmon decay near the Fermi edge (see text).

the experiment and reproduced by our calculation: 1) the polarization of low-energy electrons increases with increasing primary energy and 2) the largest polarization values (up to 50%) are reached at emission energies below 5 eV. The latter feature is quite remarkable as the mean polarization of the occupied magnetic band structure does not exceed  $\sim 35\%$ . It is obviously the result of a high degree of spin selectivity due to the spin-filter effect of Stoner excitations. Neglecting Stoner excitations, a much reduced degree of polarization would result (see Fig. 3.28).

Our simulation can quantitatively account for the increase of the spin polarization with increasing primary electron energy. This is to a large degree due to the increased statistical weight of spin polarized secondary electrons relative to that of the unpolarized primary electrons. The latter is the result of two trends: at higher energies, backscattering into vacuum of the primary electrons is suppressed as the penetration depth increases and the number of low-energy secondary electrons generated by primary electrons increases with energy. The decreasing importance of backscattered primaries with increasing impact energy is clearly visible in Fig. 3.29. Saturation will be reached when the secondary electron cascade has fully evolved and the number of backscattered primaries  $(N_p)$  becomes negligible so that  $N_s + N_p \simeq N_s$  where  $N_s$  is the number of emitted secondaries. In the absence of explicitly spin-dependent interactions, backscattered primary electrons keep their original polarization  $\mathcal{P}_p = 0$  while secondary electrons are emitted with the average polarization of the conduction band  $\mathcal{P}_s = \bar{\mathcal{P}} \simeq 35\%$ . The polarization of emitted electrons therefore lies between 0 and 35% depending on the ratio  $N_s/(N_p + N_s)$ as long as Stoner excitations are not taken into account (dashed lines in Fig. 3.28). Polarization values above  $\bar{\mathcal{P}}$  originate from Stoner excitations. The polarization values at very low energies depend on the asymmetry between  $\lambda_{in\uparrow}$  and  $\lambda_{in\downarrow}$ . Along with the saturation for the weight of secondaries, a saturation must also appear for the polarization at high primary energies which has been observed in experiment [64]. For  $E_p = 500$  eV backscattered primary electrons are still visible in the lowenergy spectrum (Fig. 3.29) so that we are not yet in the saturation regime which was experimentally determined to be at about  $E_p = 1$  keV [64].

Overall, experiment and simulation are in reasonable agreement (Fig. 3.28). There is, however, a systematic discrepancy at emission energies between about 10 and 20 eV visible for both primary energies  $E_p = 90$  eV and  $E_p = 500$  eV. The origin of this "hump" was experimentally investigated by additional measurements on oxygen exposed Fe. Since the hump between 10 and 20 eV was still visible, it was concluded that this feature is related to bulk and not to surface excitations. As this energy window coincides with the electron energy expected for plasmon decay ( $\omega_p \approx 15 \text{ eV}$ ) into particle-hole excitations, it is suggestive to relate this feature to the decay of volume plasmons. In order to explain the enhancement of the polarization, a spin-selective decay mode has to be invoked. We therefore introduce the plausible hypothesis that the decay of plasmons involves electrons preferentially near the Fermi edge where the intrinsic momentum distribution (Compton



Figure 3.29: Emission spectrum after impact of 90 eV (upper panel) and 500 eV (lower panel) primary electrons on Fe, separated into contributions of secondary electrons (solid lines) and backscattered primaries (dashed lines).

profile) minimizes the required momentum transfer for the decay to take place. To test our hypothesis, we have slightly increased the probability to excite secondary electrons from a narrow window  $(E_F - 0.3 \text{ eV} < E < E_F)$  around the Fermi edge when created via plasmon decay  $(\omega \approx \omega_p)$ . Assuming a fixed value of 0.7 for the probability that the plasmon decays via electron emission from this energy window, the polarization distribution is, indeed, in better agreement with the experiment (Fig. 3.28b). However, a more detailed study of the plasmon decay dynamics is required to validate this hypothesis.

## 3.2.4 Kinetic emission

The trajectory of the projectile ion penetrates the target electron gas between the jellium edge and the topmost atomic layer. The target electrons tend to shield this impurity charge inducing a screening cloud around the projectile (Fig. 3.30a). The spin polarization of the cloud depends on the polarization of the unperturbed electron gas. Due to binary collisions of the projectile with electrons of the screening cloud, part of these electrons is kinetically emitted (Fig. 3.30b).

Recently, the properties of the screening cloud have been investigated by Vincent and Juaristi [94]. Using DFT for a static impurity in a free electron gas they



Figure 3.30: Kinetic emission, schematically: a) a polarized screening cloud is induced by the impurity ion, b) electrons of the screening cloud are scattered at the induced potential of the ion.

determined the screened potential induced by  $N^{Q+}$  ions as well as the induced screening charge self-consistently including the spin-polarization of the screening cloud. In a second step the induced electron cloud was scattered at the calculated potential where a relative velocity corresponding to 150 keV kinetic energy of the ion and  $r_s = 2.12$  a.u. were assumed. This choice of  $r_s$  corresponds to an iron target if only the two 4s electrons are ascribed to the conduction band. However, in Fe the six 3d electrons also contribute to the conduction band. If  $r_s = (3/4\pi\rho)^{1/3}$ is calculated using a FEG density according to eight instead of two electrons, we obtain  $r_s = 1.335$  a.u. Using the FEG model this choice of  $r_s$  may therefore be more appropriate. However, the optimal choice for  $r_s$  is still an open question. For gold e.g., a typical choice is  $r_s \approx 1.5$  a.u. [95, 96] in order to find best agreement with experimental data. For iron  $r_s = 2.07$  a.u. has been used in other studies [96]. To study the influence of the choice of  $r_s$  on our results for kinetic emission, we have performed calculations using both limiting cases  $r_s = 2.12$  a.u. and  $r_s = 1.335$ a.u.

The input for our KE simulation was calculated by R. Vincent [97] with the above described method using a polarization of the unperturbed FEG of 45% which is the mean polarization for Fe at the topmost atomic layer. The calculation was performed for all possible electronic configurations of the N ion. The results show that, on the average, configurations with a hole in the K-shell induce an electron cloud with higher polarization than configurations with a filled K-shell. In the case of  $r_s = 1.335$  a.u.,  $\bar{\mathcal{P}} = 29.08\%$  and  $\bar{\mathcal{P}} = 23.82\%$  for configurations with and without a K-shell hole, respectively. For  $r_s = 2.12$  a.u., the difference is smaller, i.e.  $\bar{\mathcal{P}} = 49.06\%$  and  $\bar{\mathcal{P}} = 48.242\%$ . The overall higher polarization for  $r_s = 2.12$  a.u. compared to  $\bar{\mathcal{P}}$  for  $r_s = 1.335$  a.u. is a consequence of the dependence of exchange and correlation effects on the density  $\rho = (\frac{4}{3}r_s^3\pi)^{-1}$  of the electron gas. At high densities the total energy is dominated by the kinetic term. For low densities,



Figure 3.31: Upper panel: number of electrons excited per unit of time (a.u.), angle and energy by a nitrogen ion ( $E_{kin} = 150$  keV) with a K-shell hole traveling through an electron gas with  $r_s = 2.12$  a.u. and a background polarization of 45%. Lower panel: spin polarization of these electrons. The energy is measured with respect to the Fermi edge. Shown are electrons with energies exceeding the work function W = 4.7 eV.

the contributions from the exchange-correlation term become important. As spincorrelation effects favor screening by parallel spin, a higher spin polarization for the screening cloud in low-density (large  $r_s$ ) materials than in high-density (small  $r_s$ ) materials is expected [98].

Fig. 3.31 shows the probability distribution for the excitation of electrons with a certain energy and angle  $\theta$  with respect to the ion trajectory as well as their spin polarization averaged over all configurations with a K-shell hole and  $r_s =$ 2.12 a.u [97]. As electrons with energies lower than the work function W do not contribute to KE, only electrons with E > W are shown. The majority of electrons is excited in the forward direction of the projectile velocity, most of them with



Figure 3.32: Emission spectrum and mean polarization of electrons emitted due to KE for different  $r_s$  values of the target electron gas and a 150 keV nitrogen ion projectile.

 $\theta < \pi/2$ . This forward cone of emitted electrons is characteristic for the scattering of light particles (the electrons) at a massive particle (the projectile ion). The KE electrons have energies up to about 60 eV. This is consistent with the estimate  $E_{max} = 2v(v+v_F)+v_F^2/2$  for the maximum energy of an electron of velocity  $v_F$  after collision with a heavy ion with velocity v. This expression for  $E_{max}$  follows from energy and momentum conservation where the maximum final energy is achieved for a head-on collision with opposite directions of  $\vec{v}$  and  $\vec{v_F}$ .

The polarization of the excited electrons takes values between about 0.2 and 1. The prominent 100%-polarization band at the edge of the distribution is somewhat misleading as the excitation probability is very small in this  $E - \theta$ -range while the higher weighted areas show moderate polarization values. The average polarization (49.06%) is therefore comparable to the background polarization (45%).

Kinetic emission occurs when the ion moves through the electron gas of the target which we assume to extend up to the jellium edge. We therefore study KE along the

part of the ion trajectory between jellium edge and topmost atomic layer employing the Monte Carlo technique. The projectile spends approximately  $3 \cdot 10^{-15}$  s in the electron gas thereby exciting, on average, 15.4 electrons from the conduction band for  $r_s = 1.335$  a.u. and 15.6 electrons for  $r_s = 2.12$  a.u. The electrons produced by KE may undergo further scattering in the electron gas before they are emitted. The resulting secondary electron production is also determined using the method described in the previous section. The energy distribution for KE-emitted electrons obtained together with the average spin polarization is depicted in Fig. 3.32. Only about six electrons per ion originating from KE are emitted from the surface where the produced secondary electrons amount to 58%. This is not surprising given the fact that most of the KE electrons are excited in a direction parallel to the surface. They are only emitted if they are deflected in the right direction by elastic or inelastic scattering before they are stopped inside the solid. Due to their low energies this is, however, very unlikely. Consequently, the large difference in the polarization values depending on the choice of  $r_s$  will be of minor importance for the polarization of the total amount of electrons emitted during the interaction of the ion with the Fe surface where the emission spectrum is dominated by secondary electrons (see subsection 3.2.5).

## 3.2.5 Results for electron emission during grazing scattering of N<sup>6+</sup> ions from a magnetized Fe surface

Our results for the complete electron emission spectrum including PE, SE and KE are depicted in the left panel of Fig. 3.33. The division into the contributions of these three electron emission processes reveals the dominant role of potential emission. For the high-energy peak of the K-Auger electrons ( $E \sim 360 \text{ eV}$ ) this channel is essentially the only electron source except for a few secondaries on the tail of the peak towards lower energies. Our model for spin dependent PE can therefore best be tested in this energy regime. The comparison with experimental polarization data of Pfandzelter *et al.* [2] (Fig. 3.34) shows reasonable agreement. The experimental data show a slightly lower polarization than the simulation results. K-Auger processes involve low-*n* electrons ( $n \sim 2$ ) previously captured in the late neutralization process close to the surface where the potential barrier is low enough to allow resonant capture from all states of the Fermi sea. On the average, the polarization of the K-Auger electrons therefore reflects the mean polarization of the conduction band close to the surface. Using the SDOS of Fig. 3.18 yields an average polarization for the topmost atomic layer of  $\bar{\mathcal{P}} \sim 47\%$ .

The low-energy spectrum is more complex, showing additional contributions from KE and SE (Fig. 3.33). In the experiment [2] emitted electrons were only collected from a  $30^{\circ}$  (full width) cone perpendicular to the surface. In order to make a reliable comparison with their results, we consequently filter out all electrons with



Figure 3.33: Total emission spectrum together with its decomposition into electrons emitted due to PE, SE, and KE. PE includes electrons emitted towards the vacuum as well as PE electrons backscattered from the surface. SE includes secondary electrons produced due to PE and KE electrons in the target.

 $\theta > 15^{\circ}$  (measured from the surface normal). This results in a drastic reduction of the number of emitted electrons compared to a collection of all electrons. Approximately half of the PE electrons is emitted towards the vacuum ( $\theta < 90^{\circ}$ ) where only 2.1% lie inside the 30° cone. The other half is emitted towards the surface and produces secondaries in the target where every penetrating primary electron leads, on average, to the emission of 0.55 electrons from the surface. Out of these emitted electrons only 19% have emission angles below 15°. From the KE-emitted



Figure 3.34: Upper panel: spin polarization of K-Auger electrons with an emission angle below 15°: red dots: simulation, blue dots: experiment [2]. The energy spectrum is also shown (arbitrary units, lower panel): green line: simulation, dashed black line: experiment [2].

electrons (including the subsequently produced secondaries) about 25% are emitted with  $\theta < 15^{\circ}$  which might seem to be a surprisingly high fraction given the fact that KE electrons are predominantly emitted in forward direction of the projectile, i.e. nearly parallel to the surface. However, prior to emission they have to cross the surface potential barrier which is only allowed for  $E_{\perp} > W$  where  $E_{\perp} = E \cos^2 \theta$ is the normal energy (perpendicular to the surface) of the electron. This condition filters out the electrons with  $\theta \sim 90^{\circ}$  (i.e. moving nearly parallel to the surface) already upon passage through the surface. They have too small normal energies to overcome the surface barrier. Consequently, the weight of KE-electrons *emitted* with low angles (with respect to the surface normal) is increased compared to the weight of low-angle KE-electrons *excited* below the surface.

Taking only electrons emitted in the 30° cone changes the weight of the different emission channels (Fig. 3.33). The main contribution to the emission spectrum for  $\theta < 15^{\circ}$  comes from secondary electrons originating from the SE cascade initiated by PE as well as KE electrons in the target. The average spin polarization of the emitted electrons is therefore dominated by the the SE polarization. KE and PE electrons contribute to the average polarization with lower weights according to their contributions to the emission spectrum. Compared to the spectrum including electrons with all emission angles, the importance of PE-emitted electrons is considerably reduced after filtering out electrons with  $\theta > 15^{\circ}$ .



Figure 3.35: Polarization of electrons emitted during grazing scattering of N<sup>6+</sup> ions from magnetized Fe. Blue dots: experiment [2], red dots: simulation results using an  $r_s = 2.12$  for KE, green squares: simulation results using an  $r_s = 1.3352$  for KE.

Our simulation results for the energy-resolved polarization for low emission energies are depicted in Fig. 3.35 where results for both  $r_s = 1.335$  and  $r_s = 2.12$  (see subsection 3.2.4) used for KE are shown. For capture of PE electrons, the z-dependent SDOS was used. To study the dependence of the polarization results on the SDOS input used for the simulation, we also performed calculations using exclusively the SDOS at the topmost atomic layer [73]. The difference in the polarization of PE-emitted electrons was at most a few percent so that the influence on the average polarization of all electrons was practically negligible.

PE-electrons emitted with low energies predominantly originate from level promotion to the vacuum and high-*n* AI. In both cases, the electrons have been captured in the early neutralization process prior to emission. At that point, the barrier has been lowered slightly below the Fermi edge so that these electrons reflect the mean spin polarization around  $E_F$ . A close look at the corresponding SDOS for the surface (Fig. 3.18) explains the low polarization results: although the energyaveraged polarization for the surface SDOS is highly positive (~ 47%), for energies around  $E_F$  the polarization is reversed. While majority states still dominate over minority states in the bulk SDOS near  $E_F$ , the corresponding SDOS at the topmost layer has even negative polarization. This results in very small polarization values for low-energy PE electrons. Here, for resonant capture the SDOS at the resonance energy at the distance of the potential saddle was used to determine the spin of the captured electron. To study the sensitivity of the polarization results to variations of the saddle distance and hight, we artifically decreased the barrier hight by a few eV which led to a PE-polarization increase of at most 5%. A displacement of the saddle to smaller or larger distances to the surface by  $\pm 2$  a.u. also changed the results for PE by only a few percent.

A comparison of our polarization values with experimental data [2] in Fig. 3.35 shows, as opposed to the high-energy results, a large discrepancy between theory and experiment. The question arises if the origin of this difference in polarization results stems from problems of the theoretical model or from the experiment. From the theoretical side, the contribution of secondary electrons has been successfully tested independently from all other processes yielding good agreement with experimental data (see subsection 3.2.3). Possible uncertainties may therefore only results from KE or PE. However, for these two processes, our results strongly depend on the external input, i.e. the SDOS at and above the surface and the mean polarization of the conduction band (also following from the SDOS). Recent DFT calculations of Ernst [99] showed that small deviations in the structural relaxation of the topmost Fe layers lead to a drastic change in the SDOS near the Fermi edge and consequently in the corresponding polarization. While for the SDOS used in the present work [73] the structural relaxation of the first atomic Fe layers was determined from the DFT calculation, the distance between the first layers was taken in the new calculations of Ernst [99] from experimental measurements. Using the same method large spin effects found in Fe/MgO/Fe tunnel junctions could be explained by the corresponding SDOS [100]. While the energy-averaged polarization at the surface is the same as in the calculations used in the present work (about 47%), the polarization at the Fermi level is drastically altered. A comparison of the results for the polarization at and close to  $E_F$  as a function of the distance z to the surface (Fig. 3.36) shows that the calculations using experimental values for the separation of the atomic layers yield a strongly negative polarization around  $E_F$ . For the polarization of emitted low-energy electrons this would imply even smaller values than our present results causing even larger discrepancies with the experiment [2].

Experimental studies on the magnetic properties of iron surfaces by Hammond et al. [68] also indicate a negative polarization above the surface. There, electronspin-polarized He( $2^3S$ ) metastable atoms were scattered at a magnetized Fe(110) surface. The asymmetry between the ejected-electron currents observed with the incident He beam polarized parallel and antiparallel to the majority-spin direction of the target was measured. From the positive asymmetry obtained a negative polarization of the target electrons was derived [68]. As opposed to that, typical spin polarization results from electron capture spectroscopy where (unpolarized) positive ions are scattered under grazing incidence from Fe surfaces yield positive values. While in another work by Pfandzelter *et al.* [101] electrons emitted after scattering of singly charged ions on Fe(100) show polarization values of 25 – 65%,



from scattering of D<sup>+</sup> ions from an fcc  $\gamma$ -Fe(111)p(1×1) film polarization values of 11 – 16% were obtained [66]. The same range of polarization values was found for an Fe(110) surface derived from polarization measurement of emitted light after scattering of singly charged ions. Multiple electron capture spectroscopy on Fe(110) using He<sup>2+</sup> projectiles yielded a surface polarization of about 40% [102] derived from the KLL-Auger spectra of emitted electrons.

Another measurement of the spin polarization of ion-excited secondary electrons from Fe(110) by Kirschner *et al.* [103] showed average polarization values of emitted electrons of about 15 - 30% where the polarization was found to decrease with decreasing ion energy. As the ratio of kinetic and secondary electron yields to the potential emission yield increase with increasing projectile energy, the experimental results indicate that secondary electrons have a larger polarization than PE electrons as was found in the present work. Due to an impact angle of about  $45^{\circ}$  in the experiment, KE is not as surface sensitive as in grazing incidence measurements so that it also represents the positive polarization of the bulk. In the low-energy regime where PE dominates over SE, the polarization was reduced to about 15%[103]. Hence, the polarization decreases with increasing weight of PE electrons indicating that they have a very low or even negative spin polarization.

The large variety of polarization values found shows that a precise tool to measure the energy-dependent spin density at and above the surface has still to be established. As opposed to that, bulk properties are successfully probed by photoemission experiments which are, however, not surface-sensitive. An estimate for the validity of the SDOS inputs used in our calculations by comparison with experimental results is therefore not possible at the present.

The extremely high polarization values found by Pfandzelter *et al.* [2, 101] may suggest that the electron capture process is k-vector selective as the polarization differs for different k of the target electrons [104]. However, H. Schröder [105] showed that although capture of electrons with  $\vec{k}$  in a forward cone of the projectile is preferred, the  $\vec{k}$ -dependence is still very weak. We therefore conclude that the  $\vec{k}$ -averaged approach used in this work is appropriate. A noticeable effect of  $\vec{k}$ -selectivity would only occur if (i) there was a sharp maximum in the capture probability and (ii) the electrons with the k-values corresponding to this maximum had a polarization of about 100%. Then the spin polarization of PE electrons would be about 100% leading to such a high average polarization of emitted electrons as found in the experiment [2].

As it is experimentally very challenging to prepare a clean Fe surface as well as to keep it clean, it may be possible that the surface used in experiment was contaminated by oxygen adsorption. However, in electron spectroscopy [64] it was found that oxygen exposure leads to a reduction of the spin polarization of emitted electrons. In the limit of a magnetite (Fe<sub>3</sub>O<sub>4</sub>) surface, the predicted polarization at the Fermi level is again negative,  $\mathcal{P}_{E_F} \approx -40\%$  [106] at the surface while the bulk value is even -100% [107]. Oxygen exposure of the target can therefore be ruled out to be responsible for the high positive polarization of emitted electrons. In addition to oxygen contamination, steps in the Fe surface are a candidate for altering the electron spin polarization. However, a quantitative estimate for the influence on  $\mathcal{P}$ is not available at this point.

In summary, the discrepancy between theory and experiment for the low-energy emitted electrons (Fig. 3.35) is not well understood. There may be additional effects occurring during the interaction of ions with surfaces not accounted for in our model. One possibility would be a clear difference between the ion-electron scattering cross section (KE) for target *s*-electrons and *d*-electrons. This would lead to a change in the polarization of emitted electrons if *s*- and *d*- electrons had different spin polarizations. However, again, the difference would have to be extremely large, i.e. about 100% polarization of the dominant channel with the other channel being negligible. Only in this case, a clear increase of the average polarization data for low energies would occur.

## 4 Summary

Using classical as well as quantum methods we study ion-surface interaction thereby addressing several open questions in the field. One of them concerns the formation of trions near an LiF surface. These are quasi-molecular Coulomb complexes consisting of two holes and an excited electron. Their existence was invoked in the interpretation of recent experiments [11] where Ne<sup>+</sup> ions were scattered at an LiF surface under a grazing angle of incidence. The neutralization of Ne<sup>+</sup> not accompanied by electron emission was explained in terms of an Auger process where one surface electron is captured into a low projectile level while another surface electron is excited to a bound state within the band gap. Consequently, the excited state induced at the surface is given by two holes binding an excited electron. In the present work we confirm that such a trion indeed constitutes a bound excited state. We determine binding and excitation energies for trions in LiF by multiconfiguration self consistent field (MCSCF) calculations on embedded LiF clusters. The estimates for the excitation energies  $E_{exc}$  derived from experiment agree well with  $E_{exc} \sim 12$  eV obtained from the quantum calculations. Studying the pair correlation function of the two holes we find that the three charges of the trion form a collinear quasi-molecule in the surface with the excited electron located around a lithium ion and the holes at adjacent fluorine ions, i.e. at next-to nearest neighbor fluorine sites. Test calculations using additional basis functions located above the surface indicate that a trion configuration with the electron protruding into the vacuum may also be possible. Further studies on this subject are planned for the future.

In recent stopping power experiments on LiF using proton and antiproton projectiles it was found that the stopping power is approximately proportional to the projectile velocity v, even for relatively low energies. This was surprising given the fact that the v-proportionality is typical for metals and can be derived from free-electron gas models. A deviation from this behavior was assumed to occur for insulators at low energies due to the band gap  $E_g$  between the valence band and the conduction band. We study the influence of p and  $\bar{p}$  projectiles on the band structure of LiF using the embedded cluster approach. We perform self-consistent field as well as MCSCF calculations to include important correlation effects. While for a proton projectile a moderate reduction of the band gap is found, the influence of an antiproton on the valence band is rather dramatic. The energy threshold for excitation of an electron, when an antiproton is near an F<sup>-</sup> ion, is reduced to only 0.44 eV. Consequently, future experiments on the threshold for metallic behavior should be performed with projectile energies in the few-hundred eV range.

In the field of ion-surface collisions one topic under discussion in the last decade was the "trampoline effect" for insulator targets, i.e. the possible reflection of a slow highly charged ion approaching a surface by the repulsive force of the holes produced in the surface. Previous simulations of ion impact on LiF with projectile charge states up to Q = 10 showed that such a trampoline effect does not occur [12]. We extend the method employed there based on the classical over barrier model for insulators and study the impact of highly charged ions up to Q = 36. For all investigated initial charge states the trampoline effect is absent. The repulsive force of the holes is not strong enough to overcome the image acceleration of the ion towards the surface.

Motivated by a surprisingly high spin polarization of emitted electrons found during scattering of  $N^{6+}$  ions at a magnetized iron surface [2], we simulate this scenario using classical Monte Carlo methods. We study potential electron emission (PE) along the whole ion trajectory taking into account spin dependent electron transfer. The resulting spin polarization of K-Auger electrons emitted with high energies shows good agreement with the experimental data. The low-energy electron spectrum consists, in addition to PE electrons, of electrons emitted due to kinetic emission as well as secondary electrons produced in the target. All these emission channels are simulated including spin dependent scattering and exchange effects. Our model for the secondary electron cascade has been successfully tested independently by comparison with electron spectroscopy experiments [64]. Our results for the spin polarization of low-energy electrons emitted during scattering of N<sup>6+</sup> at magnetized Fe show a much smaller average polarization than the experimental data. Possible reasons for this discrepancy are discussed in detail where problems in the experiment cannot be ruled out. Our results should stimulate further surface sensitive experiments on magnetized iron to clarify open questions concerning the spin density above the surface.

# A Resonant Capture and Loss Rates for High Charge States

The resonant capture and loss rates for the interaction of an HCI with an LiF surface are given by  $\Gamma^{\alpha} = P_{max}^{\alpha} \gamma^{\alpha}$  with  $\alpha = c$  for capture and  $\alpha = l$  for loss. The quantities  $P_{max}^{\alpha}$  and  $\gamma^{\alpha}$  depend on four parameters (Sec. 3.1.3): the effective projectile charge,  $Q_{eff}$ , the ion-surface distance,  $R_z$ , the lattice zone,  $\vec{a}$ , and the number of holes,  $n_e$ . For  $Q \leq 18$ ,  $P_{max}^{\alpha}$  and  $\gamma^{\alpha}$  have been determined by CTMC calculations. These tabulated data have been fitted by (positive definite) analytic functions allowing the extrapolation of the dependence of the quantities  $P_{max}^{\alpha}$  and  $\gamma^{\alpha}$  on  $Q_{eff}$  and  $R_z$  for given  $\vec{a}$  and  $n_e$  to higher charge states.

Functional forms could be found depending on at most three free parameters  $(a_i, b_i, c_i)$  for given  $\vec{a}$  and  $n_e$  (we suppress the subscript " $_{eff}$ " for the effective charge in the following).

For electron capture the functional form

$$f_1(R_z, Q) = \max\{1 - \exp(-a_1 Q^{1/2} + b_1 R_z - c_1), 0\}$$
(A.1)

is used for  $P_{max}^c$  for all zones  $\vec{a}$  while  $\gamma^c$  is fitted by

$$f_2(R_z, Q) = \max\{a_2 + b_2 Q / (1 + c_2 R_z), 0\}$$
(A.2)

when the electron is captured from zone (0,0) and by

$$f_3(R_z, Q) = \max\{a_3Q + b_3R_z + c_3, 0\}$$
(A.3)

otherwise. As an example we have plotted in Fig. A.1 the Q and  $R_z$  dependence of the quantity  $P_{max}^c$  for the capture of an electron from zone (0,0) when the surface is still free of holes. The fit function is also shown which in this case has the functional form  $f_1$  (Eq. A.1) with  $a_1 = 1.37$ ,  $b_1 = 0.33$ ,  $c_1 = 0.3$ .

Although the parameters  $a_i$ ,  $b_i$ , and  $c_i$  vary with the zones and number of holes, in all cases  $a_2 \ll b_2$  and  $b_2$  is typically smaller than  $c_2$  by about a factor of ten. Consequently, the capture rate obtained by  $\Gamma^c = \gamma^c P_{max}^c$  is for zone (0,0) dominated by the term  $b_2Q/(1+c_2R_z)$  scaling approximately linearly with the effective charge Q. The same holds for the other zones where  $\Gamma^c$  is again dominated by the linear term  $a_3Q$ . This approximately linear dependence of the capture rate on the effective charge of the projectile was also found in the original COB model for metal targets



Figure A.1: The parameter  $P_{max}^c$  determining the resonant transfer rate for first electron capture from the (0,0)-zone as a function of the ion charge state  $Q_{eff}$  and ionsurface distance  $R_z$ . Red: values calculated by the CTMC method, green: fit to these data.

[5]. The capture rates increase with decreasing hight of the barrier and, equivalently, with decreasing distance  $R_z$ . This holds for both metal and insulator targets. However, while the dependence of  $\Gamma^c$  on  $R_z$  in the original COB model is dominated by a negative term in  $R_z^2$ , we found  $\Gamma^c$  to scale approximately with  $R_z^{-1}$  for the (0,0) zone. For the other zones where  $\Gamma^c = \gamma^c P_{max}^c = f_1(R_z, Q) f_3(R_z, Q)$ , all terms in  $R_z$  contribute as the parameters  $a_3$  and  $b_3$  are of the same order of magnitude with  $b_3 < 0$ .

The functional forms of the fits to  $P_{max}^l$  for the loss rates vary with lattice zone and depend, in addition, on the charge of the surface hole. The tabulated loss rate parameters show stronger fluctuations compared to the parameters for the capture rates which are characterized by an overall monotonic behavior. A two-dimensional fit of the loss rate parameters is therefore more difficult than for capture rates and the error due to the approximation of the data by the fit functions may be larger. However, as the loss rates are typically smaller than the capture rates by an order of magnitude, the simulation results for the neutralization sequence are rather sensitive to changes in the capture rates while the influence of the loss rates is comparably small.

Depending on the number of holes  $n_e$ , the loss parameters  $P_{max}^l$  for the (0,0) zone are described by different functions:

For  $n_e = 0$  and  $n_e = 1$ , the parameter  $P_{max}^l$  can be described by

$$f_4(R_z, Q) = \max\{a_4 + b_4/(1 + c_4 R_z), 0\}.$$
 (A.4)

For  $n_e = 2$  and  $n_e = 3$ , the parameter  $P_{max}^l$  can be fitted by a linear function such as  $f_3$  (Eq. A.3) and for  $4 \le n_e \le 7$  the fit function for  $P_{max}^l$  is given by

$$f_5(R_z, Q) = \max\{(a_5 - b_5 Q)/R_z - c_5, 0\}.$$
 (A.5)

In the (1,1) zone  $P_{max}^l$  for the loss rate is fitted by

$$f_6(R_z, Q) = \max\{1 - \exp(-a_6Q) + b_6R_z + c_6, 0\}$$
(A.6)

if  $n_e = 0$  or  $n_e = 2$ . For all other numbers of holes  $(n_e = 1 \text{ and } n_e = 3 - 7) P_{max}^l$ can be fitted by a linear function such as  $f_3$  (Eq. A.3). The same applies for  $P_{max}^l$ for the (2,0) zone. The functional form describing  $P_{max}^l$  for the (2,2) zone is given by

$$f_7(R_z, Q) = \max\{0.5 - \exp(-a_7Q + b_7) + c_7R_z, 0\}$$
(A.7)

if  $n_e = 0$  and for  $n_e > 0$  by a linear function  $(f_3, \text{Eq. A.3})$ .

All parameters  $\gamma^l$  for the loss rates can be approximated by a linear fit function such as  $f_3$  (Eq. A.3). By analyzing the fit parameters  $a_i$ ,  $b_i$ , and  $c_i$  we have found that, typically, the terms linear in Q dominate the loss rates with additional contributions from quadratic terms. This stronger than linear increase of the loss rates is again in accordance with the original COB model where  $\Gamma^l$  approximately scales as  $Q^{3/2}$ . The  $R_z$  dependence of the loss rate in the original COB model is given by an approximately linear increase with decreasing  $R_z$ . Also for insulator targets, we find increasing loss rates with decreasing distance to the surface. However, the analysis of the parameters  $a_i$ ,  $b_i$ , and  $c_i$  has shown that the  $R_z$  dependence is more complicated than for metal targets as all terms in  $R_z$  contribute to the loss rate.

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