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Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Towards an ab initio description of the charge transfer between a proton and a lithium fluoride surface: A quantum chemistry approach



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ARTICLE INFO

Article history: Received 24 September 2012 Received in revised form 20 November 2012 Available online 30 January 2013

Keywords: Charge transfer Lithium fluoride Ion surface scattering

1. Introduction

Many effects in heavy particle-surface scattering can be described within the adiabatic (or Born–Oppenheimer) approximation when the projectile velocity v_p is much smaller than the characteristic speed of the target electronic motion v_e (see, e.g. [1–3]). In this case a single potential energy surface (PES) corresponding to the electronic ground state of the system governs the interaction dynamics. Standard approaches to calculate the ground state PES are the Hartree–Fock (HF) approximation and density functional theory. In the regime where v_p becomes comparable to v_e one leaves the validity range of the Born–Oppenheimer approximation and non-adiabatic effects are no longer negligible.

The inclusion of non-adiabaticity gives rise to many interesting physical effects but requires advanced methods. In this work we focus on a prototypical non-adiabatic effect, the charge transfer between a projectile and a crystal. Resonant charge transfer between ions and metal surfaces (see, e.g., [4–7] and references in [8]) as well as ion neutralization and negative ion conversion of neutral atoms in front of wide band gap insulator surfaces have been extensively studied in many theoretical and experimental works (see, e.g., [9–16]). Most of the theoretical models in the latter case, however, are based on the HF approximation, i.e. single configuration, calculations which, by definition, cannot account for correlation effects and are known to poorly describe excited electronic states of a system. Furthermore, many of these models fix the tra-

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ABSTRACT

We study the non-adiabatic charge transfer dynamics during the collision of a slow proton with a lithium fluoride surface employing a quantum-chemistry based dynamics approach. The surface is modeled by an $\text{Li}_5\text{F}_1 + \text{H}^+$ cluster embedded in a large matrix of point charges. Going beyond the adiabatic (or Born–Oppenheimer) approximation, we apply multi-reference configuration-interaction methods that allow for the calculation of ground and excited states of the embedded cluster as well as of the non-adiabatic couplings between them. This information serves as input for the determination of the neutralization probability of a proton scattered off a LiF surface using Tully's semi-classical surface hopping algorithm. © 2013 Elsevier B.V. All rights reserved.

jectory of the incident projectiles during the interaction to straight lines with constant velocities.

In this work we go beyond the Born–Oppenheimer approximation by applying high level quantum chemistry methods, such as configuration interaction, which have proven to be a powerful tool to describe the transient quasi-molecule during ion–atom collisions and to accurately calculate charge transfer cross sections including correlation and polarization effects in binary collisions (see, e.g. [17]). We use these methods within the framework of the embedded cluster approach (ECA) followed by a semi-classical surface hopping algorithm for the dynamics to determine the charge transfer probability for a slow proton ($E_{kin} \leq 300 \text{ eV}$) directed onto a lithium fluoride (LiF) surface at perpendicular incidence.

The calculation of the interaction dynamics involves two steps: first, we calculate the potential energy surfaces of ground and excited states of a Li_5F_1 + H⁺ cluster embedded in point charges and the non-adiabatic coupling vectors between the PES (Section 2). This information serves as input for the second step, the determination of the neutralization probability for the proton using Tully's semi-classical surface hopping algorithm [18] (Section 3). Within this approach a detailed analysis of the dynamics of the projectile in front of the surface is possible the results of which are shown and discussed in Section 4.

2. LiF + H^+ , quantum chemistry and the embedded cluster approach

Fig. 1 schematically shows the electronic bandstructure of a LiF crystal/surface together with the electronic energy levels in the

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Fig. 1. Electronic structure of a LiF crystal and the electronic energies in the Coulomb potential of a proton. The capture level (H(1s) level) of the proton lies within the valence band of the LiF crystal which leads to resonant charge transfer upon motion of the proton towards the surface. W_{LiF} and W_{H} indicate the work function (in eV) of the crystal and the ionization potential of a hydrogen atom, respectively.

Coulomb potential of a proton. At large distances between the proton and the surface, the capture level of the projectile lies at $E_{cap} = -13.6 \text{ eV}$, approximately in the center of the valence band of LiF (-15.5 eV $< E_{val} < -12.0 \text{ eV}$) [19–21]. This allows for resonant charge transfer from the valence band of LiF to the H(1s) level of the proton upon motion of the projectile towards the surface. The level diagram for large distances between projectile and surface further suggests to consider the initial state LiF + H⁺ to be an excited state of the combined system which can deexcite by removing an electron from the upper part of the valence band and placing it into the capture level of the proton, i.e. forming the configuration (LiF)⁺ + H.

LiF is an ionic crystal and a wide band gap insulator in which valence band electrons as well as holes in the valence band are localized at the anionic sites and screening effects are rather weak. These properties favor the application of the so-called embedded cluster approach (ECA) [15,16]. An active cluster of a few atoms treated by ab initio high level quantum chemistry methods is embedded into an environment representing the residual, infinitely extended, crystal. We simulate the environment by a large matrix of positive and negative point charges located at the lattice positions of an unperturbed crystal. The total number of lattice ions (point charges plus active ions) is 486 ($n_x \times n_y \times n_z = 9 - \times 9 \times 6$). This matrix accounts for the Madelung potential with an accuracy better than 10^{-2} eV [15] in the region of the active cluster and enforces charge neutrality of the unperturbed surface.

The valence band of the LiF crystal is formed by the F(2p) orbitals. Approximating the infinite crystal by an embedded cluster, the valence band becomes discrete and the number of valence band states equals three times the number of F⁻ ions in the active region. In the model presented in this work, the active cluster consists of a single F⁻ ion and its five nearest neighboring Li⁺ ions plus the projectile (see Fig. 2). Therefore, the valence band is represented by only three states. This approximation corresponds to the binary-collision approach in [10]. Its validity is supported by the findings in [16] that only a few states of the valence band participate in the charge exchange, i.e. that the charge exchange in this system is localized. Furthermore, this small cluster size corresponds to an effectively vanishing hole mobility and to the approximation that the projectile interacts only with a single F^- ion during the collision time. The error introduced remains to be investigated in future work taking into account larger embedded clusters. A further simplification is the use of rigid surface atoms in the calculation of the surface dynamics. This excludes the excitation of phonons or surface atom displacements and limits the number of degrees of freedom to the three position coordinates (R_x , R_y , and R_z in Fig. 2) of the projectile. Furthermore, we treat the motion of the projectiles only above the surface. If a projectile comes closer than $R_z > 0.1$ a.u. to the topmost surface layer it is assumed to be



Fig. 2. Geometry of the active Li_5F_1 cluster. The active F^- ion is located at the origin and is surrounded by the five nearest neighboring Li^+ ions. The distance between F^- and each Li^+ ion is fixed at 3.8 a.u. The shaded area indicates the surface unit cell of the LiF crystal, the dashed line delimits its irreducible segment.

absorbed by the surface. Thereby, we only consider reflection and charge transfer from the topmost surface layer and neglect effects from lower lying layers of the LiF crystal.

In order to calculate PES and the non-adiabatic coupling vectors between them we employ ab initio high level quantum chemistry methods. As starting point, Hartree-Fock predicts for the (LiF + H)⁺ system an LiF + H⁺ ground state for large distances between surface and projectile. This incorrect level ordering renders HF calculations meaningless as input for dynamical charge transfer calculations. We, therefore, perform complete active space self consistent-field (CASSCF) calculations [22] followed by multi-reference configuration-interaction calculations with single and double excitations (MRCI-SD) [23]. In these approaches the many-electron wave function is, in contrast to a single determinant HF wave function, given as a linear combination of configuration state functions (symmetry-adapted linear combinations of Slater determinants). This allows for inclusion of correlation effects. In the present case, the complete active space in the CASSCF and the reference space in the MRCI-SD is given by the 10 configurations generated by distribution of the six valence electrons over the $F(2p_x)$, $F(2p_y)$, $F(2p_z)$ and H(1s) orbitals. From these reference configurations all singly and doubly excited configurations are generated to form the basis for the expansion of the many-electron wave function. For the double-zeta (DZ) basis set of Schäfer et al. [24] (consisting of two Gaussians for the H(1s) orbital, four for the Li(s) orbitals, four for the F(s) and two for each F(p) orbital) used the MRCI-SD procedure gives a total of 8200 configurations. In our calculations we employ the quantum chemistry package Columbus [25,26] which contains an effective implementation of the MRCI-SD method and allows for the calculation of the non-adiabatic coupling vectors between MRCI-SD wave functions [27].

Within the MRCI-SD method we calculate the four lowest potential energy surfaces $\epsilon_i(\vec{R})$ and all-electron eigenfunctions $\varphi_i(\vec{r}_1, \ldots, \vec{r}_N; \vec{R})$ (with i = 1,2,3,4) as well as the non-adiabatic coupling vectors $\vec{d}_{ij} = \left\langle \varphi_i(\vec{r}_1, \ldots, \vec{r}_N; \vec{R}) \Big| \frac{\partial}{\partial \vec{R}} \Big| \varphi_j(\vec{r}_1, \ldots, \vec{r}_N; \vec{R}) \right\rangle$ that parametrically depend on the position vector of the projectile \vec{R} . The functions φ_i are multi-determinant wave functions including correlation to a high degree. At large distances between the projectile and the surface, the configurations of the four states φ_i correspond to (in arbitrary order) one [(embedded Li₅F₁) + H⁺] state (in the following called the ionic state) and three [(embedded Li₅F₁)⁺ + H] states (in the following called the covalent states). In the latter case the hole is localized in one of the three different linear combinations of the F(2p_x), F(2p_y), F(2p_z) orbitals. Including only these four states in our dynamics calculation corresponds to the approximation that only charge transfer from the valence band to the H(1s) orbital is allowed. Other excitations (e.g. excitons, charge transfer to the H(2s) level or negative ion conversion) are, for simplicity, not included in the present model.

By varying \vec{R} within the irreducible surface unit cell we acquire the potential energy hypersurfaces of the four electronic states as well as the non-adiabatic coupling vectors between them. Fig. 3 shows a two-dimensional cut of the ground state and the ionic state surface along the R_z axis and the line connecting the F^- with a Li⁺ ion in the surface plane. A one-dimensional cut along the high symmetry R_z -axis ($R_x = R_y = 0$ (top F position)) is shown in Fig. 4 together with the effective charge localized around the projectile (Mulliken charge) corresponding to each of the four adiabatic electronic states. Note the exact degeneracy of two states on the high symmetry axis. For the top F position at large distances between projectile and surface, the four electronic states can be characterized as follows:

state	involved hole orbital	configuration
ground state	$F(2p_z)$	$(embedded \ Li_5 F_1)^+ + H_2 F_2 + H_2 $
covalent state 1 and 2	$F(2p_x)/F(2p_y)$	$\left(embedded\ Li_5F_1\right)^+ + H$
asymptotically ionic state	H(1s)	(embedded Li_5F_1) + H ⁺

For $R_z > 8$ a.u., the ground state corresponds to the configuration [(embedded Li_5F_1)⁺ + H] in agreement with the bandstructure (Fig. 1). Note that the correct level ordering depends on the size of the Gaussian basis. The level ordering is determined by the difference of the work function of the surface, W_{LiF} , and the ionization energy of the projectile, $W_{\rm H}$. The experimental value is $\Delta E_{\text{exp}} = W_{\text{H}} - W_{\text{LiF}} = +1.6 \text{ eV}$ (see Fig. 1). Since the binding energy of hydrogen is already very well described with small basis sets, the basis set dependence of the work function of the embedded LiF cluster is controlling the level ordering. The embedded Li_5F_1 cluster would give, in the limit of large basis sets, an inverted level ordering with $\Delta E_{calc} < 0$ corresponding to a too large work function $W_{\rm LiF}$. The fact that an optimal basis set overestimates the work function in the ECA can be understood as follows: a large basis set properly reproduces the electron affinity of F⁻ ions and thus optimizes the total energy of the neutral surface. The work function is the difference between the total energy of the surface after creation of an



Fig. 3. Two-dimensional cut of the ground state and of the ionic state surface along the R_z axis and a line connecting the F⁻ with a Li⁺ ion in the surface plane.



Fig. 4. (a) 1D cut through the potential energy surfaces of ground and three excited adiabatic states for the system [(embedded Li_5F_1)^{0/+} + H^{+/0}] along the high symmetry axis R_z ($R_x = R_y = 0$, on top of the active F⁻ ion) as a function of the distance R_z between projectile and surface. Covalent states 1 and 2 are degenerate. (b) Charge localized around the projectile (Mulliken charge) for all states as a function of R_z . At large distances, the ionic state corresponds to the configuration [(embedded Li₅F₁)+H⁺] which is the entrance channel in our dynamics simulation. For $R_z < 8$ a.u. a change in configuration mixing (transfer of the ionic character) in the adiabatic ground state and the asymptotically ionic state is observed indicating the coupling between them. (c) *z*-Component of the non-adiabatic coupling vector \vec{d}_{14} between the projectile and ties component of \vec{d} couples the ground state and the isomore the discustence of the discustence and the the surface. This component of \vec{d} couples the ground state and the ionic state state state the group to the distance R_z between the projectile and the surface. This component of the distance R_z to the ground state and the ionic state upon motion of the projectile along the R_z component.

electron hole and the total energy of the neutral surface: $W_{\text{LiF}} = -E(\text{LiF}^*) - E(\text{LiF})$. In order to properly calculate $E(\text{LiF}^*)$, one has to take into account the screening of the hole. However, for small cluster sizes, long-range correlation effects are missing and the screening of the hole is incomplete. $E(\text{LiF}^*)$ is thus overestimated and the resulting W_{LiF} too large. We use the DZ Gaussian basis set of Ref. [24]. This choice is a compromise: a smaller basis set would not adequately describe the non-adiabatic coupling matrix elements. A larger basis set would lead to a wrong level ordering due to the overestimation of the work function.

In Fig. 1 ΔE_{calc} can be extracted as the difference between the ground state and the ionic state at large distances between projectile and surface. Using the DZ basis set [24] we find $\Delta E_{calc} = 1.1 \text{ eV}$ in fair agreement with experimental value of $\Delta E_{exp} = 1.6 \text{ eV}$. For distances $R_z < 8$ a.u. we observe a change in configuration mixing (transfer of the ionic character) between the ground and the asymptotically ionic state indicating the interaction between them. This indication is confirmed by the non-vanishing R_z -component of the non-adiabatic coupling vector $\vec{d}_{14} = \langle \varphi_1 | \frac{\partial}{\partial R} | \varphi_4 \rangle$ which is shown in Fig. 4(c). At $R_z \sim 2$ a.u. we observe a potential minimum in the

electronic ground state generated by Coulomb attraction of the F^- and H^+ ions.

3. Dynamics

In the semi-classical approach [18,28] to ion-surface scattering nuclei are treated as classical particles moving on classical trajectories $\vec{R}(t)$. In our model system only the projectile is allowed to move and $\vec{R}(t)$ can be identified by its three dimensional position vector. Under this assumption the time-dependent many-electron wave function can be written as

$$\psi(\vec{r}_1, \dots, \vec{r}_N, \vec{R}(t)) = \sum_{j=1}^{N=4} a_j(t) \cdot \varphi_j(\vec{r}_1, \dots, \vec{r}_N; \vec{R}(t)).$$
(1)

In the adiabatic representation $\varphi_j(\vec{r}_1, \ldots, \vec{r}_N; \vec{R})$ is the *j*th eigenfunction of the electronic Hamiltonian $H_e \varphi_j(\vec{r}_1, \ldots, \vec{r}_N; \vec{R}) = \epsilon_j(\vec{R}) \varphi_j(\vec{r}_1, \ldots, \vec{r}_N; \vec{R})$ with the eigenvalue $\epsilon_j(\vec{R})$ at a given position of the projectile. Inserting this ansatz into the time dependent electronic Schrödinger equation $i\hbar \partial_t \psi = H_e \psi$ leads to a set of coupled differential equations for the expansion coefficients

$$i\hbar\frac{\partial}{\partial t}a_{j}(t) = \epsilon_{j}(\vec{R}(t))a_{j}(t) - i\hbar\vec{V}\sum_{i}\vec{d}_{ji}a_{i}(t).$$
(2)

 $\vec{d}_{ji}(\vec{R}(t)) = \langle \varphi_j | \frac{\partial}{\partial R} | \varphi_i \rangle$ is the non-adiabatic coupling vector between the states j and i and $\vec{V}(t)$ is the projectile velocity vector. The nuclear motion at a given instance of time is governed by Newton's equation of motion on a single potential energy surface. Newton's equation of motion and the equations for the amplitudes $a_j(t)$ are integrated simultaneously. Additionally, in every time step the transition probabilities from the current state j to any other state are evaluated. By means of a stochastic algorithm proposed by Tully [18] it is decided if the system (i.e. the projectile) "jumps" onto another PES, i.e onto another electronic state i. Conservation of energy during the jump is guaranteed by rescaling the kinetic energy of the projectile. In this Monte-Carlo approach which simulates the probabilistic nature of the quantum transition, the wave function of the proton is sampled by many classical trajectories starting from identical initial conditions.

We model an infinite LiF surface by applying periodic boundary conditions for the projectile at the borders of the square spanned by the four surface Li⁺ ions of the active cluster. This small periodicity volume leads to potentials $\epsilon_j(\vec{R})$ with discontinuous first-order derivatives at the boundaries. The latter are, however, weak and can be neglected.

4. Results and discussion

We calculate the neutralization probability of a proton scattered off the topmost layer of a LiF surface under perpendicular incidence for an energy range of $20 \text{ eV} \leq E_{kin} \leq 300 \text{ eV}$. We use 2485 initial positions (R_x, R_y) uniformly distributed over the irreducible surface unit cell (Fig. 1). For a given kinetic energy and each initial position we sample 2500 trajectories. All trajectories are started on the PES corresponding to a projectile charge state of one (see Section 2) at a distance of R_{z} = 14 a.u. above the surface where the components of the non-adiabatic coupling vectors are negligible. Angular divergence of the incident trajectories is neglected. Initial energies are distributed around the nominal value according to a Gaussian with a full width at half maximum of 2.35 eV. Integration of a trajectory is stopped when the projectile reaches again R_z = 14 a.u. after being reflected from the surface or when the projectile penetrates the surface ($R_z \leq 0.1$ a.u.). Fig. 5 shows the total reflection probability (solid red line) and the frac-



Fig. 5. Probability for reflection of projectiles (solid (red) line) and of the fraction of protons (dash-dotted (green) line) from the topmost surface layer as a function of the proton momentum.



Fig. 6. Planar averaged (a) total and (b) partial neutralization probability (solid (red) lines) of a proton reflected from the topmost surface layer of a LiF surface under perpendicular incidence as a function of the initial proton momentum. Signatures of Stückelberg oscillations in the 1D neutralization probability for a proton with $R_x = R_y = 0$ (dash-dotted (green) line) can be found in both the total and the partial neutralization probability.

tion of reflected protons (dash-dotted (green) line). According to our present result, only 5% of the projectiles are reflected from the topmost surface layer for a initial proton vertical momentum of $p \sim 85$ a.u. ($E_{kin} \sim 53.5$ eV).

The total neutralization probability is determined by the fraction of trajectories reflected by the topmost surface layer and returning on PES corresponding to a neutral projectile. It is normalized to the number of initial trajectories. The solid (red) line (Fig. 6(a)) is the total neutralization probability averaged over all lateral initial positions of the trajectories. It shows a maximum at a proton momentum of $p \sim 90$ a.u. ($E_{kin} \sim 60.0$ eV) caused by two competing processes. An increasing value of p leads, on the one hand, to a stronger violation of the adiabatic approximation and, therefore, to an increase of the charge transfer, i.e. of the neutralization probability. On the other hand an increase of p leads to an increased penetration into the surface and, therefore, to a reduction of the fraction of reflected projectiles and to a decrease of the total neutralization probability for the incident beam.

Fig. 6(b) shows the partial neutralization probability (solid (red) line) determined by the fraction of neutral projectiles reflected by the topmost surface layer. It is normalized to the number of reflected trajectories only. In the energy range shown, this is a steadily increasing function of the proton momentum. At $p \sim 110$ a.u. ($\Delta E_{kin} \sim 90$ eV) 25% of the returning projectiles are neutralized.

Both neutralization probabilities show modulations for p > 100 a.u. which are traces of Stückelberg oscillations [29]. This can be seen by comparing the total and partial neutralization probabilities with the neutralization probability of a proton directed exactly ($R_x = R_y = 0$ see the PES in Fig. 4(a)) onto the F⁻ ion in the Li₅F₁ cluster (dash-dotted (green) line in Fig. 6(b)). The latter shows strong Stückelberg oscillations which coincide with the modulations of the total and partial neutralization probabilities. This indicates that a major fraction of rescattered (neutral) projectiles is reflected within a narrow region of the surface F⁻ ion.

5. Summary, conclusion and outlook

Configuration interaction methods within the framework of the embedded cluster approach combined with a semi-classical surface hopping algorithm are applied to determine the neutralization probability of a proton reflected from the topmost layer of a lithium fluoride surface. We calculate ground and excited states of the system as well as the non-adiabatic coupling vectors between them which serve as input for the dynamical treatment in a surface hopping approach. This is, to our knowledge, the first time that non-adiabatic coupling elements between surface states (localized on a single anionic site) and the capture level of the projectile are employed. Results for a proton scattered off a Li_5F_1 embedded cluster indicate the potential of such an approach in the field of particle-surface scattering.

Limitations of the model presented are the neglect of reflection and neutralization of protons from lower lying surface layers and the selection of the basis set in the quantum chemistry calculations. The latter is chosen in order to cancel out errors caused by the use of a small Li_5F_1 cluster. Investigations are under way to include effects of lower lying surface layers and to examine the electronic properties as a function of the cluster size and of the basis set. We aim at an improved ab initio determination of the work function of the LiF crystal and of the charge transfer between a proton and the LiF surface. Our method also enables us to study negative ion conversion.

Acknowledgments

This work was supported by the Austrian Science Fund (Special Research Program F41 ViCoM). The authors thank Prof. Hans Lischka and Dr. Felix Plasser for valuable discussions.

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