Energy loss of charged particles moving parallel to a magnesium surface

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We present *ab initio* calculations of the electronic energy loss of charged particles moving outside a magnesium surface, from a realistic description of the one-electron band structure and a full treatment of the dynamical electronic response of valence electrons. Our results indicate that the finite width of the plasmon resonance, which is mainly due to the presence of band-structure effects, strongly modifies the asymptotic behaviour of the energy loss at large distances from the surface. This effect is relevant for the understanding of the interaction between charged particles and the internal surface of microcapillaries.

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I. INTRODUCTION

Collective excitations at metal surfaces (surface plasmons, SP)[1] are well known to play a key role in a wide spectrum of science, ranging from physics and materials science to biology.[2] Here we focus on one specific situation where surface plasmons play a key role: the energy loss of charged particles moving near a metal surface. This work has been partially motivated by recent theoretical and experimental studies of the interaction of highly charged ions[3] with the internal surface of microcapillaries and nanocapillaries,[4,5,6] whose interpretation calls for an understanding of the asymptotic behaviour of the energy loss at large distances from the surface. Our *ab initio* calculations of the electronic energy loss of charged particles moving outside a magnesium surface indicate that the finite width of the SP resonance, which is mainly due to the presence of band-structure effects,[7] strongly modifies this asymptotic behaviour.

When a charged particle is placed in front of a metal surface, the distribution of electrons in the surface and the bulk is modified, an induced charged density is built up, and both single-particle and collective excitations are created which are ultimately responsible for the electronic energy loss of the external charged particle. Moving charged particles can also lose energy as a result of the interaction with the nuclei of the solid; however, this energy loss is negligible compared to the electronic energy loss, unless the probe charge moves at velocities that are extremely small compared to the Fermi velocity v_F of the solid.

For a weak interaction between the external charged particle and the electrons of the metal surface, the electronic response can be treated within linear-response theory. In the case of charged particles moving inside a solid, nonlinear effects are known to be crucial in the interpretation of energy-loss measurements;[8,9] however, nonlinear corrections have been shown to be less important when the charged particle moves outside the solid.[10] On the other hand, the electronic response of the metal surface is expected to be strongly dependent upon the actual structure of the ground-state electron density. Therefore, an accurate description of the electronic energy loss of charged particles moving near a metal surface lies mainly in the understanding of two basic ingredients: the electronic properties of the ground state of the target and the linear response of a many-electron system to external perturbations.

Existing self-consistent calculations of the energy-loss spectra at solid surfaces are based on either the jellium model[11] or a one-dimensional (1D) model potential that still assumes translational invariance along the surface.[12] Here we report the first three-dimensional (3D) *ab initio* calculation of the electronic energy loss that incorporates the full band structure of the solid surface. Specifically, we calculate from first principles the energy loss of charged particles that move parallel to the (0001) surface of Mg. We use the random-phase approximation (RPA),[13] and we focus on the limit in which the moving particle travels at large distances (compared to the Fermi wavelength) from the surface. We demonstrate that even for a free-electron-like metal such as Mg band-structure effects on the finite width of the SP resonance strongly modify this asymptotic behaviour.

The paper is organized as follows. First of all, in Sec. II we describe our full *ab initio* treatment of the wavevector- and frequency-dependent electronic response of valence electrons, based on a realistic description of the one-electron band structure. From the knowledge of the density-response function we derive the surface-response function of the system, whose imaginary part is related to the rate at which an external potential generates elec-

tronic excitations at the solid surface. In Sec. III, we derive an explicit expression for the electronic energy loss of charged particles moving parallel to a solid surface (stopping power of the solid), which we obtain from the knowledge of the imaginary part of the *GW* self-energy of many-body theory.[14] In Sec. IV, we present numerical calculations of the surface-response function and the electronic stopping power of a Mg(0001) surface. We compare our results with the stopping power obtained with the use of either the jellium model or a 1D model potential. In Sec. V, our conclusions are presented. Unless otherwise is stated, we use atomic units throughout, i.e., $e^2 = \hbar = m_e = 1$.

II. SURFACE-RESPONSE FUNCTION

Take a system of N interacting electrons of density $n_0(\mathbf{r})$ exposed to a frequency-dependent external potential $V^{ext}(\mathbf{r};\omega)$. Keeping terms of first order in the external perturbation and neglecting retardation effects, the rate $w(\omega)$ at which the frequency-dependent external potential $V^{ext}(\mathbf{r};\omega)$ generates electronic excitations in the many-electron system[15] is found to be given by the following expression:

$$w(\omega) = -2\,\mathrm{Im}\int d\mathbf{r}\int d\mathbf{r}'\,V^{ext}(\mathbf{r};\omega)\,\chi(\mathbf{r},\mathbf{r}';\omega)\,V^{ext}(\mathbf{r}';\omega), \tag{1}$$

where $\chi(\mathbf{r},\mathbf{r}';\omega)$ represents the so-called density-response function of the many-electron system. In the framework of time-dependent density-functional theory (TDDFT),[16] the *exact* density-response function of an interacting many-electron system is found to obey the following Dyson-type equation:

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \chi^0(\mathbf{r},\mathbf{r}';\omega) + \int d\mathbf{r}_1\int d\mathbf{r}_2\chi^0(\mathbf{r},\mathbf{r}_1;\omega) \times\{v(\mathbf{r}_1,\mathbf{r}_2) + f^{xc}[n_0](\mathbf{r}_1,\mathbf{r}_2;\omega)\}\,\chi(\mathbf{r}_2,\mathbf{r}';\omega). \tag{2}$$

Here, $\chi^0(\mathbf{r},\mathbf{r}';\omega)$ is the density-response function of noninteracting Kohn-Sham electrons, $v(\mathbf{r}_1,\mathbf{r}_2)$ is the bare Coulomb interaction, and $f^{xc}[n_0](\mathbf{r},\mathbf{r}';\omega)$ represents the so-called exchange-correlation (xc) kernel, which is the second functional derivative of the xc energy functional evaluated at the ground-state electron density $n_0(\mathbf{r})$. In the RPA, $f^{xc}[n_0](\mathbf{r},\mathbf{r}';\omega) = 0$.

In the case of a periodic surface, we introduce 2D Fourier expansions of the form

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{A}\sum_{\mathbf{q}}^{SBZ}\sum_{\mathbf{g},\mathbf{g}'} e^{i(\mathbf{q}+\mathbf{g})\cdot\mathbf{r}_\parallel} e^{-i(\mathbf{q}+\mathbf{g}')\cdot\mathbf{r}'_\parallel}\chi_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega), \tag{3}$$

where A is a normalization area, $\mathbf{q}$ is a 2D wave-vector in the surface Brillouin zone (SBZ), and $\mathbf{g}$ and $\mathbf{g}'$ denote 2D reciprocal lattice vectors. For an external potential of the form

$$V^{ext}(\mathbf{r},\omega) = -\frac{4\pi^2}{A}\sum_{\mathbf{q}}^{SBZ} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{r}-iz)}/q, \tag{4}$$

the rate $w(\omega)$ takes the form[2]

$$w(\omega) = \sum_{\mathbf{q}}^{SBZ} w(\mathbf{q},\omega), \tag{5}$$

where $w(\mathbf{q},\omega)$ denotes the rate at which the external potential generates electronic excitations of frequency ω and 2D wave vector $\mathbf{q}$:

$$w(\mathbf{q},\omega) = \frac{4\pi}{2A}\,\mathrm{Im}g(\mathbf{q},\omega), \tag{6}$$

with

$$g(\mathbf{q},\omega) = -\frac{2\pi}{q}\int dz\int dz'\,\mathrm{e}^{q(z+z')}\,\chi_{\mathbf{g}=0,\mathbf{g}'=0}(z,z';\mathbf{q},\omega). \tag{7}$$

In the RPA, the Fourier coefficients $\chi_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega)$ are found to obey the following matrix equation:

$$\chi_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega) = \chi^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega) + \sum_{\mathbf{g}_1}\int dz_1\int dz_2\,\chi^0_{\mathbf{g},\mathbf{g}_1}(z,z_1;\mathbf{q},\omega) \times v_{\mathbf{g}_1}(z_1,z_2;\mathbf{q})\,\chi_{\mathbf{g}_1,\mathbf{g}'}(z_2,z';\mathbf{q},\omega), \tag{8}$$

where $v_{\mathbf{g}}(z,z';\mathbf{q})$ denote the 2D Fourier coefficients of the bare Coulomb interaction $v(\mathbf{r},\mathbf{r}')$,

$$v_{\mathbf{g}}(z,z';\mathbf{q}) = \frac{2\pi}{|\mathbf{q}+\mathbf{g}|}e^{-|\mathbf{q}+\mathbf{g}||z-z'|}, \tag{9}$$

and $\chi^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega)$ represent the Fourier coefficients of the density-response function of noninteracting Kohn-Sham electrons.

For positive frequencies, the imaginary part of the Fourier coefficients $\chi^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega)$ is easily obtained from the spectral function $S^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega)$, as follows

$$\mathrm{Im}\chi^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega) = -\pi S^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega), \tag{10}$$

where

$$S^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega) = \frac{2}{A}\sum_{\mathbf{k}}^{SBZ}\sum_{n}^{occ}\sum_{n'}^{unocc}\langle\psi_{\mathbf{k},n}(\mathbf{r})|e^{-i(\mathbf{q}+\mathbf{g})\mathbf{r}_\parallel}|\psi_{\mathbf{k}+\mathbf{q},n'}(\mathbf{r})\rangle\langle\psi_{\mathbf{k}+\mathbf{q},n'}(\mathbf{r}')|e^{i(\mathbf{q}+\mathbf{g}')\mathbf{r}'_\parallel}|\psi_{\mathbf{k},n}(\mathbf{r}')\rangle \times \delta(\varepsilon_{\mathbf{k},n}-\varepsilon_{\mathbf{k}+\mathbf{q},n'}+\omega). \quad (11)$$

Here, the sum over n and n' run over all occupied and unoccupied bands, respectively, and $\varepsilon_{\mathbf{k},n}$ and $\psi_{\mathbf{k},n}(z)$ represent, respectively, the single-particle energies and wave functions of a Kohn-Sham Hamiltonian with an effective potential that is periodic in the plane of the surface. For the evaluation of the real part of $\chi^0_{\mathbf{g},\mathbf{g}'}(z,z',\mathbf{q},\omega)$, we perform a Hilbert transform of the corresponding imaginary part.[17]

The function $g(\mathbf{q},\omega)$ of Eq. (7) is the so-called surface-response function, which represents a key quantity in the description of both single-particle and collective excitations at solid surfaces, and whose imaginary part [see Eq. (6)] yields the rate at which an external potential generates electronic excitations. Equation (7) shows that only the diagonal Fourier coefficient $\chi_{\mathbf{g},\mathbf{g}}(z,z';\mathbf{q},\omega)$ with $\mathbf{g}=0$ enters the expression for the surface-response function. Nevertheless, the full matrix nature of $\chi^0_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega)$ and $\chi_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega)$ is involved when solving Eq. (8). These are the so-called local-field effects,[18] which typically play an important role in the presence of strong electron-density inhomogeneities but are found to be negligible in the case of simple metals like Mg.[7]

III. ELECTRONIC STOPPING POWER

Let us consider a probe particle of charge Z_1 moving in an inhomogeneous many-electron system. The decay rate τ_i^{-1} of the particle in the state $\phi_i(\mathbf{r})$ with energy ε_i is obtained from the knowledge of the imaginary part of the self-energy $\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i)$, according to[19]

$$\tau_i^{-1} = -2\int d\mathbf{r}\int d\mathbf{r}'\phi_i^*(\mathbf{r})\mathrm{Im}\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i)\phi_i(\mathbf{r}'). \quad (12)$$

In the GW approximation of many-body theory,[14] and replacing the probe-particle Green function by that of a noninteracting particle, one finds:

$$\tau_i^{-1} = -2Z_1^2\int d\mathbf{r}\int d\mathbf{r}'\phi_i^*(\mathbf{r}) \times\sum_f \phi_f^*(\mathbf{r}')\mathrm{Im}W(\mathbf{r},\mathbf{r}';\varepsilon_i-\varepsilon_f)\phi_f(\mathbf{r})\phi_i(\mathbf{r}'), \quad (13)$$

where the sum is extended over a complete set of final states $\phi_f(\mathbf{r})$ of energy ε_f. $W(\mathbf{r},\mathbf{r}';\varepsilon_i-\varepsilon_f)$ is the screened interaction of the system, which is related to the interacting density-response function as follows

$$W(\mathbf{r},\mathbf{r}';\omega) = v(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}_1\int d\mathbf{r}_2 v(\mathbf{r},\mathbf{r}_1)\chi(\mathbf{r}_1,\mathbf{r}_2;\omega)v(\mathbf{r}_2,\mathbf{r}'). \quad (14)$$

In the case of a recoilless point particle moving at a given impact vector $\mathbf{b}$ with nonrelativistic velocity $\mathbf{v}$, the probe-particle initial and final states can be described by plane waves in the direction of motion and a Dirac δ function in the transverse direction, i.e.,

$$\phi(\mathbf{r}) = \frac{1}{\sqrt{A}}e^{i\mathbf{v}\cdot\mathbf{r}}\sqrt{\delta(\mathbf{r}_\perp-\mathbf{b})}, \quad (15)$$

where $\mathbf{r}_\perp$ represents the position vector perpendicular to the projectile velocity. One then finds that the decay rate of Eq. (13) can be written as follows

$$\tau_i^{-1} = \frac{1}{\mathrm{T}}\sum_{\mathbf{q}} P_{\mathbf{q}}, \quad (16)$$

where T is a normalization time and $P_{\mathbf{q}}$ is given by the following expression:

$$P_{\mathbf{q}} = \frac{4\pi}{\Omega}Z_1^2\int_0^\infty d\omega\int\frac{d\mathbf{q}'}{2\pi^3}e^{i\mathbf{b}\cdot(\mathbf{q}+\mathbf{q}')} \times \mathrm{Im}W(\mathbf{q},\mathbf{q}',\omega)\delta(\omega-\mathbf{q}\cdot\mathbf{v})\delta(\omega+\mathbf{q}'\cdot\mathbf{v}). \quad (17)$$

Here, Ω is a normalization volume and $W(\mathbf{q},\mathbf{q}';\omega)$ represents the double Fourier transform of the screened interaction $W(\mathbf{r},\mathbf{r}';\omega)$.

The quantity $P_{\mathbf{q}}$ entering Eq. (16) can be interpreted as the probability for the probe particle to transfer momentum $\mathbf{q}$ to the many-electron system. Hence, the stopping power of the many-electron system, i.e, the average energy lost by the particle per unit path length is found to be given by the following expression:

$$-\frac{dE}{dx} = \frac{1}{L}\sum_{\mathbf{q}}(\mathbf{q}\cdot\mathbf{v})P_{\mathbf{q}}, \quad (18)$$

where L is a normalization length and $\mathbf{q}\cdot\mathbf{v}$ represents the energy transfer associated to the momentum transfer $\mathbf{q}$.

Now we restrict our attention to the case of charged recoilless particles moving with constant velocity $\mathbf{v}$ along a definite trajectory at a fixed distance z from a periodic solid surface. If one introduces 2D Fourier expansions of the form of Eq. (3), then Eqs. (17) and (18) yield the

following expression for the stopping power:

$$-\frac{dE}{dx}(z) = -\frac{2Z_1^2}{vA}\sum_{\mathbf{g},\mathbf{K}}\sum_{\mathbf{q}}^{SBZ} e^{i\mathbf{K}\cdot\mathbf{b}}\,\mathbf{q}\cdot\mathbf{v} \times \mathrm{Im}W_{\mathbf{g},\mathbf{g}+\mathbf{K}}(z,z;\mathbf{q},\mathbf{q}\cdot\mathbf{v}), \quad (19)$$

the sum over $\mathbf{K}$ being restricted to those reciprocal lattice vectors that are perpendicular to the velocity of the projectile, i.e., $\mathbf{K}\cdot\mathbf{v}=0$.

At this point, we focus on the special situation where the coordinate z is located far from the surface into the vacuum. Equation (14) shows that under such conditions the Fourier coefficients $W_{\mathbf{g},\mathbf{g}'}(\mathbf{q},\omega)$ take the following form:

$$W_{\mathbf{g},\mathbf{g}'}(z,z;\mathbf{q},\omega) = v_{\mathbf{g}}(z,z,\mathbf{q})\delta_{\mathbf{g},\mathbf{g}'} - \frac{2\pi q}{|\mathbf{q}+\mathbf{g}||\mathbf{q}+\mathbf{g}'|}g_{\mathbf{g},\mathbf{g}'}(\mathbf{q},\omega)e^{-(|\mathbf{q}+\mathbf{g}|+|\mathbf{q}+\mathbf{g}'|)z}, \quad (20)$$

where

$$g_{\mathbf{g},\mathbf{g}'}(\mathbf{q},\omega) = -\frac{2\pi}{q} \times \int dz \int dz'\, \mathrm{e}^{|\mathbf{q}+\mathbf{g}|z}\,\chi_{\mathbf{g},\mathbf{g}'}(z,z';\mathbf{q},\omega)\mathrm{e}^{|\mathbf{q}+\mathbf{g}'|z'}, \quad (21)$$

which for $\mathbf{g}=\mathbf{g}'=0$ yields the surface-response function entering Eq. (6).

The symmetry of the one-particle Bloch states results in the following identity:

$$g_{\mathbf{g},\mathbf{g}'}(S\mathbf{q},\omega) = g_{S^{-1}\mathbf{g},S^{-1}\mathbf{g}'}(\mathbf{q},\omega), \quad (22)$$

with S representing a point group symmetry operation in the periodic crystal. As a consequence, the stopping power of Eq. (19) can be evaluated from the knowledge of the screened interaction corresponding to wave vectors lying in the irreducible element of the surface Brillouin zone (ISBZ). If crystal local-field effects are neglected altogether, introducing Eq. (21) into Eq. (19) yields

$$-\frac{dE}{dx}(z) = \frac{2Z_1^2}{vA}\sum_{\mathbf{q}}^{ISBZ}\sum_{S} \frac{2\pi}{|S\mathbf{q}|}(S\mathbf{q}\cdot\mathbf{v})e^{-2|S\mathbf{q}|z}\mathrm{Im}\,g(S\mathbf{q},\mathbf{q}\cdot\mathbf{v}), \quad (23)$$

where $g(\mathbf{q},\omega)$ represents the surface-response function of Eq. (7).

In the simplest possible model of a solid surface, in which a semi-infinite electron gas described by a Drude dielectric function $\epsilon(\omega)=1-\omega_p^2/\omega^2$ is separated by a planar interface at $z=0$ from a semi-infinite vacuum, both Eqs. (19) and (23) reduce, for particle trajectories outside the solid ($z>0$), to the classical expression:[20]

$$-\frac{dE}{dx}(z) = Z_1^2\,\frac{\omega_s^2}{v^2}\,K_0(2\omega_s z/v), \quad (24)$$

where $K_0(x)$ in the zero-order modified Bessel function,[21] and ω_s is the SP frequency $\omega_s=\omega_p/\sqrt{2}$. This expression, which is known to hold for high particle velocities ($v >> v_F$) at large distances from the surface ($z >> \lambda_F$) shows that under these conditions the energy loss is dominated by the excitation of surface plasmons.

IV. RESULTS

Magnesium ($1s^22s^22p^63s^2$) is a monoatomic solid with the hexagonal close-packed crystal structure. The input of our parameter-free first-principles stopping-power calculations is the surface-response function $g(\mathbf{q},\omega)$ of Eq. (7), which we have calculated for the (0001) surface of Mg. The results presented below have been found to be well converged for all velocities under study. The single-particle Kohn-Sham orbitals $\psi_{\mathbf{k},n}(\mathbf{r})$ entering Eq. (11) were expanded in a plane-wave basis set with a kinetic-energy cutoff of 13 Ry. In the Fourier expansion of the noninteracting density-response matrix $\chi^0_{\mathbf{g},\mathbf{g}'}(g_z,g'_z,\mathbf{q},\omega)$ we included 101 g_z-vectors and the components with $\mathbf{g}=\mathbf{g}'=0$ only because of the negligible local-field effects along the surface.[7] In Eq. (11) all occupied and unoccupied energy bands up to 50 eV above the Fermi level were taken into account. Numerically, in the evaluation of $S^0_{\mathbf{g},\mathbf{g}'}(g_z,g'_z,\mathbf{q},\omega)$ the δ-function was replaced by a Gaussian with a broadening parameter $\sigma=0.1$ eV. The sampling of the SBZ required for the evaluation of both the surface-response function of Eq. (7) and the stopping power of Eq. (23) has been performed including 7812 mesh points in the SBZ. We set $Z_1=\pm1$, but our results can be used for arbitrary values of Z_1, as the stopping power is, within linear-response theory, proportional to Z_1^2.

We compare our first-principles calculations with the results that we have also obtained by replacing the actual (0001) surface of Mg by (i) a jellium surface with an electron-density parameter $r_s=2.66$ (corresponding to an electron density equal to that of valence electrons in Mg) and (ii) a model surface described by the 1D potential of Ref. 22. This potential describes the main features of the surface electronic structure of Mg: the energy gap and the Shockley surface state at the $\bar{\Gamma}$ point ($\mathbf{k}=0$) of the SBZ; in this case, we have used films of up to 41 layers of atoms with a lattice parameter $a=4.923$ a.u. corresponding to a film thickness of 100.92 a.u., and the work function has been taken to be $\Phi=3.66$ eV.

Our first-principles calculations employ a supercell geometry with slabs containing 16 atomic layers of Mg that are separated by vacuum intervals. The slab geometry imposes a low limit for the momentum $\mathbf{q}$ below which the SP splits into two slab excitations of the form[15]

$$w_{\pm}(\mathbf{q}) = w_{sp}(1\mp e^{-qL})^{1/2}, \quad (25)$$

with L representing here the slab thickness. This drawback can be softened by increasing the slab thickness.

Figure 1 shows the self-consistent calculations of the imaginary part of the surface-response function, Im$g(\mathbf{q},\omega)$, that we have obtained from Eq. (7) in the RPA for (i) a semi-infinite jellium surface (dashed lines), (ii) the 1D model surface potential of Ref. 22 (thin solid lines), and (iii) the actual (0001) surface of Mg (thick solid lines). For the low 2D wave vectors $\mathbf{q}$ under study, the energy-loss spectra are clearly dominated by a SP contribution at $w_s \sim 8\,\mathrm{eV}$, which seems to first shift to lower frequencies, as q increases, and then, from $q \sim 0.02$ on, towards higher frequencies. This figure shows that for the small values of q considered here both jellium and 1D model calculations (dashed and thin solid curves) overestimate the SP energy; our calculations show, however, that for larger values of the 2D wave vector these simplified models predict accurate values of the SP energy.

The important message of Fig. 1 is that at small values of q the actual linewidth of the SP is considerably larger than that obtained with the use of 1D jellium-like models. This important effect is expected to impact considerably the actual stopping power of the solid surface, especially at large distances from the surface where the energy loss is dominated by the excitation of surface plasmons associated to very low wave vectors.

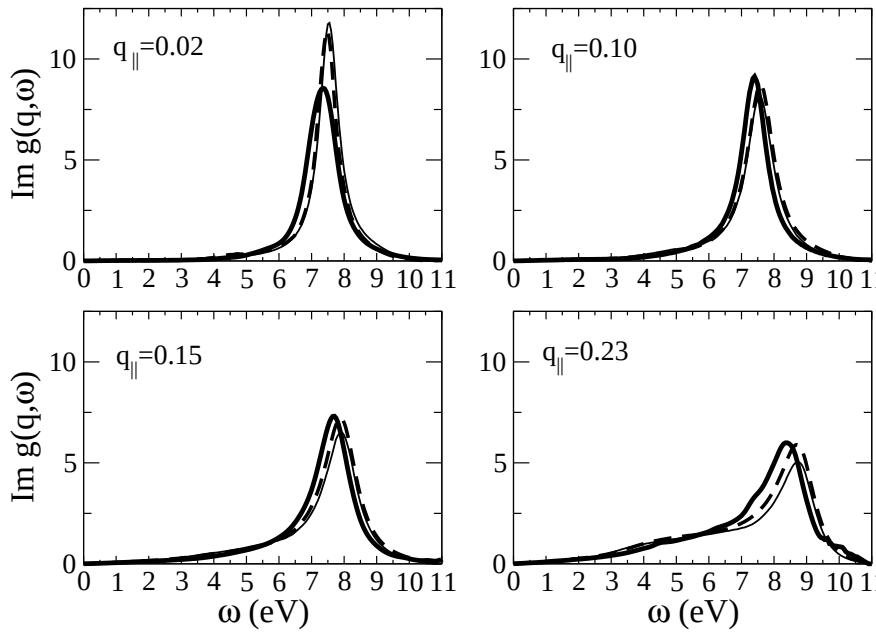

Figure 1: Imaginary part of the RPA surface-response function of Mg(0001), Im$g(\mathbf{q}_\parallel,\omega)$, as a function of ω, for various values of the magnitude q of the wave vector. The thick solid line represents self-consistent *first-principles* calculations, the dashed line represents the corresponding results obtained for a semi-infinite jellium surface, and the thin solid line represents the corresponding results obtained by using the 1D model potential of Ref. 22.

Now we focus on the special situation where an external recoilless particle of charge $Z_1 = 1$ is moving with constant velocity along a definite trajectory at a fixed distance z far from the surface into the vacuum. Fig. 2 exhibits the stopping power of Mg(0001) for this moving particle, as obtained from Eq. (23) in the RPA for (i) a semi-infinite jellium surface (dashed lines), (ii) the 1D model surface potential of Ref. 22 (thin solid lines), and (iii) the actual (0001) surface of Mg (thick solid lines). At the velocities under consideration ($v > v_F$), the energy-loss spectrum of charged particles moving far from the surface into the vacuum is dominated by long-wavelength surface excitations (small q), i.e., by the excitation of surface plasmons. Hence, we might be tempted to conclude

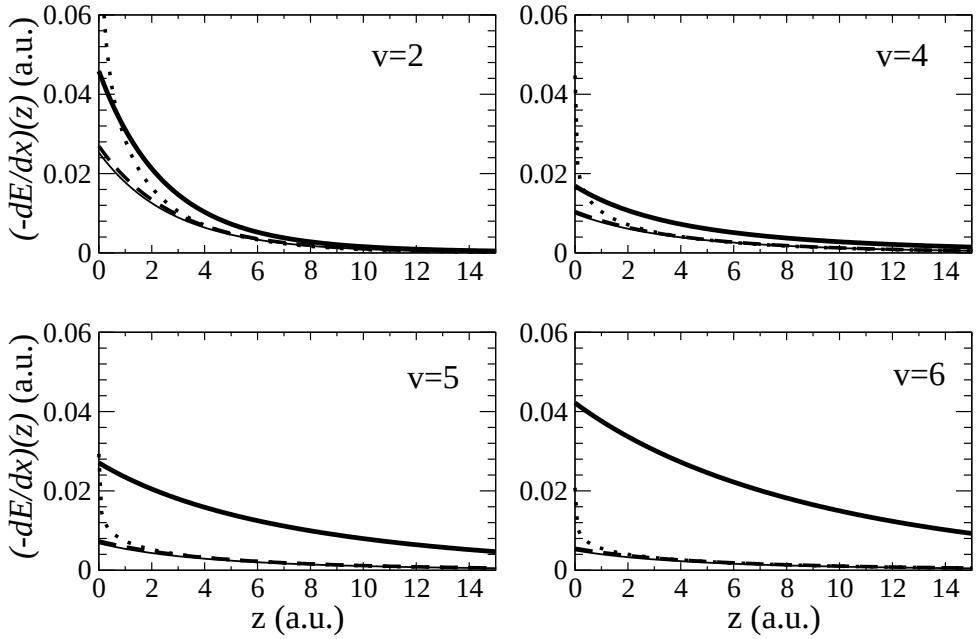

Figure 2: Stopping power of Mg(0001), versus z, for a recoilless particle of charge $Z_1 = 1$ moving with various velocities. The thick solid line represents self-consistent *first-principles* calculations. The dashed and thin solid lines represent the corresponding results obtained for a semi-infinite jellium surface and by using the 1D model-potential of Ref. 22, respectively. The dotted lines represent the classical energy loss of Eq. (24).

that Eq. (24) (represented in Fig. 2 by a dotted line) should be a good representation of the actual stopping at $z >> \lambda_F$. Indeed, Fig. 2 shows that this classical limit is in excellent agreement at large values of z with the results obtained with the use of 1D jellium-like models (dashed and thin solid lines). However, it is important to note that these models do not account for the intrinsic linewidth of surface plasmons which, as a result of interband transitions that are absent in these simplified models, dominates the energy loss at large distances. As the velocity increases (see the lower panels of Fig. 2), lower values of the wave vector enter the excitation spectrum leading to an increased impact of the intrinsic surface-plasmon linewidth on the stopping power and, therefore, more pronounced differences between the stopping power of a jellium-like surface (dashed and thin solid lines) and the real surface (thick solid lines).

Figure 3 shows the ratio between the *first-principles* stopping power of the real Mg(0001) surface and the stopping power of the corresponding jellium surface [which at large distances coincides with the classical result of Eq. (24)] for the four values of the velocity considered in Fig. 2. The *ab initio* energy loss is considerably larger than that obtained from the classical Eq. (24) at all large distances from the metal surface. As $z \to \infty$, the classical Eq. (24) (which assumes the linewidth of the surface plasmon to be zero) decays exponentially; indeed, at these large distances from the surface the stopping power is dominated by the finite intrinsic linewidth of the surface plasmon, leading to a ratio that increases exponentially. This exponential increase also occurs when

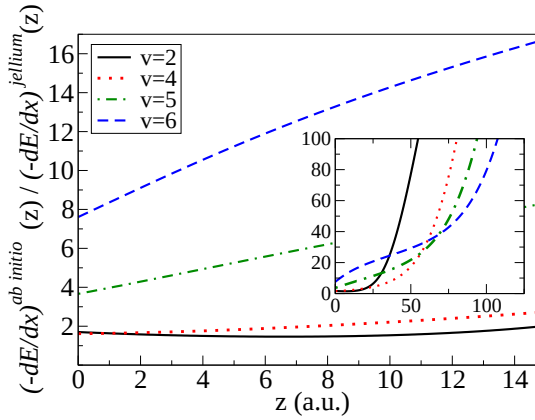

Figure 3: (Color online) Ratio $(-dE/dx)^{ab\ initio}(z)/(-dE/dx)^{jellium}(z)$, versus z, for a recoilless particle of charge $Z_1 = 1$ moving with various velocities outside theMg(0001) surface. In the inset, larger distances z from the surface are considered.

the stopping power of the real surface is replaced by that of a semi-infinite electron gas described by a Drude dielectric function of the form $\epsilon(\omega) = 1 - \omega_p^2/\omega(\omega + i\gamma)$, γ being a damping parameter that would give account approximately for the finite surface-plasmon linewidth.[23]

V. SUMMARY AND CONCLUSIONS

We have carried out first-principles self-consistent calculations of the surface-response matrix and the stopping power of the (0001) surface of Mg. Our results indicate that band-structure effects (and, in particular, interband transitions) play a key role in the description of the asymptotic behaviour of the stopping power far from the surface, even in the case of a free-electron-like metal such us Mg. In particular, we find that the linewidth of the surface-response function is considerably enhanced at small wave vectors, which yields an increased energy loss of charged particles moving far from the surface that cannot be described by simplified 1D jellium-like models. This important effect, which should be present in the case of all metal surfaces, is expected to be relevant for the understanding of the interaction between charged particles and the internal surface of microcapillaries. New experiments along these lines would be desirable.

VI. ACKNOWLEDGMENTS

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[1] R. H. Ritchie, Phys. Rev. **106**, 874 (1957).
[2] J. M. Pitarke, V. M. Silkin, E. V. Chulkov, and P. M. Echenique, Rep. Prog. Phys. **70**, 1 (2007).
[3] A. Arnau, F. Aumayr, P. M. Echenique, M. Grether, W. Heiland, J. Limburg, R. Morgenstern, P. Roncin, S. Schippers, R. Schuch, N. Stolterfoht, P. Varga, T. J. M. Zouros, and H. P. Winter, Surf. Sci. Rep. **27**, 113 (1997).
[4] Y. Yamazaki, *Photonic, Electronic and Collisions*, edited by F. Aumayr and H. P. Winter, World Scientific, Singapore, p. 693 (1998).
[5] N. Stolterfoht, J. H. Bremer,V. Hoffmann, R. Hellhammer, D. Fink, A. Petrov, and B. Sulik, Phys. Rev. Lett. **88**, 133201 (2002).
[6] K. Tökési, X-M Tong, C. Lemell, and J. Burgdörfer, Phys. Rev. A **72**, 022901 (2005).
[7] V. M. Silkin, E. V. Chulkov, and P. M. Echenique, Phys. Rev. Lett. **93**, 176801 (2004).
[8] V. U. Nazarov, J. M. Pitarke, C. S. Kim, and Y. Takada, J. Phys.: Condens. Matter 16, 8621 (2004); Phys. Rev. B **71**, 121106(R) (2005).
[9] V. U. Nazarov, J. M. Pitarke, Y. Takada, G. Vignale, and Y.-C. Chang, Phys. Rev. B 76, 205103 (2007).
[10] A. Bergara, J. M. Pitarke, and R. H. Ritchie, Phys. Rev. B **60**, 16176 (1999).
[11] A. García-Lekue and J. M. Pitarke, Phys. Rev. B **64**, 035423 (2001); **67**, 089902(E) (2003); Nucl. Instrum Methods **182**, 56 (2001); J. Electron. Spectrosc. **129**, 223 (2003).
[12] M. Alducin, V. M. Silkin, J. I. Juaristi, and E. V. Chulkov, Nucl. Instrum. Methods **193**, 585 (2002); M. Alducin, A. Arnau, and I. Nagy, Phys. Rev. A **68**, 014701 (2003).
[13] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (New York: McGraw-Hill, 1971).
[14] L. Hedin and S. Lundqvist, in *Solid State Physics: Advances in Research and Applications*, edited by E. H. Ehrenreich and D. Turnbull, vol. 23 p. 1, Academic, New York (1969).
[15] A. Liebsch, *Electronic Excitations at Metal Surfaces*, (Pleum Presss, New York, 1997).
[16] E. K. U. Gross, C. A. Ullrich, and U. J. Gossmann, *Density Functional Theory of Time-Dependent Systems*, edited by E. K. U. Gross and R. M. Dreizler, Plenum Press, New York (1995).
[17] V. M. Silkin, J. M. Pitarke, E. V. Chulkov, B. Diaconescu, K. Pohl, L. Vattuone, L. Savio, Ph. Hofmann, D. Farías, M. Rocca, and P. M. Echenique, Phys. Stat. Sol. (a) **205**, 1307 (2008).
[18] S. L. Adler, Phys. Rev. **126**, 413 (1962).
[19] I. Campillo, J. M. Pitarke, and A. G. Eguiluz, Phys. Rev. B **58**, 10307 (1998).
[20] P. M. Echenique and J. B. Pendry, J. Phys. C: Solid State Phys. **8**, 2936 (1975).
[21] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1964).
[22] E. V. Chulkov, V. M. Silkin, and P. M. Echenique, Surf. Sci. **391**, L1217 (1997); **437**, 330 (1999).
[23] R. Nuñez, P. M. Echenique, and R. H. Ritchie, J. Phys. C: Solid State Phys. **13**, 4229 (1980).