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Dynamical effects on image-induced surface resonances at nearly-free-electron metal surfaces

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A mechanism for surface image-state formation in inverse-photoemission spectroscopy at free-electron-like metal surfaces is proposed and applied explicitly to Al(111). In the analysis, a multiple-scattering approach is used where the substrate (jellium) reflectivity to an electron virtual-photon field (or bremsstrahlung electromagnetic radiation) produced in the inverse-photoemission experiment is calculated via the Fresnel equations with the nonlocal surface corrections using the *d*-parameter formalism. In contrast to earlier statements, we assign the measured peak on inverse-photoemission spectra at Al(111) to the $n=2$ image surface state only.

Among problems of an external electron interacting with the semi-infinite polarizable medium the question of bound-electron states at metal surfaces is important. In fact, apart from the well-known Shockley or Tamm (crystal-induced) surface states[1] the electron can be trapped by its own image potential $(4z)^{-1}$ outside the solid. Such potential allows an infinite Rydberg-like series of electronic states (image- or barrier-induced surface states) to exist.[2,3]

A clear picture of the image- and crystal-induced surface states can be obtained in terms of the scattering theory as suggested by Echenique and Pendry[2] and Radny.[4] In both cases, the surface states are created by multiple scattering between the atomic potential of the crystal and the surface potential barrier. If $R_C=r_C e^{i\phi_C}$ and $R_B=r_B e^{i\phi_B}$ are the reflection coefficients at the crystal and surface potential, respectively, the bound surface states arise in the energy region of the band gap if[2]

$$r_C r_B=1 \quad \text{and} \quad \phi_C(E)+\phi_B(E)=2\pi n\ , \qquad n=0,1,2,\ldots\ . \tag{1}$$

To properly analyze the surface resonances that arise in the energy region outside the crystal band gap ($r_C<1$) the density of states $n_{k_\parallel=0}(z;E)$ should be calculated[4,5]

$$n_{k_\parallel=0}(z;E)=[1/\pi k(z)]\left[1-(r_C r_B)^2+r_C(1-r_B^2)\cos\left[2\int_0^z k(z')dz'+\phi_C\right]\right.$$
$$\left.+r_B(1-r_c^2)\cos\left[\phi_B-2\int_0^z k(z')dz'\right]\right]\left|1-r_B r_C e^{i(\phi_C+\phi_B)}\right|^{-2}\ , \tag{2}$$

where $k(z)=\{2[E-V_B(z)]\}^{1/2}$ and $V_B(z)$ describes the surface potential barrier shape (Hartree atomic units are used throughout).

As follows from the analysis performed by Radny[5] the image surface-state formation can be understood in terms of a high substrate reflectivity. Namely, as long as the amplitude r_C is equal or close to unity the multiple-scattering effects are strong and the electron trapping discussed here can be understood as effected by the diffraction of the incident electron via a reciprocial surface lattice vector into the image state (Bragg scattering). If the bulk lattice corrugation [determined via the low-energy electron-diffraction process (LEED)] is weak, r_C decreases rapidly outside the small band gap [cf. Al(111), Fig. 2 in Ref. 6] and acts as a relatively weak perturbation in Eq. (2). In other words, far from the metal band gap the static crystal potential does not provide enough reflectivity for the image-induced surface states (resonances) to form. However, the image states have been observed close to the vacuum level, far from any metal band gap, at the clean surface of Al(111).[7] On the other hand, in the theoretical analysis performed so far no mechanism was identified that could provide the necessary reflectivity for such states to form.[6–11] Only recently,[12] and independently of this work, this discrepancy was attributed to the fact that the measurements were carried out by the inverse photoemission spectroscopy (IPES) where the dynamic screening properties of the metal surface should be taken into account. Such effects have recently received considerable attention because of the importance for many low-energy surface spectroscopies like ultraviolet photoemission, low-energy-electron loss, differential reflectance, as well as chemically important phenomena like sticking and desorption.[13]

Generally, in inverse photoemission an incident electron is trapped by a temporary but long-lived image-dipole-induced surface state in the intermediate stage of the scattering (bremsstrahlung) process and then photons with fixed energy are observed. At the free-electron metal like Al, in the intermediate stage of the bremsstrahlung process the incident electron can be scattered into the image state via virtual surface-plasmon excitation instead of Bragg scattering.[9]

We consider a model which consists of a metal filling the space $z<0$ and a vacuum filling $z>0$. The metal [jellium: $r_{C(\mathrm{LEED})} \cong 0$ in Eq. (2)] is represented by a dispersionless Drude model with a simple local dielectric function

$$\epsilon(\omega)=1-(\omega_p/\omega)^2 \ . \tag{3}$$

So, the surface is represented here by a step function change of dielectric function from $\epsilon(\omega)$ for $z<0$ [Eq. (3)] to $\epsilon(\omega)=1$ in the vacuum.

The surface dielectric response is significant for low-energy scattering processes where the electrons of a solid can follow the time variation of an external imposed field (nonretarded, long-wavelength regime). In this case ω is below the emission threshold, i.e., a photon does not carry enough momentum at any given energy to excite the real plasmon, so that virtual plasmons can be induced. It is known that at metal surfaces such excitations effectively screen out the external fields from the bulk and that the image potential may be considered to arise from the interaction of the electron with these surface modes. The contribution to the total potential (correlation and exchange energy) is real in this case and should be added to the crystal potential for any electronic structure calculations.[14,15]

The electron and solid must communicate via the exchange of real or virtual photons and this interaction can be completely describable in terms of the reflection amplitudes like in the classical Fresnel approach. In general, a slowly moving electron is a white source of photons and the bremsstrahlung electromagnetic radiation (or virtual photon field)[16] consists of rather long-wavelength field components. In this limit the key quantity that characterizes the electron response to the electromagnetic fields is the function $d(\omega)$ of the screening charge density induced by an electric field applied to the surface. Among the quantities that are directly determined by $d(\omega)$ are the nonlocal surface corrections to the classical Fresnel reflectivity formulas[13,17,18]

$$R_s=\frac{1-(\epsilon)^{1/2}-i[1+(k_z/k_x)^2]}{1-(\epsilon)^{1/2}+i[1+(k_z/k_x)^2]}\,\frac{[(k_x^2)/k_z]}{[(k_x^2)/k_z]}\,\frac{d_\parallel(\epsilon-1)}{d_\parallel(\epsilon-1)} \ , \tag{4}$$

$$R_p=\frac{\epsilon-(\epsilon)^{1/2}-i[(k_x^2/k_z)d_\perp-k_z d_\parallel]}{\epsilon-(\epsilon)^{1/2}+i[(k_x^2/k_z)d_\perp+k_z d_\parallel]}\,\frac{(\epsilon-1)}{(\epsilon-1)} \ , \tag{5}$$

where subscripts s and p denote the s- and p-polarized light; k_x and k_z are components of the wave vector of the impinging photon, while $d_\parallel$ and $d_\perp$ denote the parallel and perpendicular component of $d(\omega)$, respectively.

In general, the function $d(\omega)$ determines forces on charged particles near the surface. It is complex because there are dissipating forces involved. In classical terms $d(\omega)$ is related to the dynamic image plane position $z_i(\omega)$, i.e., is a measure of the centroid of the induced surface charge density with respect to the jellium edge below the plasma frequency. After Feibelman[13]

$$z_i(\omega)=\mathrm{Re}\{\epsilon(\omega)d_\perp/[\epsilon(\omega)+1]\} \ , \tag{6}$$

because for jellium $d_\parallel$ vanish by conservation of the parallel momentum.[17]

Quantum mechanically $d(\omega)$ describes the surface excitation of electron-hole pairs. Because the phase space for such excitation grows proportionally to ω, after[18,19]

$$\mathrm{Im}[d_\perp(\omega)]=\xi(\omega/\omega_p) \ , \tag{7}$$

where the low-frequency slope ξ was calculated within the time-dependent local-density approximation (TDLDA) and for $r_s=2$ (for Al, $r_s=2.07$) $\xi=0.85$.[18]

Now, let us consider the picture presented above as a whole. The solid [Eq. (3)] is flat with an x-y plane at $z=0$. According to the electrodynamics of moving charge we can assume that the electron approaching the solid along the surface normal is a source of photons that have projections of a wave vector parallel to v not restricted to any particular value from 0 (measured from the Fermi level) to $\hbar k_z=m_e v$. The parallel component is determined from the requirement $\hbar k_x(k_y)=m_e v$. The problem now is how to determine the value of the induced electric field outside the metal surface. In general the macroscopic electric field in this region can take the form[13,17]

$$E_\omega^{\mathrm{ext}}=e^{i\bar{k}_\parallel-\bar{r}_\parallel}(E^I e^{-ik_z z}+E^R e^{ik_z z}), \quad z>0 \tag{8}$$

where E^I and E^R are the amplitudes of incident and reflected electric fields, respectively (magnetic effects are negligible). Due to the long wavelength of the bremsstrahlung radiation, the scale of length describing the spatial variation of the induced fields is correspondingly large and only the large wavelength limit of the reflection amplitudes will be necessary to describe the interaction. So, according to the discussion performed by Langreth[17] the induced electric field can be simply treated as the (x,y,z) component field with the wave-vector components (k_x,k_y,k_z) equal to zero, and consequently the reflectivity coefficients can be expressed as

$$R_s=E_x^R/E_x^I \ , \tag{9}$$

$$R_p=E_z^R/E_z^I \ , \tag{10}$$

where the explicit expressions for R_s and R_p are given in Eqs. (4) and (5), respectively. In other words, although excited virtual plasmons decay into photons each time as the electron represented by the electromagnetic field of frequency $\omega<\omega_p$ impinges on a solid, in the long-wavelength limit Eqs. (9) and (10) represent the response of the surface to a constant external electric field in the z direction (see also Ref. 20).

The direct measurement of the total crystal reflectivity $|R|$ to the bremsstrahlung radiation is not easy. However, its relation to the light intensity is simply[21]

$$I \simeq I_i |R|^2 \ , \tag{11}$$

where I and I_i are intensities of the reflected and incident light beams, respectively. It is known that the intensity of the IPES spectra comparison with, e.g., the photoemission one is very small.[22] On the other hand, translation invariance parallel to the surface means that the electric field of the induced surface plasmons have p polarization.[23] Moreover, for the jellium surface the energy dependence of the reflected-light intensity for the p-polarized and unpolarized beam are the same.[22] An approximate but physically instructive treatment embodying the above picture is to take the dynamical jellium reflectivity $|R|$ with the R_s and R_p contribution from Eqs. (4) and (5) in the form[24]

$$|R|e^{i\phi}=||R_s|e^{i\phi_s}+|R_p|e^{i\phi_p}|e^{i\phi_{sp}}=|R_{sp}|e^{i\phi_{sp}} \; . \qquad (12)$$

Notice that because R_s from Eq. (4) for incoming electron states between the Fermi energy E_F and the vacuum level E_V is very close to -1 ($d_\parallel=0$), in the case discussed here [$r_{C(\mathrm{LEED})}\cong 0$ in Eq. (2)], the energy dependence of $|R|$ for the unpolarized light is the same as for p-polarized beam; only the intensities will drastically change.

The effect of the surface scattering is seen from Eq. (12) explicitly—when the response function $d(\omega)$ is zero we recover the standard Fresnel formulas and the effect of the dielectric surface response is negligible—only the LEED reflectivity r_C should be taken into account. The numerical verification of this static effect—for r_C in Eq. (2) calculated from the two-band nearly-free-electron model[5,6]—is presented in Fig. 1(b) [in all calculations presented in Fig. 1 the static ($\omega=0$), shifted image-potential barrier with a smooth transition to its bulk value U_0 is used with the parameters appropriate for aluminium,[25] $U_0=0.54$ a.u., the distance over which the image potential saturates $\lambda=1.0$ a.u. and the static image plane $z_i(\omega=0)=2.95$ a.u.]. In Fig. 1(a) the LEED reflectivity r_C as well as the surface dielectric response discussed here $|R_{sp}|$ are equal to zero (static jellium). It is easy to see that although the electronic band structure with the band gap at ~ 7 eV for the proper $r_C(E)$ dependence is created [Fig. 1(b)], the local density of states (LDOS) above the Fermi level E_F (>11 eV) characterizes *delocalized* states like at the jellium surface [Fig. 1(a)]. Oscillations of LDOS curves arise due to the barrier phase shift $\phi_B(E)$ which describes the surface barrier shape (see Ref. 5).

The effect of the dynamical screening of the moving electron (10 eV above the vacuum level) toward a jellium surface along its normal was calculated from Eqs. (3)–(5), (12), and (2). The calculations have been performed for $\omega_p=15$ eV, $d_\parallel=0$; $\mathrm{Re}[d_\perp(\omega)]$ was determined from Eq. (7) for $z_i(\omega=0)=2.95$ a.u. as an input parameter, and $\mathrm{Im}[d_\perp(\omega)]$ from Eq. (8) for ω from 0 at E_F up to the vacuum level E_v (15.21 eV). The results of calculations are presented in Fig. 1(c), where $r_{C(\mathrm{LEED})}e^{i\phi_C}$($\cong 0$) in Eq. (2) was added to $|R|e^{i\phi}$ from Eq. (12). In contrast to the LDOS picture from Figs. 1(a) and 1(b), it is clear now how different LDOS build up the image-induced surface resonances at Al(111) surface.

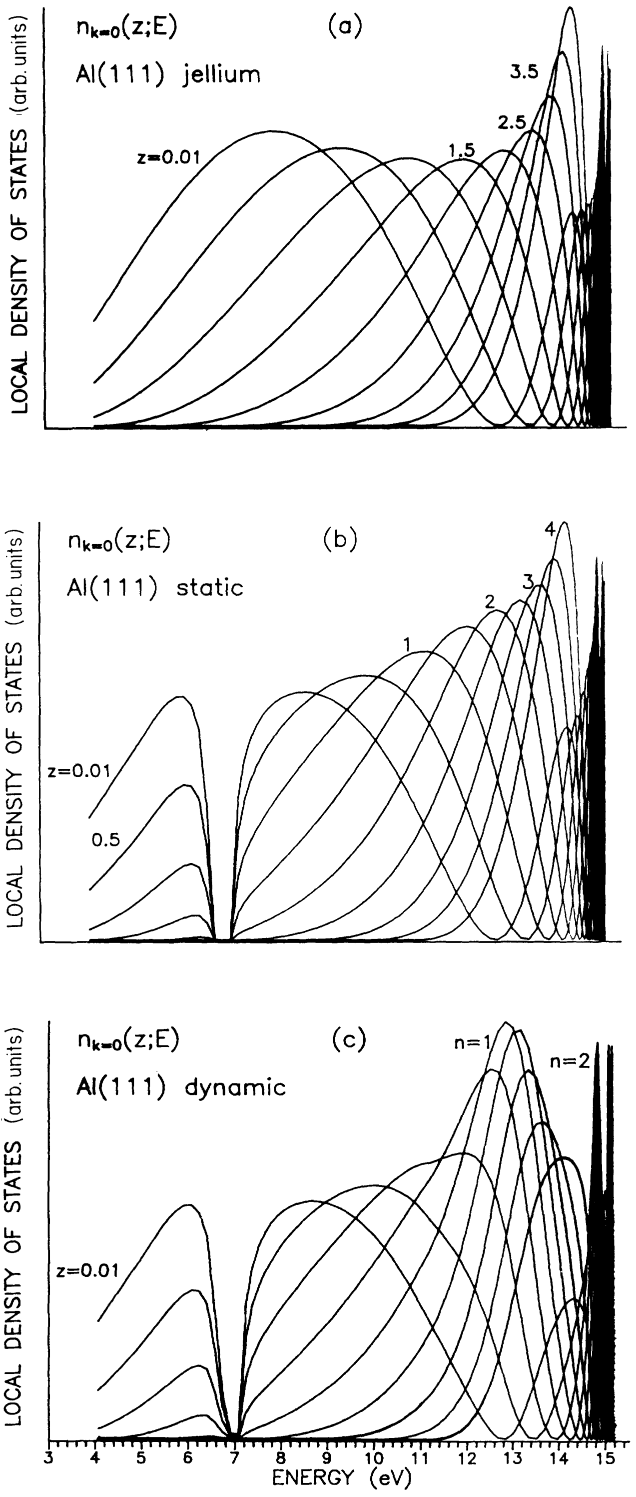

FIG. 1. The static [(a) and (b)] and dynamic (c) local density of states calculated from Eq. (2) for (a) the jellium model: $r_C(E)=0$; (b) the proper $r_C(E)$ (LEED) dependence obtained from the two-band nearly-free-electron model (Refs. 5 and 6); (c) the same $r_C(E)$ dependence as in (b) with the dynamic surface corrections; $n=1,2$ denotes the image-barrier-induced surface resonances. Presented calculations are performed for $z=0.01$, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 a.u. and, the *JJJ* surface barrier model [parameters appropriate for Al(111)—Ref. 25].

The experimentally measured value of the image-induced resonant state at Al(111) is 0.39 eV below E_v.[7] It is clear from our results that such binding energy is relevant to image states numbered by $n=2$ (-0.37 eV). The image state numbered $n=1$ (-1.92 eV), probably due to the smallness of the phase space for the electron-hole excitation [Eq. (8)], is evidently to broaden (very short life time) to be resolved in an IPES experiment. Although without an analysis concerning damping effects ($R_C=1$), a very similar energy distribution for $n=1,2,3,\ldots$ image states has been discussed by Gies.[8]

We conclude with several comments. The first is that because in the low-energy scattering on charged particles from surfaces the gradient of a scalar potential always has a significant component along the surface normal, the surface dielectric behavior should be considered in any surface scattering calculations [see Eqs. (4), (5), and (12) and Refs. 13, 23, and 20].

The next is that a large part of the literature about the image states is devoted to the search for improved surface potential barrier models for the binding-energy calculation of the hydrogenlike series—$E_s=(n+\delta)^{-2}$, where $n=1,2,\ldots$ and δ is level and barrier model-dependent quantum defect.[3,15,25–27] We want to point out that we were mainly interested here in the possibility of resolving the Rydberg series at free-electron metal surfaces ($R_C=?$) and not in the actual binding ($\phi_B=?$). However, after Tamura and Feder[27] we can state that because the dynamic effects on the surface potential barrier shape are small for the image states numbered $n>1$, the static surface barrier model is good enough even for the quantitative IPES Al(111) data analysis. On the other hand, a better model would be taken into account for the solid-vacuum interface by taking, for example, a more adequate dielectric function for such a system.[13] We were, however, more concerned here with the mechanism involved which already appears in this simple treatment.

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