Analysis of plasmon resonances on a metal particle

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Abstract

An analytical representation of plasmon resonance modes of a metal particle is developed in the basis of the null-field method and its modal expansion of the particle optical response. This representation allows for the characterization of plasmon modes properties, as their spectral position, bandwidth, amplitude and local field enhancement. Moreover, the derivation of a phenomenological equation governing such resonances relates them to open resonator behavior. The resonance bandwidth corresponds to the plasmon life-time, whereas its amplitude is related to the coupling coefficient with the incident excitation. An efficient algorithm is used to compute and characterize the resonance parameters of silver spheroids as function of the particle geometry. The normal modes present on spheres are split into different azimuthal resonant modes in the case of spheroids, with amplitude depending on the incident polarization and position dependent on the particle aspect ratio.

1. Introduction

Optical properties of metal nanoparticles differ significantly from that of bulk materials [1] and are characterized by resonances in the spectral response of the particle which contribute to both absorption and scattering. The surface plasmons of a particle, associated with collective oscillations of surface charge density at the metal/dielectric interface, can be coupled with an electromagnetic excitation in the form of surface plasmon polaritons (SPPs) resulting in a multimode resonant electromagnetic response of the particle [2], where each mode corresponds to a plasmon-polariton coupled state. The modal characteristics (the number of excited modes, their spectral position and width) intrinsically depend on the particle shape, size and on the optical properties of the host medium [3]. In the case of noble metal particles, resonances occur in the visible spectrum and their excitation at resonant frequencies induces a large near-field enhancement confined at nanoscale. This property and the high sensitivity of the resonance spectral position relative to the particle surrounding refractive index, make such particles used in an increasing range of applications like surface-enhanced Raman spectroscopy [4,5], bio-sensing [6], bio-medicine [7] and nano-photonics [8].

Modeling the optical properties of metal particles appears to be important for understanding the mechanisms underlying the SPPs and for the design of plasmonic structures for a specific application. In the particular case of a perfectly spherical particle, the Mie theory is an efficient tool to study the SPPs resonances because it provides an exact electromagnetic solution of the scattering problem in spherical coordinates. The more general and realistic case of light scattering by a non-spherical particle has been considered for few decades through many theoretical developments [9]. Among the large number of available methods, the null-field method (NFM) [10–12], also called the extended boundary condition method (EBCM), is an efficient surface integral equation method. It gives the solution of the scattering problem for non-spherical particles.
problem through a transition matrix (T-matrix) relating incident and scattered waves. Like the Mie formulation, this method is particularly well suited to study the modal response of localized plasmons. There are different approaches in the literature concerning study of SPP’s modal characteristics, based on the Mie theory for spheres [13,14] and on the surface integral eigenvalue technique [15] or the plasmon hybridization theory [16] for more complex structures, but none of them using the NFM.

This paper is mainly concerned with the description of single particle plasmon modes based on the NFM calculation and using an analytical representation of the resonant part of optical response in form of singular functions. Each function corresponds to a particular mode and contains all resonant modal characteristics (position, bandwidth and amplitude).

The proposed approach presents following advantages. First it is based on the null-field method which permits a rigorous vector analysis of the electromagnetic problem. Secondly it uses a recent development [17,18] in resonance characteristic investigation by polar representation of the system resonant optical response. This formulation based on an efficient and accurate algorithm allows for the computation of modal characteristics as well as of plasmon fields around the particle. Finally, a notable physical description of plasmon resonances is derived, relating them to an open resonator behavior. The case of silver spheres and spheroids, widely used in practical applications, is considered to illustrate the capabilities of our theoretical approach.

2. Scattering problem statement

Consider an incident monochromatic plane wave with electric field \( E_{inc} e^{jkr - j\omega t} \), interacting with an isolated and non-concave particle occupying a volume of space \( D_s \) bordered by a regular surface \( S \). This particle is defined by its permittivity \( \varepsilon_2 \), magnetic permeability \( \mu_2 \) and its surface \( S \) is expressed in spherical coordinates by radial function \( r = R(\theta, \varphi) \). The particle is surrounded by non-absorbing medium in external space \( D_i \) having dielectric permittivity \( \varepsilon_1 \) and magnetic permeability \( \mu_1 \). Both media are supposed to be linear, homogeneous and isotropic. The incident wave is linearly polarized with \( E_{0\varphi} \) and \( E_{0\theta} \), the components of the electric field parallel and orthogonal to the incidence plane, and directed by \( \theta_0 \) (zenith) and \( \varphi_0 \) (azimuthal) angles in spherical coordinates, respectively. The wavenumber in \( D_i \) is given by \( k_i = \sqrt{\varepsilon_1 \mu_1} \), \( k_0 \) is the wave number in free space.

The scattering problem consists in finding both scattered \( \mathbf{E}_{scat}, \mathbf{H}_{scat} \) and internal \( \mathbf{E}_{int}, \mathbf{H}_{int} \) fields. All considered electromagnetic fields are time-harmonic, satisfying Maxwell’s equations

\[
\begin{align*}
\nabla \times \mathbf{E} &= j\omega\mu\mathbf{H} \\
\nabla \times \mathbf{H} &= -j\omega\varepsilon\mathbf{E}
\end{align*}
\]

and the boundary conditions on the particle surface

\[
\begin{align*}
\mathbf{E}_{inc}(\mathbf{r}) + \mathbf{E}_{scat}(\mathbf{r}) &= \mathbf{E}_{int}(\mathbf{r}) \\
\mathbf{h}_{inc}(\mathbf{r}) + \mathbf{h}_{scat}(\mathbf{r}) &= \mathbf{h}_{int}(\mathbf{r})
\end{align*}
\]

where \( \mathbf{e} = n \times \mathbf{E} \) and \( \mathbf{h} = n \times \mathbf{H} \) are the tangent surface fields with \( \mathbf{n} \) the unit vector normal to the surface \( S \).

When illuminating a small particle, some energy is lost from the incident light through the scattering (radiation) and/or absorption (heating) process. A way to characterize this energy transformation is to introduce the scattering and absorption cross-sections \( C_{sca} \) and \( C_{abs} \), respectively, defined as the power removed from the incident light by scattering or absorption normalized to the incident wave intensity. Extinction cross-section \( C_{ext} \), which is the sum of these two quantities, represents the total lost power.

3. The null-field method

This section presents a brief description of the null-field method following the derivation by Doicu et al. [12] and using their notations. Fields are expanded on the basis of localized spherical vector wave functions \( \mathbf{M}_{mn}^1(\mathbf{k} \mathbf{r}) \) and \( \mathbf{N}_{mn}^1(\mathbf{k} \mathbf{r}) \) with indices 1 and 3 corresponding to regular (at the origin) and radiating solutions, respectively (see Appendix A). Electric fields of incident, scattered and internal waves are written in spherical coordinates

\[
\begin{align*}
\mathbf{E}_{inc}(\mathbf{r}) &= \sum_{n=1}^{\infty} \sum_{m=-n}^{n} a_{mn} \mathbf{M}_{mn}^1(\mathbf{k} \mathbf{r}) + b_{mn} \mathbf{N}_{mn}^1(\mathbf{k} \mathbf{r}) \\
\mathbf{E}_{sca}(\mathbf{r}) &= \sum_{n=1}^{\infty} \sum_{m=-n}^{n} f_{mn} \mathbf{M}_{mn}^1(\mathbf{k} \mathbf{r}) + g_{mn} \mathbf{N}_{mn}^1(\mathbf{k} \mathbf{r}) \\
\mathbf{E}_{int}(\mathbf{r}) &= \sum_{n=1}^{\infty} \sum_{m=-n}^{n} c_{mn} \mathbf{M}_{mn}^1(\mathbf{k} \mathbf{r}) + d_{mn} \mathbf{N}_{mn}^1(\mathbf{k} \mathbf{r})
\end{align*}
\]

Using this formalism, each field can be viewed as a superposition of spherical waves \( \mathbf{M}_{mn} \) and \( \mathbf{N}_{mn} \), weighted by expansion coefficients, and corresponding respectively to TE (i.e. with no radial component) and TM (with radial component) polarization. These waves are also known as magnetic and electric waves.

Scattering parameters can be expressed by means of expansion coefficients. The optical cross-sections are given using their definition and orthogonality of spherical functions

\[
\begin{align*}
C_{sca} &= \frac{\pi}{k_i^2} \sum_{n=1}^{\infty} \sum_{m=-n}^{n} (|a_{mn}|^2 + |g_{mn}|^2) \\
C_{ext} &= \frac{\pi}{k_i^2} \sum_{n=1}^{\infty} \sum_{m=-n}^{n} \text{Re}(f_{mn} a_{mn}^* + g_{mn} b_{mn}^*)
\end{align*}
\]

where the asterisk denotes the complex conjugate.

Determining the scattering expansion coefficients through the null-field method results from the general null-field equation

\[
-\mathbf{E}_{inc}(\mathbf{r}) = \nabla \times \int_{\mathcal{S}} \mathbf{h}_{int}(\mathbf{r'}) (g(k_1, \mathbf{r}, \mathbf{r'}) d\mathbf{S}(\mathbf{r'}) \\
+ \frac{j}{k_i} \nabla \times \nabla \times \int_{\mathcal{S}} \mathbf{h}_{int}(\mathbf{r'}) (g(k_1, \mathbf{r}, \mathbf{r'}) d\mathbf{S}(\mathbf{r'}) \quad \mathbf{r} \in D_2
\]

and the expression of the scattered field from Huygens’ principle:

\[
\mathbf{E}_{scat}(\mathbf{r}) = \nabla \times \int_{\mathcal{S}} \mathbf{h}_{int}(\mathbf{r'}) (g(k_1, \mathbf{r}, \mathbf{r'}) d\mathbf{S}(\mathbf{r'}) \\
+ \frac{j}{k_i} \nabla \times \nabla \times \int_{\mathcal{S}} \mathbf{h}_{int}(\mathbf{r'}) (g(k_1, \mathbf{r}, \mathbf{r'}) d\mathbf{S}(\mathbf{r'}) \quad \mathbf{r} \in D_1
\]
with the Green function:
\[ g(k, r, r') = \frac{e^{ik|r-r'|}}{4\pi|r-r'|} \] \hspace{1cm} (10)

The dyadic Green function is expressed in terms of vector wave functions as
\[ g(k, r, r') = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} \left[ \begin{array}{c} M^i_{nm}(kr)M^j_{nm}(kr')^* + N^i_{nm}(kr)N^j_{nm}(kr')^* \\ + \text{irrotational terms, } r < r' \\ + \text{irrotational terms, } r > r' \end{array} \right] \] \hspace{1cm} (11)

Considering the null-field Eq. (4), with \( r \) restricted on a spherical surface included into the volume of the particle \( D_2 \), and using the expansions of both incident field and green dyadic function together with the orthogonality of vector spherical wave functions on a spherical surface we get
\[ \frac{jk^2}{\pi} \int_{S} \left[ \mathbf{e}_{im}(r') \cdot \left( M^i_{nm}(kr) \right) + j\frac{\mu^2}{\epsilon}\mathbf{h}_{im}(r') \right] \cdot \left( \begin{array}{c} M^i_{nm}(kr') \\ N^i_{nm}(kr') \end{array} \right) dS(r') = - \mathbf{a}_{mn} \mathbf{b}_{mn} \] \hspace{1cm} (12)

Inserting the spherical expansion of interfield and the definition of surface fields, one obtains the matrix relation between incident and internal expansion coefficients
\[ Q^{31}(k_1, k_2) \left( \begin{array}{c} c_{mn} \\ d_{mn} \end{array} \right) = - \mathbf{a}_{mn} \mathbf{b}_{mn} \] \hspace{1cm} (13)

where matrix \( Q^{31}(k_1, k_2) \) is defined in Appendix B.

The scattered field expansion coefficients are determined by Huygens’ principle and the vector spherical wave expansion of surface fields, leading to the matrix relation:
\[ \left( \begin{array}{c} f_{mn} \\ g_{mn} \end{array} \right) = Q^{11}(k_1, k_2) \left( \begin{array}{c} c_{mn} \\ d_{mn} \end{array} \right) \] \hspace{1cm} (14)

The transition matrix relating the expansion coefficients of scattered and incident fields is found by combining Eqs. (13) and (14)
\[ \left( \begin{array}{c} f_{mn} \\ g_{mn} \end{array} \right) = -Q^{11}(k_1, k_2)(Q^{13}(k_1, k_2))^{-1} \left( \begin{array}{c} a_{mn} \\ b_{mn} \end{array} \right) = T \left( \begin{array}{c} a_{mn} \\ b_{mn} \end{array} \right) \] \hspace{1cm} (15)

In the case of axially symmetric particles, all \( Q \) and \( T \) matrices are diagonal with respect to the azimuthal indices, i.e. \( T^{ij}_{mmnn} = T^{ij}_{mmnn} \delta_{mnr} \). In the particular case of a spherical particle, the \( T \)-matrix is diagonal due to the orthogonality of spherical functions, and non-zero elements are given analytically
\[ T^{11}_{mmnn} = -a_n b_n = \frac{j_{m}(k_1 R j_{m}(k_2 R) - j_{-m}(k_1 R j_{m}(k_2 R))}{h_{m}^{(1)}(k_1 R j_{m}(k_2 R) - h_{-m}^{(1)}(k_1 R j_{m}(k_2 R))} \delta_{mnr} \delta_{mnr} \] \hspace{1cm} (16)

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4. Representation of plasmon resonances

The surface plasmon polaritons, corresponding to the incident electromagnetic excitation of the surface plasmons, are characterized by the resonant optical response of the particle. From general point of view, several polariton states exist, each one corresponding to an eigenmode of the system and appearing in the form of a resonant band in the spectral response of the particle. As an example, Fig. 1 shows the extinction efficiency of a silver sphere versus the incident wavelength and the particle radius. Different resonant bands appear in the spectrum, with maximum wavelength and bandwidth depending on the sphere size. The aim of our analysis is to provide an analytical tool to describe and to characterize each resonant mode of a particle.

All the particle response information including resonances is contained into the scattering expansion coefficients calculated by the null-field method. Moreover, plasmon resonances are assumed to correspond to TM modes, and then only \( g_{mn} \) expansion coefficients contain the resonance information. The key idea is to express each

![Fig. 1. Extinction efficiency of a silver sphere versus the wavelength and the particle size.](image-url)
of these coefficients as a singular function of the pulsation
\[ g_{mn}(\omega) = \frac{p_{mn} \omega_{mn}}{\omega - \omega_{mn}} + \sum_{k=0}^{\infty} q_{mnk}(\omega - \omega_{mn})^k \]  
(18)

This representation assumes that each considered coefficient exhibits a resonance, characterized by the singular part with complex pulsation \( \omega_{mn} \) and amplitude \( p_{mn} \) of the plasmon resonance. The real part of \( \omega_{mn} \) corresponds to the spectral position of the resonance whereas the imaginary part equals its half-bandwidth.

An efficient algorithm has been developed [17,18] to compute accurately both amplitude and complex pulsation by filtering the regular part in Eq. (18). The general idea of this method is to perform a \( N \)th order numerical derivation of Eq. (18) with respect to the pulsation with \( N \) sufficiently large to nullify the regular part, permitting the computation of the plasmon resonance pulsation and amplitude. This numerical derivation is done by discretizing the particle response using \( N \) pulsations around the resonance position and by applying Newton’s divided differences on the system obtained by considering Eq. (18) for all points. Finally, resonance parameters are expressed in function of discretized values of pulsation and response.

Then we decompose firstly Eq. (18) in \( N+1 \) linear equations by taking \( N+1 \) different values of the pulsation \( \omega_i \). Multiplying each equation by \( \omega_i - \omega_{mn} \), yields

\[ (\omega_i - \omega_{mn})g_{mn}(\omega_i) = p_{mn} \omega_{mn} + \sum_{k=0}^{\infty} q_{mnk}(\omega_i - \omega_{mn})^k + 1 \]  
(19)

Applying now the \( (N+1) \)th order Newton’s divided difference operator to (19) leads to

\[ \sum_{i=0}^{N} \frac{\omega_i - \omega_{mn}g_{mn}(\omega_i)}{\prod_{j \neq i}^{N} (\omega_i - \omega_j)} \approx 0 \]  
(20)

This equation specifies the resonant pulsation

\[ \omega_{mn} = \sum_{i=0}^{N} \frac{\omega_i - \omega_{mn}g_{mn}(\omega_i)}{\prod_{j \neq i}^{N} (\omega_i - \omega_j)} \]  
(21)

Coming back now with the expression (18) multiplied by \( \omega - \omega_{mn} \) and taking Lagrange’s form of the left-hand side

\[ (\omega - \omega_{mn})g_{mn}(\omega) = \sum_{i=0}^{N} \frac{\omega_i - \omega_{mn}g_{mn}(\omega_i)}{\prod_{j \neq i}^{N} (\omega_i - \omega_j)} \]  
(22)

it gives the resonant amplitude in the limit \( \omega \rightarrow \omega_{mn} \)

\[ p_{mn} = \sum_{i=0}^{N} \frac{\omega_i - \omega_{mn}g_{mn}(\omega_i)}{\omega_{mn}g_{mn}(\omega_i)} \prod_{j \neq i}^{N} \frac{\omega_{mn} - \omega_j}{\omega_i - \omega_j} \]  
(23)

Here we can introduce the plasmon expansion coefficient

\[ g_{\delta mn}(\omega) = \frac{p_{mn}}{\omega - \omega_{mn}} \]  
(24)

and the plasmon field in the basis of scattered field expansion in term of spherical vector wave functions

\[ E_p(r, \omega) = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} g_{\delta mn}(\omega) N_m^3(k_1 r) \]  
(25)

In general, all resonant pulsations \( \omega_{mn} \) are not distinct for all couples \((m, n)\), and the plasmon expansion coefficients having the same complex pulsation \( \omega \) contribute to a single plasmon mode. The \( l \)th plasmon field can then be written as

\[ E_p(r, \omega) = \frac{\alpha_l}{\omega - \omega_0} \sum_{\mu} p_{\mu} N_l^3(k_1 r) \]  
(26)

where \( \mu \) corresponds to all \((m, n)\) indexes providing \( \omega_{mn} = \omega_0 \). This last relation will be used to compute the plasmon fields of individual plasmon modes.

The main advantage of this method is its ability to extract the pure resonant response from the overall response of a particle, with an efficient filtering of scattering or interference effects. The plasmon fields can be computed, giving the exact contribution of resonances in the total near-field.

5. Phenomenological analysis

The description of the resonant response of a metal particle as a singular function of the pulsation permits to derive a phenomenological approach of the plasmon excitation.

If we define the plasmon expansion coefficient of the \( l \)th mode as a singular part of the response to an excitation

\[ g_l(\omega) = \frac{p_{l\omega l}}{\omega - \omega_l} f_0(\omega) \]  
(27)

with \( f_0(\omega) \) the excitation function (e.g. the incident field) and \( \omega_0 = \omega_1 + j \omega_2 \) (the plasmon pulsation, its representation, as well as its derivative, in time domain is given through the Fourier transforms

\[ G_l(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{p_{l\omega l}}{\omega - \omega_l} f_0(\omega) e^{-j\omega t} d\omega \]  
(28)

\[ \frac{dG_l(t)}{dt} = -\frac{1}{2\pi} \int_{-\infty}^{\infty} j \omega_0 \frac{p_{l\omega l}}{\omega - \omega_l} f_0(\omega) e^{-j\omega t} d\omega \]  
(29)

A particular combination of these expressions gives

\[ \frac{dG_l(t)}{dt} + j \omega_0 G_l(t) = -j \omega_0 p_{l\omega l} F_0(t) \]  
(30)

Both \( G_l(t) \) and \( F_0(t) \) are time-harmonic functions. If we consider these functions at resonance position pulsation \( \omega_1 \), we obtain

\[ F_0(t) = \tilde{F}_0(t) \exp(-j \omega_1 t) \]  
(31)

\[ G_l(t) = \tilde{G}_l(t) \exp(-j \omega_1 t) \]  
(32)

\[ \frac{dG_l(t)}{dt} = -\frac{d\tilde{G}_l(t)}{dt} \exp(-j \omega_1 t) - j \omega_1 \tilde{G}_l(t) \exp(-j \omega_1 t) \]  
(33)
with $\tilde{F}(t)$ and $\tilde{G}(t)$ the temporal shapes of $F_0(t)$ and $G_0(t)$ functions at the resonance pulsation $\omega_1$. By equalizing (29) and (33), and inserting (31) and (32), yields after simplification to

$$\frac{d\tilde{G}(t)}{dt} = \omega_2 \tilde{G}(t) - j\omega_1 p_l \tilde{F}(t)$$

(34)

The latter relation can be interpreted as the coupled mode equation [18]:

$$\frac{dG(t)}{dt} = -\frac{1}{\tau} G(t) + \kappa G_0(t)$$

(35)

describing the response $G(t)$ to an excitation $G_0(t)$ of an open resonator with decay time $\tau$ and coupling coefficient $\kappa$. Eq. (34) is of major importance to understand the physical behavior of plasmon modes. For a given particle geometry, each plasmon mode acts as an open resonator with a decay time, also called life-time, related to the resonance bandwidth $\tau = -1/\omega_2$, and a coupling coefficient corresponding to the plasmon amplitude $\kappa = -j\omega_1 p_l$.

The computation of plasmon amplitude and pulsation then permits to determine phenomenological parameters in (35) and to describe thereby the physical behavior of each plasmon resonance mode.

6. Results

We consider first the simplest case of a spherical particle. The scattering expansion coefficients corresponding to the TM modes are given in function of the Lorentz–Mie coefficients

$$g_{mn} = -a_b b_{mn}$$

(36)

Since the incident expansion coefficients depend only on the incident polarization, the plasmon resonance information are totally contained in $a_b$. According to their expression (17), the different plasmon modes do not depend on azimuthal order $m$, i.e. the $l$th resonance mode includes contribution of all azimuthal modes $g_{lm}$ with $-l \leq m \leq l$. In other words, all $g_{lm}$ expansion coefficients exhibit the same complex pulsation $\omega_l$ corresponding to the eigen pulsation of the $l$th plasmon mode. For computations, we consider a $z$-directed and $x$-polarized incident plane wave. In this case, the incident expansion coefficients are non-null only for $|m| = 1$ modes; therefore, only $g_{l \pm 1}$ scattering coefficients are excited. The algorithm described in Section 4 is used to plot resonance position, half bandwidth and amplitude of silver spheres for the (arbitrary) first five plasmon modes versus the particle size (Fig. 2). When increasing the particle radius, the resonance position (Fig. 2a) of each mode is characterized by a redshift, more pronounced for modes of lower order. Such a redshift is accompanied by a widening of the resonance band (Fig. 2b), corresponding physically to an increase of the decay time (or the life time) of the plasmon. We can note here that similar results can be obtained by finding the complex pulsations satisfying the dispersion relation of a sphere corresponding to the complex zeroes of $a_n$ coefficient denominator [13,14]:

$$\varepsilon_2 \tilde{h}_n^{(l)}(k_1 r_1, k_2 R) - \varepsilon_1 \tilde{h}_n^{(l)}(k_1 r_1, k_2 R) = 0$$

(37)

The other parameter characterizing the resonance is its amplitude $\rho \pm 1$: physically related to the coupling coefficient of the resonator, or in other words to the overlapping of the incident excitation with the plasmon mode. Dependence of the absolute values of the plasmon modes coupling coefficients $|\log \rho_0| = |\log \rho_{-1}|$ (Fig. 2c) shows an increase of resonance amplitudes in the range of considered particle sizes. In the case of the first mode, the amplitude reaches a maximum at sphere radius 56 nm and then decreases. Small spheres, e.g., less than 10 nm in radius, are well-known to exhibit the fundamental plasmon resonance mode only.

In the case of a 40 nm radius silver sphere, only the three first resonance modes appear in the extinction spectrum (Fig. 3a), the others do not couple sufficiently with the incident wave to appear in the spectrum, whereas the found resonances positions match with the resonances maxima. The plasmon field of each resonance mode on the particle surface is plotted in Fig. 3b–f for the first five resonance modes at their resonance position using the following formula derived from Eq. (26):

$$E_{\rho}(r, \text{Re} (\omega n)) = j \frac{a_n}{\text{Im} (\omega n)} \sum_{m = -1}^{1} p_{ml} N_{ml}(k_1 r)$$

(38)

The $l$th mode is characterized by 2l local maxima of the plasmon field intensity on the particle surface, reflecting the corresponding surface charge density oscillations. The fundamental plasmon mode ($l = 1$) is known as a dipolar
mode, because it radiates in the far-field as a dipole. In the same manner, the next mode \((l=2)\) is called quadrupolar mode. The positions of local field maxima as well as their maximum intensity vary greatly from one mode to another, with a larger field enhancement for the quadrupolar mode in this particular example.

Next, we consider silver spheroids with a given incident polarization. Computation of the resonant complex pulsations for scattering expansion coefficients shows that each plasmon resonance of the \(l\)th order is split into \(l+1\) different azimuthal modes when the particle is aspherical. For example, the dipolar mode \(l=1\) appears as two different modes corresponding to poles in scattering expansion coefficients for \(n=1, m=0\) and \(n=1, |m|=1\). The positions of the split dipolar and quadrupolar modes are plotted in Fig. 4 in the case of prolate and oblate particles (with a constant volume equal to a sphere of 40 nm radius). For dipolar modes, the resonance position is strongly dependent on the aspect ratio of the particle. In the case of silver particles, this property permits to tune the resonance positions over the entire visible spectrum by changing the geometrical form of the particle.

Contrary to spheres, where resonant properties are independent of the incident polarization, each plasmon mode amplitude depends on the incident polarization. Fig. 4c and d depicts the amplitude of the split dipolar and quadrupolar modes versus the incident angle for a prolate particle with a 1.5 aspect ratio. Results show in the case of a dipolar mode that the overlapping of the incident wave with each mode is strongly dependent on the incident polarization. Thus, the mode corresponding to \(n=1, m=0\) has a minimum excited amplitude for an incident wave polarized along the largest particle dimension and a maximum one along the smallest dimension. This mode is therefore a transverse mode and similarly, the mode corresponding to \(n=1, |m|=1\) is a longitudinal.

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mode. Hence, for a given particle geometry, varying incident polarization permits to identify the best coupling polarization for each mode.

Still considering a prolate particle with an aspect ratio of 1.5, the several resonant bands appearing in the extinction spectrum (Fig. 5a) match with the resonant wavelength positions computed for dipolar and quadrupolar modes (other peaks in the spectrum correspond to higher resonant modes). As in the case of silver sphere, surface plasmon field of each mode for a prolate particle with an aspect ratio of 1.1 (for which the computation of scattered field on the particle surface using Eq. (4) is possible) is shown in Fig. 5b–f calculated by the following relation:

\[
E_p^{imn}(\mathbf{r}, \omega) = j \frac{\omega |\alpha|}{\Im \omega |\alpha|} \sum p_{mn} N_{mn}(k_1 \mathbf{r})
\]

Again, local maxima of the plasmon fields appear on the particle surface, where the number and the localization of these maxima depend on the considered mode.

7. Conclusion

An analytical representation of plasmon resonant modes of metal particles is developed on the basis of the null-field method and a modal expansion of the particle optical response. The description of the resonant response by a singular function of the pulsation permits to characterize the plasmon modes and calculate their spectral position, bandwidth, amplitude as well as the local field enhancement. This approach takes the advantage of an efficient filtering of the regular part in the particle response, and leads to
a phenomenological equation governing plasmon resonances and relating them to an open resonator behavior. Thus, the resonance bandwidth corresponds to the plasmon life-time, and its amplitude is related to the coupling of the incident excitation to the plasmon mode. An accurate algorithm is used to compute and characterize resonant parameters of silver spheroids as a function of the particle geometry. The plasmon mode of a sphere is split into different azimuthal resonant modes in the case of spheroids. The amplitude of these modes varies with the incident polarization whereas the resonance positions finely depend on the particle geometry. Plasmon fields are given for different resonance modes with different localizations and intensities of maxima around the particle. This paper provides an efficient numerical tool to design plasmonic structures for specific applications. We plan to extend it to multiple particle systems in future publications.

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**Appendix A**

Spherical vector wave functions are solution to the vector wave equation $\Delta A + k^2 A = 0$ and are expressed in terms of spherical functions [20]

$$M_{mn}^{1,2}(kr) = \frac{1}{\sqrt{2n(n+1)}} \left\{ \begin{array}{l}
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \right\} e^{jmn} \\
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \right\} e^{jmn}
\end{array} \right. (A1)$$

$$N_{mn}^{1,2}(kr) = \frac{1}{k} \nabla \times M_{mn}^{1,2}(kr)$$

$$= \frac{1}{\sqrt{2n(n+1)}} \left\{ \begin{array}{l}
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\end{array} \right\} e^{jmn} (A2)$$

where $j^m_1$ is the spherical Bessel function $j_m$ (corresponding to a regular solution) and $j^m_2$ denotes the Hankel spherical functions $h^m_1$, (radiated waves). $\xi_{mn}^{1,2}(kr)$ corresponds to the derivative $[k r \xi_{mn}^{1,2}(kr)]$. Normalized associated Legendre functions $P_n^m$ are defined as [21]

$$P_n^m(\xi) = \sqrt{\frac{(2n+1)(n-m)!}{2(n+m)!}} (1-\xi)^{m/2} d^n \nabla P_n(\xi) (A3)$$

with $P_n(\xi)$ the Legendre polynomials. Spherical functions $\xi_n^m(\theta)$ and $r_n^m(\theta)$ are expressed in terms of Legendre functions:

$$\xi_n^m(\theta) = \frac{P_n^m(\cos \theta)}{\sin \theta} (A4)$$

$$r_n^m(\theta) = \frac{d}{d\theta} P_n^m(\cos \theta) (A5)$$

The incident expansion coefficients in Eq. (4) are [22]

$$a_{mn} = -\frac{4\pi}{2n(n+1)} \left[ j_m \xi_n^m(\beta_0)E_\beta + r_n^m(\beta_0)E_\beta \right] e^{-jmn} (A6)$$

$$b_{mn} = -\frac{4\pi}{2n(n+1)} \left[ r_n^m(\beta_0)E_\beta - j_m \xi_n^m(\beta_0)E_\beta \right] e^{-jmn} (A7)$$

**Appendix B**

Matrix elements $Q^{pq}(k_0, k_0)$ are following:

$$Q^{pq}(k_0, k_0) = \left[ \begin{array}{c}
Q_{mm}^{pq} \quad Q_{mp}^{pq} \quad Q_{mq}^{pq} \quad Q_{qq}^{pq} \end{array} \right]$$

$$= \left[ \begin{array}{c}
\frac{4\pi}{\sqrt{2n(n+1)}} \left\{ \begin{array}{l}
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\end{array} \right\} e^{jmn} \\
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\frac{\sqrt{\frac{n}{2}}}{} j^m \left[ n \right] e^{-j(n+1)} \\
\end{array} \right\} e^{jmn} \right] (B1)$$

$$= \frac{j k_d^2}{\pi} \int_S \left\{ \begin{array}{c}
\left[ M_{mm}^{pq}(k_0, r') \times N_{mp}^{pq}(k_0, r') \right] \cdot \mathbf{n}(r') \\
+ \sqrt{\frac{n_0}{\varepsilon_0}} N_{mm}^{pq}(k_0, r') \times \left[ M_{mp}^{pq}(k_0, r') \times N_{mp}^{pq}(k_0, r') \right] \cdot \mathbf{n}(r') \\
\end{array} \right\} dS(r') (B2)$$

$$= \frac{j k_d^2}{\pi} \int_S \left\{ \begin{array}{c}
\left[ N_{mm}^{pq}(k_0, r') \times N_{mp}^{pq}(k_0, r') \right] \cdot \mathbf{n}(r') \\
+ \sqrt{\frac{n_0}{\varepsilon_0}} M_{mm}^{pq}(k_0, r') \times \left[ M_{mp}^{pq}(k_0, r') \times N_{mp}^{pq}(k_0, r') \right] \cdot \mathbf{n}(r') \\
\end{array} \right\} dS(r') (B3)$$

**Appendix C**

Permittivity of silver particles is defined by the modified Drude model [1]:

$$\epsilon(\omega) = \epsilon_0 - \frac{\omega_p^2}{\omega^2 + i\Gamma \omega} (C1)$$

with $\Gamma = \Gamma_0 + AV_F/r$ the modified damping constant which takes into account the particle dimensions. $\Gamma_0$ is the damping constant of bulk silver ($\Gamma_0 = 17.6$ meV). $\Lambda$ is a multiplicative constant ($A=1$), $V_F$ is the Fermi velocity of electrons ($V_F = 1.39 \times 10^5$ m/s) and $r$ is the radius of the equivalent volume sphere radius of the particle. $\epsilon_0$ is the contribution of interband transitions ($\epsilon_0 = 3.7$ eV, supposed constant in the visible spectrum), $\omega_p$ is the plasma pulsation of silver $\omega_{pp}$ = 8.89 eV.

**References**


