Energy loss in electronic emission from solid surfaces

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We investigate the energy loss from inelastic losses due to excitation of the substrate and neighboring atoms during the emission of electrons from atoms weakly adsorbed at solid surfaces. The ionization losses are important only for trajectories close to the surface; for greater electron escape angles the substrate gives the main contribution. [S0163-1829(97)04532-3]

In x-ray photoemission spectroscopy of solids, satellites due to discrete losses can be observed near the core-level peaks.[1–4] These losses (excitation of collective modes, bulk and surface plasmons, and single-particle transitions in the medium) may have two origins: the movement of the emitted electron, which accounts for the extrinsic losses (important in hot-electron scattering[5,6]) and the atomic optical ionization process, which accounts for the intrinsic part of the energy loss. However, experimentally, these processes are not separable because they are coherent and interfere, but, from the theoretical point of view, we are able to identify all the different contributions to the energy loss of the photoelectrons. This concept of intrinsic, extrinsic and interference was introduced by Chang and Langreth.[7] On the other hand, dealing with adsorbate core levels, the ionization of the neighboring adsorbed atoms can also take place.

Since the early 1970s, several theoretical calculations have been presented using the so-called Hamiltonian model[8] and assuming a straight-line trajectory for the photoelectron.[7,9–13] Although the dispersion can be implemented through the energy of the plasma modes, the Hamiltonian models are unable to account for single-particle transitions. Bradshaw *et al.*[2] estimated an experimental intrinsic effect to be about one order of magnitude smaller than the prediction of the Hamiltonian model with an undispersive surface plasmon energy for the $1s$ level of oxygen adsorbed on an Al(111) surface. Inglesfield[14,15] took into consideration the wave nature of the photoemitted electron and confirmed the validity of assuming classical straight electron trajectories. It turns out to be a good approximation since the recoil of the electron is not so important in plasmon excitation. Seymour and collaborators[3] studied the plasmon satellites in core-level photoemission from sodium overlayers on Al(111) using a semiclassical hydrodynamic model to describe the response of the substrate-overlayer system. Karlsson *et al.*[16] stressed the importance of final-state effects in photoelectron spectroscopy, particularly in the Schottky-barrier formation. The core-level shifts were calculated within a wave-vector-dependent image-screening model. More recently, related matter has been reported by Chen and Chen,[17] who derived a deconvolution formula including surface effects in the Landau formula for the background subtraction of electron spectra.

In this paper we study the case of emission processes from adsorbed atoms at solid surfaces within linear-response theory together with the dielectric response function formalism[18] in order to calculate the energy loss associated with the first surface plasmon satellite. The specular reflection model of Ritchie and Marusak[19] allows one to take into account nonlocal effects in the surface response: Dispersion in the surface collective modes and the continuum of electron-hole pairs are included. This approach supplies expressions that allow the use of optical experimental data as well.

The energy losses due to the ionization of the neighboring adsorbates have been calculated within the first Born approximation. The ionization process involves the creation of a photoelectron and an ionized atom left behind. We consider the electron and the atomic hole (charge equal to $+1$) created at time $t=0$ and at a distance $z=z_0$ from the surface that is located at $z=0$. The solid corresponds to the $z<0$ region, where the z direction is perpendicular to the surface. While the electron has a velocity $\mathbf{v}=(\mathbf{v}_x, v_z)$ at an angle θ to the surface, the hole characterizing the ionized atom remains at $z=z_0$. A scheme of the situation can be seen in Fig. 1.

A charged particle in the proximity of a surface modifies the distribution of charge in the material medium. This leads to an induced potential that plays an important role in the dynamics of the moving charged particles.[20–22] The interaction between the electron, the hole, and the solid surface has been treated within the well-known specular reflection model (SRM). In this model the induced charge density and image potential are given in terms of a surface response function $g_s(Q,\omega)$, which in turn can be obtained from the wave-vector-dependent response function $\epsilon(q,\omega)$ of the bulk system. The surface response function reads[23,24]

$$g_s(\mathbf{Q},\omega) = \frac{\epsilon_s(\mathbf{Q},\omega)-1}{\epsilon_s(\mathbf{Q},\omega)+1}, \qquad (1)$$

where

$$\epsilon_s(\mathbf{Q},\omega) = \frac{Q}{\pi}\int_{-\infty}^{\infty} dq_z \frac{1}{q^2}\frac{1}{\epsilon(\mathbf{q},\omega)}. \qquad (2)$$
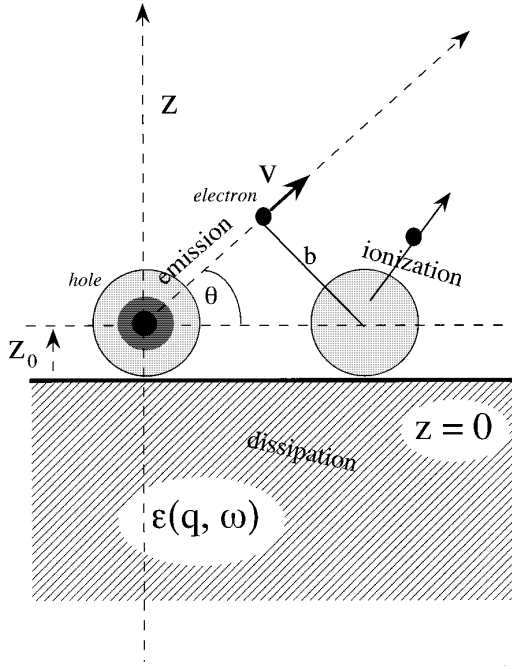
FIG. 1. Emission and channels of the energy loss scheme under investigation.

Following previous authors,[25] the rate of energy loss per unit time for a charge Z_1 moving with spatial coordinates $\mathbf{r}_{Z_1}(t)$ is given, in terms of its induced potential, by

$$w(t) = Z_1 \mathbf{v} \cdot \nabla \phi^{ind}(\mathbf{r},t)_{\mathbf{r}=\mathbf{r}_{Z_1}}. \tag{3}$$

This rate has two contributions, one conservative and the other dissipative:[26]

$$w = w_{cons} + w_{diss}, \tag{4}$$

with

$$w_{cons}(t) = Z_1 \frac{d\phi^{ind}}{dt}(\mathbf{r},t)_{\mathbf{r}=\mathbf{r}_{Z_1}} \tag{5}$$

and

$$w_{diss}(t) = -Z_1 \frac{\partial \phi^{ind}}{\partial t}(\mathbf{r},t)_{\mathbf{r}=\mathbf{r}_{Z_1}}. \tag{6}$$

Since the polarization and, consequently, the induced potential vanish at $t=0$ and $t=\infty$, the total energy loss undergone by the photoelectron will be given by integrating along the whole trajectory the rate given by Eq. (6) for the total potential (the potential induced by the electron plus the potential induced by the positively charged hole). The electron-hole-surface system is a coupled system and thus the energy spectrum of the emitted electrons depends on all the dissipative processes taking place. This means that together with the energy dissipated by the electron due to the total potential there will exist an energy shift that precisely corresponds to the screening energy of the core hole. The total amount of energy dissipated by the hole due to its sudden creation is twice its screening energy: One-half shifts the photoelectron loss spectrum and the other half is spent in its screening in front of the surface.

Taking the induced potentials given by the SRM, one finds $\Delta E = \Delta E_{ext} + \Delta E_{inter} + \Delta E_{int}$, where

$$\Delta E_{ext} = \int \frac{d\mathbf{Q}}{(2\pi)^2} \int_0^\infty \frac{d\omega}{2\pi} \frac{2\pi}{Q} \frac{2\omega e^{-2Qz_0}}{\Omega^2 + (Qv_z)^2} R_s(\mathbf{Q},\omega), \tag{7a}$$

$$\Delta E_{inter} = \int \frac{d\mathbf{Q}}{(2\pi)^2} \int_0^\infty \frac{d\omega}{2\pi} \frac{2\pi}{Q} \frac{-4\Omega e^{-2Qz_0}}{\Omega^2 + (Qv_z)^2} R_s(\mathbf{Q},\omega), \tag{7b}$$

and

$$\Delta E_{int} = \frac{1}{2} \int \frac{d\mathbf{Q}}{(2\pi)^2} \frac{2\pi}{Q} e^{-2Qz_0} \mathrm{Re}[-g_s(\mathbf{Q},\omega)]. \tag{7c}$$

These terms are the extrinsic, the interference, and the intrinsic loss, respectively. $\Omega = \omega - \mathbf{Q}\mathbf{v}_x$ and $R_s = \mathrm{Im}[-g_s]$. Assuming a Drude bulk dielectric function, one has $\mathrm{Im}[-g_s(Q,\omega)] = (\pi/2)\omega_s \delta(\omega - \omega_s)$ in the limit of zero damping. ω_s is the surface plasmon energy. Taking $v \to \infty$ in Eqs. (7) the energy loss is given by[2]

$$\Delta E = \frac{\pi\omega_s}{2v}\left(\frac{1}{2\sin\theta} - 1 + \frac{Q_c v}{\pi\omega_s}\frac{1 - e^{-2Q_c z_0}}{2Q_c z_0}\right). \tag{8}$$

Q_c is the parallel momentum cutoff that accounts for the minimum wavelength of the surface polarization waves in the electron gas.[27] In this expression the first term is the extrinsic loss,[28,29] the second the interference loss and the last one corresponds to the screening energy of the core hole, i.e., the intrinsic shift.

The energy loss due to the ionization of the neighboring adsorbate is found in terms of the transition amplitude $a_{if}(\epsilon,\mathbf{b})$ from the electronic atomic state i, with ionization potential ϵ_i, to the state f, with energy ϵ above the vacuum level, as

$$\Delta E_{ion}(b) = \sum_i \sum_f \int_0^\infty d\epsilon(\epsilon + \epsilon_i) \int_0^{2\pi} \frac{d\varphi}{2\pi} |a_{if}(\epsilon,\mathbf{b})|^2 \tag{9}$$

In this formula b is the minimum distance from the photoelectron trajectory to the neighboring atom, i.e., the impact parameter. The transition amplitude has been calculated within the first Born approximation. In this approximation one has[30,31]

$$a_{if}(\epsilon,\mathbf{b}) = \frac{1}{4\pi^2 v} \int d\mathbf{k}_\perp e^{i\mathbf{k}_\perp \cdot \mathbf{b}} \frac{4\pi}{q^2} \langle f|e^{i\mathbf{q}\cdot\mathbf{r}}|i\rangle, \tag{10}$$

where $\mathbf{r}$ is the electron vector position relative to the target atom and $\mathbf{q}$ is the transferred momentum in the interaction

$$\mathbf{q} = \frac{(\epsilon + \epsilon_i)}{v}\hat{\mathbf{v}} + \mathbf{k}_\perp, \tag{11}$$

with

$$\mathbf{k}_\perp \cdot \mathbf{v} = 0. \tag{12}$$

Both the electron energies and wave functions have been approximated to those of the isolated neutral atom. For their
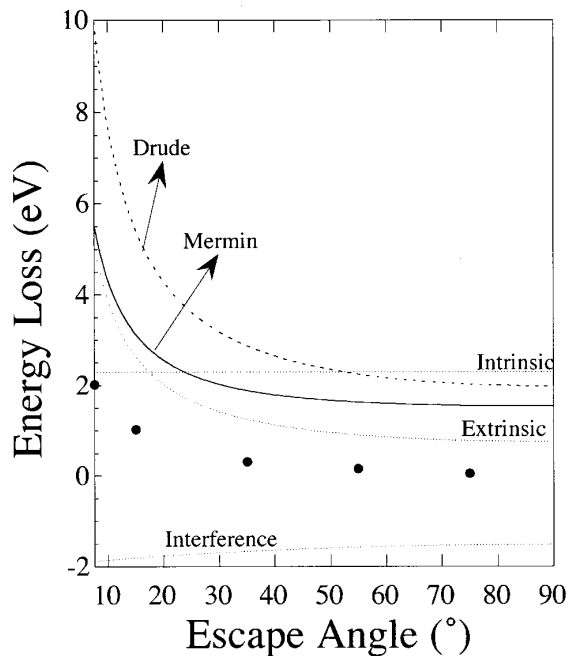
FIG. 2. Electron energy loss due to the dissipation at the substrate and the contribution of the different processes depicted as functions of the angle of emission. The continuous line represents the energy loss assuming the Mermin prescription in the bulk response function $\epsilon(q,\omega)$ and the dashed line the same for a Drude-like approximation with zero damping. The core site is $z_0=2$ a.u. and the kinetic energy of the electron is 730 eV. The substrate is aluminum simulated with an electron mean radius $r_s=2.07$ a.u. and a electron damping rate $\gamma=1.35$ eV. The points are the experimental data obtained by Bradshaw, Domcke, and Cederbaum (Ref. 2).
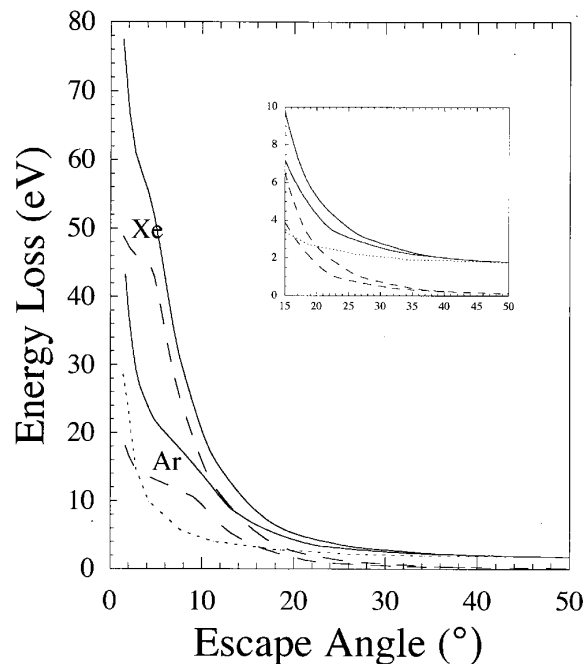

FIG. 3. Energy loss due to the substrate (dotted line) and the energy loss due to the ionization of a neighboring atom (broken line) depicted as functions of the escape angle for two different adsorbates (Ar and Xe). The continuous line represents the total loss in each case. The kinetic energy of the photoelectron is 1 keV and the substrate is graphite ($r_s=1.447$ a.u. and $\gamma=10$ eV). The distance between the adsorbates is twice its atomic radius (3.6 a.u. for Ar and 4.1 a.u. for Xe) and the core site is $z_0=2$ a.u. For both adsorbates, only the ionization of the outer shells have been considered: for Ar, the $3s$ and $3p$ levels and for Xe the $4d$, $5s$, and $5p$ levels. The inset shows the behavior at large angles.

calculation we have used a Hartree-Fock-Slater model potential together with a Numerov algorithm.[32]

For the surface response function $g_s(Q,\omega)$, the Mermin prescription to the random-phase approximation has been considered in $\epsilon(\mathbf{q},\omega)$.[33] In Fig. 2 the energy loss as a function of the escape angle of the photoelectron with a kinetic energy of 730 eV is shown for emission from aluminum. The nonlocal effects shift down the energy loss and give different results mainly for trajectories closer to the surface where the scattering processes with greater transferred momentum take place.

In Fig. 3 the energy loss taking into account the ionization of a neighboring atom is shown. As can be observed, only for very close trajectories (in fact, the electron crosses the electronic cloud) is the relevant contribution the ionization. This means that the effect of the absorbate excited core in the ionization of the neighboring atom is negligible. For angles greater than $\sim45°$ the screening is completely dominated by the substrate. In any case, the energy loss indeed is expected

to be lower because repulsion between valence electronic clouds of the adsorbate and the screening electrons of the medium occurs and the intrinsic shift is overestimated in our model.

To summarize, the energy loss due to the excitation of surface plasmons and single-particle transitions and due to the ionization of neighboring atoms in the electronic emission from adsorbates at solid surfaces has been calculated. Nonlocal effects in the surface response have been included through the SRM. The energy loss due to the ionization of the neighboring atoms has been found to be relevant only for very close trajectories.

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