

The effect of the projectile intra-site Coulomb repulsion in the surface scattering of many-electron ions

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Abstract

In this work a theoretical study of the collision of many-electron ions with a surface is performed. The case of large angle collisions with respect to the surface and projectiles with an open shell is treated. Two important ingredients are considered in the theoretical model. One is the calculation of the interaction terms by considering the orientations of the projectile orbitals with respect to the reference frame provided by the surface. In this form the different symmetry considerations with respect to an isolated two-atom collision are introduced. The other one is the Coulomb repulsion between the electrons in the ion site, which is taken into account within a Hartree–Fock description of the time-dependent evolution. In this way our model calculation is able to reproduce the experimental trends observed in the scattering of N^+ by a LiF surface.

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1. Introduction

The neutralization of ions colliding with surfaces has been noticed to be strongly dependent on the projectile–target system [1–4], being this fact originated in the varied characteristics of the electronic structure of both, target and projectile. The metallic or ionic nature of the surface, and the presence of inner states that can promote the projectile state, lead to different behaviors of the neutralization probability as a function of the energy of the in-

coming projectile [1,2,5–7]. Light projectiles like H^+ and He^+ in collisional processes where the neutralization by electronic capture to the ground state is expected to be the most probable mechanism, are well described by only one active orbital. The neutralization is in this case very dependent on the relative position of the atom energy level with respect to the band and core energy levels of the surface, and on the variation of the energy level of the projectile along its trajectory [6–8]. It has been found that the resonant charge-transfer is an important mechanism of neutralization in large angle collisions, not only in the case of ionic surfaces where the Auger mechanism is highly suppressed, but also in the case of He^+ scattered by metal surfaces where a significant hybridization of the projectile state with target core-states takes place [1,2,9].

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For collisions involving trajectories with large angles with respect to the surface, a binary picture by considering only the scatterer surface atom is expected to describe correctly the collisional process. However the natural reference frame is provided by the surface. Then, the relative orientations of the projectile orbitals in this frame become an ingredient to be considered for a more realistic description of the angular dependence of the charge transfer process. The charge transfer to an open shell of a many-electron projectile leads to different final electronic configurations that may occur with similar probabilities. This represents a complex many-body problem in which the intra-site two-electron terms have to be taken into account in some order of a perturbative calculation. As an example of a collisional system presenting these features we have the ion survival probability of N^+ scattered by the F atoms of a LiF surface measured by Khvostov et al. [10]. The range of projectile kinetic energies is between 200 and 1000 eV, the scattering angle is 90° and the incident angle with respect to the surface is 45° . An oscillatory behavior of the ion survival probability as a function of the primary ion energy is observed. Khvostov et al. explain these oscillations through a model for the ion neutralization based on two different positions of the hole in the N-2p orbitals with different orientations respect to the surface. They use a time-dependent Anderson–Newns model where two orbitals (a and b) with constant energies located on the impinging ion are considered. The hopping with the valence band states of the LiF surface are calculated as the overlap integrals between the N-2p and the F-2p orbitals, but it is not clear neither the model used for describing the band states nor the energy values they are considering for the two orbitals located on the ion. They introduce only the following three kind of many-electron functions as the basis set to solve the time-dependent Schrödinger equation: (i) one electron in the a-state of the projectile and N electrons in the valence band, (ii) two electrons in the projectile and $N - 1$ in the valence band, (iii) one electron in the b-state of the projectile and N in the valence band. Then, they are not considering neither the electron-loss channel given by the wave function with none electron in the projectile, N in the valence band and one electron in

the conduction band, nor the surface excitation channels. Their discussion is rather confuse, but they conclude that an specific polarization of the electron orbitals occurs, because about the 80% of the scattered ions have electron orbitals oriented normally to the surface.

The proposal of this work is to perform a Hartree–Fock (HF) treatment of the intra-site two-electron terms in a consistent way with the dynamical evolution of the collisional process. By assuming that the most probable initial state of the nitrogen ion is the 3P configuration, the hole in the 2p shell of the nitrogen atom can be in any of the 2p orbitals (p_x , p_y or p_z) with the same initial probability. Different hybridizations between the N-2p orbitals and the 2p and 2s orbitals of the F atom will take place depending on the orientations of the N-2p orbitals with respect to the surface. By the other hand, in a mean-field picture each N-2p energy level is strongly dependent on the occupation of the other two 2p orbitals due to the direct and exchange Coulomb interactions between the 2p electrons. A description of the collisional process within a time-dependent HF approximation that allows to vary the 2p one-electron energy levels of nitrogen according with their corresponding dynamical occupations, means surely an improvement respect to one that neglects completely the correlations between the N-2p electrons. This kind of calculation is finally the main objective of the present work. We perform a detailed HF calculation of the interaction parameters for the collisional system, by considering the LiF surface described as a F^- atom embedded in a semi-infinite point-charge distribution that resembles the Madelung potential of the ionic lattice. In the description of the dynamical collisional process there are included not only the surface band-states, but also the core states of the surface atoms that can promote the projectile energy levels through the hybridizations occurring in the short-distance encounters. The Green function-technique used for solving the time-dependent evolution allows to introduce all the electronic channels consistently with the HF description of the interacting system. By exploring only the transition $^3P \rightarrow ^4S$ as the neutralization channel, we found that the Coulomb interaction between the 2p electrons can explain the

oscillations observed in the dependence of the ion survival probability with the primary ion energy.

This work is organized as follows: in Section 2 the model calculation is explained in detail; Section 3 is devoted to the discussion of the results, and Section 4 to the concluding remarks.

2. Theory

A second-quantized description of an interacting two-atom system that involves a symmetric orthogonalization procedure [13] and an expansion up to a second-order in the atomic overlap is first performed [11,12]. Then, by assuming that the solid can be assimilated to one of the two atoms (with extended and localized states), the Hamiltonian finally obtained is an Anderson-like one where the term associated with the energy of the projectile open shell in the non-interacting atom–surface limit reads:

$$\sum_{\alpha,\sigma} \left\{ \varepsilon_{\alpha}^0 + \frac{1}{2} U_{\alpha\alpha} \hat{n}_{\alpha-\sigma} + \frac{1}{2} \sum_{\beta \neq \alpha} \left[J_{\alpha\beta} \hat{n}_{\beta-\sigma} + (J_{\alpha\beta} - J_{\alpha\beta}^x) \hat{n}_{\beta\sigma} \right] \right\} \hat{n}_{\alpha\sigma} \quad (1)$$

where α and β run over the 2p atomic orbitals; ε_{α}^0 is the one-electron contribution, and $U_{\alpha\alpha}$, $J_{\alpha\beta}$, $J_{\alpha\beta}^x$ are the direct and exchange intra-site Coulomb integrals respectively. These all two-electron terms appearing in expression (1) account for the different electronic configurations of the N^+ , N^0 and N^- species. The lowest order of a perturbative calculation corresponds to the HF approximation of these two-electron terms. In this approximation, Eq. (1) results:

$$\sum_{\alpha,\sigma} \left\{ \varepsilon_{\alpha}^0 + U_{\alpha\alpha} \langle \hat{n}_{\alpha-\sigma} \rangle + \sum_{\beta \neq \alpha} \left[J_{\alpha\beta} \langle \hat{n}_{\beta-\sigma} \rangle + (J_{\alpha\beta} - J_{\alpha\beta}^x) \langle \hat{n}_{\beta\sigma} \rangle \right] \right\} \hat{n}_{\alpha\sigma} \quad (2)$$

where now the energy of each p-orbital depends on the average occupations $\langle \hat{n}_{\beta\sigma} \rangle$ of the other ones.

The use of the complete expression (2) allows to treat in a HF approximation the all possible

neutral channels related with the transitions ${}^3P \rightarrow {}^4S$, ${}^3P \rightarrow {}^2D$ and ${}^3P \rightarrow {}^2S$, and also the negative ion formation (1D). To contemplate all them represents a formidable task. Then, in this work we propose to consider only the neutralization channel ${}^3P \rightarrow {}^4S$ and to analyze the effect of the Coulomb repulsion between the p-electrons treated within a mean-field approximation. We will show that the oscillatory dependence of the ion survival probability with the incoming kinetic energy of the projectile is well reproduced when these Coulomb terms are included. In this case the expression (2) is reduced to the following form:

$$\sum_{\alpha,\sigma} \left\{ \varepsilon_{\alpha}^0 + \sum_{\beta \neq \alpha} (J_{\alpha\beta} - J_{\alpha\beta}^x) \langle \hat{n}_{\beta\sigma} \rangle \right\} \hat{n}_{\alpha\sigma}$$

The value of the $(J_{\alpha\beta} - J_{\alpha\beta}^x)$ integrals is obtained from the difference between the HF total energies of $N^0({}^4S)$ and $N^+({}^3P)$:

$$J_{\alpha\beta} - J_{\alpha\beta}^x = E({}^4S) - E({}^3P)$$

In the interacting situation and within the HF approximation, the Hamiltonian that describes the collision between the N^+ projectile and the LiF surface including the interactions of the valence and core states of the surface with the p-orbitals of the N^+ ion, is

$$\begin{aligned} H = & \sum_k \varepsilon_k \hat{n}_k + \sum_c \varepsilon_c \hat{n}_c + \sum_{\alpha} E_{\alpha}(t) \hat{n}_{\alpha} \\ & + \sum_k \left[V_{k\alpha}(t) \hat{c}_k^+ \hat{c}_{\alpha} + H.c. \right] \\ & + \sum_c \left[V_{c\alpha}(t) \hat{c}_c^+ \hat{c}_{\alpha} + H.c. \right] \end{aligned} \quad (3)$$

The first two terms correspond to the extended band states with energies ε_k and to the core-band states with energies ε_c of the LiF surface respectively. The third term describes the $2p_x$, $2p_y$ and $2p_z$ orbitals of the nitrogen projectile with HF energies E_{α} . The last two terms account for the hybridization among the surface and ion states. The occupation number operators are defined as: $\hat{n}_k = \hat{c}_k^+ \hat{c}_k$ for the band states, $\hat{n}_c = \hat{c}_c^+ \hat{c}_c$ for the core states, and $\hat{n}_{\alpha} = \hat{c}_{\alpha}^+ \hat{c}_{\alpha}$ for the ion states.

The hopping terms $V_{k\alpha}$ are calculated by using a LCAO expansion of the k -states of the solid. In this form the projectile–surface hopping term is

written as a superposition of projectile–target atom hopping integrals weighted by the coefficients of the LCAO expansion. These coefficients determine the partial and local density of states of the LiF surface. By considering only the interaction with the scatterer atom at the surface:

$$V_{k\alpha}(t) \simeq \sum_i c_{i,0}^k V_{i\alpha}(R(t) - R_0) \quad (4)$$

where $R(t)$ is the ion position at time t , while R_0 is the position of the scatterer F atom that we assume at the origin of the reference frame ($R_0 = 0$). The $c_{i,0}^k$ coefficients are the weights of the 2p-states of the F atom at $R_0 = 0$ in the k -state of the surface; and the $V_{i\alpha}$ are the off-diagonal matrix elements of the Hamiltonian between the symmetrically orthonormalized F and N atomic orbitals. The core-bands are assumed as localized states, then the $V_{c\alpha}$ in expression (3) correspond to the hopping between the core orbitals of the F atom (1s and 2s states) and the N-2p orbitals.

2.1. Model calculation of the Hamiltonian parameters

The terms of the Hamiltonian (3) are calculated by considering the F^- atom embedded in the semi-infinite point-charge distribution that reproduces the Madelung potential of the LiF ionic surface. The in- and out-trajectories of the N^+ ion are roughly simulated by two broken straight lines with the correct incidence and exit angles (45°) with respect to the surface (see Fig. 1). For each incoming kinetic energy the distances of closest approach are previously obtained from the interaction energy of the N^+F^- system embedded in the point-charge distribution, and considering a perpendicular ion movement. These all calculations are performed by considering an adiabatic evolution without charge transfer between the two atoms. Depending on which N-2p orbital the hole is, we have that the unrestricted HF calculation gives an energy corresponding to this orbital which is approximately 0.6 a.u. (the value of $J_{\alpha\beta} - J_{\alpha\beta}^x$) larger than the energies of the other two 2p orbitals (the asymptotic values are respectively -0.55 and -1.15 a.u. relative to the vacuum level).

We only write the explicit expression of the projectile on-site energy term for understanding

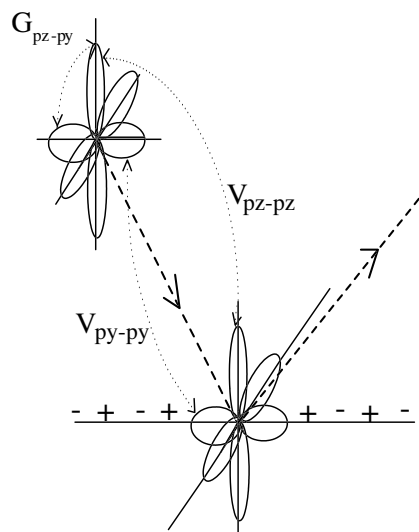


Fig. 1. Diagrammatic description of the collisional system. The yz is the collision plane and the yx is the surface plane. V_{zm} are the atomic hopping integrals between the projectile ion and the scatterer target atom; $G_{\alpha\beta}$ are the Coulomb integrals in the projectile site. The in- and out straight trajectories are indicated by the dashed lines. The plus and minus symbols indicate the point-charge distribution of the ionic surface.

the time-dependent HF approximation after performed:

$$E_{\alpha\sigma}^{ad} = \zeta_{\alpha\sigma} + \sum_{\beta \neq \alpha} (J_{\alpha\beta} - J_{\alpha\beta}^x) \langle \hat{n}_{\beta\sigma} \rangle + \sum_j \left(\tilde{J}_{\alpha j} \langle \hat{n}_{j-\sigma} \rangle + \tilde{G}_{\alpha j} \langle \hat{n}_{j\sigma} \rangle \right) \quad (5)$$

where β runs over the p-orbitals of the projectile, while j runs over the surface atom states; and the different parameters are defined as:

$$\tilde{J}_{ij} = J_{ij}^0 - S_{ij}^2 J_{ij}^{x0}$$

$$\tilde{G}_{ij} = (J_{ij}^0 - J_{ij}^{x0})(1 + S_{ij}^2)$$

with S_{ij} the overlap between the atomic states of the two atoms involved, and the Coulomb integrals J_{ij}^0 and J_{ij}^{x0} are defined in the atomic basis set from the general expression of the two-electron integrals:

$$v_{ijkl} = \left\langle \phi_i(r) \phi_j(r') \left| \frac{1}{|r - r'|} \right| \phi_k(r) \phi_l(r') \right\rangle$$

as $J_{ij} = v_{ijij}$, and $J_{ij}^x = v_{iijj}$. The $\zeta_{z\sigma}$ term includes the expected corrections due to the overlap in a second-order expansion [12]:

$$\begin{aligned} \zeta_{z\sigma} = & \varepsilon_z^0 - \sum_j S_{zj} V_{zj}^\sigma + \frac{1}{4} \sum_j S_{zj}^2 \\ & \times \left\{ \left[\varepsilon_z^0 + \sum_k J_{zk}^0 \langle \hat{n}_{k-\sigma} \rangle + \sum_{k \neq j} G_{zk}^0 \langle \hat{n}_{k\sigma} \rangle \right] \right. \\ & \left. - \left[\varepsilon_j^0 + \sum_k J_{jk}^0 \langle \hat{n}_{k-\sigma} \rangle + \sum_{k \neq i} G_{jk}^0 \langle \hat{n}_{k\sigma} \rangle \right] \right\} \quad (6) \end{aligned}$$

The one-electron term ε_z^0 in Eq. (6) includes now the interaction of the electron with the point-charge distribution. We will take into account in the dynamical evolution of the collisional system the three p-orbitals of the N^+ ion, by introducing the energy variation of each one accordingly with the occupation of the other two. This is performed within a time-dependent HF approximation by considering:

$$\begin{aligned} E_{p_z}(t) = & E_{p_z\sigma}^{\text{ad}}(t) + \sum_{\beta \neq z} \left(J_{p_z p_\beta} - J_{p_z p_\beta}^x \right) \\ & \times \left[\langle \hat{n}_{p_\beta\sigma} \rangle_t - \langle \hat{n}_{p_\beta\sigma} \rangle_{-\infty} \right] \quad (7) \end{aligned}$$

where $E_{p_z\sigma}^{\text{ad}}(t)$ is given by the expression (5) and calculated from the adiabatic evolution without charge transfer between the N and F atoms. The time dependence of this parameter is due to the classical trajectory of the N^+ ion, $R = R(t)$, assumed with a constant velocity. Only one spin projection (the σ chosen for the occupied p-orbitals) enters in the calculation due to the nature of the Coulomb interaction term considered, justifying in this form the spin-less picture of the time-dependent Hamiltonian (Eq. (3)). The average occupations $\langle \hat{n}_{p_\beta\sigma} \rangle_t$ are provided by the dynamical calculation at each time t , while $\langle \hat{n}_{p_\beta\sigma} \rangle_{-\infty}$ are the occupations of the p_β orbitals in the 3P configuration of the incoming ion.

2.2. Quantum mechanical calculation of the ion survival probability

A time-dependent formalism based on the following Green functions is used [14]:

$$G_{z\sigma M}(t, t_0) = -i\Theta(t - t_0) \langle c_M^+(t_0) c_z(t) + c_z(t) c_M^+(t_0) \rangle$$

The index M runs over the eigenstates of the non-interacting collisional system at the initial time t_0 , these are the k-band states and c-core states of the surface, and the β -orbitals of the projectile. The index α runs over the $2p_x$, $2p_y$ and $2p_z$ orbitals of the projectile. These Green functions give the amplitudes of the α -state in the time-dependent wave functions that evolve from the M -eigenstates of the system at time t_0 . The motion equations of the $G_{z\sigma M}(t, t_0)$ functions determined by the Hamiltonian (3), are derived in the following way:

$$i dG_{z\sigma M}(t, t_0)/dt = \delta(t - t_0) \delta_{z\sigma M} + \sum_K V_{zK}(t) G_{KM}(t, t_0)$$

$$i dG_{KM}(t, t_0)/dt = \delta(t - t_0) \delta_{KM} + \sum_\beta V_{K\beta}(t) G_{\beta M}(t, t_0)$$

By performing the phase transformations:

$$G_{qM}(t, t_0) = g_{qM}(t, t_0) e^{-i \int_{t_0}^t E_q dx}$$

the differential equation for the $G_{KM}(t, t_0)$ is integrated and the result is replaced in the equation for the $G_{z\sigma M}(t, t_0)$. The final result is

$$\begin{aligned} i d g_{z\sigma M}(t, t_0)/dt = & \delta(t - t_0) \delta_{z\sigma M} \\ & - i \sum_{K, \beta} V_{zK}(t) e^{-i \int_{t_0}^t (e_K - E_z) dx} \\ & \times \int_{t_0}^t d\tau V_{K\beta}(\tau) e^{i \int_{t_0}^\tau (e_K - E_\beta) dx} g_{\beta M}(\tau, t_0) \\ & - i V_{z\sigma M}(t) e^{-i \int_{t_0}^t (e_M - E_z) dx} \quad (8) \end{aligned}$$

where the index K runs over the surface states, β over the projectile states, and the orbital energy levels $E_z(t)$ of the projectile are the $E_{p_z}(t)$ given by the expression (7).

The hopping with the k-band states are calculated through the expansion (4) by using the following simple form proposed for the $c_{i,0}^k$ coefficients [15]:

$$c_{i,0}^k = \sqrt{2n_v} \sin(\pi k/2) / \sqrt{3}; \quad i = 2p_x, 2p_y, 2p_z$$

with k varying from 0 to 1; and n_v equal to 0.9 for the valence band, and equal to 0.1 for the conduction band. In this form we take into account the negative charge of the F atom in the surface,

equal to 0.9, and the small but not null weight of the F-2p states in the conduction band of the LiF surface. The energy dispersion relation of the band states is also taken from this very simplified linear-chain model [15], by considering an energy gap value equal to 13 eV and a valence band-width equal to 5 eV.

The average occupation number $\langle n_{p_x}(t) \rangle$ of each 2p-orbital of the projectile is given by

$$\langle n_{p_x}(t) \rangle = \sum_{M \text{ occupied}} |G_{zM}(t, t_0)|^2 \quad (9)$$

where M runs over the initially occupied eigenstates of the non-interacting system: the k-valence states of the LiF surface and the c-core states of the F atom (1s and 2s states), and the two 2p-orbitals initially occupied in the N^+ (3P). These $\langle n_{p_x}(t) \rangle$ values are used to calculate the variations of the HF energy levels due to the occupations of the 2p orbitals at the time t , accordingly with expression (7).

Within the time-dependent HF approximation, the many-body wave function is a Slater determinant evolving in time from the corresponding initial configuration state. Then, the calculation of the probabilities of the different charge-states of the projectile leads to the following expressions:

$$\begin{aligned} P^0 &= \langle n_{p_x}(t) \rangle \langle n_{p_y}(t) \rangle \langle n_{p_z}(t) \rangle \\ P^+ &= \langle 1 - n_{p_x}(t) \rangle \langle n_{p_y}(t) \rangle \langle n_{p_z}(t) \rangle \\ &\quad + \langle n_{p_x}(t) \rangle \langle 1 - n_{p_y}(t) \rangle \langle n_{p_z}(t) \rangle \\ &\quad + \langle n_{p_x}(t) \rangle \langle n_{p_y}(t) \rangle \langle 1 - n_{p_z}(t) \rangle \\ P^{++} &= \langle 1 - n_{p_x}(t) \rangle \langle 1 - n_{p_y}(t) \rangle \langle n_{p_z}(t) \rangle \\ &\quad + \langle 1 - n_{p_x}(t) \rangle \langle n_{p_y}(t) \rangle \langle 1 - n_{p_z}(t) \rangle \\ &\quad + \langle n_{p_x}(t) \rangle \langle 1 - n_{p_y}(t) \rangle \langle 1 - n_{p_z}(t) \rangle \\ P^{+++} &= \langle 1 - n_{p_x}(t) \rangle \langle 1 - n_{p_y}(t) \rangle \langle 1 - n_{p_z}(t) \rangle \end{aligned} \quad (10)$$

being P^0 the probability of neutral N atoms, P^+ , P^{++} and P^{+++} the probabilities of N atoms with one, two and three holes in the 2p shell respectively. The sum equal to 1 of these all probabilities provides a good numerical test for our calculation.

3. Results and discussion

The adiabatic evolutions along the ion trajectory of the 2p one-electron HF energy levels $E_{p_x, \sigma}^{\text{ad}}(R)$ given by the expression (5) without considering charge exchange between the surface and the ion projectile, are shown in Fig. 2 as a function of the normal distance to the surface z measured respect to the turning point (the trajectory takes place in the yz plane). In this case the N^+ (3P) initial configuration has the hole in the $2p_x$ orbital, and the turning point ($R = 0.76$ a.u.) corresponds to an incoming kinetic energy equal to 300 eV. In the dynamical evolution, the occupation of the $2p_x$

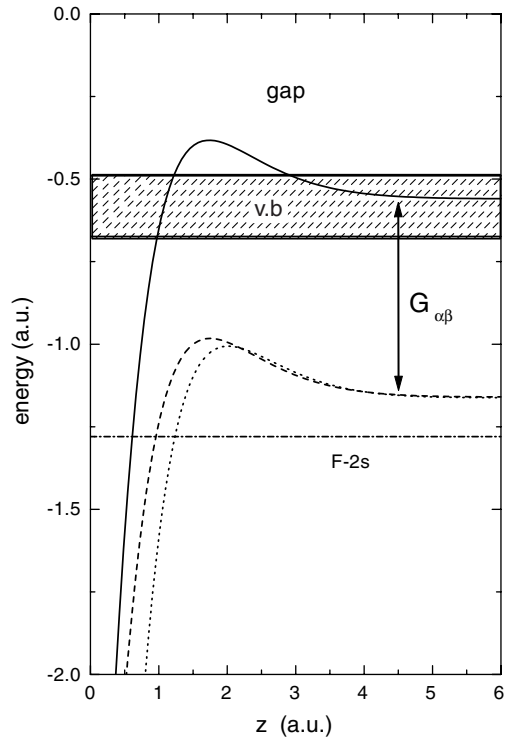


Fig. 2. The energy levels of the projectile orbitals given by Eq. (5), as a function of the z -distance measured with respect to the turning point. The initial charge-state configuration of N^+ corresponds to a hole in the p_x -orbital, and the incoming ion energy is 300 eV. The solid line corresponds to $E_{p_x}^{\text{ad}}$, the dashed line to $E_{p_y}^{\text{ad}}$ and the dotted line to $E_{p_z}^{\text{ad}}$. The dott-dashed line indicates the boundaries of the valence band of LiF surface. The Coulomb repulsion term $G_{\alpha\beta}$ accounts for the difference between the p-orbital energies in the asymptotic situation.

orbital produces an energy promotion of the other two 2p levels according to expression (7), and consequently a possibility of electron transfer from these orbitals to the conduction band, also favored by the hybridizations with the F core states.

The $V_{\alpha m}(R)$ hopping interactions between the α -orbitals of the N^+ ion ($\alpha = 2p_x, 2p_y, 2p_z$) and the m -orbitals of the F atom ($m = 2p_x, 2p_y, 2p_z, 2s, 1s$) are shown in Fig. 3 also as a function of the normal distance to the surface z . The negative values of z only indicate the incoming part of the ion trajectory. According to the magnitudes of the hopping terms with the core states of the F atom shown in Fig. 3b, it is concluded that the promotion of the N- p_z energy level will be the most significant. There is no hybridization between the N- p_x and the F core orbitals.

The total ion survival probability obtained by averaging with equal probabilities the ion survival probabilities for each degenerate possibility of the

initial electronic configuration 3P of the N^+ ion, is shown in Fig. 4 as a function of the incoming projectile energy. The main contribution comes from P^+ that corresponds to the single ions (Eqs. (10)), being P^{++} and P^{+++} negligible (less than 3%). It is shown in the same figure the results obtained from the following two other calculations: (I) By considering the collision as occurring between only two atoms for calculating the atom–atom interaction parameters (E_α and $V_{i\alpha}$). In this case the internuclear axis is the natural symmetry axis for the two-atom interaction. Then, this calculation is ignoring completely the presence of the surface. (II) The orientations of the projectile orbitals respect to the surface along its trajectory are taken into account by calculating the interaction parameters in the reference frame provided by the surface. In both calculations, (I) and (II), we consider the initially empty 2p orbital of the N^+ as the only one active state on the projectile site,

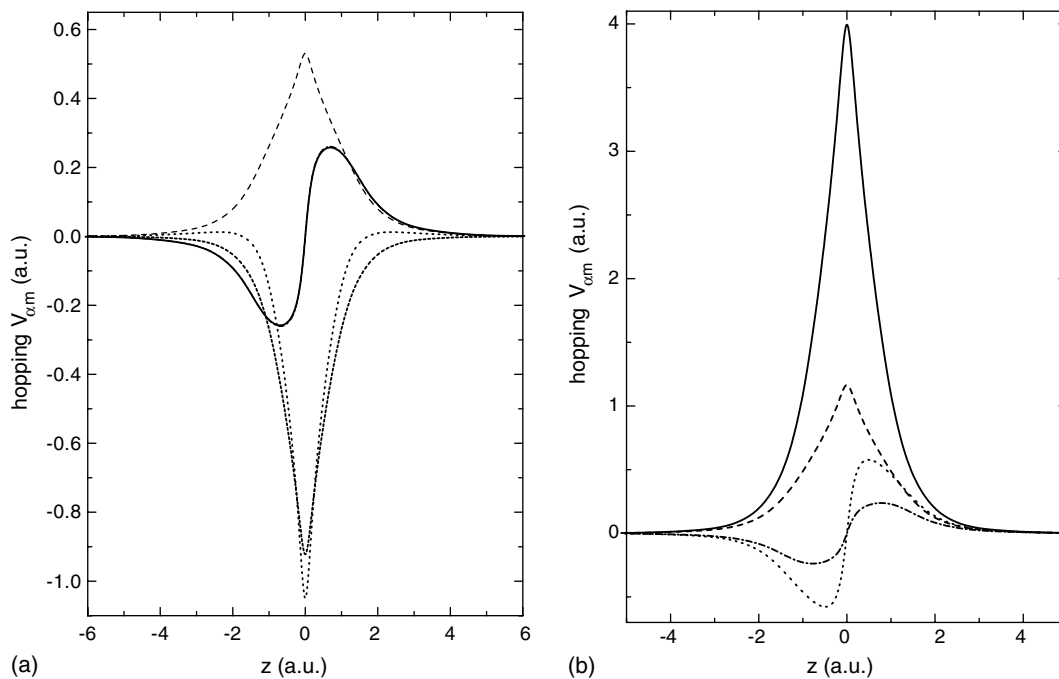


Fig. 3. Hopping interaction terms $V_{\alpha m}$ as a function of the z -distance with respect to the turning point. (a) With the valence states m of the F-atom: the solid line corresponds to $\alpha = p_z, m = p_y$, the dashed line to $\alpha = p_z, m = p_z$, the short-dashed line to $\alpha = p_x, m = p_x$, and the dotted line to $\alpha = p_y, m = p_y$. The hopping terms with $\alpha = p_y, m = p_z$ and $\alpha = p_z, m = p_y$ result to be equal. (b) With the core states m of the F atom: the solid line corresponds to $\alpha = p_z, m = 1s$, the dashed line to $\alpha = p_z, m = 2s$, the dotted line to $\alpha = p_y, m = 1s$, and the dott-dashed line to $\alpha = p_y, m = 2s$.

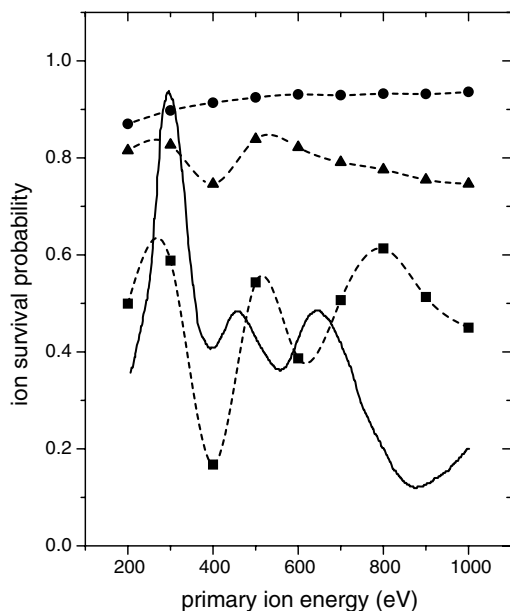


Fig. 4. Total ion survival probability as a function of the primary ion energy. The full circle curve corresponds to the calculation that ignores the surface as the reference frame and neglects the correlation between the p electrons of the N^+ ; the full triangle curve also neglects the electronic correlation but introduces the relative orientations of the p-orbitals with respect to the surface; the full square curve corresponds to the complete calculation that introduces the surface as the reference frame, and a HF treatment of the intra-site Coulomb repulsion. The experimental data are indicated by the solid line curve.

neglecting in this form any correlation between the N-2p electrons. We can observe that the option calculation (I) gives very large values (around 0.9) of the ion survival probability and a very smooth dependence with the incoming ion energy. The option (II) gives lower values (around 0.8) and shows slight oscillations as a function of the projectile energy. While the calculation that involves the three p-orbitals of the N atom by using a mean-field approximation of the Coulomb interaction between them, reproduces fairly the values and the pronounced oscillations with the projectile energy of the measured ion survival probability [10] (also shown in this figure).

The ion survival probabilities for each initial charge-state configuration of N^+ (3P) are shown in Fig. 5. All them present similar oscillatory behaviors as a function of the incoming ion energy,

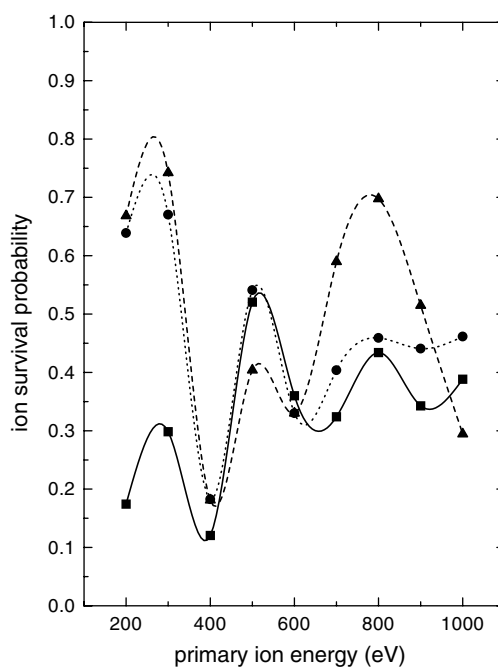


Fig. 5. The ion survival probabilities for each initial charge-state configuration of the N^+ ion. The full square curve corresponds to the hole in the p_x orbital, the full circle curve to the hole in the p_y orbital, and the full triangle curve to the hole in the p_z orbital.

being different their partial contributions to the total ion survival probability. The ion neutralization is due to the resonant process of charge exchange between the projectile orbitals and the surface band states. The only role of the core states of the surface atom is to promote the energy levels of the projectile.

The HF energy levels of the 2p orbitals of N^+ vary along the ion trajectory with respect to the adiabatic values (Fig. 2), due to the Coulomb interaction treated within the time-dependent mean field approximation (Eq. (7)), and also due to the interaction with the core states of the target atom that becomes effective during the close encounter. In Fig. 6 we can observe the N- p_z energy level as a function of the z-distance for the case of the initial N^+ (3P) configuration with a hole in this orbital, and a kinetic energy of 300 eV. Here the following situations are shown: the energy level values given by Eq. (7) with the average occupations determined

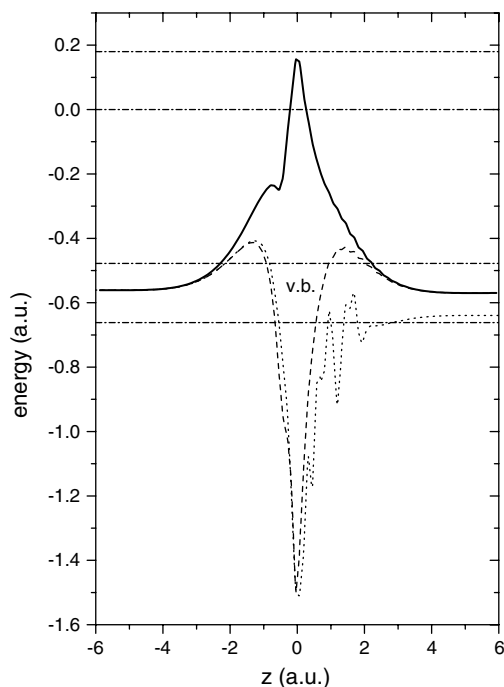


Fig. 6. The dynamical evolution of the energy level of the p_z orbital, in the case of a N^+ initial configuration with a p_z hole and an incoming ion energy of 300 eV. The short-dashed curve corresponds to the energy given by Eq. (7) when the F core states are not considered; the dashed curve to the same energy expression but considering the F core states, and the solid curve to the p_z energy level promoted by the hybridization with the core states of the F atom. The dot-dashed lines indicate the boundaries of the LiF band states.

by either considering or not the interaction with the core orbitals of the F atom in the dynamical evolution; and the promoted p_z energy level that results from the hybridization between the N- p_z HF orbital (with energy given by Eq. (7)) and the F core states. The presence of the F core states in this case leads to a less capability of electron capture to the N- p_z due to its significant energy promotion. This is observed in the average occupations of the N-p orbitals as a function of the z -distance for this initial electronic configuration, shown in Fig. 7. In Fig. 7a the core states of the target atom are considered, while in Fig. 7b they are not. The electron loss processes by the energy promotion due to the presence of the core states is clearly evidenced in the evolution of the p_z -orbital occupation observed

in Fig. 7a. While the occupation of the p_z in the case of neglecting the interaction with the core orbitals of the target atom (Fig. 7b), grows to a value around 0.9 accordingly to an energy level that is always practically resonant with the valence band (Fig. 6). In Fig. 7b the energy levels of the p-orbitals used are those given by the Eq. (7), being their variations with respect to the adiabatic value only determined by the dynamical evolution of the average occupations. The energies of the p_x and p_y orbitals, for which the hybridizations with the F core states are either null or small, are well described in any case by Eq. (7). Fig. 8 shows the results of the total ion survival probability obtained by either including or not the F-core states. It is evidenced the importance of the hybridizations with the localized core states for achieving a better agreement with the experimental results.

There is another point to take into account: the large value of the energy loss of the projectile in the laboratory frame, when colliding with a target atom of similar mass. For the N-F system and a scattering angle equal to 90° , this means a reduction by a factor of 0.15 in the kinetic energy of N after the collision. We are actually considering the laboratory frame provided by the surface, but neglecting the recoil of the target atom. Therefore, this is not at all a correct description of the collision process. But in order to see how much sensitive to the velocity changes the behavior of the ion survival probability is, we have taken into account the energy loss by considering different ion velocities for the in- and out-trajectories. The results of the ion survival probability obtained in this form are compared to the calculation without energy loss in Fig. 9. The qualitative behavior has not changed; it is observed an improvement for the largest primary ion energies when compared to the experimental data, while for the lowest energy values the results are worst. The constant velocity approximation we have used is probably not the most appropriate one for this range of low kinetic energy values; a better calculation including the velocity variations along the ion trajectory is expected to give results that include features of these both present calculations.

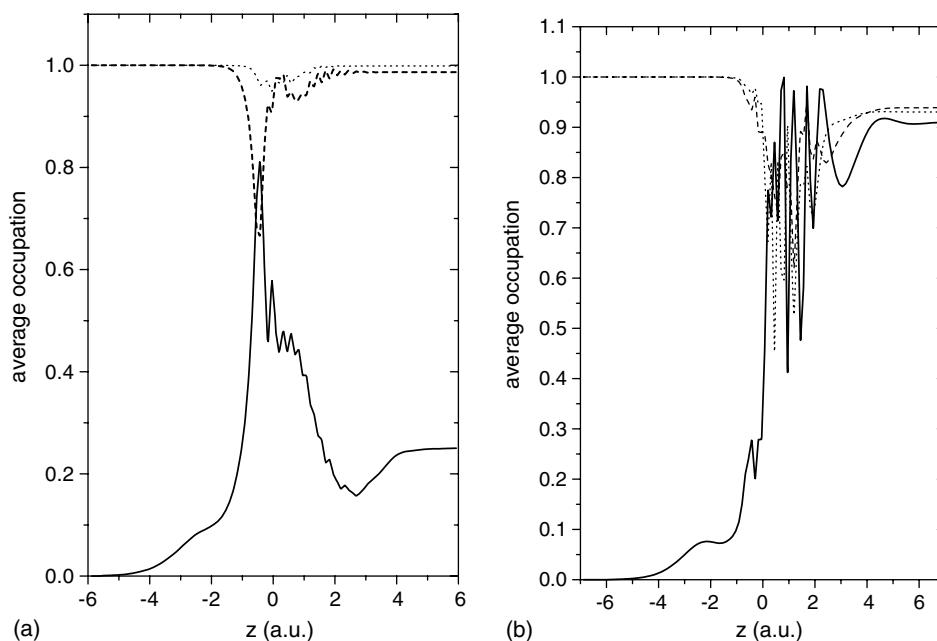


Fig. 7. The average occupation of the p-orbitals of the nitrogen as a function of the z -distance in the case of a N^+ initial configuration with a p_z hole and an incoming ion energy of 300 eV. The solid curve corresponds to $\langle n_{p_z} \rangle$, the dashed curve to $\langle n_{p_x} \rangle$ and the dotted curve to $\langle n_{p_y} \rangle$. By considering (a), or not (b), the core states of the F atom.

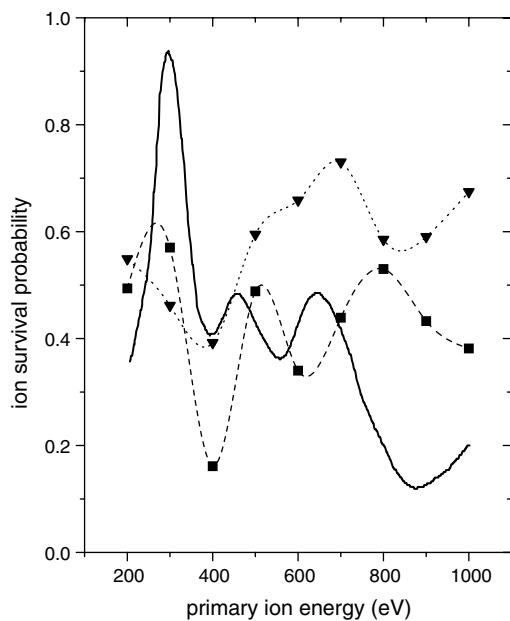


Fig. 8. The total ion survival probability as a function of the primary ion energy. The full square curve includes the core states of the F atom, while the full inverted triangle curve does not. The experimental curve corresponds to the solid line.

4. Conclusions

We have studied the neutralization process in large angle collisions of a many-electron ion with an open shell against a ionic surface. Two ingredients have been considered, the orientations of the ion orbitals respect to the surface along the trajectory for a good description of the angular dependence; and the electron–electron interaction in the projectile site treated within a HF approximation. The interaction parameters have been obtained by using an unrestricted HF calculation previously developed. A time-dependent calculation of the ion survival probability has been performed in the specific case of N^+ against a LiF surface for which there are experimental results. Our formalism allows to perform a time-dependent HF calculation of the all possible neutralization channels from an initial ionic configuration assumed as the 3P one ($^3P \rightarrow ^4S, ^2D, ^2S$), and also of the negative ion formation (1D) that has been found to be important as temporary ions in electron emission experiments [16]. In this work only

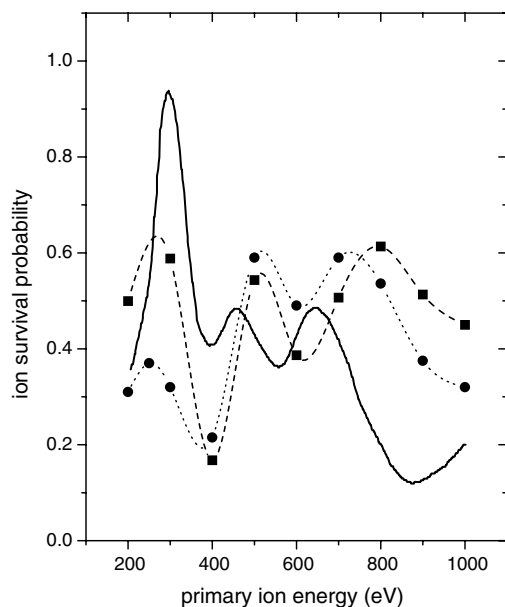


Fig. 9. The total ion survival probability as a function of the primary ion energy. The full circle curve introduces the kinetic energy loss that the N^+ ion suffers in the collision with the F atom, while in the the full square curve this energy loss is not taken into account. The solid curve corresponds to the experimental data.

the $^3P \rightarrow ^4S$ transition has been considered. Nevertheless, we can conclude that this kind of model including basically the interactions with not only the surface band states but also with the core states, and the electronic Coulomb repulsion in the projectile site treated within a HF approximation, is able to reproduce fairly the experimentally observed behavior of the ion survival probability as a function of the incoming ion energy. This result is encouraging for a future work where the all possible final configurations are simultaneously included.

Acknowledgements

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