Ab-initio calculations of charge exchange in ion-surface collisions: an embedded-cluster approach

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Abstract
We discuss the feasibility of the embedded cluster approach for ab-initio calculations of charge exchange between ions and a LiF surface. We show that the discrete density of valence states in embedded clusters converges towards the continuum limit of the density of states in the valence band of an infinitely extended LiF surface. Screening of the holes that are left in the surface after electron transfer to the projectile plays an important role for the correct level ordering in the calculation of potential energy surfaces. We discuss to which extent the hole screening is taken into account by different levels of approximations which are customarily employed in quantum chemistry. The central result of the paper is the convergence of potential energy curves with respect to cluster size: Out of the increasing number of potential energy curves (converging towards a continuum for infinite cluster size), only a small number of states effectively interacts with the capture level of the projectile and determines the charge transfer efficiency.

1.1 Introduction
Charge exchange plays a major role in collision of ions with surfaces. An observable readily accessible in experiments is the final charge state of an ion after scattering at the surface. Also for the description of other experimentally observable quantities, a detailed knowledge of the charge transfer dynamics is desirable: For example, the instantaneous charge state of the projectile determines the interaction potential with the surface and thereby influences the projectile trajectory, i.e. the energy and the angle of backscattered ions. Furthermore, in insulators with strong electron-phonon coupling, electron transfer to the projectile can lead to formation of self-trapped defects (electron holes, excitons) which, in turn, can result in the
ablation of secondary particles from the surface \[1\].

Despite the importance of charge transfer for virtually all phenomena involving ion-surface collision, an accurate \textit{ab-initio} treatment is still missing. This is, of course, due to the complexity of the problem. In particular, in the case of insulator surfaces, where the description of the surface in terms of the jellium model (assuming a homogeneous positive background charge instead of localized atomic cores) is not suitable, the dynamics of a many-nuclei and many-electron system must be explicitly treated. The interaction of (discrete) projectile states with the continuum of states in the surface valence band entails both the properties of the infinitely extended surface and the localized projectile state. The former is usually achieved by using Bloch wavefunctions and describing the system in a supercell (consisting of a two-dimensional unit cell parallel to the surface and a large slab of bulk and vacuum in perpendicular direction). In contrast, the localized interaction of the projectile ion with one or several atoms of the surface is more appropriately described by the methods of ion-atom/ion-molecule collision. There are two possibilities to combine both approaches: One possibility would be to treat the ion-surface collision in a supercell. However, apart of the exceedingly large size of the supercell, additional difficulties would arise due to the positive net charge of the projectile. The long-range Coulomb potential of the periodically repeated positive projectile would have to be artificially screened in order not to affect neighboring unit cells and a negative background charge would have to be introduced in order to render the supercell neutral. Alternatively, in the approach pursued in the following we choose the second option which is the calculation of a projectile-collision with a cluster of surface ions embedded into a large array of point charges that represents the residual (infinitely extended) surface and bulk.

In order to render the embedded-cluster approach valuable for the description of the interaction of the projectile with an infinitely extended surface, several criteria have to be met:

1. The (discrete) density of states of the embedded cluster should - in the limit of large cluster size - approach the continuum limit of the density of states of the infinite system.

2. The ionization energy of the embedded cluster should agree with the workfunction of the surface. This point is important for the proper energetic ordering of the projectile state relative to the valence band. This is a highly non-trivial requirement as the Hartree-Fock theory is well-known to overestimate the band gap of insulators by up to several eV while density functional theory (DFT) underestimates it by about the same amount \[2\]. The proper treatment of electron correlations is therefore indispensable. The main effect of correlation in the current context is the screening of the hole that is left behind in the surface when an electron leaves the surface. This screening, i.e., the polarization of the environment, reduces the interaction of the hole with the emitted electron and reduces the ionization energy by up to several eV with respect to the value obtained by the Hartree-Fock approximation.

3. The potential energy curves that determine the charge exchange between projectile and surface must have converged as a function of cluster size.

Requirement (1) is analyzed in section \[1,2\] where we compare the density of states (DOS) in the limit of large cluster size with the DOS obtained by a supercell calculation. Fulfilling the second criterion requires obviously a methodology that goes well beyond both Hartree-Fock theory and ground-state DFT. In section \[1,3\] we summarize our approach \[3\] which is based on...
1.2 Convergence of the density of states as a function of cluster size

We present in this section a systematic study of the convergence of the density of states (DOS) of the valence electrons in a (bulk) embedded cluster of LiF towards the DOS of the infinitely extended system. We have performed Hartree-Fock (also referred to as self consistent field, SCF) calculations for cubic clusters containing from $1^3$ (single embedded $F^-$) up to $5^3$ atoms \cite{7}. In order to simulate the Madelung potential of the residual infinite crystal, the active clusters are embedded in a cubic array of negative and positive point charges at the positions of the $F^-$ and $Li^+$ ions, respectively \cite{10}.

Table 1.1 shows the clusters for which we have performed calculations. The positive point charges at the border between active cluster and surrounding point charges are replaced by active Li$^+$ ions such that all active fluorines are fully coordinated by six lithium atoms. This prevents an artificial distortion of the electron density at the border of the active cluster due to missing Pauli repulsion from the positive point charges.

In Fig. 1.1 a) we present the orbital energies of the highest and lowest $F_{2p}$-like orbitals (valence orbitals) of the clusters listed in Table 1.1. The three $F_{2p}$ orbitals of the embedded Li$^+_5F^-$ cluster are degenerate at an orbital energy of -15.5 eV. The transition to the next larger cluster with four $F^-$ ions introduces a splitting of almost 1.5 eV. With increasing size, the band width increases more slowly and converges towards a value of 3.5 eV as can be seen

| size | cluster                  | cluster with coordinated ions |
|------|--------------------------|-------------------------------|
| $1^3$| $F$                      | $Li_5F$                       |
| $2^3$| $Li_4F_4$                | $Li_{16}F_4$                  |
| $3^3$| $Li_{14}F_{13}/Li_{13}F_{14}$ | $Li_{38}F_{13}/Li_{43}F_{14}$ |
| $4^3$| $Li_{32}F_{32}$          | $Li_{80}F_{32}$               |
| $5^3$| $Li_{63}F_{62}/Li_{62}F_{63}$ | $Li_{135}F_{62}/Li_{146}F_{63}$ |

Table 1.1: Clusters used in the convergence study of the valence DOS. For clusters with odd ion number we calculate both the case with a fluorine in the center and with a lithium in the center.
Figure 1.1: a) Orbital energy of highest and lowest $F_2p$-like orbital as a function of the number of $F^-$ contained in the cluster. b) Average density of $F_2p$ states in the $Li_{135}^+F_{62}^-$ and $Li_{146}^+F_{63}^-$ clusters. Each discrete state is represented by a Gaussian peak with a full width at half maximum of 0.4 eV. c) DOS of infinite LiF calculated with DFT-LDA in a periodic supercell approach.

by plotting the band width as a function of the inverse linear dimension of the cluster [3]. This value agrees with the value obtained by photoelectron spectroscopy [11] and with quasiparticle band-structure calculations [12]. Panel b) of Fig. 1.1 shows the average of the (orbital energy) DOS of the embedded $Li_{135}^+F_{62}^-$ and $Li_{146}^+F_{63}^-$ clusters [13]. In addition to the main peak at -15.2 eV, the DOS displays a side peak at -16.8 eV. This secondary peak is also seen in the experiment [11]. We compare the cluster DOS of panel b) with the DOS of an infinitely extended LiF crystal in panel c) for which the calculation [14, 15] has been performed using density functional theory (DFT) in the local density approximation (LDA). The good agreement leads us to conclude that, in the limit of large clusters, the embedded cluster approach does indeed reproduce bulk quantities.

1.3 Going beyond Hartree-Fock

According to Koopmans’ theorem, the energy of the highest occupied molecular orbital (HOMO) should be a good approximation to the ionization energy of the system, i.e. the work function of the infinitely extended surface. The experimental work function has a value of about $W_{LiF} = 12.3$ eV [16] which is smaller by more than 2 eV than the value of the HOMO energy (Fig. 1.1) extrapolated to infinite cluster size. Increasing basis set would lower the orbital energies by an additional eV upon convergence with respect to basis set size and render the discrepancy between experimental value and the HOMO energy even larger. This discrepancy is not a failure of the embedded cluster approach but a failure of the Hartree-Fock method and is in line with the overestimate of the band gap of insulators by up to several eV [17, 2]. The underlying reason is the neglect of screening of a hole left behind in the surface after ionization. The screening, i.e., the polarization of the environment, reduces the interaction of the hole with the emitted electron and thereby lowers the ionization energy. Screening cannot be properly described in a quasi-one particle picture underlying the Hartree-Fock approximation.
Instead, methods that go beyond Hartree-Fock and include many-body effects are required.

Beyond the level of a mean-field approximation, the picture of orbital energies which is frequently invoked in the description of charge exchange phenomena and which is intrinsically connected to the one-particle picture, looses its meaning. Let us consider, e.g., the case of a $\text{H}^+$ ion colliding with a LiF surface as depicted schematically in Fig. 1.2 a. The valence band extends from $W_{\text{LiF}} = -12.3$ eV down to about -15.8 eV. The lowest projectile level into which an electron can be captured is the ground state of hydrogen at -13.6 eV which is thus, at large projectile-surface distance, energetically positioned inside the valence band. Therefore, a strong interaction of this “capture level” with the valence band of LiF is expected facilitating charge exchange at small ion-surface distances. However, since on the Hartree-Fock level the top of the valence band lies too low by 2-3 eV, the capture level lies well above the valence band during the approach to the LiF surface and charge exchange is suppressed at this level of description [3]. The proper level ordering in the combined ion-surface system is thus directly determined by the value of the work function of the system and requires the use of methods going beyond the Hartree Fock approximation. In turn, the concept of orbital energies which is related to the effective one-particle character of Hartree-Fock theory (or similarly, DFT) is no longer well-defined. The appropriate framework to describe charge exchange is therefore the calculation of total potential energy surfaces along ionic trajectories, i.e., the energies of ground and excited states of the system comprising the embedded cluster and the projectile ion with the position of the projectile as an adiabatic parameter. One of these N-electron states, the “ionic” state, corresponds at large distances $R \to \infty$ to the neutral surface with the positive ion in front while all the other states correspond to the projectile in a neutralized state with a hole left behind in the surface (see Fig. 1.2 b). Inclusion of correlation effects allows for a proper calculation of the work function of LiF and leads to a correct ordering of the total
energies of ionic and covalent states of the combined projectile-surface system.

Our numerical approach has been described in detail in Ref. [3]. Here, we just give a brief summary of the method. We employ the quantum chemistry code COLUMBUS which is specifically designed for the calculation of ground and excited states through multi-reference and multi-configuration methods. The first step beyond Hartree-Fock or the single Slater-determinant self consistent field (SCF) method is the multi-configuration self-consistent field (MCSCF) method [18] which expands the many-electron wave function in different configurations. An active space is chosen which comprises the F2p-like orbitals of the cluster and the projectile orbital(s) into which an electron can be transferred. All the orbitals of the active space can be unoccupied, singly, or doubly occupied. The occupation numbers define the different configurations of the system. One of these configurations has ionic character (positively charged projectile and all band-states doubly occupied) while all other configurations have covalent character (projectile neutralized and a hole in the surface). The MCSCF method solves self-consistently both for the orbital wavefunctions and the expansion coefficients at the same time. In a state-averaged calculation both the ground state (which is dominated by either the ionic or one of the covalent configurations) and several excited states are calculated simultaneously. The MCSCF method thus accounts - at least on a qualitative level - for the interaction between different electronic configurations. However, quantitatively correct results can only be achieved if also the energetic ordering of the levels for large projectile distance is properly described. As explained above, the latter requires the inclusion of hole screening. This, in turn, requires the inclusion of a prohibitively large number of configurations. Therefore, the energetic ordering of the ionic and covalent states may still be incorrect on the MCSCF level, as is the case for the system of H+ colliding with a LiF surface (see Fig. 1.3 a below).

The description of screening effects can at least partially be achieved by a multi-reference configuration interaction (MR-CI) method. The many-electron wave function is expanded in terms of a number of excitations of reference configurations (customarily the configurations from the preceding MCSCF run). The expansion coefficients yielding the lowest energy are then determined while the orbital wavefunctions are kept constant. This allows the inclusion of many more configurations than in the MCSCF calculation. Through the virtual excitation of electrons into intermediate states, correlation of electrons within the active cluster is taken into account. However, only single and double excitations are included in the expansion - as the inclusion of higher excitations becomes computationally prohibitive for big systems. As a consequence, for larger clusters, the MR-CI method suffers strongly from the violation of size consistency, i.e. the correlation energy does not scale linearly with the number of atoms since only single and double excitations are taken into account. One may go beyond the MR-CI method by employing methods that account for size-consistency on an approximate level: the extended Davidson correction [19, 20], Møller-Plesset perturbation theory (MRPT), or the multi-reference averaged quadratic coupled cluster method (MR-AQCC) [21].

We have tested the different quantum chemistry approaches for the calculation of potential energy surfaces and demonstrated that proper inclusion of correlation (i.e. screening of the holes) leads indeed to a proper energetic ordering of the levels of the system H+ → LiF [3]. The results of our calculations are summarized in Fig. 1.3 where we present the potential energy curves for H+ in vertical incidence on top of the central Li+ ion of an embedded Li26 F9− cluster [22]. On the MCSCF level (Fig. 1.3 a), the lowest-lying state in energy corresponds at all distances to the ionic configuration. In the orbital energy picture this would mean that
1.3 Going beyond Hartree-Fock

Figure 1.3: Potential energy curves for H\(^+\) approaching an embedded Li\(_{20}\)F\(_9\) cluster (vertical incidence, touch-down on Li site). Comparison of different levels of approximation: a) MCSCF, b) MR-CISD, c) MR-CISD with Davidson correction, d) MR-AQCC, e) MRPT2, f) MRPT3. The absolute energy scale is chosen such that the energy of the ionic state at large distance is 0. The dashed line indicates the diabatic energy curve corresponding to the ionic configuration.

the capture level of H\(^+\) lies above the valence band edge. As pointed out above, this wrong level ordering is due to the nearly complete neglect of screening effects on the MCSCF level. On the MR-CI level with single and double excitations (MR-CISD, Fig. 1.3 b), screening of the holes leads to a lowering of the binding energy of all covalent states (i.e. of all states where a hole is left behind in the surface) by 0.75 eV with respect to the ionic state. The shift due to the correlation energy leads to avoided crossings between the ionic entrance channel and some of the covalent states representing the exit channel. The dashed line indicates the diabatic energy curve of the ionic state which crosses several of the covalent curves. Since in large clusters the correlation energy is often underestimated, we also apply the Davidson correction \([19][20]\) to approximately correct for size consistency. The Davidson correction affects the covalent states more than the ionic state and leads to an additional downward shift in energy of the covalent states at large distance by 0.25 eV (Fig. 1.3 c). The ionic state is
now clearly embedded into the “band” of covalent states. The energetic difference between
the asymptotic ionic and lowest covalent level is 0.5 eV compared to the experimental value
of 1.3 eV. A calculation on the MR-AQCC level (Fig. 1.3 d) yields an even stronger asymptotic
lowering of the covalent states. The resulting asymptotic energy difference between the
lowest covalent and the ionic level is 0.63 eV and confirms the expectation that methods con-
taining size consistency corrections such as AQCC should yield converged potential energy
curves for charge exchange, provided that a calculation with larger cluster size and basis set
becomes numerically feasible with further advances in computing power. For completeness,
we present in Fig. 1.3 e) and f) calculations of the potential energy curves with Möller-Plesset
perturbation theory to second order (MRPT2) and to third order (MRPT3). While MRPT2
leads to a considerable downward shift of the covalent levels by 1.8 eV, MRPT3 cancels this
shift to a large extent and leads to a result similar to that of the MRCI-SD approximation.
The large difference between MRPT2 and MRPT3 indicates that the perturbation series only
slowly converges and higher order corrections should be taken into account. We presume that
higher orders will lead again to a downward shift of the covalent levels and will eventually
converge towards the result obtained by other methods such as the MR-AQCC method.

The screening effect is enhanced when larger active clusters are used but converges only
slowly with cluster size since screening due to polarization of the environment is a long-range
effect. It would therefore be desirable to combine the accurate, but computationally very de-
manding description of a small active cluster in the region around the point of projectile impact
with a somewhat “cheaper” description of the larger environment which mainly contributes
only through its polarizability. This leads us to the question which will be treated in the next
section: if we describe the environment of the active cluster by static point charges and/or
by a polarizable environment, how large must the active cluster itself be in order to properly
describe the interaction of the projectile with the band structure.

1.4 Convergence of potential energy curves as function of
cluster size

Due to the computational complexity of methods that properly describe screening which are
still prohibitively expensive for larger clusters we have performed a convergence study of
the embedded cluster method as a function of cluster size on the MCSCF level. This allows
us to include a large number of reference configurations in order to explore the continuum
limit of the valence states. Since the MCSCF method suffers - in principle - from a wrong
level ordering for our sample system $H^+ \rightarrow LiF$, we can artificially enforce the correct level
ordering by choosing a very small basis for the $F^-$ ions. The additional benefit of this
small basis is that we can include large active clusters in our study. The embedded clusters of
our study are shown in Fig. 1.4. They range from a cluster containing only one active $F^-$ up to
a cluster with 13 active $F^-$ in the topmost atomic layer. The active clusters are surrounded by
an array of point charges such that the total system (active cluster and point charges together)
consists of 196 ($7 \times 7 \times 4$) force centers. This renders the system neutral and reproduces the
Madelung potential for an electron at the center site in the surface with sufficient accuracy.

As a first test we calculate the ionization potentials of different embedded clusters in the
1.4 Convergence of potential energy curves as function of cluster size

absence of the \( H^+ \) projectile through the energy difference \( \Delta E \) between the total energy of the neutral systems and of the ionized systems \cite{25}:

\[
\begin{align*}
\text{Li}_5^+ \text{F}^- & : \Delta E = 9.61 \text{ eV} \\
\text{Li}_{10}^+ \text{F}_5^- & : \Delta E = 10.64 \text{ eV} \\
\text{Li}_{25}^+ \text{F}_9^- & : \Delta E = 10.65 \text{ eV} \\
\text{Li}_{37}^+ \text{F}_{13}^- & : \Delta E = 10.82 \text{ eV}
\end{align*}
\]

In all cases, the ionization potential remains smaller than the ionization potential of hydrogen (13.6 eV). This corresponds to a correct level ordering in the presence of the projectile, i.e., the ionic state is higher in energy than the lowest covalent state. The correct level ordering is a prerequisite for performing a convergence study with respect to cluster size on the MCSCF level.\(^1\)

Fig. 1.4 presents potential energy curves for the ionic and the covalent states of an \( H^+ \) ion impinging on clusters containing an increasing number of active \( F^- \) ions in the topmost surface layers. All \( F^- \) ions are fully coordinated by active \( \text{Li}^+ \) ions in order to prevent artificial distortion of the electron density at the border between the active cluster and the surrounding point charges. We present curves for the projectile in vertical incidence on top of a \( F^- \) ion in the surface layer. For this geometry, the complete system comprising the embedded cluster and the projectile is described by the \( C_{4v} \) symmetry group. The ionic state (neutral surface plus bare \( H^+ \)) corresponds to a closed shell configuration and possesses therefore \( A_1 \) symmetry. Due to the Wigner-von Neumann non-crossing rule it can only interact with covalent states of the same symmetry. Therefore we show in Fig. 1.4 only potential curves of \( A_1 \) symmetry.

In the smallest system containing only one active \( F^- \), there are only two states of \( A_1 \) symmetry: one ionic and the other covalent (Fig. 1.4 a). At large projectile distance \( z \), the two curves run in parallel with a distance in energy of 4 eV. At \( z = 5 \) a.u. the two curves start to separate. In order to determine the character of the avoided crossing, we show the (approximate) electronic charge localized at the hydrogen projectile for both states in the panel below. This charge can be easily calculated from the total electronic dipole of the system. A value of \( q = 1 \) at large distances signifies one electron located at the projectile and therefore characterizes the ionic state. Likewise, a value of 0 characterizes the ionic state. The lower state in the potential energy diagram (dashed line) has covalent character at large distance and the upper state (dash-dotted line) is ionic. This asymptotic energetic ordering is consistent with the fact that the calculated ionization energy of the embedded cluster (9.61 eV, see above) is lower than the ionization potential of hydrogen. At small distances, the two states exchange their character as can be seen from the corresponding curve crossing in the charge diagram (lower panel). The lower state has now taken on ionic character which gives rise to the \( 1/z \) like slope before the curve reaches a minimum at 1.8 a.u. where the nuclear repulsion starts to dominate the interaction potential. Another way to verify that the two curves do indeed perform an avoided crossing is the analysis of the expansion coefficients of the MCSCF wavefunction. The ionic state at large distance corresponds to a configuration where the 1s orbital of hydrogen is unoccupied and the 2p\(_z\) orbital (with the \( z \)-axis perpendicular to

\(^1\)However, we emphasize that the level ordering is only correct due to the artificially small basis chosen. Choosing a realistic basis will lead to much lower orbital energies of the \( F_2p \)-like orbitals corresponding to higher ionization potentials reaching up to 15 eV. This is because large basis sets including diffuse and polarization functions lead to a better accommodation of the electrons in the anionic state of the fluorines. The proper level ordering using a correct basis can only be restored by including a more sophisticated level of hole screening.
Figure 1.4: Potential energy curves for a $\text{H}^+$ ion interacting with embedded clusters of LiF of increasing size: a) Li$_5^+$F$^-$, b) Li$_{17}^+$F$_5^-$, c) Li$_{25}^+$F$_9^-$, d) Li$_{37}^+$F$_{13}^-$. Only curves of $A_1$ symmetry (within the $C_{4v}$ symmetry group) are displayed. The insets display the clusters embedded into a lattice of point charges (black: F$^-$ ions, white: Li$^+$ ions). In the lower panels we show the distance-dependent electronic charge state $q$ of the projectile. Dashed-dotted line: state with ionic character at large distance; dashed line: covalent state strongly interacting with the ionic state; solid lines: residual covalent states of $A_1$ symmetry.
the surface) of the fluorine is doubly occupied. In the covalent state, both orbitals are singly occupied. At small distances, the two atomic-like orbitals start to hybridize accompanied by a configurational mixing. At a distance of about 4 a.u. the two configurations contribute about 50% to each states which is a clear indication of an avoided crossing.

The addition of the 4 nearest neighbor fluorines to the active cluster in Fig. 1.4 (b) adds two additional states of $A_1$ symmetry. These states (solid lines) interact only weakly with the other two states. The corresponding potential energy curves are mostly flat (until the repulsive regime at small distances is reached) and have covalent character for all projectile distances as can be seen in the charge plot. The charge transfer proceeds between the two states marked by dashed and dashed-dotted lines. An analysis of the MCSCF wavefunctions reveals the underlying reason: the half-occupied molecular orbital of the strongly interacting covalent state is mostly localized at the central fluorine while in the other two states the half-occupied orbitals have a larger weight at the surrounding $F^-$ ions.

Adding more fluorines to the active cluster (Figs. 1.4 (c) and d) does not change the emerging scenario that charge transfer is dominated by predominantly two channels. The additional levels of $A_1$ symmetry are almost independent of the distance, have delocalized wavefunctions, and remain covalent in character. This observation clearly indicates the suitability of the embedded cluster approach to describe the charge-transfer between a projectile ion and an extended surface: even though the capture state of the projectile can - in principle - interact with a continuum of states, in practice it only interacts with one state. For other scattering geometries where the projectile is not incident on top of a fluorine, there may be several states interacting, but still only a small number of localized states is expected to contribute. The slope of the two states that represent the charge transfer channels at small distance (dashed and dashed-dotted lines) appears to be to converged as a function of cluster size. Also the crossing point of the charge of these two states has become cluster-size independent. Fig. 1.5 illustrates the localization of the interacting state for the system $H^+ \rightarrow Li^{2+} F_9^-$. It displays the wavefunction of the half-occupied molecular orbital that gives the dominant contribution to the interacting covalent state. It corresponds to the wavefunction of the hole left behind in the surface after transfer of an electron to the projectile. At large distances ($z = 8$ a.u.) the hole is almost evenly distributed over the $2p_z$ orbitals of all fluorines contained in the active cluster. At $z = 5$ a.u., the orbital is mostly localized at the central fluorine and shows a small admixture from the $1s$ orbital of the hydrogen projectile. At small distances ($z = 2$ a.u.), the hole is completely localized in a hybrid orbital comprising the $2p_z$ orbital of the central fluorine and the $1s$ hydrogen orbital. At this distance, the covalent configuration only contributes to the highest state (dashed-dotted line) in Fig. 1.4 (c) while at larger distances it contributes to both lowest energy curve (dashed line). The analysis of the MCSCF wavefunctions underlines the scenario that out of the many covalent states with a hole delocalized in the surface, one state localizes and represents the main charge transfer channel with the ionic state.

### 1.5 Conclusions

The accurate *ab-initio* treatment of charge-transfer in ion-surface collisions still poses a considerable computational challenge. Using the example of hydrogen ions impinging on a LiF surface, we have investigated in this paper the feasibility of an approach where the (infinite)
surface is represented by a finite embedded cluster only. With increasing cluster size, the discrete density of valence states of (bulk) embedded clusters converges towards the continuum DOS of LiF. The valence band of LiF is thus well represented by embedded clusters. We present a convergence study of potential energy curves for an H\(^+\) ion interacting with clusters of increasing size. The projectile level can interact - in principle - with a continuum of valence states. An accurate description would then require embedded clusters of infinite size. In practice, however, our model calculations demonstrate that one or at most a few states localize in the region of impact as the projectile approaches the surface. The potential energy curves corresponding to these states clearly converge as a function of cluster size and display only weak interaction with the delocalized states. We have thus demonstrated that the embedded cluster approach is, indeed, feasible for the calculation of charge exchange in ion-surface collision. In practical calculations, the proper inclusion of correlation energy is important. Correlation effects lead to hole-screening, i.e., the polarization of the environment of a hole in the surface after transfer of an electron to the projectile. Within the region of the active cluster, correlation can be described to a good degree of approximation by size-consistent methods from quantum chemistry such as a multi-reference CI (including the Davidson correction) or coupled-cluster methods. A complete solution of the problem will, however, require the inclusion of polarization effects in the surrounding medium, at least on a phenomenological level. For the future, we plan the calculation of non-adiabatic coupling-matrix elements in order to solve the time-dependent Schrödinger equation and obtain cross sections for the neutralization of particles in ion-surface collisions.

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[23] The basis is taken from [24]. For F a contraction (10S,7P) → [2S,1P] is used and for Li a contraction (10s) → [2s]. The basis is so small that the electron affinity of fluorine calculated within this basis carries the wrong sign. This leads to an artificial upwards shift of the valence band by about 3 eV. For the present model calculation this shift is desired because it compensates for the absence of strong correlation effects in the MCSCF calculations.

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