Properties of Hybridized Modes in Core–Shell Scatterers

Ari Sihvola*, Dimitrios C. Tzarouchis, Pasi Ylä-Oijala, and Henrik Wallén
Department of Electronics and Nanoengineering, Aalto University, Finland

Abstract

The character of resonances in plasmonic core–shell structures is analyzed. In particular, the focus is on the behavior of the weaker (antibonding) resonance. Using the residue expansion of the polarizability, it is shown that to maximize the effect of the antibonding resonance, the ratio of the core radius to the whole sphere radius should be 0.596. The polarizability-based results are compared with full Mie scattering calculations showing fair agreement up to size parameters $x = 1/3$.

1 Introduction

A beautiful correspondence exists between mixing theories and the polarizability response of core–shell structures [1]: in terms of the dipolar response, a core–shell sphere can be replaced by a homogeneous sphere whose permittivity is exactly the same as the effective permittivity computed according to the Maxwell Garnett mixing principle [2] of a mixture with shell material as environment and the core material dispersed as inclusions. The volume fractions between the two materials are the same in the mixture and in the composite sphere.

Hence, all analyses on Maxwell Garnett mixing translate directly into the studies of core–shell spheres. In particular, there are interesting results on how mixing affects dispersion, in other words the frequency dependence of the effective medium may be qualitatively different from the dispersion of its constituent material permittivities. Therefore, also core–shell scatterers can be engineered, with a clever combination of material pairs, to display dispersion and resonance spectrum that does not appear in easily available materials.

In the following, we will focus on a special case of this phenomenon: the resonance structure of a plasmonic shell. Due to the afore-mentioned correspondence, this case is dual to a "Swiss-cheese" mixture where a negative-permittivity bulk material (silver, for example) is impurified with spherical holes, and as shown in [3], such a mixture seems promising for broadband tuning of dispersion. A plasmonic layer can also be exploited in cloaking applications [4] and in the design of electrically small antennas [5]. In the following, our particular interest is in the character of the antisymmetric resonance of the composite sphere.

2 Modes in a plasmonic core–shell particle

The (normalized) polarizability of a two-phase composite sphere of Figure 1 reads [6, Eq. (4.33)]

$$\alpha = 3\frac{(\varepsilon_1-1)(\varepsilon_2+2\varepsilon_1)+r^3(2\varepsilon_1+1)(\varepsilon_2-\varepsilon_1)}{(\varepsilon_1+2)(\varepsilon_2+2\varepsilon_1)+2r^3(\varepsilon_1-1)(\varepsilon_2-\varepsilon_1)} \quad (1)$$

where $r = a/b$ is the ratio of the core radius to the whole-sphere radius (r^3 is the core–particle volume fraction). The shell is of relative permittivity ε_1 and core of ε_2 (all permittivities are relative and dimensionless).
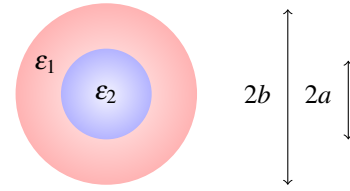
Figure 1. A composite sphere with core and shell.

Consequently, the polarizability for a hollow-core particle (with core being $\varepsilon_2 = 1$ and the shell $\varepsilon_1 = \varepsilon$) reads

$$\alpha = 3\frac{(\varepsilon-1)(2\varepsilon+1)(1-r^3)}{(\varepsilon+2)(2\varepsilon+1)-2r^3(\varepsilon-1)^2} \quad (2)$$

showing the zeros: in addition to the obvious $\varepsilon = 1$ and $r = 1$, there is another one, independent of core size: $\varepsilon = -1/2$. There are two poles:

$$\varepsilon_{\mp} = -\frac{5+4r^3\pm3\sqrt{1+8r^3}}{4(1-r^3)} \quad (3)$$

where ε_- and ε_+ resonances refer to the symmetric (bonding) and antisymmetric (antibonding) modes, according to the so-called plasmonic hybridization model [7, 8].

For a very small core ($r \to 0$), the symmetric resonance appears at $\varepsilon_- = -2$ and the antisymmetric one at $\varepsilon_+ = -1/2$. It is worth noting that the antisymmetric resonance vanishes for vanishing core, because the zero at $\varepsilon = -1/2$ cancels the resonance $\varepsilon_+ = -1/2$.

When the core increases, ε_- moves towards minus infinity, and ε_+ increases towards zero. Figure 2 visualizes these observations, including the invisibility for shell permittivity $\varepsilon = -1/2$, independently of core size.
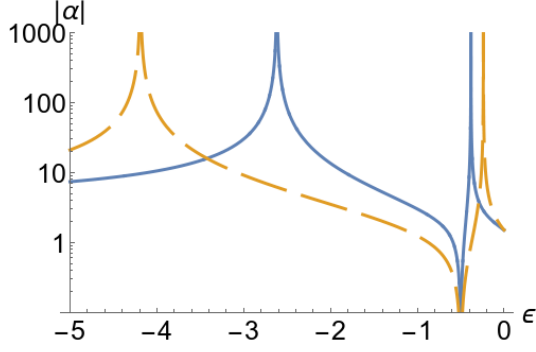
Figure 2. The absolute value of the polarizability of a hollow plasmonic shell as a function of the shell permittivity ε. Core volume $(a/b)^3 = 0.1$ (solid blue), 0.3 (dashed orange.)

Connecting the permittivity with a Drude dispersion model with plasma frequency ω_p as $\varepsilon(\omega) = 1 - \omega_p^2/\omega^2$, we can see that the symmetric resonance starts from $\omega \approx 0.577\omega_p$ and redshifts, while the antisymmetric one appears at $\omega \approx 0.815\omega_p$ and blueshifts with increasing hollow core.

The antibonding resonance is clearly weaker and narrower than the bonding one. Since plasmonic materials are dispersive, they are lossy, and an obvious question is how this resonance is affected by losses. Inserting a complex-valued shell permittivity into (2) leads to a very convoluted function for the absolute value of the complex polarizability as a function of $\varepsilon', \varepsilon''$ and r, and an analytical solution of the maximum amplitude of neither of the resonances cannot be found.

3 Residue expansion

An approach to determine the character of the antibonding resonance is the following. Starting from the observation that this resonance vanishes for vanishing core ($r \to 0$) and vanishing shell ($r \to 1$), we can try to find its evolution by expanding the polarizability (2) with its residues. Knowing the poles (Equation (3)), we can write down a pole expansion of the polarizability:

$$\alpha_{\text{norm}} = 3 + \frac{A_-}{\varepsilon - \varepsilon_-} + \frac{A_+}{\varepsilon - \varepsilon_+} \tag{4}$$

Here the constant accounts for the polarizability approaching 3 in the PEC limit $\varepsilon \to \pm\infty$.

The residues are

$$A_{\mp} = -\frac{9(3 \pm \sqrt{1+8r^3})(\sqrt{1+8r^3} \pm 1 \pm 2r^3)}{8(1-r^3)\sqrt{1+8r^3}} \tag{5}$$

which expressions clearly show the dominance of the bonding mode amplitude A_- over the antibonding one A_+. (For $r = 0$, we have $A_- = -9$ and $A_+ = 0$.)

However, in the neighborhood of the antibonding resonance ($\varepsilon \approx \varepsilon_+$), the polarizability can be well approximated with

the last term of the three in (4). Then the expression for α simplifies considerably, and is much easier to analyze in the complex domain than the original polarizability expression.

Given a lossy dielectric shell ($\varepsilon = \varepsilon' - j\varepsilon''$), the question we ask is how strong the antibonding resonance can be. The approximation using the antibonding residue shows us that for a given core volume r^3, the maximum polarizability has the amplitude

$$|\alpha|_{\text{max}} = \frac{|A_+|}{\varepsilon''} \tag{6}$$

The increase of the imaginary part of ε brings the maximum polarizability down. However, always a maximum exists. But it is interesting that this maximum polarizability has a maximum, as can be seen in Figure 3 where the $|\alpha|_{\text{max}}$ is shown as a function of r^3.
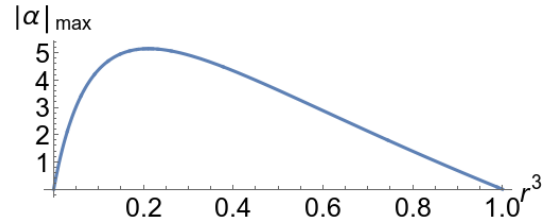
Figure 3. The absolute value of the maximum of polarizability of the antibonding resonance for $\varepsilon'' = 0.05$ as a function of the relative core volume.

The resonance maximum takes place at

$$r^3 = \frac{4}{49} + \frac{9\sqrt{2}}{98} \approx 0.212 \tag{7}$$

for which $A_+ \approx -0.257$. In other words, to trigger the antisymmetric resonance in a plasmonic shell most strongly, the core radius should be a factor $a \approx 0.596b$ from the outer radius. The needed permittivity for the maximum antibonding polarizability can be computed from ε_+ in (3); it is $\varepsilon' \approx -0.293$. In the ideal Drude model, this corresponds to the frequency $\omega \approx 0.879\omega_p$.

The approximation for the maximum is rather accurate as can be seen in Figure 4 which shows the exact behavior of the absolute value of the polarizability in the case $r^3 = 0.212$ and $\varepsilon'' = 0.05$.

4 Comparison with full-wave solution

The results so far have been based on concepts based on electrostatic fields and the manipulation of Laplace and Poisson equations. However, they carry over into electrodynamics, to some extent. In the following, let us compare the above results with full-wave Mie scattering computations.

Figure 5 shows the comparison for the scattering efficiency Q_{sca} of a hollow sphere with relative core size treated before, $(a/b)^3 = 0.212$, and the size parameter $x = k_0 b = 1/3$.
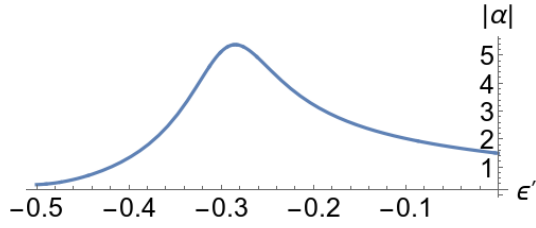
Figure 4. The absolute value of the polarizability in the antibonding range for $\varepsilon'' = 0.05$ and $r^3 = 0.212$ as a function of the real part of the permittivity. Note that the maximum agrees well with the maximum in Figure 3 which is based on the truncated residue approximation.

The polarizability-based approximation for the scattering efficiency is [9]

$$Q_{\mathrm{sca}} \approx \frac{8}{27}|\alpha|^2 x^4 \qquad (8)$$
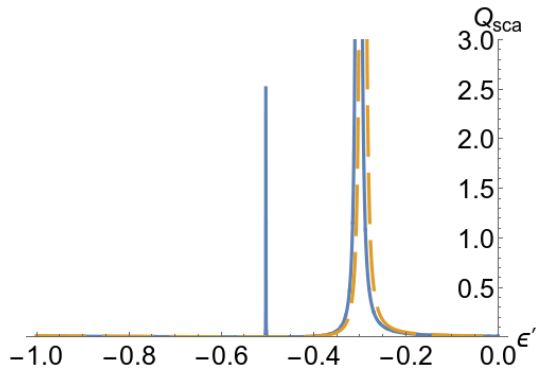
Figure 5. Quasistatic approximation (dashed orange) and full Mie solution (solid blue) for the scattering efficiency of a hollow sphere with optimized antibonding resonance. Lossless case.

The quasistatic result predicts the behavior fairly well. It does not capture the narrow quadrupolar antisymmetric mode. Furthermore, in the dipolar mode there is a slight shift to more negative permittivity values (redshift).

When losses are included, the quadrupolar mode is washed away. Figure 6 shows the comparison of the absorption efficiency of the particle with the same size ($x = 1/3$) but now with shell permittivity $\varepsilon = \varepsilon' - \mathrm{j} \cdot 0.05$. Again, the polarizability-based approximation for the absorption efficiency is [9]

$$Q_{\mathrm{abs}} \approx \frac{4}{3}|\mathrm{Im}\{\alpha\}|\,x \qquad (9)$$

5 Conclusions

The analysis about character of the antisymmetric resonance in hollow plasmonic spheres has shown that to optimize the amplitude of this resonance, the hollow core should occupy a fraction of 0.212 of the total sphere. This value is independent of the losses and leads to a resonance at the frequency $0.879\omega_p$.
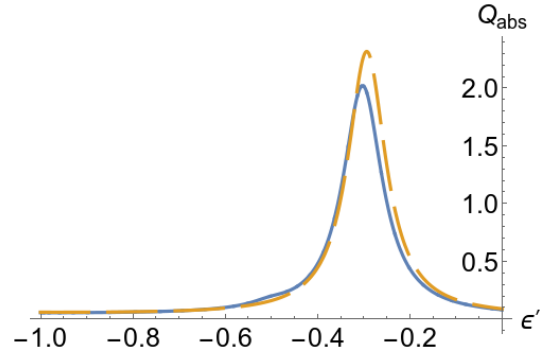
Figure 6. The same comparison as in Figure 5, but for the absorption efficiency, and in the case that the shell has losses: $\varepsilon'' = 0.05$.

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