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Optical excitation of acoustic surface plasmons in metallic nanoparticles

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Acoustic surface plasmons are low energy collective excitations occurring at metallic surfaces. These excitations show a linear dispersion which can be described using realistic quantum-mechanical models. The response function of Ag(111) films is calculated and an effective dielectric function of the films is obtained. With use of this dielectric function the scattering of silver nanoparticles in the infrared range is calculated, with focus on the possibility of excitation of localized acoustic surface plasmons. Our calculations show that it is possible to excite optically localized acoustic surface plasmons in silver spheres, although the efficiency is very low.

1 Introduction

The response of materials to electromagnetic radiation can vary dramatically with the frequency of the radiation, reflecting the presence of different excitations which can be induced within a particular material. In the visible region and UV range electronic transitions are the main excitations in semiconductors and dielectrics. In the case of metals collective oscillations of conduction electrons, so called plasmons [1–3], can also be excited. In the infrared range of the spectrum excitations are usually connected with phonons in crystals [4] or vibrational modes in organic molecules and their spectroscopic information provides a powerful tool for chemical analysis [5].

The bulk response of metals is governed by the behaviour of valence electrons and in the infrared part of the spectrum this response is usually approximated by a Drude model $\varepsilon = 1 - \omega_{\mathrm{p}}^2/(\omega^2 + i\omega\gamma)$, where ε is the bulk dielectric function, ω_{p} the plasma frequency of the free electron gas, ω the frequency of the electromagnetic radiation and γ the damping in the metal [6, 7]. A material described by such a dielectric function only sustains conventional bulk plasmons and surface plasmons

when the metal is bounded by interfaces. However when the behaviour of electrons contained in the metal close to a surface is treated within a more realistic quantum-mechanical model, novel features in the electrodynamical response appear. These feeatures are a consequence of the interaction between the 3D electron plasma of the bulk of the metal and the 2D electron gas formed by the surface electronic states [8–10]. As a result, the metal surface can support low energy plasmonic excitations, so called *acoustic surface plasmons* [11]. The terminology of acoustic plasmon is due to the sound-like linear dispersion curve of these excitations, which significantly differs from the dispersion of an ordinary surface plasmon polariton [6, 7]. Acoustic surface plasmons were predicted to exist on some simple and noble metal surfaces [11, 12] and have been experimentally observed in a variety of metals using electron energy loss spectroscopy [13–17]. The possibility of exciting such modes in small nanoparticles was already pointed out in Ref. [18].

In this paper we study the possibility of optical excitation of these plasmons in silver nanoparticles to estimate how effectively light can couple to a localized acoustic plasmon excitation. The electrodynamical response of silver was extracted from a realistic quantum-mechanical model of thin Ag(111) slabs [19]. This response which incorporates the quantum features is then assumed to describe the optical response of a surface in classical electrodynamics. The interaction of electromagnetic radiation with the nanoparticles is described

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by solving Maxwell's equations within Mie theory, providing a quantitative evaluation of the scattering and extinction efficiency of these excitations. We explore whether localized acoustic surface plasmons might serve as novel fingerprints to identify surface quantum states optically.

2 Surface response function

In order to fully grasp the electrodynamical response of metals including surface states and band structure, a quantum-mechanical treatment of the electrons is necessary. Such a treatment was developed by Silkin et al. [19], who calculated the electron wavefunctions for thin Ag(111) films described by a model potential based on the real band structure of silver. The electrodynamical response of this system was subsequently obtained using the random phase approximation [20].

When dealing with surface excitations it is convenient to introduce an energy transfer $\hbar\omega$ and momentum transfer q dependent surface response function $g(q,\omega)$ [21], which characterizes the field induced outside the material due to the polarization. The absorption suffered by an external electromagnetic field due to the scattering by the surface can be related to the imaginary part of the surface response function $\mathrm{Im}\{g(q,\omega)\}$. In Fig. 1 we show the normalized surface loss function $\mathrm{Im}\{g(q,\omega)\}/q\omega$ for a Ag(111) film of 8 monolayers (approximately 2.5 nm). The bright curves represent dispersion curves of various surface excitations. The dispersion curve of the acoustic surface plasmon (ASP) lies in the low energy region and is characterized by a linear dispersion dependence. This dispersion is significantly different from the dependences of ordinary 3D or 2D electron gases. This points out that the acoustic surface plasmon is not simply a collective oscillation of the 2D electron gas formed at the surface of the metal, but a result of the interaction between bulk and surface states [22]. The remaining dispersion curves observed in Fig. 1 belong to the conventional anti-symmetric plasmon polariton mode ω_{sp}^{-} [7] and excitations arising from the quantum effects caused by the very small thickness of the film.

3 Localized surface response

The possibility of optical excitation of acoustic surface plasmons is a natural question that has not been unraveled up to date. Since the excitation of surface plasmons at perfectly flat interfaces is possible only with use of special techniques, we focus on structures with
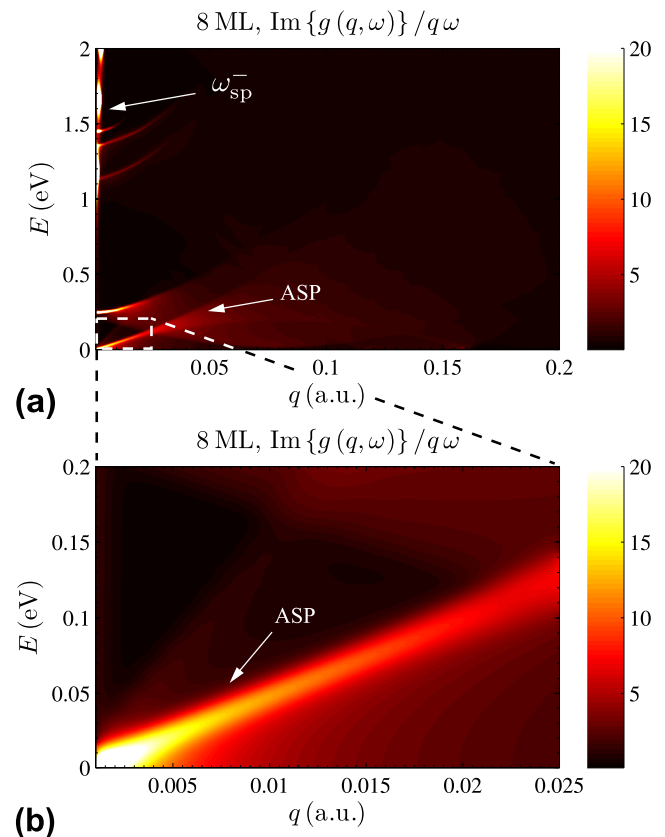

Figure 1 (a) Normalized surface loss function $\mathrm{Im}\{g(q,\omega)\}/q\omega$ of a Ag(111) film of 8 monolayers. The acoustic surface plasmon dispersion is labeled as ASP. The remaining dispersion curves belong to the conventional anti-symmetric plasmon polariton mode ω_{sp}^{-} and excitations related to the quantization effects present in very thin films. (b) Zoom-in of the low energy part of the upper contour plot showing the acoustic surface plasmon dispersion (ASP) in more detail.

closed boundaries. The confined geometry of these structures provides the additional momentum necessary to fulfill the momentum conservation and thus to become optically active. The response of nanostructures to electromagnetic radiation is determined by their geometry and size-dependent bulk dielectric function $\varepsilon(\omega)$. In order to incorporate surface effects we obtain the dielectric function from the surface response function $g(q,\omega)$, where the particular value of the wavevector component q parallel to the surface is given by the geometry and size of the structure. In this study we investigate spheres and shells with defined radius R. Since we assume the dipolar mode is the dominant excitation, we require the wavelength associated with the wavevector q to be equal

to the perimeter of the particle $2\pi R$, thus setting the wavevector component q as

$$q \approx \frac{2\pi}{2\pi R} = \frac{1}{R}. \tag{1}$$

We will consider two particular structures schematically represented in Fig. 2.

First we study a homogeneous silver sphere with radius $R_{sph} = D_{sph}/2 = 10\,\text{nm}$ (Fig. 2 (a)) and dielectric function $\varepsilon_{R_{sph}}(\omega)$. The dielectric function $\varepsilon_{R_{sph}}(\omega)$ is derived from the surface response function g_{31ML} of a 10 nm thick silver film (31 monolayers), for which the quantization effects vanish, characterizing well the situation of a semiinfinite system. This procedure is an attempt to reproduce the main quantum features of the particle response from an exact surface response.
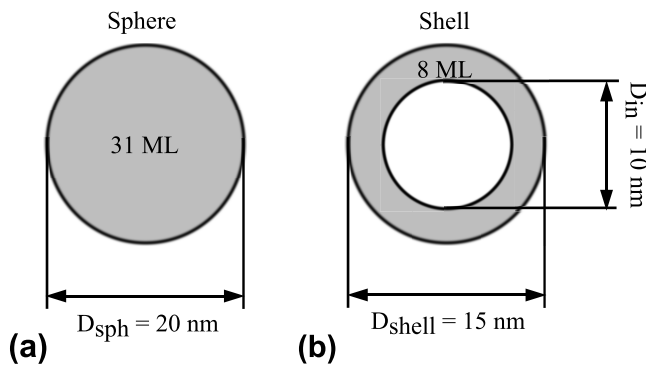
Sphere   Shell

8 ML

31 ML $D_{in} = 10\,\text{nm}$

(a)   **(b)**

$D_{sph} = 20\,\text{nm}$ $D_{shell} = 15\,\text{nm}$

Figure 2 (a) Sphere of radius $R_{sph} = D_{sph}/2 = 10\,\text{nm}$ with a dielectric function corresponding to 31 monolayers (31ML) of silver Ag(111). (b) Hollow shell with inner radius $R_{in} = D_{in}/2 = 5\,\text{nm}$ and outer radius $R_{shell} = D_{out}/2 = 7.5\,\text{nm}$ and a dielectric function derived from the 8 monolayers (8ML) thick Ag(111) slab.

The relationship between $\varepsilon_{R_{sph}}(\omega)$ and g_{31ML} can be obtained from the solution of Maxwell's equations for a semiinfinite system [21]. Let us assume that the solid occupies the lower half space $z < 0$ and an external charge located at z_0 in the region $z > 0$ polarizes the material and gives rise to an induced field. Within the quasistatic approach the external and induced fields can be described by the respective external Φ_{ext} and induced Φ_{ind} potentials.

The external potential Φ_{ext} in the region $z > 0$ has to fulfill Poisson's equation $\nabla^2 \Phi_{ext} = \rho_{ext} = \delta(z - z_0)\delta(\mathbf{r}_\parallel)$, where ρ_{ext} is the charge density and $\mathbf{r}_\parallel$ is the position vector parallel to the interface. The solution to this equation can be written as

$$\Phi_{ext}(\mathbf{q}_\parallel, z, \omega) = \mathscr{A}(\omega)\frac{e^{q_\parallel(z-z_0)}}{q_\parallel} = A(\mathbf{q}_\parallel, \omega)e^{q_\parallel z} \qquad z > 0, \tag{2}$$

where $\mathbf{q}_\parallel$ is a wavevector parallel to the interface, $\mathscr{A}(\omega)$ is the frequency-dependent amplitude of the external field and the coefficient $A(\mathbf{q}_\parallel, \omega)$ is given by $A(\mathbf{q}_\parallel, \omega) = \mathscr{A}(\omega)e^{-q_\parallel z_0}/q_\parallel$. The solution for the induced potential Φ_{ind} in this region is given by

$$\Phi_{ind}(\mathbf{q}_\parallel, z, \omega) = -g(\mathbf{q}_\parallel, \omega)A(\mathbf{q}_\parallel, \omega)e^{-q_\parallel z} \qquad z > 0, \tag{3}$$

where we have introduced the surface response function $g(\mathbf{q}_\parallel, \omega)$, which will be determined by the boundary conditions.

Analogously, in the region $z < 0$ the total potential $\Phi_{tot} = \Phi_{ext} + \Phi_{ind}$ can be expressed as

$$\Phi_{tot}(\mathbf{q}_\parallel, z, \omega) = B(\mathbf{q}_\parallel, \omega)e^{q_\parallel z} \qquad z < 0, \tag{4}$$

where $B(\mathbf{q}_\parallel, \omega)$ is a coefficient determined by the boundary conditions. From the continuity requirement of the total potential and the normal component of the electric displacement at the interface, we obtain the relationship between the non-local dielectric function $\varepsilon(\mathbf{q}_\parallel, \omega)$ and the surface response function $g(\mathbf{q}_\parallel, \omega)$:

$$\varepsilon(\mathbf{q}_\parallel, \omega) = \frac{1 + g(\mathbf{q}_\parallel, \omega)}{1 - g(\mathbf{q}_\parallel, \omega)}, \tag{5}$$

We now assume for the parallel momentum $\mathbf{q}_\parallel$ a value given by the inverse of the size of the sphere as pointed out in Eq. (1) $\mathbf{q}_\parallel = q_{R_{sph}} = 1/R_{sph} = 0.005$ a.u. (atomic units). This sets the value of the surface response function for the 31ML thick silver film $g_{31ML}(q_{R_{sph}}, \omega)$. The dielectric function of the sphere $\varepsilon_{R_{sph}}(\omega)$ with radius R_{sph} can then be expressed as a function of the corresponding surface response function $g_{31ML}(q_{R_{sph}} = 1/R_{sph}, \omega)$ following Eq. (5) as:

$$\varepsilon_{R_{sph}}(\omega) = \frac{1 + g_{31ML}(q_{R_{sph}}, \omega)}{1 - g_{31ML}(q_{R_{sph}}, \omega)}. \tag{6}$$

The spectral dependence of the surface loss function $\text{Im}\{g_{31ML}(q_{R_{sph}} = 0.005\,\text{a.u.}, \omega)\}$ (31ML) is represented by the blue solid line in Fig. 3 (a) showing a distinct peak at an energy $E = 0.015$ eV corresponding to the acoustic surface plasmon. The real and imaginary parts of the corresponding dielectric function, as obtained from Eq. (6), are plotted in Fig. 3 (b). Unlike the standard Drude model, the real part of the dielectric function considering surface states of silver is positive in the low energy range of the spectrum and crosses zero around $E = 0.015$ eV.

We consider now a hollow shell structure with inner radius $R_{in} = D_{in}/2 = 5\,nm$ and a $2.5\,nm$ thick silver shell (8 monolayers) (Fig. 2 (b)). The dielectric function $\varepsilon_{R_{shell}}(\omega)$ was obtained from the surface response function corresponding to a thin film structure of thickness $R_{shell} - R_{in}$ that mimics the geometry of the shell. This results in a modified expression for the dielectric response

$$\varepsilon_{R_{shell}}(\omega) = \frac{(1+\alpha^2)\,g_{8ML} + \sqrt{4g_{8ML}^2\,\alpha^2 + (1-\alpha^2)^2}}{(1-g_{8ML})(1-\alpha^2)}, \qquad (7)$$

where g_{8ML} is the surface response function of the 8ML silver film $g_{8ML}(q_{R_{shell}},\omega)$. The particular value of the wavevector component $q_{R_{shell}} = 0.007\,a.u.$ corresponds to the inverse of the size of the shell $R_{shell} = 7.5\,nm$ and α is an exponential factor $\alpha = \exp(-q_{R_{shell}}d)$, where d is the thickness of the shell. The spectral dependence of the surface loss function $Im\{g_{8ML}(q_{R_{shell}} = 0.007\,a.u.,\omega)\}$ (8ML) is plotted in Fig. 3 (a) as a green solid line. Together with the distinct peak at an energy $E = 0.035\,eV$ corresponding to the acoustic surface plasmon additional features related to the quantum confinement appear around $E = 0.1\,eV$. In Fig. 3 (c) the real and imaginary parts of the respective dielectric function $\varepsilon_{R_{shell}}(\omega)$ (8ML) as obtained from Eq. (7) are shown. The spectral dependence is dominated by a Lorentz-shaped resonance structure around $E = 0.1325\,eV$.

4 Extinction and scattering efficiency

In order to estimate the possibility of detecting the excitation of localized acoustic surface plasmons using optical techniques, we calculate the scattering and extinction efficiencies of the sphere and shell geometries adopting the quantum-mechanically calculated surface response function to obtain the dielectric function as shown in the previous section and using Mie theory [23] to solve the classical electromagnetic scattering with use of those dielectric functions. The results are shown in Fig. 4.

When a semiinfinite system (resp. slab) is transformed into a sphere (resp. shell), the confinement generally results in a frequency shift of the absorption peak. This can be explained through the change in the resonance conditions for the respective eigenmodes. For a surface plasmon mode on a flat interface between a metal and vacuum the absorption peak is associated with the maximum in the imaginary part of the surface response function

$$Im\{g\} = \frac{2\varepsilon''}{(\varepsilon'+1)^2 + \varepsilon''^2}, \qquad (8)$$
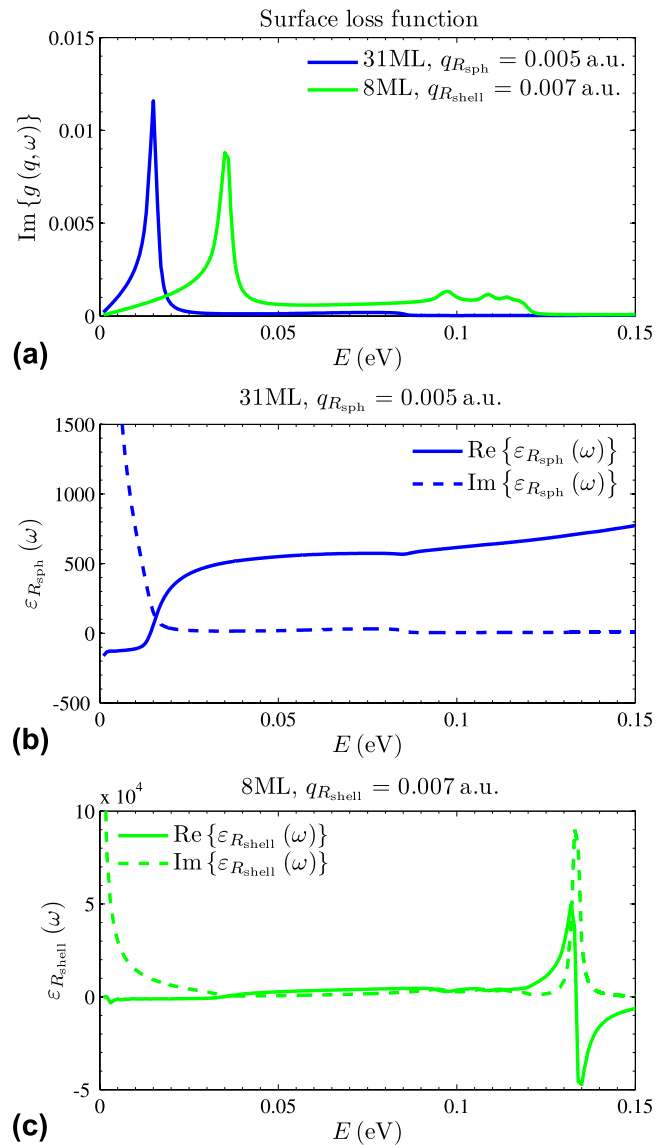

(a)

(b)

(c)

Figure 3 (a) Spectral dependence of the surface loss function $Im\{g(q,\omega)\}$ for 31ML (blue) and 8ML (green) slabs. The values of the wavevector $q_{R_{sph}} = 0.005\,a.u.$ (31ML) and $q_{R_{shell}} = 0.007\,a.u.$ (8ML) correspond to the particular sizes of sphere ($R_{sph} = 10\,nm$) and shell ($R_{shell} = 7.5\,nm$) respectively. (b) Real (solid) and imaginary (dashed) parts of the dielectric function $\varepsilon_{R_{sph}}(\omega)$ characterizing the response of a silver sphere of radius $R_{sph} = 10\,nm$. (c) Real (solid) and imaginary (dashed) parts of the dielectric function $\varepsilon_{R_{shell}}(\omega)$ characterizing the response of a silver shell with inner radius $R_{in} = 5\,nm$ and outer radius $R_{shell} = 7.5\,nm$. The dielectric function for the sphere is derived following Eq. (6) under the assumption of the resemblance of the surface to a semiinfinite system. In the case of the shell, the interaction between the two interfaces of the slab is taken into account while deriving the dielectric function (Eq. (7)).

where ε' and ε'' are real and imaginary parts of the dielectric function of the metal respectively. In the case of a small metallic sphere the dipolar extinction peak is related to the maximum of the imaginary part of the polarizability of the sphere α_{sph}

$$\text{Im}\{\alpha_{sph}\} \sim \frac{3\varepsilon''}{(\varepsilon'+2)^2 + \varepsilon''^2}. \tag{9}$$

Since the change in resonance conditions for a surface and for an electrostatic sphere is almost negligible compared to the absolute values of both the real and imaginary parts of the dielectric functions, we do not expect any perceptible shift in the resonance frequency between the planar interface and the particle resonance. This can be directly observed by comparing the surface loss functions of Fig. 3 (a) and the calculated extinction efficiencies in Fig. 4 (a,b).

According to our calculations, the efficiency of the optical excitation of acoustic surface plasmons in spherical particles is very low (with the extinction efficiency of the order of $Q_{ext} \approx 10^{-5}$), which makes these excitations difficult to detect from simple optical methods. The damping γ of the localized acoustic surface plasmons can be estimated from the width of the corresponding peaks. Similarly to the acoustic surface plasmons, the damping γ acquires values around $\gamma \approx 0.004$ eV and is basically associated with intrinsic losses.

The additional features in the extinction spectrum of the shell structure observed in Fig. 4 (b) are the consequence of the spectral features in the respective dielectric function. The intense peak at an energy $E = 0.1325$ eV, marked as *MD* in the extinction spectra of the 8ML shell in Fig. 4 (b), can be associated with the magnetic dipolar mode and it comes from the Lorentz-shaped resonance feature in the corresponding dielectric function shown in Fig. 3 (c).

Another way to quantify the excitation efficiency of acoustic surface plasmons in nanoparticles is to compare the extinction spectra obtained with use of the quantum-mechanically calculated response function to the spectra of silver nanoparticles characterized by a standard Drude model, which does not incorporate surface states. In Fig. 4 (c) the extinction efficiencies from Fig. 4 (a,b) are normalized to the results calculated for nanoparticles of the same size characterized by a Drude dielectric function $\varepsilon = 1 - \omega_p^2/(\omega^2 + i\omega\gamma)$ with parameters $\omega_p = 9$ eV and $\gamma = 0.02$ eV. The spectral resonances of the normalized extinction efficiencies $\widetilde{Q}_{ext}$ suggest that in principle it would be possible to identify optically surface reconstructions in nanoparticles by distinguishing those presenting surface states from those, which do not support such states.
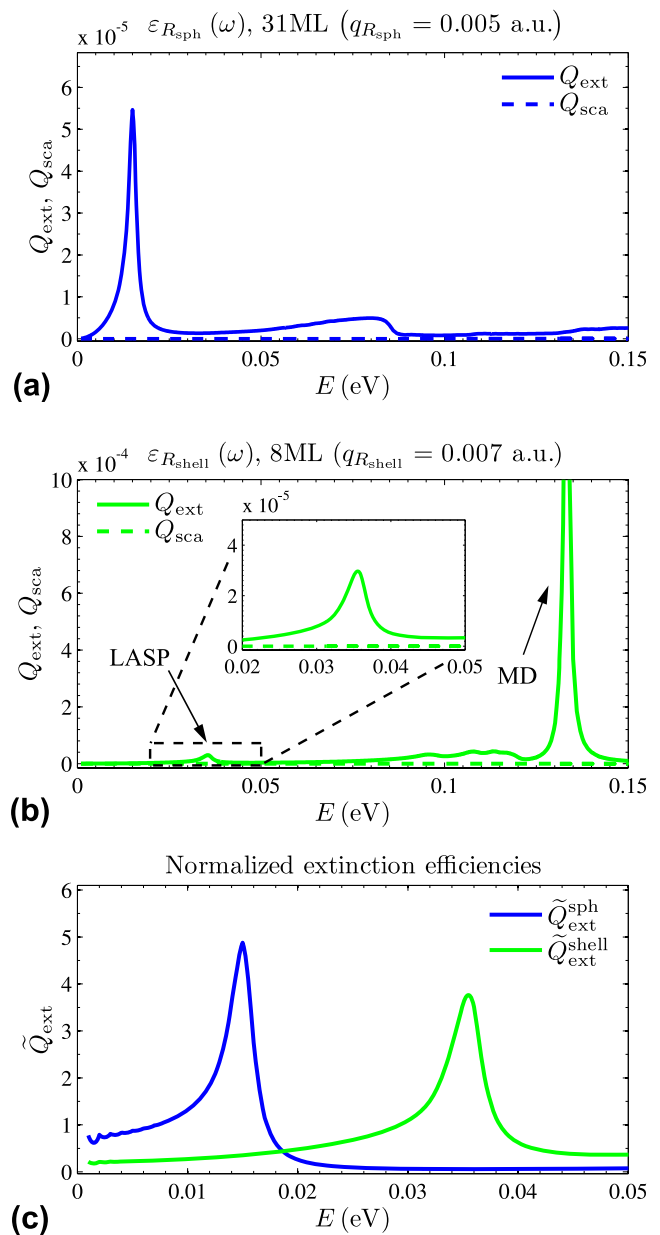

Figure 4 (online color at: www.ann-phys.org) (a) Extinction Q_{ext} (solid) and scattering Q_{sca} (dashed) efficiencies for a silver sphere of radius $R_{sph} = 10$ nm characterized by the corresponding dielectric function $\varepsilon_{R_{sph}}(\omega)$. (b) Extinction Q_{ext} (solid) and scattering Q_{sca} (dashed) efficiencies for a hollow silver shell with inner radius $R_{in} = 5$ nm and outer radius $R_{shell} = 7.5$ nm characterized by the corresponding dielectric function $\varepsilon_{R_{shell}}(\omega)$. The peak corresponding to the excitation of the localized acoustic surface plasmon is labeled LASP. The peak marked MD can be associated to a magnetic dipolar mode. (c) Extinction efficiency $\widetilde{Q}_{ext}$ for the sphere (blue) and the shell (green) normalized to the values obtained with use a Drude dielectric response.

Our electrodynamical calculations of scattering for spherical particles are based on the use of a dielectric function obtained from quantum-mechanical calculations for thin metallic films. We assume that the change from the planar to the spherical geometry has no effect, which is not necessarily accurate, since the requirement of the pure Ag(111) surface can not be met for particles of spherical shape. Nevertheless the choice of the geometry seems to have only minor effects on the scattering properties in comparison with the electrodynamical response of silver in this spectral region, thus we think that the use of the spherical geometry is relevant for the estimation of the light excitation efficiency of localized acoustic surface plasmons in small nanoparticles [18]. Ideally the electrodynamical response should be obtained from quantum-mechanical calculations for each particular geometry in consideration, but this exceeds the current capabilities of quantum-mechanical calculations at hand.

5 Conclusion

Analytical calculations based on Mie theory were performed to investigate the possibility of excitation of localized acoustic surface plasmons in small spherical nanoparticles characterized by dielectric functions obtained from quantum-mechanical calculations and thus accounting for the presence of surface electronic states. From the calculated scattering and extinction efficiency spectra we are able to estimate the excitation efficiency and the damping of the localized acoustic surface plasmons. The values obtained suggest that the detection of this excitation process by standard optical techniques might be difficult, but improved optical techniques with use of enhanced fields might access this phenomenon.

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