Universidad de Cantabria

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ON LIGHT SCATTERING BY NANOPARTICLES WITH CONVENTIONAL AND NON-CONVENTIONAL OPTICAL PROPERTIES

PH.D. THESIS

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Theoretical Overview

"Cuanto más avanzan la técnica y el materialismo, más nos damos cuenta de que hay algo que hemos dejado atrás sin comprenderlo".
—Enrique Moriel, La Ciudad Sin Tiempo.

2.1. Introduction

In this chapter, the fundamental principles used to study light scattering by particles are introduced and briefly explained. For the special case of spherical particles, Mie theory is the basic theoretical tool. We will discuss shortly this scheme following the presentation as given by C. Bohren and D. Huffman [14]. Since the object of this thesis is centered on the study of small particles compared with the incident wavelength, some approximations to Mie theory will be introduced.

2.2. The Light Scattering Problem

An electromagnetic field incident on an object will be scattered in all directions. Hence, incident and scattered fields have different properties, which depend on the physical (optical properties) and geometrical (size and shape) characteristics of the target and its surroundings.

In other words, the characteristics of the target are encoded in the scattered field. Herein lays the interest of the classical light scattering. One can distinguish two main approaches to this problem:

- One adapts the properties of the object in order to obtain scattered radiation with convenient properties.
- Or, one studies the characteristics of the scattered radiation to infer properties of the object that is illuminated.

The second item is known as *The Inverse Problem* [86]. During the last years, research in this field helped the development of new techniques enabling the analysis of different materials, organic and inorganic, in a non-invasive way.

For our study we have considered the simplest geometry: a sphere. As we said before, the most usual theoretical tool to handle electromagnetic scattering by a sphere is Mie theory.

2.3. Mie Theory for Light Scattering by a Sphere

Mie theory presents the solution for the electromagnetic scattering by a sphere of radius *R* embedded in a homogeneous and isotropic medium illuminated by a plane wave.

2.3.1. Solutions to the Wave Equation

A time harmonic electromagnetic field $[\vec{E}(\vec{r},t), \vec{H}(\vec{r},t)]$ in a linear, isotropic and homogeneous medium, satisfies the well-known wave equation

$$\nabla^2\vec{E} + k^2\vec{E} = 0 \qquad \nabla^2\vec{H} + k^2\vec{H} = 0, \tag{2.1}$$

where $k^2 = \omega^2\epsilon\mu$, ω is the frequency of the incident field, ϵ and μ are the electric permittivity and the magnetic permeability, respectively.

Since the charge density is zero, electric and magnetic fields, $\vec{E}$ and $\vec{H}$, are divergence-free

$$\nabla \cdot \vec{E} = 0, \qquad \nabla \cdot \vec{H} = 0, \tag{2.2}$$

Furthermore, considering the time harmonicity of the fields, Faraday's and Ampère's laws become

$$\nabla \times \vec{E} = i\omega\mu\vec{H}, \qquad \nabla \times \vec{H} = -i\omega\epsilon\vec{E}. \tag{2.3}$$

The solution of the wave equation (2.1), considering the previous conditions, is not straightforward. Thereto, an intermediate vector function, $\vec{M}$ is introduced

$$\vec{M} = \nabla \times (\vec{c}\psi), \tag{2.4}$$

$\vec{c}$ being a constant vector and ψ a scalar function.

This definition warrants that $\vec{M}$ is divergence-free since the divergence of the curl of any vector is zero. Hence

$$\nabla \cdot \vec{M} = 0. \tag{2.5}$$

If the operator $\nabla^2 + k^2$ is applied to (2.4), we obtain

$$\nabla^2 \vec{M} + k^2 \vec{M} = \nabla \times [\vec{c}(\nabla^2 \psi + k^2 \psi)]. \tag{2.6}$$

Comparing equations (2.6)) and (2.1), we see that $\vec{M}$ verifies the wave function if ψ is a solution to the scalar equation

$$\nabla^2 \psi + k^2 \psi = 0. \tag{2.7}$$

When this condition and the previous ones are satisfied, the intermediate function, $\vec{M}$, is equivalent with the electric or the magnetic field. To represent the other field, we can generate another divergence-free vector function that verifies the vector wave equation

$$\vec{N} = \frac{\nabla \times \vec{M}}{k}, \tag{2.8}$$

or equivalently

$$\nabla \times \vec{N} = k\vec{M}. \tag{2.9}$$

In summary, the so-called *Vector Spherical Harmonics (VSHs)*, $\vec{M}$ and $\vec{N}$, have all the requirements of an electromagnetic field in vacuum:

- both satisfy the wave equation (2.1)

- both are divergence-free

- the curl of $\vec{M}$ is proportional to $\vec{N}$

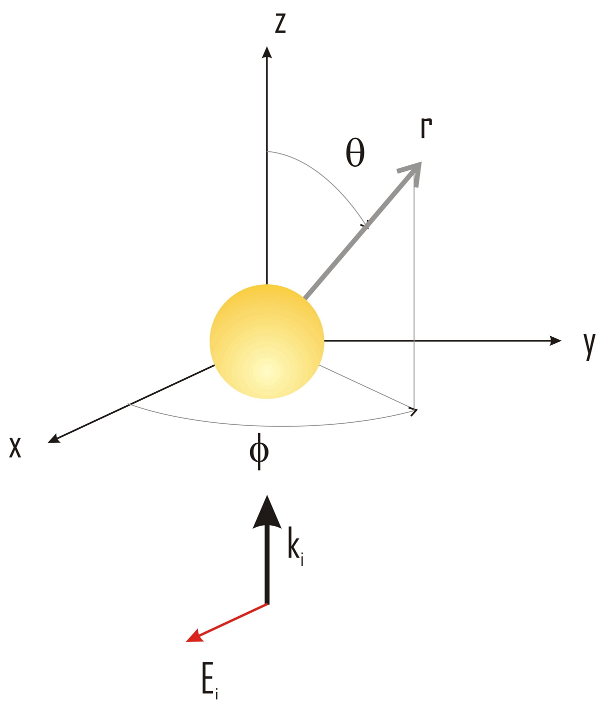

Figure 2.1: Scheme of the geometry of the scattering problem. The spherical coordinates are included

- the curl of $\vec{N}$ is proportional to $\vec{M}$

But this is true only when ψ is solution of the equation (2.7). Thus, the problem of solving the vector wave equation, equation (2.1), is reduced to solving the scalar wave equation where ψ is called the *Generating Function* and $\vec{c}$ the *guiding* or *pilot vector*.

In order to solve the scalar equation, equation (2.7), the use of spherical coordinates (r, θ, ϕ) is very convenient since the geometry of our problem (we are considering an isolated spherical particle) presents spherical symmetry (See Figure 2.1). The choice of the *guiding vector* is arbitrary. A convenient and easy alternative is to choose $\vec{c} = \vec{r}$, where $\vec{r}$ is the vector position.

In spherical coordinates, the scalar wave equation can be written as:

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial \psi}{\partial r}) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}(\sin\theta\frac{\partial \psi}{\partial \theta}) + \frac{1}{r^2 \sin\theta}\frac{\partial^2 \psi}{\partial \phi^2} + k^2\psi = 0, \tag{2.10}$$

By considering a particular form of the scalar function ψ:

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\psi). \tag{2.11}$$

And by introducing the previous function, equation (2.11), in the scalar wave equation given by equation (2.10), three separated equations, one for each coordinate, are obtained. The solution of these equations, must satisfy the conditions of linear independence and must be *single-valued*. Hence the complete solution of the scalar wave equation (2.7) is given by

$$\psi_{emn}(r,\theta,\phi) = \cos m\phi P_n^m(\cos\theta) z_n(kr), \tag{2.12}$$

$$\psi_{omn}(r,\theta,\phi) = \sin m\phi P_n^m(\cos\theta) z_n(kr), \tag{2.13}$$

where *e* and *o* mean *even* and *odd* respectively, P_n^m are the *associated Legendre functions* [4] of first kind of degree *n* and order *m* and z_n represents any of the four spherical *Bessel* functions: j_n, y_n, $h_n^{(1)}$ or $h_n^{(2)}$. Every solution of the scalar equation, (2.7), may be expanded as an infinite series of the functions (2.12) and (2.13).

Thus, *VSH's* can be expressed as

$$\vec{M}_{emn} = \nabla \times (\vec{r}\psi_{emn}) \quad \vec{M}_{omn} = \nabla \times (\vec{r}\psi_{omn}), \tag{2.14}$$

$$\vec{N}_{emn} = \frac{\nabla \times (\vec{r}\psi_{emn})}{k} \quad \vec{N}_{omn} = \frac{\nabla \times (\vec{r}\psi_{omn})}{k}. \tag{2.15}$$

The component forms of the *VSHs* can be consulted in [14]. The main conclusion of this theory is that any solution of the wave equation (equation 2.1) can be written as an infinite series of the vector harmonics given by equations (2.14) and (2.15).

2.3.2. Incident and Scattered Fields

The incident field is considered to be a plane wave linearly polarized parallel to the *x* axis and propagating in the *z* direction, (Figure 2.1). It can be written in spherical coordinates as:

$$\vec{E}_i = E_0 e^{ikr\cos\theta}\hat{e}_x, \tag{2.16}$$

where E_0 is the amplitude of the electric field, *k* is the wavenumber and $\widehat{e_x}$ is the unit vector in the polarization direction:

$$\widehat{e_x} = \sin\theta\cos\phi\widehat{e_r} + \cos\theta\cos\phi\widehat{e_\theta} - \sin\theta\widehat{e_\phi}. \tag{2.17}$$

The incident magnetic field can be obtained, directly, from the curl of the electric field (equation 2.16) using equation (2.3).

Given the incident field, it can be then expanded as an infinite series of the *Vector Spherical Harmonics (VHSs)* as follows.

$$\vec{E_i} = \sum_{m=0}^{\infty}\sum_{n=m}^{\infty}(B_{emn}\vec{M}_{emn} + B_{omn}\vec{M}_{omn} + A_{emn}vecN_{emn} + A_{omn}\vec{N}_{omn}) \tag{2.18}$$

B_{emn}, B_{omn}, A_{emn} and A_{omn} being the expansion coefficients. Using the orthogonality of the vector harmonics and the finiteness of the incident field at the origin, the expansion can be reduced to

$$\vec{E_i} = \sum_{n=1}^{\infty}(B_{o1n}\vec{M}_{o1n}^{(1)} + A_{e1n}\vec{N}_{e1n}^{(1)}), \tag{2.19}$$

where the superscript (1) means that the spherical Bessel function j_n*(kr)* is used for the radial part of the generating functions (ϕ_{olm} and ψ_{elm}), warranting that the incident field is finite at the origin.

After some manipulations, we obtain the final form of the expansion coefficients

$$B_{o1n} = i^n E_0 \frac{2n+1}{n(n+1)}, \tag{2.20}$$

$$A_{e1n} = -i^n E_0 i^n \frac{2n+1}{n(n+1)}. \tag{2.21}$$

Substituting these expression in equation (2.19), the expansion of the incident electric field becomes

$$\vec{E_i} = E_0 \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)}(\vec{M}_{o1n}^{(1)} - i\vec{N}_{e1n}^{(1)}), \tag{2.22}$$

and the corresponding incident magnetic field

$$\vec{H}_i = \frac{-k}{\omega\mu} E_0 \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (\vec{M}^{(1)}_{e1n} + i\vec{N}^{(1)}_{o1n}). \tag{2.23}$$

In what follows, to simplify the notation, we will use $E_n = E_0 i^n \frac{2n+1}{n(n+1)}$.

The scattered field ($\vec{E}_s$, $\vec{H}_s$) and the field inside the particle ($\vec{E}_l$, $\vec{H}_l$) can be obtained from the incident one by applying the boundary conditions between the sphere and the surrounding medium [18]

$$(\vec{E}_i + \vec{E}_s - \vec{E}_l) \times \widehat{e}_r = (\vec{H}_i + \vec{H}_s - \vec{H}_l) \times \widehat{e}_r = 0. \tag{2.24}$$

The scattered fields are then given by

$$\vec{E}_s = \sum_{n=1}^{\infty} E_n (i a_n \vec{N}^{(3)}_{e1n} - b_n \vec{M}^{(3)}_{o1n}), \tag{2.25}$$

$$\vec{H}_s = \sum_{n=1}^{\infty} E_n (i b_n \vec{N}^{(3)}_{o1n} + a_n \vec{M}^{(3)}_{e1n}), \tag{2.26}$$

where the superscript (3) refers to the radial dependence of the *generating* function, ψ, which is given by the *spherical Hankel* function $h_n^{(1)}$. The coefficients, a_n and b_n, are the so-called Mie coefficients for the scattered field. Again, by applying the boundary conditions (equation 2.24) at the surface of the sphere, we obtain four equations from which the analytical expressions for the Mie coefficients are deduced:

$$a_n = \frac{\mu m^2 j_n(mx)[x j_n(x)]' - \mu_l j_n(x)[mx j_n(mx)]'}{\mu m^2 j_n(mx)[x h_n^{(1)}(x)]' - \mu_l h_n^{(1)}(x)[mx j_n(mx)]'}, \tag{2.27}$$

$$b_n = \frac{\mu_l j_n(mx)[x j_n(x)]' - \mu j_n(x)[mx j_n(mx)]'}{\mu_l j_n(mx)[x h_n^{(1)}(x)]' - \mu h_n^{(1)}(x)[mx j_n(mx)]'}, \tag{2.28}$$

where μ_l and μ are the magnetic permeabilities of the sphere and the surrounding medium, respectively. Furthermore, *x* is the size parameter and *m* the relative refractive index between the sphere and the medium in which it is embedded, and are defined as

$$x = kR = \frac{2\pi R n}{\lambda} \qquad m = \frac{n_l}{n} \tag{2.29}$$

respectively. In equation (2.29), R is the radius of the sphere, λ the incident wavelength and n_l and n the refractive index of the sphere and the surrounding medium, respectively.

The previous form of the Mie coefficients for the scattered field, equations (2.27) and (2.28), can be simplified using the *Ricatti-Bessel* functions [14]

$$\psi_n(\rho) = \rho j_n(\rho), \qquad \xi_n(\rho) = \rho h_n^{(1)}(\rho). \tag{2.30}$$

The most common case is obtained when the magnetic permeabilities of the particle and the surrounding medium are equal to one. Under this condition, the Mie coefficients can be expressed as

$$a_n = \frac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n'(x) - \xi_n(x)\psi_n'(mx)}, \tag{2.31}$$

$$b_n = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n'(x) - m\xi_n(x)\psi_n'(mx)}. \tag{2.32}$$

Our interest goes mainly to the general case, when the particle present electric and magnetic properties. In other words the electric permittivity and the magnetic permeability can present values different from 1. For this general situation the expressions for the Mie coefficients are [69, 39]

$$a_n = \frac{\widetilde{m}\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{\widetilde{m}\psi_n(mx)\xi_n'(x) - \xi_n(x)\psi_n'(mx)} \tag{2.33}$$

$$b_n = \frac{\psi_n(mx)\psi_n'(x) - \widetilde{m}\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n'(x) - \widetilde{m}\xi_n(x)\psi_n'(mx)} \tag{2.34}$$

where $\widetilde{m} = \frac{m}{\mu_l}$ considering $\mu = 1$.

2.3.3. Scattering, Absorption and Extinction Cross Sections

Important physical quantities can be obtained from the previous scattered fields. One of these is the cross section, which can be defined as *the net rate at which electromagnetic energy (W) crosses the surface of a imaginary sphere of radius $r \geq R$ centered on the particle divided by the incident irradiance (I_i)* [14].

To quantify the rate of the electromagnetic energy that is absorbed (W_{abs}) or scattered (W_{sca}) by the diffuser, the absorption (C_{abs}) or scattering cross sections (C_{sca}) can be defined.

Where

$$C_{abs} = \frac{W_{abs}}{I_i}, \qquad C_{sca} = \frac{W_{sca}}{I_i}. \tag{2.35}$$

The sum of these is the *extinction* cross section

$$C_{ext} = C_{sca} + C_{abs}, \tag{2.36}$$

which gives an idea of the amount of energy removed from the incident field due to scattering and/or absorption generated by the particle.

These parameters can be expressed as a function of the Mie coefficients as follows [14]

$$C_{sca} = \frac{W_{sca}}{I_i} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2), \tag{2.37}$$

$$C_{ext} = \frac{W_{ext}}{I_i} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\boldsymbol{Re}(a_n + b_n), \tag{2.38}$$

$$C_{abs} = C_{ext} - C_{sca}. \tag{2.39}$$

By dividing these cross sections by the geometrical cross area of the particle projected onto a plane perpendicular to the incident beam, *G*, we obtain the scattering, extinction and absorption efficiencies. For a sphere, $G = \pi R^2$, and the expressions for the efficiencies become

$$Q_{sca} = \frac{C_{sca}}{G} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2), \tag{2.40}$$

$$Q_{ext} = \frac{c_{ext}}{G} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\boldsymbol{Re}(a_n + b_n), \tag{2.41}$$

$$Q_{abs} = Q_{ext} - Q_{sca}. \tag{2.42}$$

2.3.4. Scattered Intensity

The light intensity scattered by the particle, can also be expressed as a function of the Mie coefficients described above.

The expansion of the scattered field (equations (2.25) and (2.26)) can be truncated. If a high enough number of terms are taken into account, the error can be made arbitrary small. Using this truncation, the transverse components of the scattered electric field can be written as

$$\vec{E}_{s\theta} \sim E_0 \frac{e^{ikr}}{-ikr} \cos\phi S_2(\cos\theta), \tag{2.43}$$

$$\vec{E}_{s\phi} \sim -E_0 \frac{e^{ikr}}{-ikr} \sin\phi S_1(\cos\theta). \tag{2.44}$$

The terms S_1 and S_2 relate the incident and the scattered field amplitudes in the following way

$$\begin{pmatrix} \vec{E}_{||s} \\ \vec{E}_{\perp s} \end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{pmatrix} S_2 & 0 \\ 0 & S_1 \end{pmatrix} \begin{pmatrix} \vec{E}_{||i} \\ \vec{E}_{\perp i} \end{pmatrix} \tag{2.45}$$

and are expressed as [14]

$$S_1 = \sum_n \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n), \tag{2.46}$$

$$S_2 = \sum_n \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n). \tag{2.47}$$

A scheme that includes the polarizations of the scattered electric field is depicted in Figure 2.2. π_n and τ_n are called "the angle-dependent functions" because they introduce this dependence in the Mie coefficients through the scattering angle, θ, and are defined as

$$\pi_n = \frac{P_n^1}{\sin\theta}, \qquad \tau_n = \frac{dP_n^1}{d\theta}. \tag{2.48}$$

Remember that P_n^1 is the *associated Legendre function* of first kind of degree *n* and first order (equations (2.12) and (2.13)).

To perform numerical computations in an efficient way, it is useful to apply the known recurrence relations of which we give the expressions for clarity. Considering that $\pi_0 = 0$

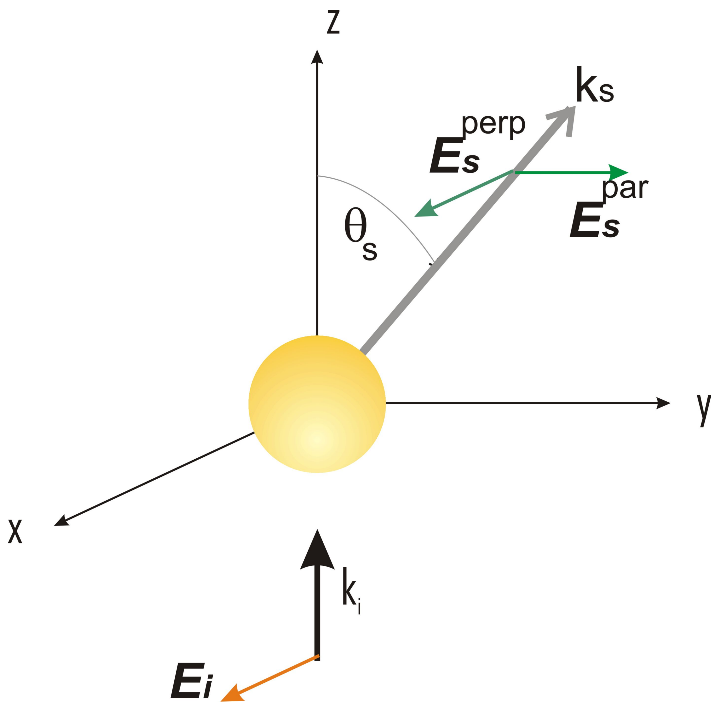

Figure 2.2: Scheme of the polarized components of the scattered field by a sphere illuminated by a linearly polarized plane wave.

and $\pi_1 = 1$ the higher order functions can be obtained as follows

$$\pi_n = \frac{2n+1}{n-1}\cos\theta\pi_{n-1} - \frac{n}{n-1}\pi_{n-2}, \tag{2.49}$$

$$\tau_n = n\cos\theta\pi_n - (n+1)\pi_{n-1}, \tag{2.50}$$

and

$$\pi_n(-\cos\theta) = (-1)^{n-1}\pi_n(\cos\theta), \quad \tau_n(-\cos\theta) = (-1)^n\tau_n(\cos\theta). \tag{2.51}$$

The polarized components of the scattered irradiance (normalized to the incident intensity) are [14]

$$i_{||} = |S_2|^2 = |\sum_n \frac{2n+1}{n(n+1)}(a_n\tau_n + b_n\pi_n)|^2 \tag{2.52}$$

if the incident light is polarized *parallel* to the scattering plane

$$i_{\perp} = |S_1|^2 = |\sum_n \frac{2n+1}{n(n+1)}(a_n \pi_n + b_n \tau_n)|^2 \tag{2.53}$$

if the incident light is polarized *perpendicular* to the scattering plane

2.4. Scattering by Small Particles compared with the Incident Wavelength: Rayleigh Approximation

During the last years, researchers have focused their attention on very small objects and more precisely on systems at the nanometer scale. Mie theory, as described above, is valid for all particle sizes and incident wavelengths. However, for very small particles compared to wavelength, some approximations can be applied, which simplify the expressions given in the previous section. Since in this work we have analyzed such "small" systems, we will discuss the most common approximations.

2.4.1. Scattering by Dipole-Like Particles

Light scattering by a very small particle compared with the incident wavelength (λ) can be calculated using an approximation of Mie theory known as *the Rayleigh approximation*. Here, the particle scatters as an electric and/or magnetic dipole, depending on its optical properties.

Two important conditions must be fulfilled by the scatterer in order to be valid the Rayleigh approximation:

- $x \ll 1$
- $|m|x \ll 1$

where m is the refractive index of the particle relative to the surrounding medium and x the size parameter (equation 2.29).

Under the previous conditions, the expressions of the scattered electric and magnetic field, (2.25) and (2.26), are reduced to the first term of the expansion, and higher order terms can be neglected.

$$\vec{E}_s = E_1(ia_1 \vec{N}_{e11}^{(3)} - b_1 \vec{M}_{o11}^{(3)}), \tag{2.54}$$

$$\vec{H}_s = E_1(ib_1\vec{N}^{(3)}_{o11} + a_1\vec{M}^{(3)}_{e11}). \tag{2.55}$$

where $E_1 = 3i/2E_0$ (see equations 2.22 and 2.23). Only the first two Mie coefficients, a_1 and b_1 have been considered. Furthermore, their expressions can be simplified, such that only the smallest power of the size parameter (x^n with $n < 5$) is kept.

$$a_1 = -i\frac{2x^3}{3}\frac{\epsilon - 1}{\epsilon + 2} + \bigcirc(x^5), \tag{2.56}$$

$$b_1 = -i\frac{2x^3}{3}\frac{\mu - 1}{\mu + 2} + \bigcirc(x^5), \tag{2.57}$$

$$a_n \approx b_n \approx 0; n \geq 2 \tag{2.58}$$

We see, from those expressions, that the scattered radiation is similar to the one emitted by either an electric or a magnetic dipole. The values of the electric permittivity and/or the magnetic permeability establish the electric or magnetic behavior of the scattered radiation.

The electric behavior of the scattered radiation is commonly associated to a_n coefficients, while the magnetic one is related with b_n coefficients. For instance in relation (2.56) and (2.57), a_1 includes only the electric permittivity, ϵ, and b_1 includes only the magnetic permeability, μ. For this reason, we may refer to the a_n and b_n terms as electric and magnetic terms, respectively.

By using the previous relations, the expressions of the efficiencies and scattered intensity [(2.40), (2.41), (2.42), (2.52) and (2.53)] can be simplified. Extinction, scattering and absorption efficiencies are now expressed as

$$Q_{ext} = \frac{6}{x^2}Re(a_1 + b_1), \qquad Q_{sca} = \frac{6}{x^2}(|a_1|^2 + |b_1|^2) \qquad Q_{abs} = Q_{ext} - Q_{sca}. \tag{2.59}$$

From equations (2.49) and (2.50), we obtain the first order terms of the angular functions

$$\pi_1 = 1, \qquad \tau_1 = \cos(\theta), \tag{2.60}$$

Now the components of the scattered intensity can be written as

$$i_{\|} = |\frac{3}{2}(a_1 + b_1 \cos\theta)|^2 \qquad i_{\perp} = |\frac{3}{2}(a_1 \cos\theta + b_1)|^2 \tag{2.61}$$

2.5. Second Order Approximation of Mie Theory

In 1990, G. Videen and W. Bickel [139] showed that very small particles, not satisfying the second condition of the Rayleigh approximation ($|m|x \ll 1$), present interesting features in the way they scatter light. These authors considered a dielectric and non magnetic ($\epsilon > 0$ and $\mu = 1$) spherical particle whose size and optical properties are such that $x \ll 1$ but $mx \not< 1$. For this situation, the expressions derived in the last section are no longer valid.

To analyze this kind of systems, the authors developed a second order approximation of Mie theory. This approximation consists in retaining the first four Mie coefficients, a_1, b_1, a_2 and b_2, in the series expansion of the scattered field (equations (2.25) and (2.26)). Starting with equations (2.31) and (2.32), simplified expressions were derived.

The Ricatti-Bessel functions with $n = 1, 2$ appearing in the Mie scattering coefficients are expressed as

$$\begin{aligned} \psi_1(\rho) &= \frac{\sin(\rho)}{\rho}, \\ \xi_1(\rho) &= e^{ix}(-i\rho^{-1} - 1, \\ \psi_2(\rho) &= (\frac{3}{\rho^2} - 1)\sin(\rho) - \frac{3}{\rho}\cos(\rho), \\ \xi_2(\rho) &= e^{ix}(-3i\rho^{-2} - 3\rho^{-1} - i). \end{aligned} \tag{2.62}$$

When $x \ll 1$, $\sin(x)$, $\cos(x)$, and $\exp(x)$ can be replaced by the first term of their power expansion. However, for spheres which don't verify $|m|x \ll 1$, the functions $\sin(mx)$, $\cos(mx)$, and $\exp(mx)$ cannot be simplified as just described. After these considerations, the authors present in [139] new approximate expressions for the four first Mie coefficients:

$$\begin{aligned} a_1 &\sim \frac{\cos(mx)[x(\frac{1+2m^2}{3m}) - x^3(\frac{1+4m^2}{30m})] + \sin(mx)[-(\frac{1+2m^2}{3m^2}) + x^2(\frac{1+14m^2}{30m^2})]}{\cos(mx)[x^{-2}(\frac{-i+im^2}{m}) - (\frac{i+im^2}{2m})] + \sin(mx)[x^{-3}(\frac{i-im^2}{m^2}) + x^{-1}(\frac{i-im^2}{2m^2})]} \\ b_1 &\sim \frac{\cos(mx)(x - x^3/6) + \sin(mx)[-1/m + x^2(\frac{1+2m^2}{6m})]}{\cos(mx)(-i + x) + \sin(mx)[x^{-1}(\frac{i-im^2}{m}) - 1/m - x(\frac{i+im^2}{2m})]} \end{aligned} \tag{2.63}$$

and similarly for the second-order coefficients:

$$a_2 \sim \frac{A_{num}}{A_{den}} \tag{2.64}$$

$$\begin{aligned}A_{num} = \cos(mx)[-x(\frac{2+3m^2}{5m^2}) + x^3(\frac{6+29m^2}{210m^2})]+ \\ + \sin(mx)[(\frac{2+3m^2}{5m^3}) - x^2(\frac{2+19m^2+14m^4}{70m^3})]\end{aligned}$$

$$\begin{aligned}A_{den} = \cos(mx)[x^{-4}(\frac{18i-18im^2}{m^2}) + x^2(\frac{3i-3im^2}{m^2})]+ \\ + \sin(mx)[x^{-5}(\frac{18i-18im^2}{-m^3}) + x^{-3}(\frac{-3i+9im^2-6im^4}{m^3})]\end{aligned}$$

$$b_2 \sim \frac{\cos(mx)[-/m - x^3(\frac{3+2m^2}{30m})] + \sin(mx)[-1/m^2 - x^2(\frac{1+4m^2}{10m^2})]}{\cos(mx)[x^{-2}(\frac{3i-3im^2}{m}) + (\frac{3i-im^2}{2m})] + \sin(mx)[x^{-3}(\frac{3im^2-3i}{m^2}) + x^{-1}(\frac{3im^2-3i}{2m^2})]} \tag{2.65}$$

However, the authors limited their study to dielectric ($\epsilon > 0$) and non-magnetic ($\mu = 1$) spherical particles. Following their idea, we have generalized this approximation to very small particles with arbitrary values of the optical constants.

Considering the general expressions for the Mie scattering coefficients, equations (2.33) and (2.34), and those of the first and second order Ricatti-Bessel functions, equation (2.62), we have rewritten the first four Mie coefficients, a_1, b_1, a_2 and b_2. To do this, we have considered the Taylor expansion of $\sin(x)$, $\cos(x)$, and $\exp(x)$ up to the second order instead of the first one. After substituting these approximations in equations (2.33) and (2.34), we have checked the contribution of each term in order to eliminate those whose value can be neglected. The resulting equations are as follows

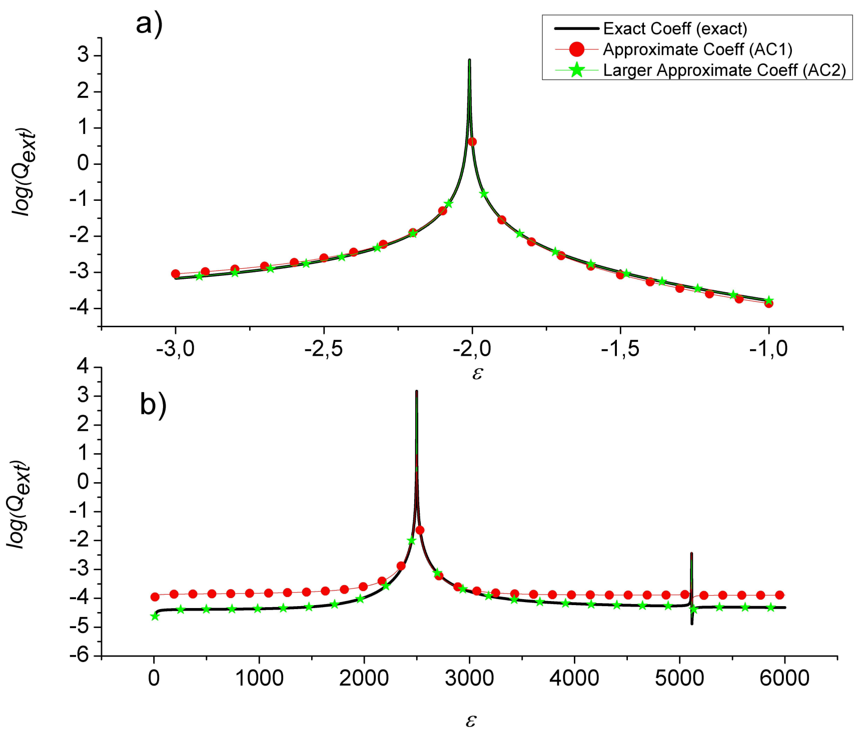

Figure 2.3: Plot of Q_{ext} for three different expressions of the Mie coefficients: Exact (solid line), approximate using (2.66) and (2.67) $(AC1)$ and approximate using more terms in the expansion of the functions sine and cosine $(AC2)$. In (a) we consider a metallic particle $(\epsilon < 0)$ and in (b) a dielectric particle $(\epsilon > 0)$ with a radius $R = 0.01\lambda$

Due to the spherical symmetry of the particles, a_n and b_n are related in the following way

$$a_n(\widetilde{m}, m, x) = b_n(\frac{1}{\widetilde{m}}, m, x) \tag{2.68}$$

Since both coefficients a_n and b_n are related by the previous expression, we only present the results for a_n.

In order to show the reliability of our expressions, we show in Figure 2.3, in semi-logarithmic scale, the extinction efficiency as a function of the electric permittivity for a small particle of radius $R = 0.01\lambda$ with nonmagnetic properties $(\mu = 1)$ and a resonant behavior. As can be seen, in the metallic range (Figure 2.3a) our expressions for the scattering coefficients reproduce very accurately the resonance (position and shape). In the dielectric range (Figure 2.3b), both the position and shape of resonances are well reproduced. Outside the resonances, the values of Q_{ext} calculated using the reduced expression $(AC1)$, differ

$$a_1 \sim \frac{\widetilde{m}mx^3(mx\cos(mx) - \sin(mx))}{\cos(mx)[-\widetilde{m}m^2x^2 - i\widetilde{m}m^2x^2 + imx^3 + imx] + \sin mx[\widetilde{m}mx^3 + i\widetilde{m}m - ix^2 + im^2x^4 - i + im^2x^2]} \tag{2.66}$$

$$a_2 = \frac{A_{num}}{A_{den}} \tag{2.67}$$

$$\begin{aligned} A_{num} = {} & \cos(mx)[6\widetilde{m}m^2x^2 - 6mx^2 + m^3x^4]+ \\ & + \sin(mx)[6x - 3m^2x^2 - 6\widetilde{m}mx + 2\widetilde{m}m^3x^3] \end{aligned}$$

$$\begin{aligned} A_{dem} = {} & \cos(mx)[3i\widetilde{m}m^3x^2 + 2\widetilde{m}m^3x^3 - i\widetilde{m}m^3x^4 + 6i\widetilde{m}m^3 - 9i\widetilde{m}m - 6\widetilde{m}mx]+ \\ & + 3i\widetilde{m}mx^2 + 18\frac{i\widetilde{m}m}{x^2} - (-\frac{3i}{x^2} - 2i - x)(6 - 3m^2x^2) + \sin(mx)[9i\widetilde{m}m^2x+ \\ & + 6\widetilde{m}m^2x^2 - 3i\widetilde{m}m^2x^3 + 18\frac{i\widetilde{m}m^2}{x} - (-\frac{3i}{x^2} - 2i - x)(-6mx + m^3x^3)] \end{aligned}$$

slightly from the exact values. To reproduce more accurately the exact extinction, it is necessary to include additional terms in the Taylor expansion of sine, cosine and exponential functions. In Figure 2.3, we have included the extinction efficiency using the first four terms of the power expansion of these functions to approximate Mie coefficients ($AC2$). As can be seen, these other approximate coefficients reproduce more accurately the exact values in and outside the resonances in both ranges (metallic and dielectric). However, these expressions are more complex than our expressions, (2.66) and (2.67). As our purpose is to obtain the simplest expressions allowing a qualitative analysis of the scattering features, such as the excitation of resonances, we prefer to use the formulas proposed by us and given by equations (2.66) and (2.67).