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Distance of Excited-State Formation in Ion-Surface Collisions

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We present the first numerical results of a multichannel theory for resonant charge exchange in ion-surface scattering at grazing incidence. The time-dependent Schrödinger equation describing resonant exchange can be solved in the adiabatic approximation for the slow perpendicular motion. As an initial application the state dependence of the distance of formation in the $H(n=2)$ following specular reflection of protons at a gold surface is determined.

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Charge-exchange processes in ion-surface scattering at small grazing angles ($\theta \leq 5°$) provide the unique opportunity to study collision processes under unusual conditions not easily accessible by other means: Projectile ions reflected specularly at clean surfaces undergo an array of extremely soft collisions at the surface layer with distances of closest approach selected by the normal component of the projectile velocity. An even more interesting feature is that the electron capture from the conduction band of the metal into atomic orbitals is simultaneously characterized by two different time (or velocity) scales: a fast motion of the projectile ($v_{\parallel} \cong v_F$) in the surface plane and the near-adiabatic motion along the surface normal ($v_{\perp} \ll v_F$) where the characteristic internal velocity of the target electrons is the Fermi velocity v_F. Both low- and high-energy methods therefore must be combined to describe inelastic electronic processes near the surface at intermediate velocities.

The technique of ion-surface scattering at grazing incidence has recently been used in a large number of investigations in a broad range of different subfields such as the polarization characteristics of excited atomic manifolds,[1-3] the production of nuclear spin polarization,[4] surface channeling,[5] and the diagnostics of surface magnetic order.[6] For the understanding of the production mechanism of excited states itself as well as its application as a potential tool of surface diagnostics, detailed knowledge of the distance dependence of the formation process is required.

As a first application of a new multichannel treatment of resonant charge transfer we calculate the formation distance from the surface of all substates $H(n=2,lm)$ following $p \rightarrow \mathrm{Au}$ collisions at intermediate projectile speeds ($v \cong 1$ a.u.). The quantization axis is chosen to coincide with the surface normal. The gold surface is described by a (nearly) free-electron jellium model. The motion of the proton can be quite accurately approximated by a classical trajectory since the de Broglie wavelength λ_d is small compared to characteristic distances in the target or projectile. In the following we will be concerned only with the outward portion of the trajectory of the receding ion which is taken as a straight line. Deviations near the turning point as well as the inward portion are irrelevant for the formation of excited states for reasons to be discussed below. The electron transfer from a conduction-band state $\phi_{\mathbf{k}}$ to an atomic orbital ϕ_j is then governed by a time-dependent Schrödinger equation. Because of the fast parallel motion, the orbitals belonging to different frames of reference have to be properly Galilei transformed by use of translation factors well known from high-energy ion-atom collisions.[7] We choose the projectile as the frame of reference. The distance between the proton and the jellium surface is denoted by $R(t)$. For solid surfaces with perfect translation symmetry such as jellium the effect of the relative motion is now to bring about degeneracies between discrete atomic levels and the Galilei-shifted occupied conduction-band levels[8,9] (Fig. 1) to which we will refer in the following as kinematic resonances. While at $v=0$ the occupied levels are nondegenerate with the entire spectrum of the hydrogen atom, at velocities $v \simeq v_F$ excited states are in resonance simultaneously with portions of the occupied as well as empty levels of the Galilei-shifted band structure. A continual creation by resonant capture and subsequent destruction by resonant ionization is therefore expected to dominate the formation process. We note, however, that capture from inner shells resembling binary ion-atom collisions becomes important at high velocities $v > 1$ a.u.

Our treatment of charge transfer through a kinematic resonance follows closely standard resonance theory for radiative decay[10] except for two important modifications: Charge transfer is an intrinsic multichannel scattering process with asymptotic initial ($\phi_{\mathbf{k}}$) and final states (ϕ_j)

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belonging to different channel Hamiltonians. This requires the proper identification of relevant channel perturbations and the inclusion of contributions due to the nonorthogonality of the initial and the final states. Furthermore, the resonance scattering becomes explicitly time dependent as a result of the classically prescribed trajectory.

The Hamiltonian can be written as

$$H=H_i+V_i+H_f+V_f, \tag{1}$$

where $H_{i\,(f)}$ is the entrance (exit) channel Hamitonian and $V_{i\,(f)}$ is the corresponding channel perturbation. For the numerical calculation we will later choose the Sommerfeld Hamiltonian H_i for the semi-infinite electron gas[11] and the hydrogenic Hamiltonian H_f. In the channel perturbation we will also include the interactions of the transferred electron with the proton image charge and with the electronic self-image in order to take into account the collective response effects of the electron gas to lowest order. The use of a classical image potential is justified[12] for distances larger than the surface-plasmon wake wavelength $\lambda_s=v/\omega_s$ (ω_s is the surface-plasmon frequency).

In the independent-particle model (IPM) for charge transfer, the exact wave function can be expanded in an overcomplete basis as

$$\Psi(t)=\sum_j a_j(t)\phi_j+\sum_{\mathbf{k}} b_{\mathbf{k}}(t)\phi_{\mathbf{k}}(t). \tag{2}$$

The equation of motion for the amplitudes $a_j(t)$ with the Hamiltonian (1) can now be solved for slow perpendicular motion in two steps. In the first step, we determine the exact solution for $v_\perp=0$ and fixed $R(t)=R_0$ and finite time intervals $(0,t)$. In the second step, the parametric dependence of all matrix elements through the time-dependent distance $R(t)=R_0+v_\perp$ is treated in the adiabatic approximation, thus allowing the determination of asymptotic scattering amplitudes $a_j(t\to\infty)$.

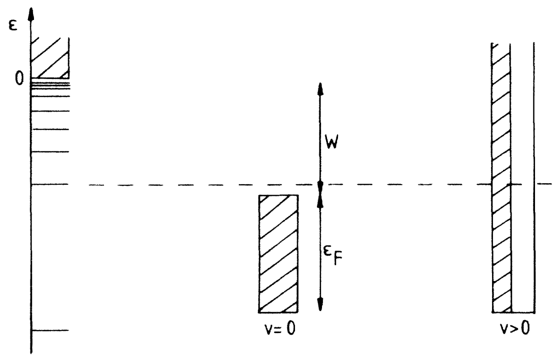

FIG. 1. Kinematic resonance as seen in the projectile frame, schematically. At $v=0$ occupied levels (shaded area) are nondegenerate with atomic spectrum (ε_F: Fermi energy; W=work function). At intermediate velocities atomic levels are in resonance with both occupied and empty levels of the Galilei-shifted band structure.

In the first step, the Schrödinger equation can be converted to a matrix equation by standard Laplace transformation techniques.[10,13] Upon solution of the eigenvalue problem for the self-energy matrix

$$\Sigma_{j,j'}(s)=\langle\phi_j|V_f|\phi_{j'}\rangle+\sum_{\mathbf{k}} M_j(s)M_{j'}^{\dagger}(s)/(is-\bar{\varepsilon}_{\mathbf{k}}), \tag{3}$$

where

$$M_j(s)=\langle\phi_j|V_i|\phi_{\mathbf{k}}\rangle-(is-\varepsilon_{\mathbf{k}})\langle\phi_j|\phi_{\mathbf{k}}\rangle \tag{4}$$

are coupling matrix elements including nonorthogonality corrections due to nonvanishing overlap $\langle\phi_j|\phi_{\mathbf{k}}\rangle$, the inverse Laplace transform can be performed. In Eqs. (3) and (4) the variable of the Laplace transform is denoted by s. Restricting ourselves for simplicity to the subspace of a (near) degenerate manifold of atomic substates of dimension N with energy ε_a, we find for the new amplitudes

$$c_j(t)=-i\sum_{|\mathbf{k}-\mathbf{v}_\parallel|\le k_f}\int_0^t dt'\,B_j(-i\bar{\varepsilon}_{\mathbf{k}})\exp\Big[i\int_{t_0}^{t'}dt''\bar{\varepsilon}_{\mathbf{k}}-i\int_{t'}^{t}dt''(\varepsilon_a+\Sigma_j)\Big], \tag{5}$$

where the vector of new coupling matrix elements $\mathbf{B}=(B_j)_{1\le j\le N}$ is given in terms of the original coupling matrix elements by

$$\mathbf{B}=U^{-1}\mathbf{M} \tag{6}$$

and $\bar{\varepsilon}_{\mathbf{k}}=\varepsilon_{\mathbf{k}}+\langle\phi_{\mathbf{k}}|V_i|\phi_{\mathbf{k}}\rangle$ denotes the conduction-band energies including distortion. Similarly, the vector of new state amplitudes, $\mathbf{C}=(c_j)_{1\le j\le N}$ is related to the unperturbed atomic amplitudes $\mathbf{A}=(a_j)_{1\le j\le N}$ by

$$\mathbf{C}=U^{-1}\mathbf{A}. \tag{7}$$

The amplitudes $\mathbf{C}$ describe the population amplitudes of strongly perturbed atomic states in the vicinity of the surface. These perturbed states are eigenstates of Σ. The eigenvector matrix U is nonunitary because of the coupling of the atomic system to the infinite degrees of freedom in the solid. The initial condition $b_{\mathbf{k}}(t=0)=\Theta(k_f-|\mathbf{k}-\mathbf{v}_\parallel|)$ restricts the $\mathbf{k}$ sum (integral) on the right-hand side of Eq. (5) to the occupied jellium states. Σ_j denotes the complex eigenvalues of the self-energy matrix of the perturbed atomic energy level in the vicinity of the surface.

Equation (5) is now well suited for application of the adiabatic approximation in a second step. The integrands in the time integrals are treated as implicitly time dependent through the $R(t)$ dependence of all matrix elements (e.g., M_j,Σ_j). The probability for capture into a projectile state j, the diagonal element of the density matrix, is given by

$$\rho_j(R_0)=\langle c_j(t\to\infty)c_j^*(t\to\infty)\rangle, \tag{8}$$

where the amplitudes c_j are to be correlated to the asymptotic unperturbed atomic-state amplitudes a_j through the nonintersecting adiabatic self-energy curves $\mathrm{Re}(\Sigma_j)$. The dependence of ρ on the initial value R_0 of the evolution will be discussed below.

Recall that the result [Eqs. (5) and (8)] is based on three essential assumptions: the independent-particle model, the perfect planar symmetry of the surface, and the adiabatic approximation for the perpendicular motion. It allows, however, the calculation of the resonant charge transfer between atomic levels and the solid for a broad class of input matrix elements characterizing the static structure of the atom and of the surface at various levels of sophistication.

As an initial test we have evaluated Eqs. (5) and (8) for the formation of $H(n=2)$ near a gold surface using the following input: (a) Sommerfeld model for the conduction-band states,[11] (b) the multipole expansion of the image charge potentials including the quadrupole term in the channel perturbation, and (c) self-energy matrix in Wigner-Weiskopf approximation,[10] i.e., $\Sigma(s)\cong\Sigma(-i\varepsilon_a)$. We also have taken into account nonresonant loss processes due to electron-electron scattering using a mean-free-path approximation.[13]

The capture probability $\rho_{2p\pm1}(R_0)$ as a function of the initial distance R_0 of the evolution on the outward trajectory displays a characteristic saturation behavior for $R_0\lesssim3$ a.u., i.e., ρ becomes independent of R_0 (Fig. 2). At small distances the continual creation and destruction of excited states leads to an excitation equilibrium. We also have observed small oscillations in $\rho(R_0)$ around the equilibrium value at small R_0 and higher v.[13] This loss of memory justifies the crude approximation for the trajectory near the point of closest approach ($\cong 1$ a.u.) mentioned above. At large values of R_0, ρ approaches the first-order (Born) approximation results[14] (Fig. 2). In the present case, the validity of the Born approximation for the transfer at large distances is based on the weakness of the coupling rather than the high projectile speed used as the perturbation parameter in high-energy ion-atom collisions. We also note that second-order Thomas double scattering[15] is not important in this case since the planar channel potential V_f does not support a 60° scattering event into the forward direction as required for the kinematics of the Thomas process.

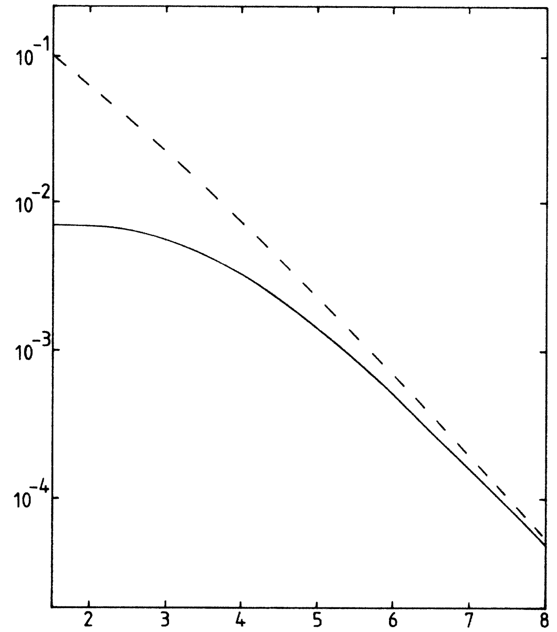

FIG. 2. Probability $\rho(R_0)$ for capture into the $2p\pm1$ state for $p\to\mathrm{Au}$ ($v=1$, $\theta=5°$) as function of the lower limit R_0 of the outward $R(t)$ integration. The surface normal is the quantization axis. (dashed line) Born approximation; (solid line) present multichannel resonance theory (see text).

The most probable distance for the formation can be inferred from the rate of change in probability, $-d\rho/dR_0$ (Fig. 3). Roughly, capture takes place at a distance $R\cong\langle r\rangle_{n=2}\cong5$ a.u. from the jellium surface, corresponding to distance of $R=\langle r\rangle_{n=2}+a/2$ (a is the lattice constant) from the outermost atomic layer of a real metal surface. This quantitatively confirms experimental data[3,16] and explains the good qualitative agreement with Born-approximation calculations[14] when a phenomenological cutoff $R_0\gtrsim\langle r\rangle_n$ was introduced. We also note a qualitative similarity of the present ($-d\rho/dR_0$) curve for $2p\pm1$ with the spatial weighting function[17] for capture derived within a fixed-ion approximation for hyperthermal surface scattering. In more detail, we find the peak of ($-d\rho/dR_0$) to be state and velocity dependent. For the $2s$ and the $2p_0$ states we observe oscillatory

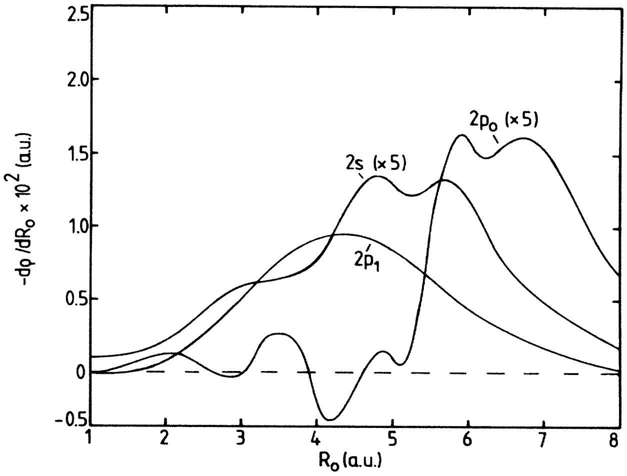

FIG. 3. Rate of change of capture probability ($-d\rho/dR_0$) for all substates $H(2lm)$ for $p\to\mathrm{Au}$ ($v=0.7$ a.u., $\theta=5°$).

structures due to strong state mixture near the surface. The distance of formation is fairly delocalized with a typical width of $\Delta R \cong 3-4$ a.u.

A simple physical picture emerges: At distances $R \ll \langle r \rangle_n$ the coupling of atomic levels to the unoccupied levels in the solid due to the overlap is so strong that the formation of excited states is followed by loss. At large distances, the coupling is so weak that the probability flux in both directions is small despite the resonant nature of the process. The final state formation effectively takes place in the transition region between these two regions.

The present treatment can be extended to a calculation of the complete density matrix of the excited-state manifold including substate coherences and the polarization characteristics of the subsequent photon emission.[13]

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