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Multipolar plasmon modes of sodium sphere: constrain on the minimal sphere radius

Krystyna Kolwas and Anastasiya Derkatchova

Institute of Physics of the Polish Academy of Sciences
Al.Lotników 32/46, 02-668 Warsaw, Poland

ABSTRACT

We re-examine the usual expectations for multipolar plasmon modes of a simple-metal sphere within a classical picture. We show that according to rigorous solution of the eigenvalue problem the complex eigenfrequencies of plasmon modes can be attributed to the sphere of size larger than the minimum size at given multipolarity, the feature not known from widely used "low radius limit".

Keywords: Free-electron clusters, alkali nano-spheres, plasmon modes, Mie theory.

1. INTRODUCTION

Nanoscale metal particles are well known for their ability to sustain collective electron plasma oscillations - plasmons. When we talk of plasmons, we have in mind the eigenmodes of the self-consistent Maxwell equations with appropriate boundary conditions in the absence of an external electromagnetic field (e.g.[1–3]). We reconsider the eigenvalue problem of a free-electron metal sphere as a function of sphere radius within the rigorous model (no assumption concerning the particle size). We study the dipole ($l = 1$) and the higher polarity plasmon eigenfrequencies $\omega_l(R)$, $l = 1, 2, ...10$ as well as the plasmon radiative decay rates $\omega_l''(R)$ as a function of the particle radius R. In particular we re-examine the usual expectation for multipolar plasmon frequencies in the so called "low radius limit".

2. FORMULATION OF THE EIGENVALUE PROBLEM

The system of interest is a sphere of optical and electric properties described by the frequency dependent dielectric function $\varepsilon_{in}(\omega) = 1 - \omega_p^2/\omega^2$ assumed to have the constant bulk value up to the sphere border. The sphere is embedded in a nonconducting and nonmagnetic medium of the dielectric function assumed to be $\varepsilon_{out} = 1$ in all numerical illustrations. We are interested in the electrodynamic properties of the sphere in the frequency regime of anomalous dispersion $\varepsilon_{in}(\omega) < 0$. The dynamic, linear response of the sphere material is described within standard optics. We look for solutions of self-consistent Maxwell's equations with no external sources. For harmonic, transverse waves ($\nabla \cdot \mathbf{E} = 0$) in two homogeneous regions inside and outside the sphere the wave equation reduces to the Helmholtz equation: $\nabla^2\mathbf{E}(\mathbf{r}) + q^2\mathbf{E}(\mathbf{r}) = 0$, where: $q = q_{in} = q_0\sqrt{\varepsilon_{in}}$ inside the sphere, $q = q_{out} = q_0\sqrt{\varepsilon_{out}}$ in the sphere surroundings, and $q_0 = \frac{\omega}{c}$. The well known scalar solution of the corresponding scalar equation (e.g.[4,5]) in spherical coordinates reads: $\psi_{lm}(r, \theta, \phi) = Z_l(qr)Y_{lm}(\theta, \phi)$, where $l = 1, 2, ..., m = 0, \pm1, ..., \pm l$, $Y_{lm}(\theta, \phi)$ are spherical harmonics, and $Z_l(qr)$ are spherical Bessel functions $j_l(q_{in}r)$ inside the sphere and the spherical Hankel functions $h_l(q_{out}r)$ outside the sphere.

We focus our attention on TM mode only. The explicit expressions for the solution with the nonzero radial component of the electric field $E_r \neq 0$ read:

$$\begin{aligned}
E_r(r,\theta,\phi) &= B_{lm} l(l+1)(qr)^{-1} Z_l(qr) Y_{lm}(\theta,\phi), \\
E_\theta(r,\theta,\phi) &= B_{lm}(qr)^{-1}[qrZ_l(qr)]' \partial Y_{lm}/\partial\theta, \\
E_\varphi(r,\theta,\phi) &= B_{lm} im(qr\sin\theta)^{-1}[qrZ_l(qr)]' Y_{lm}(\theta,\phi), \\
H_r(r,\theta,\phi) &= 0, \\
H_\theta(r,\theta,\phi) &= B_{lm}[\varepsilon(\omega)]^{1/2}(m/\sin\theta) Z_l(qr) Y_{lm}(\theta,\phi), \\
H_\varphi(r,\theta,\phi) &= iB_{lm}[\varepsilon(\omega)]^{1/2} Z_l(qr)\partial Y_{lm}/\partial\theta,
\end{aligned} \quad (1)$$

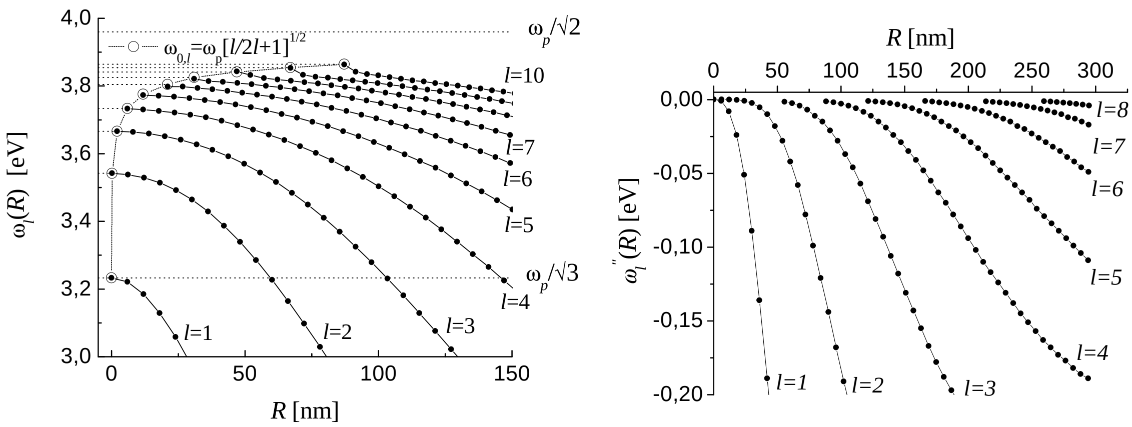

Figure 1. Plasmon oscillation frequencies $\omega_l(R)$ and radiative damping rates $\omega_l''(R)$ as a function of sodium sphere radius R for $l = 1, 2, ...10$ resulting from exact radius dependence. The coincidence of the plasmon frequencies $\omega_l(R_{\min,l})$ with the corresponding value $\omega_{0,l}$ obtained within vanishing size approximation (open circles) is illustrated.

A_{lm} and B_{lm} are constants that take different values A_{lm}^{in} and B_{lm}^{in} inside and A_{lm}^{out} and B_{lm}^{out} outside the sphere. The prime indicates differentiation in respect to the argument, which is $q_{in}r$ or $q_{out}r$ correspondingly. The continuity relations for the tangential components of the electric and magnetic field lead to:

$$B_{lm}^{in}(z_B)^{-1}[z_B j_l(z_B)]' = B_{lm}^{out}(z_H)^{-1}[z_H h_l(z_H)]', \quad B_{lm}^{in}\sqrt{\varepsilon_{in}}j_l(z_B) = B_{lm}^{out}\sqrt{\varepsilon_{out}}h_l(z_H), \tag{2}$$

where the spherical Bessel functions: $j_l(z) = \sqrt{\frac{\pi}{2z}}J_{l+\frac{1}{2}}(z)$, $h_l(z) = j_l(z) - i\cdot n_l(z) = \sqrt{\frac{\pi}{2z}}H^{(1)}_{l+\frac{1}{2}}(z)$ and $n_l(z) = \sqrt{\frac{\pi}{2z}}N_{l+\frac{1}{2}}(z)$. The functions $J_{l+\frac{1}{2}}(z)$, $H^{(1)}_{l+\frac{1}{2}}(z)$ and $N_{l+\frac{1}{2}}(z)$ are Bessel, Hankel and Neuman cylindrical functions of half order of the standard type according to the convention used e.g. in[6] . $z_B = q_{in}R = \frac{\omega}{c}R\sqrt{\varepsilon_{in}}$ is the argument of the Bessel function j_l, and $z_H = q_{out}R = \frac{\omega}{c}R\sqrt{\varepsilon_{out}} = z_B\sqrt{\varepsilon_{out}}/\sqrt{\varepsilon_{in}}$ is the argument of the Hankel function for $r = R$. The continuity relations lead to non-trivial solutions (e.g. non-zero field amplitudes B_{lm} inside and outside the sphere) only when:

$$D_l(z) \equiv \sqrt{\varepsilon_{out}}\xi_l(z_H)\psi_l'(z_B) - \sqrt{\varepsilon_{in}}\psi_l(z_B)\xi_l'(z_H) = 0, \tag{3}$$

where $\psi_l(z) = z\cdot j_l(z)$ and $\xi_l(z) = z\cdot h_l^{(1)}(z)$ are Riccati-Bessel functions. In the region of anomalous dispersion only the TM eigenmodes exist. $Z_l(qr) = j_l(q_{in}r)$ is then a function of a complex argument. The boundary conditions are then satisfied only by a discrete set of characteristic complex values z_l which are the roots of the complex function $D_l(z)$ of complex argument $z = z_l(\omega, R)$. Discretization of complex roots z_l means the discretization of corresponding values $\omega = \Omega_l = \omega_l + i\omega_l''$, $l = 1, 2, 3...$. They define discrete eigenmode frequencies ω_l and damping rates ω_l'' for the TM mode being the sum of corresponding components of (1) multiplied by $e^{i\Omega_l t} = e^{i\omega_l t}e^{\omega_l'' t}$. The analytic form of $z_l = z_l(\Omega_l(R), R)$ is not known, nor the analytic form of the relation $\Omega_l(R)$. Let's notice, that neither $z_H(\omega)$ nor $z_B(\omega)$ separately are appropriate to define the set of discrete characteristic values, contrary to what is suggested in[7] .

We solved the dispersion relation (3) with respect to Ω_l numerically by treating the radius R as an external parameter. Riccati-Bessel functions ψ_l, χ_l and ξ_l and their derivatives with respect to the corresponding arguments z_H and z_B were calculated exactly with use of the recurrence relation: $F_l(z) = \frac{2l-1}{z}F_{l-1}(z) - F_{l-2}(z)$, $F_l'(z) = -\frac{l}{z}F_l(z) + F_{l-1}(z)$, with the two first terms of the series in the form:

$$\begin{array}{cc} \psi_0(z) = \sin(z), & \chi_0(z) = \cos(z), \\ \psi_1(z) = \frac{1}{z}\sin(z) - \cos(z), & \chi_1(z) = \frac{1}{z}\cos(z) + \sin(z). \end{array} \tag{4}$$

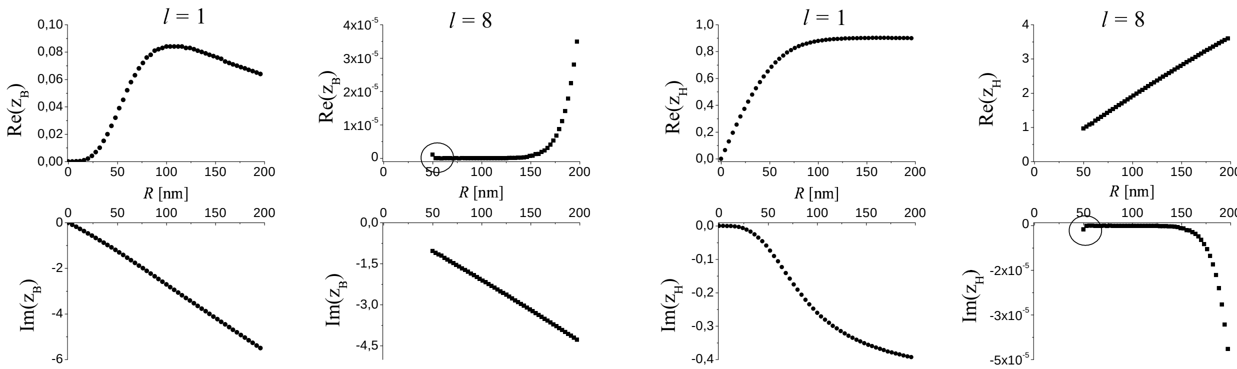

Figure 2. The lower range of variation of the arguments of the Bessel and Hankel functions due to the nonapproximated dispersion relation $D_l(z) = 0$, examples for $l = 1$ and $l = 8$.

We have used the Müller method of secants of finding numerical solutions of the function $f(v) = 0$ when one knows the starting approximated values lying in the vicinity of the exact function parameter v,which can be complex (the "root" function of the Mathcad program). For given l and given R, the complex eigenvalue Ω_l was treated as the parameter to find, successive values of R were external parameters and where changed with the step $\Delta R \approx 2$nm up to the final radius value $R = 300$nm. The values for $\omega_l(R)$ and $\omega_l''(R)$ were searched for by starting from approximate values of the root procedure chosen from the range from $\omega_p\sqrt{3}$ up to $\omega_p\sqrt{2}$ correspondingly and for negative values of ω_l''. The numerical illustrations have been made for a sodium sphere described by the Drude dielectric function with $\omega_p = 5.6$eV.

3. RESULTS

If one employs the widely used rough approximation retaining only the first term of the expansion (see e.g.[2,8]):

$$\begin{aligned} j_l(z) &= \frac{z^l}{(2l+1)!!}\left[1 - \frac{0.5z^2}{1!(2l+3)} + \frac{\left(0.5z^2\right)^2}{2!(2l+3)(2l+5)} - ....\right] \\ h_l(z) &= -i\frac{(2l-1)!!}{z^{l+1}}\left[1 - \frac{0.5z^2}{1!(1-2l)} + \frac{\left(0.5z^2\right)^2}{2!(1-2l)(3-2l)} - ....\right] \end{aligned} \tag{5}$$

where $(2l \pm 1)!! \equiv 1 \times 3 \times 5 \times ... \times (2l \pm 1)$, the dispersion relation (3) is fulfilled for any radius R of the sphere, and gives real discrete eigenfrequencies $\Omega_l = \omega_{0,l}$ (see Fig. 1):

$$\omega_{0,l} = \omega_p\sqrt{\frac{l}{2l+1}}. \tag{6}$$

According to our rigorous solutions there exist no purely real solution for Ω_l: surface plasmons are always damped, even if the dielectric function $\varepsilon_{in}(\omega)$ is real. Fig. 1 (solid lines with closed spheres) illustrate the obtained $\omega_l(R)$ and $\omega_l''(R)$ dependencies for $l = 1, 2, 3, ...10$ starting from $\omega_l(R_{\min,l})$ and $\omega_l''(R_{\min,l})$ values. For $R < R_{\min,l}$ there are no eigenvalues $\Omega_l(R)$. This behavior of the $\Omega_l(R)$ dependence is due to the property of the $\xi_l(z_H)$ function entering the dispersion relation (3) in the range of interest of the variability of the z_H parameter. Figs. 2 illustrate the variation ranges of arguments $z_B(\Omega_l(R), R)$ and $z_H(\Omega_l(R), R)$ of the corresponding functions $\psi_l(z_B)$ and $\xi_l(z_H)$ down to the limiting value for $R = R_{\min,l}$. The non-monotonic behavior at some of the initial values is notable (circles in Fig. 2). In contrary to the $\psi_l(z_B)$ function, $\xi_l(z_H)$ is divergent approaching the

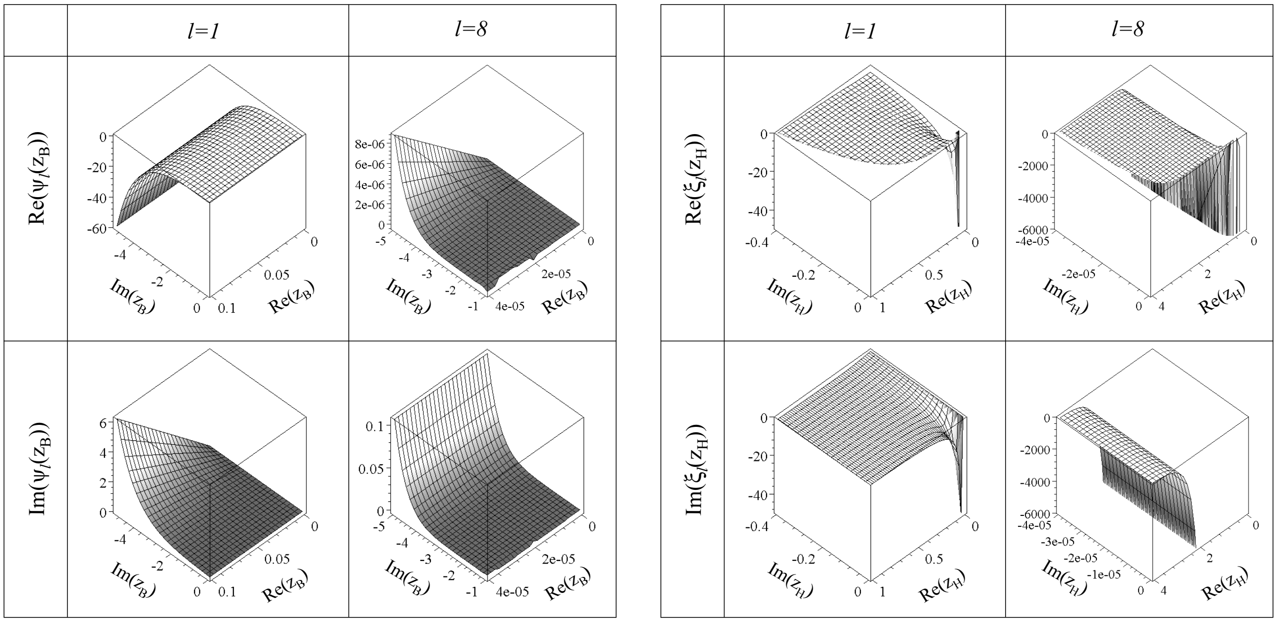

Figure 3. The Riccati-Bessel function $\psi_l\,(z_B)$ and of the Riccati-Bessel function $\xi_l(z_H)$ for the studied range of arguments, examples for $l = 1$ and $l = 8$.

origin, and the region of divergency increases with increasing order l, as illustrated by the examples of $l = 1$ and $l = 8$ in Fig. 3. Divergence of the function $\xi_l(z_H)$ is responsible for the limitation on the existence of roots of the dispersion relation (3) for $R < R_{\min,l}$, as well as for necessity for the nonzero damping rate: $\omega_l''(R_{\min,l}) \neq 0$ (in spite that it can be by orders smaller than $\omega_l(R_{\min,l})$). Our numerical experiment shows that $R_{\min,l}$ dependence on l can be described as $R_{\min,l} \approx C\,[l\,(2l+1)]^{3/2}$ with the proportionality constant C depending on density of free electrons through plasma frequency value ω_p. $R_{\min,l}$ can be e.g.: $R_{\min,l=4} = 6$nm, but it can be as large as $R_{\min,l=10} = 87.2$nm (the size parameter $2\pi R/\lambda \simeq 1$ for optical wavelength λ).

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