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# Time-dependent quantum calculations of negative ion formation in scattering of atoms from alkali-halide surfaces

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# Abstract

Wavepacket methods have been applied to study the motion of atoms above insulator surfaces. In this approach, no assumptions need be made about the motion, energy is conserved and the correct balance of normal and parallel momenta can be maintained, when a non-adiabatic transfer between potential energy surfaces (PESs) occurs. Ion formation probabilities are shown to be sensitive to the coupling between diabatic PESs, in particular, manipulation of the coupling is required to produce a threshold. Trapping is found to be important in the results at low energies, but this is not seen in experiment. The introduction of screening of the hole left on the surface after charge transfer eliminates the trapping.

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# 1. Introduction

The charge transfer (CT) process in the scattering of atoms from metal surfaces has been extensively studied during the last 20 years leading to a good understanding of this fundamental reaction [1-3]. Resonant electron transfer is facile because the atom electron affinity is downshifted into resonance with the metal Fermi level by the image attraction. High negative ion fractions can result, especially for low workfunction surfaces [2]. In alkali-halides, by contrast, the valence electrons are tightly bound to the halide sites, leading to

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narrow valence bandwidths, low electron mobilities and high workfunctions [4–6]. The affinity level of the scattering atom has to decrease substantially to become resonant with the valence band of the crystal, and so one would expect a low electron transfer probability. However, the opposite has been observed in experiments; in grazing incidence scattering of O, and F atoms and positive ions from alkali-halide surfaces, Winter and co-workers [7–11] detected very high yields of negative ions above a threshold energy dependent on projectile species, target material and incidence angle. Similar results have been seen in scattering of O and F atoms from the MgO(100) surface [12,13].

The high workfunction of an ionic solid is not, in fact, a barrier to CT from the valence band to a scattering atom. Rather the affinity level of the

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atom downshifts considerably as it approaches the surface, due to the Coulomb attraction between the negative ion and the locally positive region left behind on the surface after electron transfer [14,15]. This can result in crossing or close proximity of the diabatic energy curves describing the ground state (GS) (neutral atom, neutral surface) and CT (negative ion, positive surface) configurations as determined by Borisov and Sidis [14,15] using Hartree-Fock with MNDO, and an embedded cluster description of the surface. Employing methods from gas-phase dynamics [16], they derived coupled time-dependent equations for the amplitude in each diabatic configuration. Thresholds for negative ion formation were obtained in seemingly good agreement with experiment for a range of projectiles and surfaces [14,15,17].

In the work of Borisov and Sidis, however, the dynamics of the projectile motion was only treated approximately with a classical trajectory having motions parallel to and normal to the surface decoupled. The time-dependence of the amplitudes of each electronic configuration derive from this trajectory. To treat the dynamics of a curve-hopping event accurately, we should employ quantum mechanical methods, solving the Schrödinger equation to guarantee energy conservation and the correct balance of the momentum components of the projectile during CT. This will be especially important in the threshold region. Semi-classical and classical curve hopping methods have been demonstrated to give quantitatively and even qualitatively incorrect results in multi-dimensional systems with strong non-adiabatic coupling [18]. In earlier work [19], we presented results of a timedependent wavepacket study of the F/LiF(100)system, with potential energy surfaces (PESs) obtained from a semi-empirical valence bond (SEVB) method. These showed an ion formation probability,  $P_i$ , of almost unity at all energies, and trapping of the ions formed at low energies, both in contradiction to experiment and other theory. In this paper, we return to this problem to resolve the discrepancy between our SEVB PES, wavepacket model and other work. We consider only the ionformation stage and possible trapping of ions formed. We do not include subsequent neutralization of the ion, either by electron transfer to the conduction band or by electron emission into the gas-phase [20]. Ion-formation and neutralization stages are known to occur several times over in a typical trajectory at high energy [21].

# 2. Potential energy surfaces

In this work, we employ a diabatic-like description of the interaction of the fluorine projectile, A, with the surface atoms. Since we only consider the ion-formation stage, only two electronic configurations are required: the GS, F/LiF, configuration, and the negative ion state (NIS),  $F^-/LiF^+$ , configuration. A SEVB method [22,23], using atomic, diatomic molecule and crystal parameters, was used to generate the PESs. This simple and flexible method gives all diagonal and off-diagonal PES matrix elements within the same framework. Madelung terms appear naturally, but we have added, by hand, terms accounting for the polarization of A and the image charge attraction of the  $A^-$ .

The GS PES,  $V_{11}$ , obtained from the SEVB method is a sum of pair potentials for the interaction between A and individual atoms comprising the substrate. The pair potentials are obtained [22] by fitting the SEVB energy of the GS to the known GS energy curve of the appropriate diatom.  $V_{11}$  is predominantly repulsive, more so at the halide site than at the alkali site.

The NIS PES is obtained by assuming the CT to be a local event from a halide anion in the surface to A. We write

$$V_{22} = \Phi - E_{ea}(\mathbf{A}) + V_{11} + V_{pc} + V_{dip}(\mathbf{A}^{-}) + V_{im}.$$
(1)

 $\Phi$  is the work-function of LiF,  $E_{ea}(A)$  is the electron affinity of the projectile and  $V_{dip}(A^-)$  accounts for the dipole induced in the negative ion by the surface charges.  $V_{im}$  is the image charge attraction between the negative ion and the surface. It is damped when A approaches closer than 4.1 au to the surface.  $V_{pc}$  represents the interaction of the F<sup>-</sup> with all the point-charges in the surface, given by

$$V_{\rm pc} = \sum_{\rm p} \left\{ \frac{1}{R_{\rm AX_p}} - \frac{1}{R_{\rm AM_p}} \right\} - \frac{1}{R_{\rm AX_N}}.$$
 (2)

The summation is taken over all surface sites, and so we must explicitly account for the neutral atom at the X<sub>N</sub> site by adding a 1/R Coulomb attraction into this locally positive region where CT has occurred. Asymptotically, the NIS PES lies  $(\Phi - E_{ea}(A))$  above the GS. This amounts to a separation of 8.58 eV for F/LiF ( $\Phi \approx 12$  eV [24]).

From the SEVB method the coupling between  $V_{11}$  and  $V_{22}$  is given by

$$V_{12} = \frac{1}{2} S_{AX_N} \left\{ V_{11} + V_{22} - V_{pc} + E_{mad} - \frac{1}{2} (\rho_A + \rho_X) + \frac{1}{R_{AX_N}} \right\},$$
(3)

where  $\rho_A$  and  $\rho_X$  are the screening constants of the outer electrons of A and X [25].  $S_{AX_N}$  is the overlap integral between p-orbitals on the projectile F atom and the CT site F atom. It is approximated using analytic expressions [26].

For greatest flexibility of use, the PES matrix elements are expressed as Fourier series, explicit expressions for these are given in Ref. [19]. The semi-empirical construction means that we should not expect great accuracy in the energies, and so we are free to alter the PES to explore the effects on the dynamics. Specifically, we have reduced  $V_{\rm pc}$ to affect the energy at which  $V_{11}$  and  $V_{22}$  cross, this simulates partial surface charges. Fig. 1 shows a plot of the PES matrix elements as a function of distance above the CT site when the surface charges are reduced to 0.86 [27]. The curve-crossing in this case is at  $\sim 10$  eV.  $V_{12}$  can be seen to be large, but since  $S_{AX_N}$  is determined only approximately from the overlap of favourably aligned orbitals on individual atoms, we also reduce  $V_{12}$ .

# 3. Wavepacket dynamics

To follow the quantum motion of the projectile atom, we have used time-dependent wavepacket methods with fast Fourier transforms [28]. Perpendicular to the surface (the z-direction), we removed the wavepacket from the end of the grid by



Fig. 1. The PES matrix elements as a function of distance above the CT halide site on the surface.  $V_{11}$  is almost uniformly repulsive, while  $V_{22}$  reduces from an asymptotic value of 8.58 eV due to the Coulomb attraction between the negative projectile and the positive region left on the surface after electron transfer. The horizontal lines at 0.6 and 4.1 eV indicate the normal energy for incidence projectile energies of 2 and 14 keV respectively at 1° incidence angle.

grid-cutting [29]. To ensure that the negative ion could not return (the FFT imposes periodic boundary conditions) and re-neutralize at the CT site, the grid was made sufficiently long parallel to the surface that when the ion returned, it did so at z > 5 au where  $V_{12}$  is negligible. To accommodate large grid lengths with the high parallel momenta in grazing incidence scattering, we employed the shift-theorem of Fourier transforms [30] to centre the momentum parallel to the surface at a high value,  $K_0$ .

The explicit time-dependence of the wavefunction was solved using the Chebychev method [31]. We limited the dimensionality, allowing the projectile to move only in a plane perpendicular to the surface, parallel to the incident beam direction, i.e. the calculations were two-dimensional. The initial wavefunction was taken to be the product of a plane-wave state in x (running in the (010) direction) with a Gaussian-weighted plane-wave in z. For the results presented in this paper, the parallel momentum was chosen, for convenience, to be a reciprocal lattice vector of the LiF surface. We have explicitly checked that this choice does not affect the results. The grid length in z was 23.5 au. To force  $V_{22}$  to attain its asymptotic value on this short grid, we have damped the long range Coulomb terms for z > 9 au. The grid length used in x was 228.8 au (600 × 600 (x × z) points) at the lower energies, increasing to 457.2 au (720 × 2080 points) at higher energies. In contrast to previous work [19], a projectile mass of 19 amu has been used throughout.

CT should be able to occur at every surface halide site. However  $V_{22}$  and  $V_{12}$  are centred at the CT site, therefore there are separate PES matrix elements for different active sites on the surface. Fortunately, these are related by coordinate shifts of whole lattice vectors in x, and one  $V_{22}$  and one  $V_{12}$  can be used for all of the NIS PESs. The GS wavefunction,  $\psi_1$  is a Bloch state (because  $V_{11}$  is periodic and all halide sites are equivalent). Combining this with the symmetries of the PES matrix elements, we find that the NIS wavefunction,  $\psi_2^{(na)}(x)$ , for CT at a site *na* is related to that centred at the origin by

$$\psi_2^{(na)}(x) = e^{iK_0 na} \psi_2^{(0)}(x - na).$$
(4)

Therefore, if we take account of the coordinate and phase shifts, only one  $\psi_2$  needs to be stored to represent all of the NIS wavefunctions.

#### 4. Results and discussion

The experimental results for the negative ion fraction of F scattered from LiF(100) at a grazing angle of 1° show a rise from  $\sim 0.1$  at a projectile energy,  $E \approx 2$  keV, to ~0.8 at  $E \approx 8$  keV [9]. In our earlier work [19], we obtained an ion-formation probability,  $P_i$ , of almost unity across this energy range. Changes to all of the grid parameters and different choices of parallel momenta (i.e. not reciprocal lattice vectors of the LiF unit cell) did not change this result. Indeed, allowing CT only at a single halide site still results in negative ion formation of  $\sim$ 70%, although a large fraction of the wavepacket only passes the CT site at distances where  $V_{12} \approx 0$ . It is clear from this work [19], however, that CT at threshold energies is strongly localized at the active site, occurring at approximately the classical turning point for motion in zon *V*<sub>11</sub>.

The strong localization of the CT suggests that a strategy to obtain better agreement with experiment and earlier theory would be to adjust the PES in the region of the CT site. Comparison of the original PES [19] with that of Borisov and Sidis [15] shows that the most obvious difference is a curve-crossing between  $V_{11}$  and  $V_{22}$  at  $\sim 2 \text{ eV}$  in our original PES which is absent in theirs. The curvecrossing energy can be changed by altering several components of  $V_{22}$  given by Eq. (1). The most obvious alteration is to reduce the surface charges, i.e. reduce  $V_{pc}$  in Eq. (2), thereby reducing the rate of decrease of  $V_{22}$  at the active site, cf. Fig. 1 which shows the PESs for a reduction of surface charges to 0.86. In fact, we find that the curve-crossing energy has little effect on ion formation at the experimental threshold energies. Even with no crossing the results are the same at low energy. This is not so surprising. With CT localized at the classical turning point for z-motion at the active halide site, it is the normal energy (i.e.  $p_z^2/2m$ , where  $p_z$  is the momentum component in the zdirection and *m* the mass of A) that will determine the point of CT. Incident at 1°, the normal energy at E = 2 keV is only ~0.6 eV, well below the energy of the crossing point of the original PESs. It would require  $E \approx 6.6$  keV to reach this point.

Far greater differences can be obtained by altering the off-diagonal PES elements  $V_{12}$ . Multiplying by a "coupling strength" less than one reduces the wavepacket intensity transferred to the NIS, and thus reduces  $P_i$  as shown in Fig. 2. As can be seen in Fig. 1,  $|V_{12}|$  at the classical turning points increases with E at threshold energies, therefore the effect of reducing  $V_{12}$  is greater at lower energy where there is less penetration of the surface. Continuing to decrease  $V_{12}$  in this simple fashion does eventually reduce  $P_i$  at higher energies where it should be >0.8. This demonstrates that the correct threshold dependence of  $P_i$  contains information about the magnitude and the dependence on distance above the surface of the nonadiabatic coupling  $V_{12}$ .

The negative ion once formed experiences an image charge attraction to the surface. At the lowest energies, this is sufficient to trap the negative ion at the surface in our wavepacket calculations. This can be seen in Fig. 3, which shows that the population on the NIS state remains constant at long times (i.e. the ions do not escape to large z



Fig. 2. The probability of forming a negative ion as a function of the coupling strength between the ground and NIS state PESs at projectile energies of 2 and 14 keV for the PES shown in Fig. 1. The coupling strength in the abscissa is simply a factor by which  $V_{12}$  is multiplied to reduce the overall coupling. A multiplier of ~0.25 gives a low threshold value at 2 keV, while still maintaining the high  $P_i$  required at 14 keV.



Fig. 3. Wavepacket intensities on the GS and the NIS as a function of propagation time for a projectile energy of 2 keV on the PES of Fig. 1. Above ~5000 atu, the NIS becomes populated at the expense of the GS. The reflected intensity on  $V_{11}$  is damped at the end of the grid producing the second decrease in the ground-state population above ~13,000 atu. The population on the NIS remains constant at long times, indicating trapping of the ions at the surface.

where the wavepacket is damped). Trapping is not observed in the experiment. While re-neutralization could cause such projectiles to escape into the gas-phase again, this is unlikely for F at these low energies because it has a relatively high affinity level, making it difficult to remove the electron either into the gas-phase or into the conduction band of the solid, and certainly the survival probability of  $F^-$  ions scattered from MgO is high at low energies [12]. We have attempted to eliminate trapping by changing the strength of the image attraction, but this is only successful if it is reduced almost to zero. Changes in the PES local to the CT site do not affect the trapping.

Inspection of the wavepackets during propagation shows that following CT the ion travels almost exactly parallel to the surface (as assumed in the semi-classical treatment [15]), only rebounding from the surface  $\sim 40$  au from the CT site. In this part of the scattering,  $p_z$  is almost unchanged, and throughout, the corrugation of the PES is insufficient to provide much interconvertion of normal and parallel components of momenta via diffraction at the high parallel momenta of the projectile. Therefore if A initially has insufficient normal momentum to escape the image attraction, it does not gain momentum from the parallel coordinate during scattering to enable it to escape. To do this, the ion must climb in potential away from the CT site in the x-direction to reach a potential higher than the asymptotic energy difference between  $V_{11}$ and  $V_{22}$ , i.e. it must climb to a potential energy of at least 8.58 eV. Fig. 4a shows  $V_{22}$  as a function of x for z values close to the point of CT on the PES of Fig. 1. The potential is clearly not climbing rapidly enough to reach the required value before the wavepacket reflects from the surface. The ions when formed move across the surface, eventually oscillating back-and-forth in z, trapped in the image attraction of the surface.

The slow rise with increasing x in Fig. 4a results from the 1/R Coulomb attraction between the negative ion and the positive hole left on the surface at the CT site. Previously we have assumed that this is completely unscreened by the remainder of the crystal, but the charge excess will of course polarize the surrounding ions which will in turn interact back with the hole. This can be expressed as Mott–Littleton and dielectric screening type terms some of which have competing effects and partially cancel [32]. Rather than attempting a



Fig. 4. (a) The NIS potential as a function of distance parallel to the surface away from the CT site for three values of z close to the classical turning point for motion in z at the CT site, for a projectile energy of 2 keV. The lower curve is for z = 3.65 au, the middle for z = 3.5 au and the top curve is for z = 3.35 au. Peaks occur every 7.62 au when the ion is above a surface halide site. The fine line at 8.58 eV indicates the energy required for the ion to be able to escape into the gas-phase. (b) Same as (a), but including screening of the hole lateral to the surface. The potential now reaches the required asymptotic level to permit escape of the ions into the gas-phase.

detailed computation of the screening, we have chosen to explore the possible effects by replacing the Madelung contribution to  $V_{22}$  by

$$V_{\rm pc} = \sum_{\rm p} \left\{ \frac{1}{R_{\rm AX_{\rm p}}} - \frac{1}{R_{\rm AM_{\rm p}}} \right\} - \frac{1}{R_{\rm AX_{\rm N}}} e^{-\kappa |x|}, \tag{5}$$

i.e. we damp the 1/R parallel to the surface to account in an ad hoc way for screening of the hole charge by the crystal ions between the projectile and the hole. Detailed calculations will be required to give a more realistic form for the dielectric screening. Fig. 4b shows the potential obtained with a damping constant  $\kappa = 0.067$  corresponding to a screening length of 15 au. We can see from the figure that the effect of this change is to cause a rapid rise in the potential to reach the required asymptotic energy within 20 au.

On the screened-hole PES, the negative ions still initially propagate parallel to the surface after they have been formed. Now, however, when they are 20 au from the active site, they have climbed in potential to a value greater than the asymptotic energy required for the ion to escape, as can be seen in Fig. 4b. The ion has used parallel momentum to climb out of the Coulomb attraction. Since the corrugation is not strong enough to produce substantial interconversion of normal and parallel momenta, the parallel momentum does not change further, and so the potential energy gained converts into motion normal to the surface when the  $A^-$  reverses direction in the z-coordinate. The ions now have easily enough normal energy to escape from the image charge attraction into the vacuum, and the probability of forming ions is then also the probability of obtaining them in the gas-phase. Fig. 5 shows the fraction of reflectivity composed of negative ions for a PES including the hole screening. The sharp threshold can be seen to fit the experimental results well (although averaging over other scattering planes would reduce the agreement).



Fig. 5. Negative ion fractions (probability of scattering as a negative ion) as a function of projectile energy for a PES including screening of the surface hole. The coupling function,  $V_{12}$  has been reduced far from the surface to produce a threshold in good agreement with the experimental results shown as dots (the faint line is a guide to the eye). Including averaging over different scattering planes would increase the threshold energy [19].

# 5. Conclusions

We have constructed a quatum mechanical wavepacket model to describe the negative ion formation in grazing incidence scattering of F atoms from the LiF(100) surface. The model treats CT to all surface halide sites on an equivalent footing, and the quantum treatment ensures energy conservation and the correct balance of normal and parallel momentum components during propagation. The threshold behaviour of the ion formation probability is shown to be extremely sensitive to the magnitude and distance dependence of the coupling between the PESs for the neutral and negative ion configurations. Thresholds can be achieved which match those of experiment very well, but in order for the ions to escape the surface, we have to include screening lateral to the surface of the hole remaining after CT.

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