Multipole surface-plasmon-excitation enhancement in metals

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We consider the energy losses undergone by an electron reflected inside the extended electron-density distribution at the surface of a metal. The random-phase approximation calculation of the dynamical response with a local-density approximation ground state reveals the dramatic enhancement of the multipole-plasmon intensity compared with the conventionally considered reflection in vacuum above the surface. Our calculations conciliate the theory and the electron-energy-loss spectroscopy experiment with regard to the multipole surface-plasmon intensity, which has been predicted by previous theories to be two orders of magnitude smaller than the experimental one. The influence of the nonzero electron density along the incident electron path on the surface and the bulk-plasmon generation is also discussed. [S0163-1829(99)00115-0]

Multipole-plasmon (MP) modes at metal surfaces were predicted by Bennett within the hydrodynamic approximation. In recent years, the excitation of these modes was demonstrated experimentally by the use of electron-energy-loss spectroscopy (EELS) and supported theoretically by quantum-mechanical calculations. A good agreement between theory and experiment had been achieved in these works for simple metals with regard to the monopole and multipole surface-plasmon dispersion and damping.

However, for all the metals dealt with and for all the geometries of electron scattering assumed the calculated spectra demonstrated a very weak MP peak, compared with the monopole surface-plasmon (SP) one, while experimentally (e.g., in the case of K and Na) SP and MP peaks display themselves on an equal footing.

Let us recall that the surface energy-loss function, introduced in Ref. 4 and conventionally used to describe the inelastic scattering at surfaces, by its definition pertains to the reflection in vacuum above the surface (dipole regime). This means that for models with abrupt static electron-density fall off, reflection of a charge is assumed to occur outside the electron density of the target. For self-consistent extended static electron densities, such as that of Lang and Kohn (LK), this suggests that reflection takes place at negligible charge density, mathematically at infinity above the surface. Meanwhile it is clear that the back scattering of the incident beam is due to the reflection from the lattice and LK electron density is not negligible at the turning point of incident charges (impact regime). It could be supposed then that the discrepancy between the theory and the experiment with regard to the MP intensities was due to utilizing the dipole-regime theory to account for the impact-regime experiment.

Recently the formalism accounting for ions penetrating the surface of a solid has been developed. However, these works deal with the ion-stimulated electron emission and do not address the problem of MP excitation in EELS. The purpose of the present work is to follow SP, MP, and bulk-plasmon (BP) behavior depending on the penetration depth of probing charges. We use LK densities of unperturbed jellium surfaces of K, Na, and Al to calculate the random-phase approximation (RPA) response to an external charge reflected at diverse distances to both sides of the surface. For reflection at the jellium edge we find the intensity of MP to be much larger than that obtained in Ref. 2 for reflection in vacuum. When the penetration increases under the edge, MP intensities for K and Na continue to grow, while for Al it merges with the left wing of BP, both conclusions being in agreement with experiment.

The inelastic scattering of a charge reflected at \( z = c \) can be characterized by the energy-loss function

\[
L(\omega, q_i) = \frac{q_i}{(2\pi)^2} \Im \int dq_z dk_z e^{i(q_z - k_z)c} \frac{e^{-1(q_z, k_z, q_i, \omega)}}{(k_z^2 + q_i^2)^{1/2} - \epsilon^{-1(q_z, k_z, q_i, \omega)}} \times \left[ \frac{1}{p - p' + p'q/p' + i0^+} + \frac{1}{p' - p + pq/p + i0^+} \right] \times \left[ \frac{1}{p - p' + pk/p' - i0^+} + \frac{1}{p' - p - pk/p - i0^+} \right],
\]

(1)

where \( p \) and \( p' \) are the momentum of the charge before and after the scattering, \( q_i = p_i - p_i' \) and \( \omega = p^2 - p'^2 \) are the momentum and the energy loss, and the inverse dielectric function \( \epsilon^{-1} \) is defined by the nonlocal relation

\[
\phi(q_z, q_i, \omega) = \int e^{-1(q_z, k_z, q_i, \omega)} \phi_{\text{ext}}(k_z, q_i, \omega) dk_z,
\]

where \( \phi_{\text{ext}} \) and \( \phi \) are the external and the total scalar potentials. Energy is measured in rydbergs. In real space, we have to solve the integral equation

\[
\phi(z) = \int_{-\infty}^{\infty} \Pi(z, z') \phi(z') dz' = \phi_{\text{ext}}(z),
\]

(2)

where in RPA

\[
\Pi(z, z', q_i, \omega) = \frac{2\pi}{q_i} \int_{-\infty}^{\infty} \frac{e^{-\eta|z-z'|}}{\chi_0(z'', z', q_i, \omega)} dz''.
\]
with the independent-particle susceptibility

\[
\chi^{0}(z,z') = \frac{1}{\pi} \int d\mathbf{p}_i d\mathbf{p}_z d\mathbf{p}_2 \psi_{p1}^*(z) \psi_{p1}(z') \psi_{p2}(z) \psi_{p2}^*(z') \\
\times \frac{f^2((\mathbf{p}_1 + \mathbf{p}_z)^2) - f^2((\mathbf{p}_2 + \mathbf{p}_1 + \mathbf{q}))}{\omega + i0_+ + \mathbf{p}_1^2 - \mathbf{p}_2^2 + \mathbf{p}_1^2 - (\mathbf{p}_1 + \mathbf{q})^2},
\]

where \( \psi_{p}(z) \) are the wave functions of the ground state jellium and \( f \) is the Fermi function, temperature assumed to be zero. \( \phi_{\text{ext}} \) is created by the charge density of the incident electron

\[
\rho_{\text{ext}}(\mathbf{q},z) = \frac{1}{\pi} \int \frac{d\mathbf{p}_i}{\cos \theta_f} + \frac{\sin \theta_f}{\cos \theta_f} \Theta(z-c)/4\pi.
\]

where \( \Theta(z) = 0,1 \) if \( z \leq, > 0, q_{f,i} = \pm (p' - p - q_{i}) \sin \theta_{f,i}/\cos \theta_f \), and \( \theta_f \) and \( \theta_i \) are the angles of incidence and reflection. Then by Eq. (1)

\[
L(\omega, q) = -q_1 \Im \int_{c}^{\infty} \rho_{\text{ext}}^*(z) \phi(z) dz.
\]

Susceptibility (3) can be expressed by

\[
\chi^{0}(z,z') = \frac{1}{\pi} \int d\mathbf{p}_i d\mathbf{p}_z d\mathbf{p}_2 \psi_{p1}^*(z) \psi_{p1}(z') \psi_{p2}(z) \psi_{p2}^*(z') \\
\times \frac{f^2((\mathbf{p}_1 + \mathbf{p}_z)^2) - f^2((\mathbf{p}_2 + \mathbf{p}_1 + \mathbf{q}))}{\omega + i0_+ + \mathbf{p}_1^2 - \mathbf{p}_2^2 + \mathbf{p}_1^2 - (\mathbf{p}_1 + \mathbf{q})^2},
\]

where \( \psi_{p}(z) \) are the wave functions of the ground state jellium and \( f \) is the Fermi function, temperature assumed to be zero. \( \phi_{\text{ext}} \) is created by the charge density of the incident electron

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where \( \Theta(z) = 0,1 \) if \( z \leq, > 0, q_{f,i} = \pm (p' - p - q_{i}) \sin \theta_{f,i}/\cos \theta_f \), and \( \theta_f \) and \( \theta_i \) are the angles of incidence and reflection. Then by Eq. (1)

\[
L(\omega, q) = -q_1 \Im \int_{c}^{\infty} \rho_{\text{ext}}^*(z) \phi(z) dz.
\]
starting from larger depths. In the case of Al, MP appears starting from $c' = 0.5$ a.u., grows in amplitude, and shifts to higher energies influenced by the rising BP, until the former merges with the left wing of the latter.

In Figs. 4 and 5 the theoretical curves in a qualitative agreement with the experimental spectra for K, Na, and Al are presented. For K and Na, our calculation demonstrates the pronounced MP and BP peaks in the off-specular geometry. The penetration should be about 8.5 and 4.5 a.u. for K and Na, respectively, to match the observed relative intensities of plasmons. For the $\langle 111 \rangle$ face these values lie between the second and the third atomic layers for K and between the first and the second ones for Na, the first layer assumed to be at half the interplane distance from the jellium edge. For Al, experiment does not reveal any trace of MP, which is the case with the theory starting from $c' = 2.3$ a.u. This value lies between the first ($-2.25$ a.u.) and the second ($-6.63$ a.u.) layers in this direction, much closer to the first one.

Although our jellium calculations show reasonable agreement with experiment, let us discuss the possible extensions beyond this model. Unlike BP and SP energies, which in the long-wave limit are the bulk quantities of a medium, the energy of the MP mode depends crucially on the static charge density at the surface. The general tendency is that the steeper is the density fall off the closer to unity is the ratio of MP and BP energies, until the two modes merge in the infinite barrier limit. It is also known that the electron density at the Al(111) surface becomes steeper than that of jellium if the crystalline potential is included. We have
calculated the spectrum of Al(111) with the crystalline potential from Ref. 12 (dashed line in Fig. 5). It can be seen that the crystallinity further decreases the penetration needed for MP to fade at the left wing of BP, making reflection from the first layer consistent with the experiment.

We are now in a position to explain the behavior of the SP, MP, and BP peaks in the EELS under reflection geometry. First we can assert that unlike the dipole mode calculations, for all the metals considered the account of the non-zero electron density along the incident electron path gives rise to the pronounced MP peak. The reason why MP is zero electron density along the incident electron path gives the considerable increase of MP intensity previously obtained in the dipole regime. For Al, our calculation also gives the considerable increase of MP intensity at very small penetrations, which then, in accord with experiment, disappears at experimentally achievable penetrations.

In conclusion, the multipole-plasmon excitation in the impact-regime reflection EELS is explained in the framework of the impact-regime theory. The RPA calculation of the dynamical screening of an incident charge reflected inside the distributed charge density at a simple metal surface demonstrates high sensitivity of MP amplitude to the penetration depth of the probe. Our results account for the observed MP amplitudes for K and Na, which are about two orders of magnitude larger than those previously obtained in the dipole regime. For Al, our calculation also gives the considerable increase of MP intensity with penetration.

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9For peak positions for alkali metals, two sources of discrepancy between RPA and experiment are to be taken into account: (1) \( \omega_p / \omega_s \) is not exactly \( \sqrt{2} \) experimentally and (2) RPA overestimates SP dispersion at larger \( q \parallel \) (Ref. 2).
11In the hydrodynamic approximation this had been shown by A. G. Eguiluz, S. C. Ying, and J. J. Quinn, Phys. Rev. B 11, 2118 (1975). Our recent calculations confirm this in RPA [V. U. Nazarov and Yu. V. Luniakov (unpublished)].