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Analysis of plasmon resonances on a metal particle

Saïd Bakhti, Nathalie Destouches, Alexandre V. Tishchenko*

Université de Lyon, F-42023 Saint-Etienne, France; CNRS, UMR 5516, Laboratoire Hubert Curien, Université Jean Monnet, 18 rue Pr. Lauras F-42000 Saint-Etienne, France

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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 through a transition matrix (T-matrix) relating

* Corresponding author at: Laboratoire Hubert Curien, CNRS, UMR 5516, Université Jean Monnet, 18 rue Pr. Lauras F-42000 Saint-Etienne, France.
Tel.: +33 477915819.
E-mail address: alexandre.tishchenko@univ-st-etienne.fr (A.V. Tishchenko).

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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 SPPs 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 $\mathbf{E}_{inc}e^{j\mathbf{kr}-j\omega t}$, interacting with an isolated and non-concave particle occupying a volume of space D_2 bordered by a regular surface S. This particle is defined by its permittivity ε_2, magnetic permeability μ_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_1 having dielectric permittivity ε_1 and magnetic permeability μ_1. Both media are supposed to be linear, homogeneous and isotropic. The incident wave is linearly polarized with $E_{0\beta}$ and $E_{0\alpha}$ the components of the electric field parallel and orthogonal to the incidence plane, and directed by β_0 (zenith) and α_0 (azimuthal) angles in spherical coordinates, respectively. The wavenumber in D_i is given by $k_i=\omega(\varepsilon_i\mu_i)^{1/2}$, k_0 is the wave number in free space. The scattering problem consists in finding both scattered ($\mathbf{E}_{sca}$, $\mathbf{H}_{sca}$) and internal ($\mathbf{E}_{int}$, $\mathbf{H}_{int}$) fields. All considered electromagnetic fields are time-harmonic, satisfying Maxwell's equations

$$\begin{cases} \nabla\times\mathbf{E}(\mathbf{r})=j\omega\mu_i\mathbf{H}(\mathbf{r}) \\ \nabla\times\mathbf{H}(\mathbf{r})=-j\omega\varepsilon_i\mathbf{E}(\mathbf{r}) \end{cases} \quad \mathbf{r}\in D_i \tag{1}$$

and the boundary conditions on the particle surface

$$\begin{cases} \mathbf{e}_{inc}(\mathbf{r})+\mathbf{e}_{sca}(\mathbf{r})=\mathbf{e}_{int}(\mathbf{r}) \\ \mathbf{h}_{inc}(\mathbf{r})+\mathbf{h}_{sca}(\mathbf{r})=\mathbf{h}_{int}(\mathbf{r}) \end{cases} \quad \mathbf{r}\in S \tag{2}$$

where $\mathbf{e}=\mathbf{n}\times\mathbf{E}$ and $\mathbf{h}=\mathbf{n}\times\mathbf{H}$ 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 $\mathbf{M}^{1,3}_{mn}(k\mathbf{r})$ and $\mathbf{N}^{1,3}_{mn}(k\mathbf{r})$ 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

$$\mathbf{E}_{inc}(\mathbf{r})=\sum_{n=1}^{\infty}\sum_{m=-n}^{n}a_{mn}\mathbf{M}^1_{mn}(k_1\mathbf{r})+b_{mn}\mathbf{N}^1_{mn}(k_1\mathbf{r}) \tag{3}$$

$$\mathbf{E}_{sca}(\mathbf{r})=\sum_{n=1}^{\infty}\sum_{m=-n}^{n}f_{mn}\mathbf{M}^3_{mn}(k_1\mathbf{r})+g_{mn}\mathbf{N}^3_{mn}(k_1\mathbf{r}) \tag{4}$$

$$\mathbf{E}_{int}(\mathbf{r})=\sum_{n=1}^{\infty}\sum_{m=-n}^{n}c_{mn}\mathbf{M}^1_{mn}(k_2\mathbf{r})+d_{mn}\mathbf{N}^1_{mn}(k_2\mathbf{r}) \tag{5}$$

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

$$C_{sca}=\frac{\pi}{k_1^2}\sum_{n=1}^{\infty}\sum_{m=-n}^{n}(|f_{mn}|^2+|g_{mn}|^2) \tag{6}$$

$$C_{ext}=-\frac{\pi}{k_1^2}\sum_{n=1}^{\infty}\sum_{m=-n}^{n}\mathrm{Re}(f_{mn}a^*_{mn}+g_{mn}b^*_{mn}) \tag{7}$$

where the asterisk denotes the complex conjugate.

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

$$-\mathbf{E}_{inc}(\mathbf{r})=\nabla\times\int_S\mathbf{e}_{int}(\mathbf{r}')g(k_1,\mathbf{r},\mathbf{r}')dS(\mathbf{r}') + \frac{j}{k_1}\nabla\times\nabla\times\int_S\mathbf{h}_{int}(\mathbf{r}')g(k_1,\mathbf{r},\mathbf{r}')dS(\mathbf{r}') \quad \mathbf{r}\in D_2 \tag{8}$$

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

$$\mathbf{E}_{sca}(\mathbf{r})=\nabla\times\int_S\mathbf{e}_{int}(\mathbf{r}')g(k_1,\mathbf{r},\mathbf{r}')dS(\mathbf{r}') + \frac{j}{k_1}\nabla\times\nabla\times\int_S\mathbf{h}_{int}(\mathbf{r}')g(k_1,\mathbf{r},\mathbf{r}')dS(\mathbf{r}') \quad \mathbf{r}\in D_1 \tag{9}$$