

Resonant coherent ionization in grazing ion/atom–surface collisions at high velocities

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The resonant coherent interaction of a fast ion/atom with an oriented crystal surface under grazing incidence conditions is shown to contribute significantly to ionize the probe for high enough velocities and motion along a random direction. The dependence of this process on both the distance to the surface and the velocity of the projectile is studied in detail. We focus on the case of hydrogen moving with a velocity above 2 a.u. Comparison with other mechanisms of charge transfer, such as capture from inner shells of the target atoms, permits us to draw some conclusions about the charge state of the outgoing projectiles.

Experiments designed to investigate ion–surface collisions under grazing incidence conditions have proliferated over the past years [1,2]. Within this framework, the present paper is concerned with the theoretical study of electron capture/loss to/from swift projectiles reflected on an oriented surface with glancing angle of incidence in the range of mrad.

Different mechanisms of charge transfer can be devised. Their relative importance depends on the projectile velocity v , the distance to the surface z and the type of projectile under consideration. Auger and direct resonant processes involving the solid conduction band play an essential role for $v \leq v_F$ [3], where v_F is the Fermi velocity of the medium. However, in the high velocity regime ($v \gg v_F$), for which recent experimental results are available [1,2], the capture from inner shells of individual atoms of the solid and the resonant coherent interaction with the surface lattice will be relevant. The latter contributes to both capture and loss. It originates in the periodicity of the lattice of target atoms in the case of oriented surfaces, and is related to the well-known Okorokov effect [4]. It has been recently proposed as responsible for the orientational dependence of molecule dissociation by surface interaction under surface channeling conditions [5].

Provided that the normal velocity is several orders of magnitude smaller than the parallel one under the regime of grazing incidence, the study of those processes can be in general performed assuming that the motion is parallel to the surface. The real trajectory is then incorporated through integrating the corresponding rate equation over different distances to the surface. Consequently, an impact parameter representation of the various processes that take place during the collision becomes necessary. Notice that when the turning point of a grazing trajectory is above the top-most atomic layer, this imposes a distance of closest approach to the target atoms, which makes that the very high momentum behavior of the interatomic potential (e.g., its influence in charge transfer) loses its importance with respect to the bulk.

Atomic units (a.u.) will be used throughout this work. The z -axis will be chosen parallel to the surface normal, in such a way that the top-most atomic layer is placed at $z = 0$ and the vacuum lies in the $z > 0$ region (see Fig. 1). Each state of the electron bound to the probe, $|\alpha\rangle$ of energy ϵ_α , will be considered separately.

Let us first describe the mechanism of resonant coherent loss (RCL), in which the probe loses an electron due to the coherent interaction with the surface lattice. This effect has been also accounted for in bulk calculations of charge states [6]. When the ion beam is directed along a special direction of the oriented crystal surface, it has been predicted that the RCL gives rise to electron emission with well-defined energies and directions [7]. In the present work, we

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shall address the case of a trajectory oriented in a random direction, that is, parallel to an irrational-index surface-lattice vector. A description of the interaction potential between the projectile and the target atoms, $A(r)$, is needed. The periodicity of the crystal potential in the directions parallel with the surface allows us to express it in terms of its Fourier components. The contribution of the top-most atomic layer can be written as

$$V_{CP}(r) = \sum_G \zeta_{G,z} e^{iG \cdot R}, \quad (1)$$

where

$$\zeta_{G,z} = \frac{1}{\Omega} \int dR A(r) e^{-iG \cdot R},$$

Ω is the area of the unit cell, $r = (R, z)$, $R = (x, y)$ and G is a 2D reciprocal surface-lattice vector. In many occasions, the solid can be regarded as a succession of identical parallel atomic planes equally separated by a vector $(D, -d_z)$. Then, using the ZBL [8] approximation for the interatomic potential, which have proved to be valid for explaining a number of experimental results of ion-surface collisions [9], one finds

$$\zeta_{G,z} = \frac{2\pi Z_T}{\Omega} \sum_{i=1}^4 \frac{\gamma_i}{\Gamma_i} \frac{\exp(-\Gamma_i z)}{(1 - \exp(-iG \cdot D - \Gamma_i d_z))}, \quad (2)$$

for $z > 0$, where Z_T is the atomic number of the target atoms, $\Gamma_i = \sqrt{\beta_i^2 + G^2}$, $\gamma_i = (0.02817, 0.2802, 0.5099,$

$0.1818)$, $\beta_i = (0.2016/a_{ZBL}, 0.4028/a_{ZBL}, 0.9423/a_{ZBL}, 3.2/a_{ZBL})$,

$$a_{ZBL} = 0.8854(Z_1^{0.23} + Z_T^{0.23})^{-1},$$

and Z_1 is the atomic number of the external ion. We shall focus on collisions with the (111) face of an fcc crystal of lattice constant a , so that, choosing the axis of coordinates as shown in Fig. 1, one has $\Omega = a^2\sqrt{3}/4$, $G \cdot D = 2\pi(n+m)/3$, $d_z = a/\sqrt{3}$ and $G = 2\pi\sqrt{2}/a((m+n)/\sqrt{3}, m-n)$, m and n being integers.

The rate of loss from the bound state of the ion $|\alpha\rangle$ to the orthogonalized plane wave $|\bar{k}\rangle$ can be obtained using first-order time-dependent perturbation theory. One finds

$$w_{RC}^L(z) = \frac{V}{4\pi^2} \times \sum_G \int d\Omega_k |\langle \bar{k} | \zeta_{G,z+z'} e^{iG \cdot R'} | \alpha \rangle|^2 k \theta(k^2), \quad (3)$$

where V is the normalization volume, z is the projectile-surface separation, $r' = (R', z')$ inside the form factor of Eq. (3) refers to the electronic coordinate and

$$k = \sqrt{2(\epsilon_\alpha - G \cdot V_\parallel)}$$

is the momentum of the emitted electron in the frame moving with the projectile. The fact that the binding

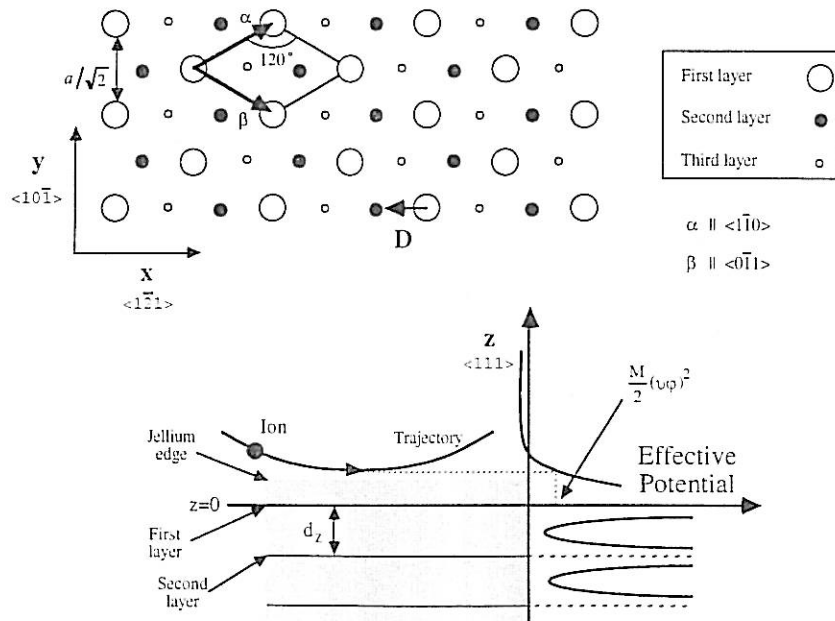


Fig. 1. Top: Schematic representation of the (111) surface of a crystal of lattice constant a . Bottom: Geometry under consideration: the energy associated to the normal motion is assumed to be conserved, so that the turning point of the trajectory is determined by equating the normal kinetic energy at infinity to the effective potential experienced by the probe.

energy ε_α depends upon the distance to the surface due to the corrections introduced by the interaction with both the conduction band (i.e., the image potential) and the target atoms (i.e., the crystal potential) has been taken into account in the calculation of Eq. (3) shown in Fig. 2 (continuous curves) [10]. The rate of RCL is high enough as to have to be considered in a

reliable description of final charge states. The dependence on the velocity is smooth, as can be observed in Fig. 2b. The rate of RCL depends on the direction of the velocity in the plane of the surface (see Fig. 2c). Nevertheless, it can be shown that the final neutral fraction, studied below, is not sensitive to this dependence.

The contribution of the resonant coherent capture (RCC) from valence band electrons is expected to be small as a consequence of the poor matching between initial and final states in momentum space. The rate for such a process can be written [6] as

$$w_{RC}^C(z) = \frac{V}{4\pi^2} \sum_G \int d\Omega_k |\langle \alpha | \xi_{-G, z+z'} e^{-iG \cdot R'} | k \rangle|^2 \times k \theta(k^2) \theta(v_F - |k + v|), \quad (4)$$

where the initial state $|k\rangle$ is a plane wave in the directions parallel with the surface and a solution of the Schrödinger equation with a square barrier potential in the z direction. The results obtained from Eq. (4) are represented in Fig. 2a (dotted curves). The RCC is seen to be negligible as compared with the mechanism discussed below.

The rate of capture from inner shells (S) of the target atoms when the ion moves parallel to the surface at a distance z from the last atomic layer can be obtained by averaging over the trajectory the total probability of capture in a single collision with a target atom as a function of the impact parameter b , $P_S^C(b)$. One finds

$$w_S^C(z) = \frac{2v}{\Omega} \int_0^\infty ds P_S^C(\sqrt{s^2 + z^2}). \quad (5)$$

The results are depicted in Fig. 2a (dashed curves when P_S^C is calculated in first-order Born approximation [11]. This seems to be the main source of capture in the range of velocities under consideration.

The charge state of the outgoing projectiles can be related to the occupancy of the bound states of the probe at $t = \infty$. For each of those states, the time-dependent occupancy $p_\alpha(t)$ is well described by the rate

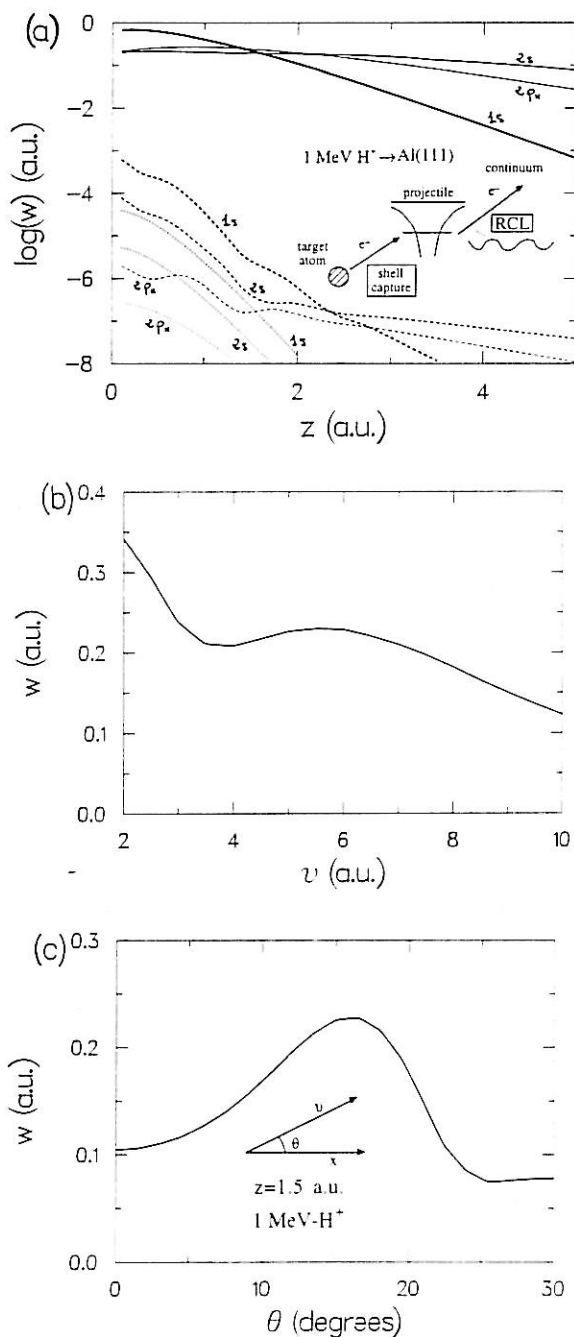


Fig. 2. (a) The rate of electron capture from inner shells of the target atoms (Eq. (5)) is represented by dashed curves as function of the distance to the top-most atomic layer of the solid z for different final electronic states of the projectile when a 1 MeV proton is moving parallel to an Al(111) surface. The axis of quantization is parallel to the velocity. Under the same conditions, the rates of resonant coherent capture and loss (Eqs. (4) and (3)) is shown by dotted and solid curves, respectively. (b) Velocity dependence of the RC from the 1s state ($z = 1.5$ a.u.). (c) Dependence of the RC on the angle between the velocity and the x axis (see Fig. 1 notice the symmetry of the lattice). The value of θ has been set equal to 17° in the rest of the calculations.

states. The dependence can be observed in the direction of the face (see Fig. 2c).

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$$|z\rangle, e^{-iG \cdot R} |k\rangle|^2 \quad (4)$$

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equation, provided that the rates of charge exchange are small, as it is the case for the velocities discussed in this work. That is,

$$\left. \begin{aligned} \frac{dp_\alpha}{dt} &= -p_\alpha w^L(z) + (1-p)w^C(z) \\ p &= \sum_\alpha p_\alpha \end{aligned} \right\} \quad (6)$$

where w^C (w^L) is the total probability of capture (loss) per unit time from (to) the bound state $|\alpha\rangle$. These equations can be integrated over the trajectory, determined by equating the normal kinetic energy at infinity to the total normal energy for each value of z as shown in Fig. 1. More precisely, the normal velocity reads

$$v_z = |dz/dt| = \sqrt{(v\varphi)^2 - \frac{2}{M}U(z)}, \quad (7)$$

where $U(z)$ is the effective potential experienced by the projectile and φ is the angle of incidence. The latter receives contributions from both the image potential (let us call $\phi^1(z)$ the image potential acting on a unit test charge) and the interaction with the target atoms (notice that the crystal potential acting on a unit test charge is given by $\xi_{0,z}$ when it is averaged over a random trajectory). The form of $U(z)$ depends on the charge state of the probe: for the bare projectile of charge Z_1 it reads

$$U(z) = Z_1^2 \phi^1(z) + Z_1 \xi_{0,z}, \quad (8)$$

whereas for a hydrogenic atom/ion with the electron in the state $|\alpha\rangle$ it takes the form

$$U(z) = (Z_1 - 1)^2 \phi^1(z) + Z_1 \xi_{0,z} - \langle \alpha | \xi_{0,z-z'} | \alpha \rangle, \quad (9)$$

where z' is the z coordinate of the electron, and we have assumed that the image potential does not change significantly along the extension of the bound state. The first term in Eqs. (8) and (9) represents the image potential (see ref. [12] for an experimental discussion on this point).

For simplicity, let us focus on H^+ projectiles from now on. The neutralization rate is quite small for the velocities under discussion (see Fig. 2). Therefore, the occupancy of the bound states will be very small. Moreover, the probability of capture followed by successive loss and capture can be neglected. Thus, the neutral charge fraction upon exit from the surface can be written as

$$[H^0]/([H^+] + [H^0]) = \sum_\alpha \int_{-\infty}^{\infty} dt w_\alpha^C(t) T_\alpha(t),$$

where $T_\alpha(t)$ is a transmission factor which accounts for possible loss events from the neutralized projectile.

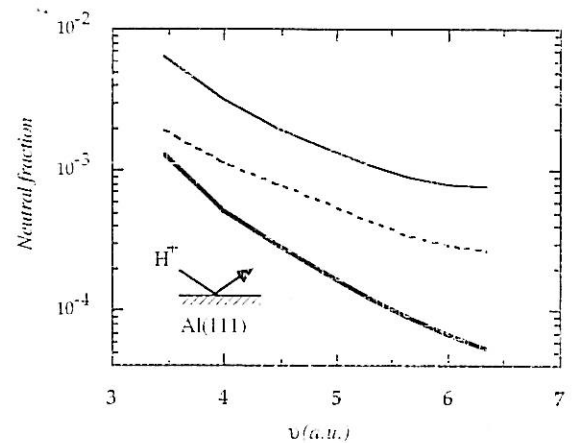


Fig. 3. Neutral fraction after specular reflection of protons on an Al(111) surface with glancing angle of 3.5 mrad along a random direction. The dashed curve stands for the experimental results [2]. The continuous curves correspond to the present theory, that is, Eq. (10) with/without inclusion of the mechanism of resonant coherent ionization (thick/narrow curve).

Using Eq. (7) to change the variable of integration from t to z , one finds

$$\begin{aligned} & \frac{[H^0]}{([H^+] + [H^0])} \\ &= \sum_\alpha \int_{z_0^-}^{\infty} \frac{dz}{v_z^0(z)} w_\alpha^C(z) \\ & \times \exp \left[- \int_z^{\infty} \frac{dz'}{v_z^0(z')} w_\alpha^L(z') \right] \\ & \times \left\{ 1 + \exp \left[- 2 \int_{z_0^0(z)}^z \frac{dz'}{v_z^0(z')} w_\alpha^L(z') \right] \right\}, \quad (10) \end{aligned}$$

where z_0^- is the larger of: (i) the turning point of the proton trajectory and (ii) the value of z such that when the neutralization occurs below it then the neutral projectile cannot escape to infinity. $z_0^0(z)$ corresponds to the turning point of the hydrogen trajectory. The latter depends on the distance to the surface z where the proton has been neutralized and also on the bound state $|\alpha\rangle$; at that distance Eq. (8) for $U(z)$ is replaced by Eq. (9) in Eq. (7). Analogously, v_z^L and v_z^0 are the velocity of the proton and the neutral projectile, respectively.

Fig. 3 shows the results obtained for the neutral fraction from Eq. (10) setting $w_\alpha^C = w_S^C$ and $w_\alpha^L = 0$ (narrow solid curve) and $w_\alpha^L = w_{RC}^L$ (thick curve). It is obvious from the figure that the resonant coherent loss process plays a crucial role in grazing ion/atom-surface collisions, reducing the final neutral fraction. Also exhibited in this figure are previous experimental results

[2] (dashed curve). When the RCL is not taken into account, the neutral fraction exceeds that of the experiment. Its inclusion reduces the final neutral fraction to values that lie 2–5 times below the experimental results. This discrepancy may be due to several reasons. Firstly, the crude description used for the region where, after neutralization, the hydrogen stays trapped (Eq. (10)). Secondly, the fact that the Fourier components of the crystal potential in Eq. (2), obtained from the ZBL approximation for the interatomic potential, may not be appropriate for describing the bound electron–target atoms interaction, because of the different way the valence band electrons screen the potential in the solid phase [13] with respect to the free Al atoms (however, the calculation of the trajectory is dominated by much shorter distances, so that the above description of the interatomic potential seems to be suitable); this is something similar to what happens in the stopping, named phase effect [14]. An inadequate treatment of such a screening leads to an enhancement of the RCL mechanism, especially at large distances. Finally, Auger processes should be studied in detail. Work in this direction is now in progress.

In summary, a description of the resonant coherent loss for atoms/ions moving parallel with an oriented solid surface has been given. This mechanism has been shown to be relevant in the description of the charge state distribution of fast projectiles scattered under grazing incidence conditions. A calculation of the neutral fraction after specular reflection of protons on Al(111) has been performed and compared to experiment.

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