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Surface effects on the electronic energy loss of charged particles entering a metal surface

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Abstract

Surface effects on the electronic energy loss of charged particles entering a metal surface are investigated within linear-response theory, in the framework of time-dependent density functional theory. Interesting phenomena occur in the loss spectra originated by the boundary (bregenzung) effect, which is as a consequence of the orthogonality of surface and bulk excitation modes. Our calculations indicate that the presence of a non-abrupt electron-density profile at the surface severely affects the nature of surface excitations, as deduced from comparison with simplified models.

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1. Introduction

A moving particle approaching a metal surface loses part of its energy as a consequence of the creation of electron–hole pairs and both bulk and surface collective excitations, i.e., plasmons [1,2]. A theoretical description of these electronic excitations is basic to understand the processes involved in several spectroscopies, such as X-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), and reflection-electron energy-loss spectroscopy (REELS) [3]. Equally, the interaction of moving ions with solids has represented an active field of basic and applied physics [4,5].

In this paper, we follow the theoretical framework developed in Refs. [6,7] and focus on the interaction of charged particles moving with constant velocity along a definite trajectory that is perpendicular to a jellium surface. Previous linear-response calculations of the energy loss of charged particles entering a metal surface were carried out with the use of simplified models [8,9]. Here we present self-consistent calculations of the energy-loss spectra, as obtained in the framework of time-dependent density-functional theory (TDDFT) [10,11]. Although in the case of charged particles moving inside a solid nonlinear effects may be crucial in the interpretation of energy-loss measurements [12–14], surface effects are expected to be well described within linear-response theory, unless the velocity of the probe particle is small compared to the Fermi velocity of the solid [15].

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Contributions to the energy loss coming from the excitation of bulk and surface plasmons are studied in detail, as well as the influence of an appropriate characterization of the electron density at the surface. The latter is found to be essential when the particle penetrates the solid, as the surface region is particularly perturbed when the particle crosses the surface. Besides, interference effects occurring between the various parts of the ion trajectory are more relevant than in the case of charged particles moving at a fixed distance from the surface, which claims for the need of a self-consistent treatment of the surface electronic response.

In Section 2, we briefly discuss general expressions for the energy-loss spectra of charged particles entering a solid surface along a trajectory that is perpendicular to the surface. In Section 3, we report the results of our full self-consistent calculations, and the effect that the electronic self-energy at a metal surface has on the energy-loss spectra is discussed by comparing our full calculations with those obtained for electron densities that drop abruptly to zero at the surface. Unless otherwise is stated, atomic units are used throughout, i.e., $e^2 = \hbar = m_e = 1$.

2. Theory

Let us consider a recoilless particle of charge Z_1 moving with non-relativistic velocity v along a definite trajectory that is perpendicular to a metal surface (see Fig. 1). The moving particle will be characterized by a classical charge distribution. The solid will be described by a bounded free-electron gas normal to the z -axis, consisting of a fixed uniform positive background plus a neutralizing cloud of interacting electrons of density $n(z)$.

Within linear-response theory, the probability per unit time and unit energy for the probe particle at z to transfer energy ω to the solid is found to be [6,7]

$$P_z(\omega) = -\frac{Z_1^2}{2\pi^2 v} \int_{-\infty}^{+\infty} dz' \times \cos[\omega(z-z')/v] \int dq q \operatorname{Im} W(z, z'; q, \omega), \quad (1)$$

where \mathbf{q} represents a wave vector parallel to the

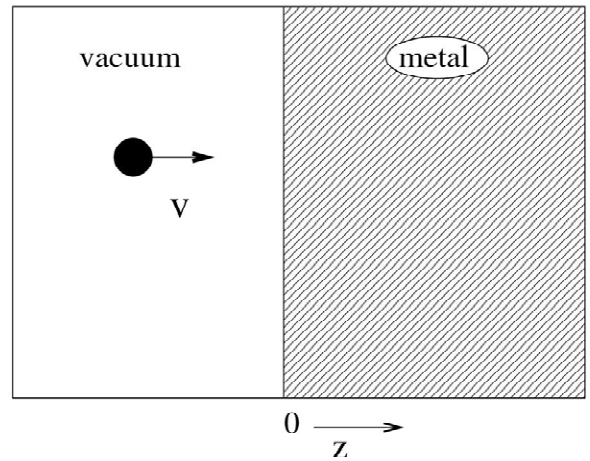


Fig. 1. Illustration of an external charged particle impinging perpendicularly on a metal surface.

surface and $W(z, z'; q, \omega)$ is the so-called screened interaction

$$W(z, z'; q, \omega) = v(z, z'; q) + \int dz_1 \int \times dz_2 v(z, z_1; q) \chi(z_1, z_2; q, \omega) v(z_2, z'; q), \quad (2)$$

$v(z, z'; q)$ and $\chi(z, z'; q, \omega)$ being two-dimensional Fourier transforms of the bare Coulomb potential and the density-response function of the solid [16], respectively. The energy that the probe particle at z loses per unit path length due to the creation of electronic excitations in the solid is simply [17,18]

$$-\frac{dE}{dz} = \frac{1}{v} \int_0^{\infty} d\omega \omega P_z(\omega). \quad (3)$$

In the framework of TDDFT, the interacting density-response function $\chi(z, z'; q, \omega)$ is fully determined from the eigenfunctions and eigenvalues of the Kohn-Sham equation of density-functional theory (DFT) [19,20] and the exchange-correlation (xc) kernel f_{xc} accounting for short-range xc effects (see, e.g., Refs. [6,7]), which in the random-phase approximation (RPA) is taken to be zero. To compute $\chi(z, z'; q, \omega)$, we first take a jellium slab of thickness $a = 6 \lambda_F$ (the results obtained for this slab thickness are well-converged and are expected to accurately describe the case of a semi-infinite free-

electron gas. $\lambda_F = 2\pi r_s / (9\pi/4)^{1/3}$) and electron density equal to the average electron density of valence electrons in Al ($r_s = 2.07$), and then solve the Kohn-Sham equation of DFT in the local-density approximation (LDA) (In this approximation, the xc potential entering the Kohn-Sham equation of DFT is given at each point by the xc potential of a uniform electron gas at the local density, which we take from the Perdew-Wang [21] parametrization of the Ceperley-Alder diffusion Monte Carlo data [22]) by following the procedure described in Ref. [23,24]. For comparison, we also consider simplified models for the screened interaction $W(z, z'; q, \omega)$ of a semi-infinite electron gas, which are derived for electron densities that drop abruptly to zero at the surface: These are a hydrodynamic model (HDM) [25], and a specular-reflexion model (SRM) [26,27] which expresses the screened interaction in terms of the bulk dielectric function $\epsilon(q, \omega)$.

3. Results

First of all, we show results for the probability $P_z(\omega)$ as a function of z and for selected values of the energy ω , which we obtain either in the full self-consistent surface RPA, in the HDM, or in the SRM with the bulk RPA dielectric function. We set the velocity $v = 4v_0$ ($v_0 = e^2/\hbar$ is the Bohr velocity) and $Z_1 = \pm 1$, and our results can then be used for arbitrary values of Z_1 , as the energy-loss probability is within linear-response theory proportional to Z_1^2 .

Fig. 2 shows the probability $P_z(\omega)$ for the moving particle to transfer either the energy $\omega = \omega_p$ [$\omega_p = \sqrt{4\pi n}$, n being the average electron density, i.e., $1/n = (4/3)\pi r_s^3$], corresponding to the excitation of a bulk plasmon, or $\omega = \omega_s$ [$\omega_s = \omega_p/\sqrt{2}$], corresponding to the excitation of a surface plasmon. When $\omega = \omega_p$ (Fig. 2a), the energy-loss probability increases as the projectile enters the surface and reaches a constant value deep inside the solid. At the surface-plasmon energy (Fig. 2b), the probability reaches a maximum when the probe particle is located near the surface, and diminishes in the interior of the solid where only electron-hole pairs can be excited with $\omega = \omega_s$.

It is well known that within a classical model consisting of a semi-infinite medium of local dielec-

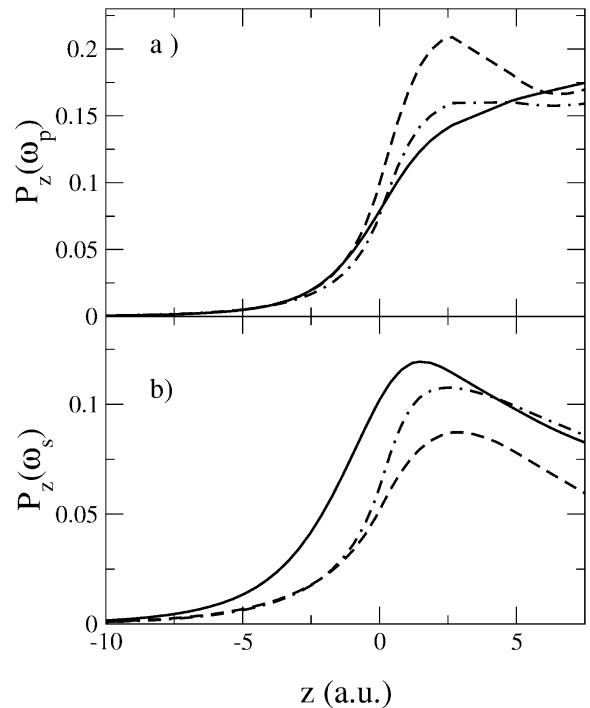


Fig. 2. Energy-loss probability $P_z(\omega)$ versus z for a particle of charge $Z_1 = \pm 1$ moving with velocity $v = 4v_0$ to transfer the energy (a) $\omega = \omega_p$ or (b) $\omega = \omega_s$ to the solid, corresponding to the excitation of a bulk and surface plasmon, respectively. The electron-density parameter r_s is taken to be that corresponding to the average density of valence electrons in Al, i.e., $r_s = 2.07$. The result of our full self-consistent RPA calculation is represented by a solid line. The results obtained with the use of HD and SR models are represented by dashed and dashed-dotted lines, respectively.

tric function $\epsilon(\omega)$ the energy-loss probability $P_z(\omega_s)$ would be maximum at $z = 0$. However, the actual dispersion of the surface plasmon, not included in the classical model, shifts the peak position of $P_z(\omega_s)$ towards the interior of the solid. Moreover, the so-called bregenzung or boundary effect reduces the coupling to bulk plasmons by the presence of surface plasmons. As the electronic selvage is changed from zero (HD and SRM) to its actual structure (RPA), the creation of electron-hole pairs increases and the bregenzung effect is more pronounced, thereby yielding larger surface-plasmon and smaller bulk-plasmon excitation probabilities.

Fig. 3 exhibits our full surface RPA (solid line), HDM (dashed line), and SRM (dashed-dotted line)

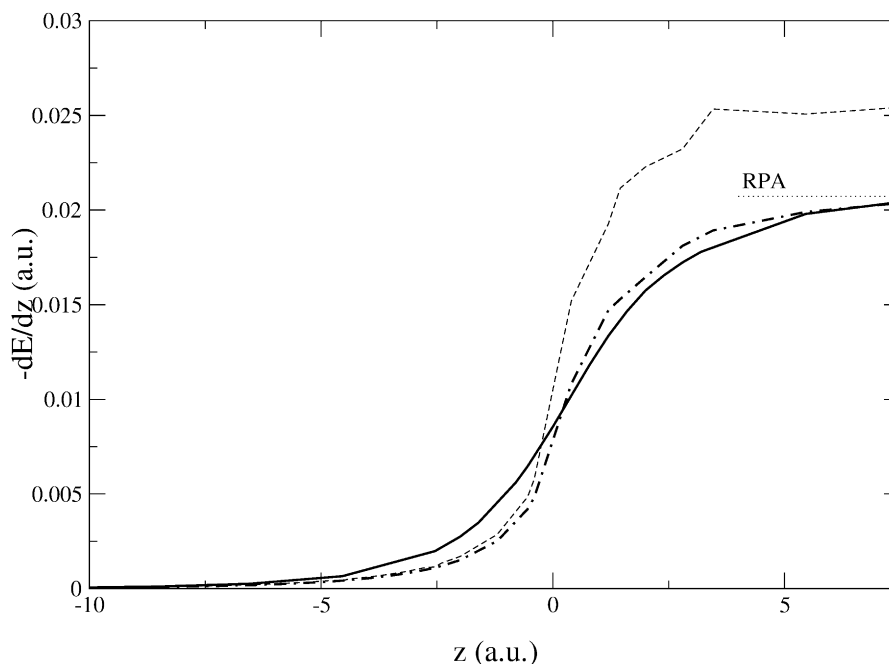


Fig. 3. Stopping power, as obtained from Eq. (3) as a function of z and with $v = 4v_0$. As in Fig. 2, solid, dashed, and dashed-dotted lines represent the result of our full self-consistent RPA calculations and those obtained with the use of HD and SR models, respectively. The horizontal dotted line represents the result of a bulk RPA calculation.

calculations of the stopping power, as obtained from Eq. (3) as a function of z and with $v = 4v_0$. As the projectile is entering the surface, our full surface RPA energy-loss calculations show a broader and smoother structure, which is mainly due to the presence of a non-abrupt electron-density profile at the surface. Before entering the surface, the selvage electronic structure yields a larger energy loss than predicted within SRM. Inside the solid the actual energy loss is smaller than in the SRM, due to the bremsstrahlung effect arising from the orthogonality of the surface and bulk plasmon modes. In the interior of the solid, where the electron density is constant, both our full surface RPA and SRM calculations coincide with the well-known RPA stopping power of a uniform electron gas (horizontal dotted line). On the other hand, the HD calculation deep inside the solid coincides with the bulk HD, which differs from the bulk RPA.

In conclusion, our full self-consistent RPA calculations of the energy loss of charged particles entering a metal surface indicate that a fully quantum-me-

chanical treatment of the electronic response of a metal surface is necessary to quantitatively describe the effect of the presence of the surface. A systematic self-consistent investigation of both RPA and beyond-RPA energy-loss spectra of charged particles moving along arbitrary trajectories is now in progress.

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