



**UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO  
POSGRADO EN CIENCIAS FÍSICAS**

**OPTICAL RESPONSE OF PARTIALLY EMBEDDED  
NANOSPHERES**

**TESIS  
QUE PARA OPTAR POR EL GRADO DE:  
MAESTRO EN CIENCIAS (FÍSICA)**

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**CIUDAD DE MÉXICO, MÉXICO, 2022**







## Abstract/Resumen

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# Background and Motivation

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It is recommended to fill in this part of the document with the following information:

Metasurfaces are bidimensional arrays of unit cells with geometrical dimensions smaller than the wavelength of the incident light. Biosensing-aimed metasurfaces are supported onto a substrate and immersed in an aqueous medium, thus its performance is limited by its washability. One alternative to decrease a metasurface's washability is to partially embed it within the substrate while allowing the metasurface to still interact with the aqueous medium. In this work, we study the optical response of a single partially embedded metallic nanosphere and extend its behavior analytically into a disordered metasurface by employing an effective medium approach.

The incrustation of the metasurface is studied by calculating the spectral behavior of a single partially embedded nanosphere with the Finite Element Method (FEM) and proposing an effective polarizability in the elements of the metasurface.

- Your field: Context about the field your are working  
**Plasmonics -> Metamaterials -> Biosensing**
- Motivation: Backgroung about your thesis work and why did you choose this project and why is it important.  
**Fabrication -> Partially embedded NPs -> No analytical (approximated) method physically introduces the incrustation degree. There are numerical solutions and Effective Medium Theories approaching the problem but the later only as a fitting method.**
- Objectives: What question are you answering with your work.  
**Can optical non invasive tests (IR-Vis) retrieve the average incrustation degree for monolayers of small spherical particles?**
- Methology: What are your secondary goals so you achieve your objective. Also, how are you answering yout question: which method or model.  
**Bruggeman homogenization theories on bidimensional systems?  
Is the dipolar approximation is enough or do we need more multipolar terms?  
Do we need the depolarization factors?**
- Structure: How is this thesis divides and what is the content of each chapter.



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# Chapter 1

# Scattering Theory of a Single Spherical Particle

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The problem addressed in this thesis corresponds to the numerical analysis of the Localized Surface Plasmon Resonances (LSPR) excited on plasmonic spherical nanoparticles (NPs) when these are under realistic experimental conditions, such as those present on plasmonic biosensors, where the NPs are partially embedded into a substrate [1]. The performed analysis consists on the numerical calculation of the absorption, scattering and extinction cross sections of a partially embedded metal NP, employing the Finite Element Method (FEM). To verify the validity of the obtained numerical results, the problem of the absorption and scattering of light by a single free-standing spherical particle is considered. In this chapter, we revisit the general solution of the light absorption and scattering by both an arbitrary particle and a spherical particle, given by the Mie Theory<sup>1</sup> [4].

## 1.1 The Optical Theorem: Amplitude Matrix and Cross Sections

Let  $\mathbf{E}^i = \mathbf{E}_0^i \exp(i\mathbf{k}^i \cdot \mathbf{r})$  be the electric field of an incident monochromatic plane wave with constant amplitude  $\mathbf{E}_0^i$  traveling through a non absorbing medium with refractive index  $n_{\text{mat}}$ , denominated as the matrix, in the direction  $\mathbf{k}^i = k\hat{\mathbf{k}}^i$ , with  $k = (\omega/c)n_{\text{mat}}$  the wave number of the plane wave in the matrix, and let  $\mathbf{E}^{\text{sca}}$  be the scattered electric field due to a particle with arbitrary shape embedded into the matrix. In general, the scattered electric field propagates in all directions but for an observation point  $\mathbf{r} = r\hat{\mathbf{e}}_r$ , the traveling direction is defined by the vector  $\mathbf{k}^{\text{sca}} = k\hat{\mathbf{k}}^{\text{sca}} = k\hat{\mathbf{e}}_r$ . Due to the linearity of the Maxwell's equations, the incident and scattered electric fields in the far field regime are related by the following linear relation [5]:

$$\mathbf{E}^{\text{sca}} = \frac{\exp(i\mathbf{k}^{\text{sca}} \cdot \mathbf{r})}{r} \mathbb{F}(\hat{\mathbf{k}}^{\text{sca}}, \hat{\mathbf{k}}^i) \mathbf{E}^i, \quad (1.1)$$

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<sup>1</sup>The term *Mie Theory* refers rather to a solution set to Maxwell's equations for the scattering of an electromagnetic plane wave due to a spherical particle, developed by Gustav Mie and published on 1907 [2]. Ludving Lorenz published beforehand an equivalent solution to the same scattering problem nevertheless, Mie's solution consists in an iterative method suited for easier computations, which boosted its spread [3].

where  $\mathbb{F}(\hat{\mathbf{k}}^{\text{sca}}, \hat{\mathbf{k}}^{\text{i}})$  is the scattering amplitude matrix from direction  $\hat{\mathbf{k}}^{\text{i}}$  into  $\hat{\mathbf{k}}^{\text{sca}}$ . Since only the far field is considered, both the incident and the scattered electric fields can be decomposed into two linearly independent components perpendicular to  $\mathbf{k}^{\text{i}}$  and  $\mathbf{k}^{\text{sca}}$ , respectively, each forming a right-handed orthonormal system. If the particle acting as a scatterer has a symmetric shape, it is convenient to define an orthonormal system relative to the scattering plane, which is the plane containing  $\mathbf{k}^{\text{i}}$  and  $\mathbf{k}^{\text{sca}}$ , since the elements of  $\mathbb{F}(\hat{\mathbf{k}}^{\text{sca}}, \hat{\mathbf{k}}^{\text{i}})$  get simplified when represented in these bases [5]. In Fig. 1.1 a plane wave traveling in the  $z$  direction illuminates an arbitrary particle centered at the origin of the coordinated system and the scattering plane is depicted in green. By defining the directions perpendicular ( $\perp$ ) and parallel ( $\parallel$ ) to the scattering plane, the incident and scattered electric fields can be written as

$$\mathbf{E}^{\text{i}} = (E_{\parallel}^{\text{i}} \hat{\mathbf{e}}_{\parallel}^{\text{i}} + E_{\perp}^{\text{i}} \hat{\mathbf{e}}_{\perp}^{\text{i}}) \exp(i\mathbf{k}^{\text{i}} \cdot \mathbf{r}), \quad (1.2)$$

$$\mathbf{E}^{\text{sca}} = (E_{\parallel}^{\text{sca}} \hat{\mathbf{e}}_{\parallel}^{\text{sca}} + E_{\perp}^{\text{sca}} \hat{\mathbf{e}}_{\perp}^{\text{sca}}) \frac{\exp(i\mathbf{k}^{\text{sca}} \cdot \mathbf{r})}{r}, \quad (1.3)$$

where a harmonic time dependence  $\exp(-i\omega t)$  has been omitted, and where it has been assumed that the scattered field is described by a spherical wave; the superscript ‘i’ (‘sca’) denotes the orthonormal system defined by the incident plane wave (scattered fields). Since  $\{\hat{\mathbf{e}}_{\perp}^{\text{i}}, \hat{\mathbf{e}}_{\parallel}^{\text{i}}, \hat{\mathbf{k}}^{\text{i}}\}$  and  $\{\hat{\mathbf{e}}_{\perp}^{\text{sca}}, \hat{\mathbf{e}}_{\parallel}^{\text{sca}}, \hat{\mathbf{k}}^{\text{sca}}\}$  —shown in purple in Fig. 1.1 along with the Cartesian (blue) and spherical (black) unit vector bases— are right-handed orthonormal systems, they are related as follows

$$\hat{\mathbf{e}}_{\perp}^{\text{i}} = \hat{\mathbf{e}}_{\perp}^{\text{sca}} = \hat{\mathbf{k}}^{\text{sca}} \times \hat{\mathbf{k}}^{\text{i}}, \quad \hat{\mathbf{e}}_{\parallel}^{\text{i}} = \hat{\mathbf{k}}^{\text{i}} \times \hat{\mathbf{e}}_{\perp}^{\text{i}}, \quad \text{and} \quad \hat{\mathbf{e}}_{\parallel}^{\text{sca}} = \hat{\mathbf{k}}^{\text{sca}} \times \hat{\mathbf{e}}_{\perp}^{\text{sca}}. \quad (1.4)$$

As Eqs. (1.4) suggest, the unit vector bases of the orthonormal systems relative to the scattering plane depend on the scattering direction. For example, if the incident plane wave travels along the  $z$  axis (Fig. 1.1), then  $\hat{\mathbf{k}}^{\text{i}} = \hat{\mathbf{e}}_z$  and  $\hat{\mathbf{k}}^{\text{sca}} = \hat{\mathbf{e}}_r$ . Thus the unit vector bases of the systems relative to the scattering plane are  $\hat{\mathbf{e}}_{\parallel}^{\text{i}} = \cos \varphi \hat{\mathbf{e}}_x + \sin \varphi \hat{\mathbf{e}}_y$ ,  $\hat{\mathbf{e}}_{\parallel}^{\text{sca}} = \hat{\mathbf{e}}_\theta$  and  $\hat{\mathbf{e}}_{\perp}^{\text{i}} = \hat{\mathbf{e}}_{\perp}^{\text{sca}} = -\hat{\mathbf{e}}_\varphi$ , with  $\theta$  the polar angle and  $\varphi$  the azimuthal angle.

When an incident plane wave interacts with a particle with a complex refractive index  $n_p(\omega)$ , the total electric field outside the particle is given by the sum of the incident and the scattered fields. Therefore, the time averaged Poynting vector  $\langle \mathbf{S} \rangle_t$ , denoting the power flow per unit area, of the total field is given by

$$\langle \mathbf{S} \rangle_t = \underbrace{\frac{1}{2} \text{Re} (\mathbf{E}^{\text{i}} \times \mathbf{H}^{\text{i}*})}_{\langle \mathbf{S}^{\text{i}} \rangle_t} + \underbrace{\frac{1}{2} \text{Re} (\mathbf{E}^{\text{sca}} \times \mathbf{H}^{\text{sca}*})}_{\langle \mathbf{S}^{\text{sca}} \rangle_t} + \underbrace{\frac{1}{2} \text{Re} (\mathbf{E}^{\text{i}} \times \mathbf{H}^{\text{sca}*} + \mathbf{E}^{\text{sca}} \times \mathbf{H}^{\text{i}*})}_{\langle \mathbf{S}^{\text{ext}} \rangle_t}, \quad (1.5)$$

with (\*) the complex conjugate operation and where the total Poynting vector is separated in three terms: the contribution from the incident field  $\langle \mathbf{S}^{\text{i}} \rangle_t$ , from the scattered field  $\langle \mathbf{S}^{\text{sca}} \rangle_t$  and from their cross product denoted by  $\langle \mathbf{S}^{\text{ext}} \rangle_t$ . By means of the Faraday-Lenz’s law and Eqs. (1.1)–(1.3), the contribution to the Poynting vector from the incident and the scattered fields can be rewritten as

$$\langle \mathbf{S}^{\text{i}} \rangle_t = \frac{\|\mathbf{E}_0^{\text{i}}\|^2}{2Z_{\text{mat}}} \hat{\mathbf{k}}^{\text{i}}, \quad \text{and} \quad \langle \mathbf{S}^{\text{sca}} \rangle_t = \frac{\|\mathbf{E}^{\text{sca}}\|^2}{2Z_{\text{mat}}} \hat{\mathbf{k}}^{\text{sca}} = \frac{\|\mathbb{F}(\hat{\mathbf{k}}^{\text{sca}}, \hat{\mathbf{k}}^{\text{i}}) \mathbf{E}^{\text{i}}\|^2}{2Z_{\text{mat}} r^2} \hat{\mathbf{k}}^{\text{sca}}, \quad (1.6)$$



**Fig. 1.1:** The scattering plane (green) is defined by the vector  $\hat{\mathbf{k}}^i$  (red) parallel to  $\hat{\mathbf{e}}_z$  —the direction of the incident plane wave—and the vector  $\hat{\mathbf{k}}^{sca}$ —the direction of the scattered field in a given point  $\vec{r}$ . The parallel and perpendicular components of the incident field relative to the scattering plane are  $\hat{\mathbf{e}}_{\parallel}^i = \cos \varphi \hat{\mathbf{e}}_x + \sin \varphi \hat{\mathbf{e}}_y$  and  $\hat{\mathbf{e}}_{\perp}^i = -\hat{\mathbf{e}}_{\varphi}$ , while the components of the scattering field relative to the scattering plane are  $\hat{\mathbf{e}}_{\parallel}^{sca} = \hat{\mathbf{e}}_{\theta}$ ,  $\hat{\mathbf{e}}_{\perp}^{sca} = -\hat{\mathbf{e}}_{\varphi}$ . The Cartesian unit vector basis is shown in blue, the spherical unit vector basis in black, while the basis of the orthonormal systems relative to the scattering plane are shown in purple.

with  $Z_{\text{mat}} = \sqrt{\mu_{\text{mat}}/\varepsilon_{\text{mat}}}$ , the impedance of the non-absorbing matrix, while the crossed contribution is given by

$$\langle \mathbf{S}^{\text{ext}} \rangle_t = \text{Re} \left\{ \frac{\exp[-i(\mathbf{k}^{sca} - \mathbf{k}^i) \cdot \mathbf{r}]}{2Z_{\text{mat}} r^2} \left[ \hat{\mathbf{k}}^{sca} (\mathbf{E}_0^i \cdot \mathbb{F}^* \mathbf{E}^{i*}) - \mathbb{F}^* \mathbf{E}^{i*} (\mathbf{E}_0^i \cdot \hat{\mathbf{k}}^{sca}) \right] \right. \\ \left. + \frac{\exp[i(\mathbf{k}^{sca} - \mathbf{k}^i) \cdot \mathbf{r}]}{2Z_{\text{mat}} r^2} \left[ \hat{\mathbf{k}}^i (\mathbb{F} \mathbf{E}^i \cdot \mathbf{E}_0^i) - \mathbf{E}_0^i (\mathbb{F} \mathbf{E}^i \cdot \hat{\mathbf{k}}^i) \right] \right\}, \quad (1.7)$$

where the scattering amplitude matrix is evaluated as  $\mathbb{F}(\hat{\mathbf{k}}^{sca}, \hat{\mathbf{k}}^i)$ .

The power scattered by the particle can be calculated by integrating  $\langle \mathbf{S}^{\text{sca}} \rangle_t$  in a closed surface surrounding the particle; if the scattered power is normalized by the irradiance of the incident field  $\|\langle \mathbf{S}^i \rangle_t\|$ , it is obtained a quantity with units of area, known as the scattering cross section  $C_{\text{sca}}$ , given by [4]

### Scattering Cross Section

$$C_{\text{sca}} = \frac{2Z_{\text{mat}}}{\|\mathbf{E}_0^i\|^2} \oint_S \langle \mathbf{S}^{\text{sca}} \rangle_t \cdot d\mathbf{a} = \oint_S \frac{\|\mathbb{F}(\hat{\mathbf{k}}^{sca}, \hat{\mathbf{k}}^i) \mathbf{E}^i\|^2}{\|\mathbf{E}_0^i\|^2} d\Omega, \quad (1.8)$$

where  $d\Omega$  is the differential solid angle.

Similarly, an absorption cross section  $C_{\text{abs}}$  can be defined as well. On the one side, the absorption cross section is given by the integral on a closed surface of  $\langle -\mathbf{S} \rangle_t$  [Eq. (1.5)] divided by the irradiance of the incident field, where the minus sign is chosen so that  $C_{\text{abs}} > 0$  if the particle absorbs energy [4]. On the other side, if an Ohmic material with conductivity  $\sigma(\omega) = i\omega n_p^2(\omega)$  [6] for the particle is assumed, through Joule's heating law [5], the absorption cross section can be computed as

#### Ohmic Particle - Absorption Cross Section

$$C_{\text{abs}} = \frac{1}{2} \int_V \frac{\text{Re}(\mathbf{J} \cdot \mathbf{E}^{\text{int}*})}{\|\mathbf{E}_0^i\|^2 / 2Z_{\text{mat}}} dV = \int_V \omega Z_{\text{mat}} \text{Im}(n_p^2) \frac{\|\mathbf{E}^{\text{int}}\|^2}{\|\mathbf{E}_0^i\|^2} dV, \quad (1.9)$$

where integration is performed inside the particle, and  $\mathbf{J}$  and  $\mathbf{E}^{\text{int}}$  are the volumetric electric current density and the total electric field in this region, respectively. Both the scattering and the absorption cross sections are quantities related to the optical signature of a particle [7], and their relation can be made explicit by performing the surface integral representation of  $C_{\text{abs}}$  and defining  $C_{\text{ext}}$ , that is,

$$\begin{aligned} C_{\text{abs}} &= -\frac{2Z_{\text{mat}}}{\|\mathbf{E}_0^i\|^2} \int_S \left( \langle \mathbf{S}^i \rangle_t + \langle \mathbf{S}^{\text{sca}} \rangle_t + \langle \mathbf{S}^{\text{ext}} \rangle_t \right) \cdot d\mathbf{a} \\ &= -C_{\text{sca}} - \frac{2Z_{\text{mat}}}{\|\mathbf{E}_0^i\|^2} \int_S \langle \mathbf{S}^{\text{ext}} \rangle_t \cdot \hat{\mathbf{e}}_r d\Omega \\ &= -C_{\text{sca}} + C_{\text{ext}}, \end{aligned} \quad (1.10)$$

where the contribution of  $\langle \mathbf{S}^i \rangle_t$  to the integral is zero since a non-absorbing matrix was assumed. From Eq.(1.10) it can be seen that  $C_{\text{ext}}$  takes into account both mechanisms for energy losses (scattering and absorption), thus it is called the extinction cross section. To solve the integral in Eq. (1.10) let us define  $\theta$  as the angle between  $\hat{\mathbf{k}}^{\text{sca}}$  and  $\hat{\mathbf{k}}^i$  as the polar angle and  $\varphi$  as the azimuthal angle, as shown in Fig 1.1. With this choice of coordinates, the extinction cross section can be computed as

$$\begin{aligned} C_{\text{ext}} &= -\text{Re} \left\{ \frac{\exp(-ikr)}{\|\mathbf{E}_0^i\|^2} \oint_S \exp(ikr \cos \theta) (1) (\mathbf{E}^i \cdot \mathbb{F}^* \mathbf{E}^{i*}) d\Omega \right. \\ &\quad + \frac{\exp(ikr)}{\|\mathbf{E}_0^i\|^2} \oint_S \exp(-ikr \cos \theta) \cos \theta (\mathbf{E}^{i*} \cdot \mathbb{F} \mathbf{E}^i) d\Omega \\ &\quad \left. + \frac{\exp(ikr)}{\|\mathbf{E}_0^i\|^2} \oint_S \exp(-ikr \cos \theta) \sin \theta (E_{0,x}^i \cos \varphi + E_{0,y}^i \sin \varphi) (\mathbb{F} \mathbf{E}^i \cdot \mathbf{k}^i) d\Omega \right\}, \end{aligned} \quad (1.11)$$

using that  $\hat{\mathbf{k}}^{\text{sca}} \cdot \hat{\mathbf{e}}_r = 1$ ,  $\hat{\mathbf{k}}^i \cdot \hat{\mathbf{e}}_r = \cos \theta$  and  $\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}_r = 0$ . The integrals in Eq. (1.11) can be solved by a two-fold integration by parts in the polar angle  $\theta$  and by neglecting terms proportional to  $r^{-2}$ . This process leads to a zero contribution from the integrand proportional to  $\sin \theta$  in Eq. (1.11) and, after rearranging the other terms in their real and imaginary parts, it follows that  $C_{\text{ext}}$  depends only on the forward direction  $\hat{\mathbf{k}}^{\text{sca}} = \hat{\mathbf{k}}^i$  ( $\theta = 0$ ). This result is known as the Optical

## 1.2 Mie Scattering

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Theorem whose mathematical expression is given by [5, 7, 8]:

### Optical Theorem - Extinction Cross Section

$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}} = \frac{4\pi}{k\|\mathbf{E}_0^i\|^2} \text{Im} [\mathbf{E}_0^i \cdot \mathbb{F}^*(\hat{\mathbf{k}}^i, \hat{\mathbf{k}}^i) \mathbf{E}^{i*}]. \quad (1.12)$$

The Optical Theorem is a general result applicable to general scattering phenomena, both quantum and classical [4, 8], and its derivation rely in the incident field being a plane wave [see Eq. (1.11)] and more precisely, in the lack of longitudinal components of the incident field [9, 10].

From Eqs. (1.5) and (1.12) it can be seen that the extinction of light, the combined result of scattering and absorption as energy loss mechanisms, is also a manifestation of the interference between the incident and the scattered fields and, remarkably, that the overall effect of the light extinction can be fully understood by analyzing the amplitude of the scattering field in the forward direction. It is worth noting that Eq. (1.12) is an exact relation but its usefulness is bond to the correct evaluation of the scattering amplitude matrix  $\mathbb{F}$  [5]. Thus, in the following Sections a scattering problem with spherical symmetry will be assumed, so that the exact solution to the scattering amplitude matrix can be developed; this solution is known as the *Mie Theory*.

## 1.2 Mie Scattering

In the previous Section, it was concluded that the extinction of light due to the interaction between a particle and a monochromatic plane wave can be determined through the amplitude of the scattered field in the forward direction. This is stated in the Optical Theorem, which is an exact relation, but inaccuracies may arise when either the scattering amplitude matrix or the extinction cross section are approximated<sup>2</sup>. A particular case in which the scattering amplitude matrix can be exactly calculated is when the scatterer has spherical symmetry. In order to address this special case, it will be introduced a vectorial basis with spherical symmetry, known as the Vector Spherical Harmonics (VSH). Once the VSH are defined, they will be used to write a monochromatic plane wave in terms of the VSH. By imposing the continuity of the tangential components of the electric and magnetic fields, the scattered field can be also written in terms of the VSH. As a particular example of interest, shown in the last Section, the optical properties of a gold nanoparticle with radius of 12.5 nm are calculated.

### 1.2.1 Vector Spherical Harmonics

The electric and magnetic fields, denoted as  $\mathbf{E}$  and  $\mathbf{B}$ , respectively, corresponds to a solution to the homogeneous vectorial Helmholtz equation when a harmonic time dependence and a spatial domain with no external charge nor current densities is assumed, that is,

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<sup>2</sup>See for example Section 2.4 from Ref. [5] on the Rayleigh Scattering, and Section 21.7 from Ref. [11] on Thompson scattering.

## Vectorial Helmholtz Equation

$$\nabla^2 \mathbf{E}(\mathbf{r}, \omega) + k^2 \mathbf{E}(\mathbf{r}, \omega) = \mathbf{0}, \quad \nabla^2 \mathbf{B}(\mathbf{r}, \omega) + k^2 \mathbf{B}(\mathbf{r}, \omega) = \mathbf{0}. \quad (1.13)$$

where the vectorial operator  $\nabla^2$  must be understood as  $\nabla^2 = \nabla(\nabla \cdot) - \nabla \times \nabla \times$ , and  $k$  is the wave number in the matrix, which follows the dispersion relation  $k = (\omega/c)n_{\text{mat}}$ , with  $n_{\text{mat}} = \sqrt{\mu_{\text{mat}}\varepsilon_{\text{mat}}/\mu_0\varepsilon_0}$  the refractive index of the matrix,  $\mu_{\text{mat}}$  its magnetic permeability and  $\varepsilon_{\text{mat}}$  its dielectric function. It is possible to build a basis set for the electric and magnetic fields as long as the elements of this basis are also solution to Eq. (1.13). One alternative is to employ the following set of vector functions [12]

$$\mathbf{L} = \nabla\psi, \quad (1.14a)$$

$$\mathbf{M} = \nabla \times (\mathbf{r}\psi), \quad (1.14b)$$

$$\mathbf{N} = \frac{1}{k} \nabla \times \mathbf{M}, \quad (1.14c)$$

that are solution to the homogeneous vectorial Helmholtz equation as long as the scalar function  $\psi$  is solution to the scalar Helmholtz equation<sup>3</sup>

$$\nabla^2\psi + k^2\psi = 0. \quad (1.15)$$

The triad  $\{\mathbf{L}, \mathbf{M}, \mathbf{N}\}$  is a set of vectors<sup>4</sup> that obey Helmholtz equation, *i.e.*, they can be directly identified as electric or magnetic fields. The elements of the vector basis from Eq. (1.14) are known as the Vector Spherical Harmonics and are defined as Stratton [12], or by Bohren and Huffman [4], and the scalar function  $\psi$  is known as the generating function of the VSH. From the definition of the VSH in Eqs. (1.14) it can be seen that  $\mathbf{L}$  has only a longitudinal component, while  $\mathbf{M}$  has only transversal components —specifically  $\mathbf{M}$  is tangential to any sphere of radius  $\|\mathbf{r}\|$ , and  $\mathbf{N}$  have both longitudinal and transversal components.

If spherical coordinates are chosen, and it is assumed that  $\psi(r, \theta, \varphi) = R(r)\Theta(\theta)\Phi(\varphi)$ , then Eq. (1.15) can be decoupled into three ordinary differential equations:

$$\frac{d^2\Phi}{d\varphi^2} + m^2\Phi = 0, \quad (1.16)$$

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \left[ \ell(\ell+1) - \frac{m^2}{\sin^2\theta} \right] \Theta = 0, \quad (1.17)$$

$$\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ (kr)^2 - \ell(\ell+1) \right] R = 0, \quad (1.18)$$

where  $\ell$  takes natural values and zero, and  $|m| \leq \ell$  so that  $\Phi$  and  $\Theta$  are uni-valued and finite on

<sup>3</sup>This result can be proved by considering the following: Let  $f$  be  $\mathcal{C}^3$  and  $\mathbf{F}$  a  $\mathcal{C}^2$ . Then, it is true that  $\nabla^2(\nabla f) = \nabla(\nabla^2 f)$ , and  $\nabla \times (\nabla^2 \mathbf{F}) = \nabla^2(\nabla \times \mathbf{F})$ .

<sup>4</sup>Using the Einstein sum convention with  $\epsilon_{ijk}$  the Levi-Civita symbol, Eq. (1.14b) can be written as follows:  $M_i = [\nabla \times (\mathbf{r}\psi)]_i = \epsilon_{ijk}\partial_j(r_k\psi) = \psi\epsilon_{ijk}\partial_j(r_k) - \epsilon_{ikj}r_k\partial_j\psi = \psi[\nabla \times \mathbf{r}]_i - [\mathbf{r} \times \nabla\psi]_i = -[\mathbf{r} \times \nabla\psi]_i = [\mathbf{L} \times \mathbf{r}]_i$ , therefore  $\mathbf{M}$  is orthogonal to  $\mathbf{L}$  and  $\mathbf{r}$ . From Eq. (1.14c)  $\mathbf{M} \cdot \mathbf{N} = 0$ , so  $\mathbf{M}$  is orthogonal to  $\mathbf{N}$ . As it will be shown in Eq. (1.22), not necessarily  $\mathbf{L}$  is orthogonal to  $\mathbf{N}$  in a geometrical sense.

a sphere. The Eqs. (1.17) and (1.18) can be rewritten as

$$(1 - \mu^2) \frac{d^2\Theta}{d\mu^2} - 2\mu \frac{d\Theta}{d\mu} + \left[ \ell(\ell + 1) - \frac{m^2}{1 - \mu^2} \right] \Theta = 0, \quad \text{with } \mu = \cos\theta, \quad (1.19)$$

$$\rho \frac{d}{d\rho} \left( \rho \frac{dZ}{d\rho} \right) + \left[ \rho^2 - \left( \ell + \frac{1}{2} \right)^2 \right] Z = 0, \quad \text{with } Z = R\sqrt{\rho} \text{ and } \rho = kr. \quad (1.20)$$

The solution to Eq. (1.19) are the associated Legendre functions  $P_\ell^m(\mu)$  and to Eq. (1.20) the spherical Bessel functions of the first ( $j_\ell$ ) and second ( $y_\ell$ ) kind, or the spherical Hankel functions of first ( $h_\ell^{(1)} = j_\ell + iy_\ell$ ) and second ( $h_\ell^{(2)} = j_\ell - iy_\ell$ ) kind. Following the convention from most Mie Scattering literature [11], the solution to Eq. (1.16) will be **decomposed** into an odd ('o') and an even ('e') **solutions**, that is, as sine and cosine functions, thus restricting the values of  $m$  to non negative integers. After this, the generating function of the VSH is given by

$\psi$ : Generating function of the vectorial spherical harmonics

$$\psi_{\text{o}\ell m}(r, \theta, \varphi) = \frac{\sin(m\varphi)}{\cos(m\varphi)} P_\ell^m(\cos\theta) z_\ell(kr), \quad (1.21)$$

where  $z_\ell$  stands for any of the four solutions to the radial equation [Eq. (1.20)]. Substituting Eq. (1.21) in Eqs. (1.14a)–(1.14c) one finds the VSH:

### Vectorial Spherical Harmonics

$$\begin{aligned} \mathbf{L}_{\text{o}\ell m} &= \frac{\cos(m\varphi)}{\sin(m\varphi)} k P_\ell^m(\cos\theta) \frac{dz_\ell(kr)}{d(kr)} \hat{\mathbf{e}}_r + \frac{\cos(m\varphi)}{\sin(m\varphi)} k \frac{z_\ell(kr)}{kr} \frac{dP_\ell^m(\cos\theta)}{d\theta} \hat{\mathbf{e}}_\theta + \\ &\quad - \frac{\sin(m\varphi)}{\cos(m\varphi)} km \frac{P_\ell^m(\cos\theta)}{\sin\theta} \frac{z_\ell(kr)}{kr} \hat{\mathbf{e}}_\varphi \end{aligned} \quad (1.22a)$$

$$\mathbf{M}_{\text{o}\ell m} = \frac{-\sin(m\varphi)}{+\cos(m\varphi)} m z_\ell(kr) \frac{P_\ell^m(\cos\theta)}{\sin\theta} \hat{\mathbf{e}}_\theta - \frac{\cos(m\varphi)}{\sin(m\varphi)} z_\ell(kr) \frac{dP_\ell^m(\cos\theta)}{d\theta} \hat{\mathbf{e}}_\varphi, \quad (1.22b)$$

$$\begin{aligned} \mathbf{N}_{\text{o}\ell m} &= \frac{\cos(m\varphi)}{\sin(m\varphi)} \frac{z_\ell(kr)}{kr} \ell(\ell + 1) P_\ell^m(\cos\theta) \hat{\mathbf{e}}_r + \frac{\cos(m\varphi)}{\sin(m\varphi)} \frac{1}{kr} \frac{d[kr z_\ell(kr)]}{d(kr)} \frac{dP_\ell^m(\cos\theta)}{d\theta} \hat{\mathbf{e}}_\theta + \\ &\quad - \frac{\sin(m\varphi)}{\cos(m\varphi)} m \frac{1}{kr} \frac{d[kr z_\ell(kr)]}{d(kr)} \frac{P_\ell^m(\cos\theta)}{\sin\theta} \hat{\mathbf{e}}_\varphi, \end{aligned} \quad (1.22c)$$

where the term  $\ell(\ell + 1)P_\ell^m$  arises since the associated Legendre functions obeys Eq. (1.19).

The choice at  $z_\ell$  in Eqs. (1.22) is due to the physical constraints of the scattering problem. On the one hand, the spherical Bessel function of first kind, unlike the other three proposed solutions to the radial equation, is finite at  $r = 0$ , thus it is appropriate for the internal electric field and plane waves. This choice at  $z_\ell$  will be denoted in the VSH with the superscript (1). On the other hand, the asymptotic behavior ( $\ell \ll \rho$ ) of the Hankel function of first kind  $h^{(1)} = j_\ell + iy_\ell$  and its derivative **represent** outgoing spherical waves [4]

$$h_\ell^{(1)}(\rho) \approx (-i)^\ell \frac{\exp(i\rho)}{i\rho} \quad \text{and} \quad \frac{dh_\ell^{(1)}(\rho)}{d\rho} \approx (-i)^\ell \frac{\exp(i\rho)}{\rho}, \quad (1.23)$$

which are well suited for the scattered field; the VSH with  $z_\ell = h_\ell^{(1)}$  will be denoted with the superscript (3).

From here on, the VSH will be those defined in Eq. (1.14) under the condition of being a solution to the vectorial Helmholtz equation, which lead to the generating function  $\psi$  to be a solution to the scalar Helmholtz equation. Nevertheless, there are other definitions for the VSH as discussed by Barrera, Estevez, and Giraldo [13]. The chosen definition of the VSH allows the VSH to be interpreted directly as electric and magnetic fields, specifically identifying  $\mathbf{N}$  with the electric contribution and  $\mathbf{M}$  with the magnetic due to its behavior in the far field regime<sup>5</sup>, as it will be shown in Section 1.2.3.1.

### 1.2.2 Incident, Scattered, and Internal Electric Fields

Let  $\mathbf{E}^i$  be a  $x$ -polarized plane wave traveling in the  $\mathbf{e}_z$  direction; its representation in the spherical unit vector basis is

$$\mathbf{E}^i(\mathbf{r}) = E_0(\sin \theta \cos \varphi \hat{\mathbf{e}}_r + \cos \theta \cos \varphi \hat{\mathbf{e}}_\theta - \sin \varphi \hat{\mathbf{e}}_\varphi) \exp(ikr \cos \theta). \quad (1.24)$$

The monochromatic plane wave is a transversal wave, thus it can be written in terms of only  $\mathbf{M}^{(1)}$  and  $\mathbf{N}^{(1)}$ , where the radial dependency is given by  $j_\ell$  since the monochromatic plane wave is finite everywhere. Even more, due to the dependence on  $\varphi$ , it is only restricted to values of  $m = 1$ . By inspection on the radial component of  $\mathbf{E}^i$ , proportional to  $\cos \varphi$ , it depends only on  $\mathbf{N}_{e1\ell}^{(1)}$ , and on the azimuthal component, proportional to  $\sin \varphi$ , it depends only on  $\mathbf{M}_{o1\ell}^{(1)}$ . Thus, Eq. (1.24) can be written as a linear combination of  $\mathbf{N}_{e1\ell}^{(1)}$  and  $\mathbf{M}_{o1\ell}^{(1)}$ . Through the orthogonality relations of the VSH [see Eqs. (A.22)–(A.25) from Appendix A], the  $x$ -polarized plane wave can be written as [12]

$$\mathbf{E}^i(\mathbf{r}) = E_0 \sum_{\ell=1}^{\infty} \frac{i^\ell (2\ell+1)}{\ell(\ell+1)} (\mathbf{M}_{o1\ell}^{(1)} - i\mathbf{N}_{e1\ell}^{(1)}), \quad (1.25a)$$

$$\mathbf{H}^i(\mathbf{r}) = \frac{-kE_0}{\mu\omega} \sum_{\ell=1}^{\infty} \frac{i^\ell (2\ell+1)}{\ell(\ell+1)} (\mathbf{M}_{e1\ell}^{(1)} + i\mathbf{N}_{o1\ell}^{(1)}). \quad (1.25b)$$

In the problem of scattering due to a spherical particle of radius  $a$ , the continuity conditions on the tangential components of the electric and magnetic fields are written as

$$(\mathbf{E}^i + \mathbf{E}^{\text{sca}} - \mathbf{E}^{\text{int}}) \Big|_{r=a} \times \hat{\mathbf{e}}_r = (\mathbf{H}^i + \mathbf{H}^{\text{sca}} - \mathbf{H}^{\text{int}}) \Big|_{r=a} \times \hat{\mathbf{e}}_r = 0, \quad (1.26)$$

with  $\mathbf{E}^{\text{sca}}$  ( $\mathbf{E}^{\text{int}}$ ) the scattered (internal) electric field and  $\mathbf{H}^{\text{sca}}$  ( $\mathbf{H}^{\text{int}}$ ) the scattered (internal) magnetic field. If the incident field  $\mathbf{E}^i$  is given by a  $x$ -polarized plane wave [Eq. (1.24)] then the scattered and internal fields can be written also as a linear combination of  $\mathbf{M}_{o1\ell}$  and  $\mathbf{N}_{e1\ell}$ . The internal field is finite inside the particle, thus the radial dependence is given by the function

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<sup>5</sup>The VSH  $\mathbf{L}$  is left out from the identification of either an electric or magnetic contribution since it is purely longitudinal and thus not suitable for the far field.

$j_\ell(k_p a)$ , with  $k_p$  the wave number inside the particle. For the scattered fields, it is chosen the spherical Hankel function of first kind  $h^{(1)}(ka)$  due to its asymptotic behavior of a spherical outgoing wave. Such a choice for the radial dependence is denoted by the superscript (3) over the VSH. To simplify the following steps, the scattered and the internal electric fields are written as

$$\mathbf{E}^{\text{sca}}(\mathbf{r}) = E_0 \sum_{\ell=1}^{\infty} \frac{i^\ell(2\ell+1)}{\ell(\ell+1)} (ia_\ell \mathbf{N}_{e1\ell}^{(3)} - b_\ell \mathbf{M}_{o1\ell}^{(3)}), \quad (1.27a)$$

$$\mathbf{E}^{\text{int}}(\mathbf{r}) = E_0 \sum_{\ell=1}^{\infty} \frac{i^\ell(2\ell+1)}{\ell(\ell+1)} (c_\ell \mathbf{M}_{o1\ell}^{(1)} - id_\ell \mathbf{N}_{e1\ell}^{(1)}), \quad (1.27b)$$

with the respective magnetic fields

$$\mathbf{H}^{\text{sca}}(\mathbf{r}) = \frac{-kE_0}{\mu\omega} \sum_{\ell=1}^{\infty} \frac{i^\ell(2\ell+1)}{\ell(\ell+1)} (ib_\ell \mathbf{N}_{o1\ell}^{(3)} + a_\ell \mathbf{M}_{e1\ell}^{(3)}), \quad (1.28a)$$

$$\mathbf{H}^{\text{int}}(\mathbf{r}) = \frac{-kE_0}{\mu_p\omega} \sum_{\ell=1}^{\infty} \frac{i^\ell(2\ell+1)}{\ell(\ell+1)} (d_\ell \mathbf{M}_{e1\ell}^{(1)} + ic_\ell \mathbf{N}_{o1\ell}^{(1)}). \quad (1.28b)$$

Since only the term  $m = 1$  is taken into account, it is convenient to define the angular functions

$$\pi_\ell(\cos\theta) = \frac{P_\ell^1(\cos\theta)}{\sin\theta} \quad \text{and} \quad \tau_\ell(\cos\theta) = \frac{dP_\ell^1(\cos\theta)}{d\theta}, \quad (1.29)$$

which are not orthogonal but their addition and subtraction are, that is  $\pi_\ell \pm \tau_\ell$  are orthogonal functions [4]; see Eq. (A.20) in Appendix A. After substitution of Eqs. (1.25), (1.27b) and (1.28) into Eq. (1.26) and considering the orthogonality between  $\mathbf{M}$  and  $\mathbf{N}$ , between even and odd VSH, and between  $\pi_\ell \pm \tau_\ell$ , it is shown that the coefficients  $a_\ell$ ,  $b_\ell$ ,  $c_\ell$  and  $d_\ell$  are given by two decoupled equation systems

$$\begin{pmatrix} [xh_\ell^{(1)}(x)] & (\mu/\mu_p)[(mx)j_\ell(mx)] \\ m[xh_\ell^{(1)}(x)]' & [(mx)j_\ell(mx)]' \end{pmatrix} \begin{pmatrix} a_\ell \\ d_\ell \end{pmatrix} = \begin{pmatrix} [xj_\ell(x)] \\ m[xj_\ell(x)]' \end{pmatrix}, \quad (1.30)$$

and

$$\begin{pmatrix} m[xh_\ell^{(1)}(x)] & [(mx)j_\ell(mx)] \\ [xh_\ell^{(1)}(x)]' & (\mu/\mu_p)[(mx)j_\ell(mx)]' \end{pmatrix} \begin{pmatrix} b_\ell \\ c_\ell \end{pmatrix} = \begin{pmatrix} m[xj_\ell(x)] \\ [xj_\ell(x)]' \end{pmatrix}, \quad (1.31)$$

where  $m = k_p/k = n_p/n_{\text{mat}}$  is the contrast between the sphere and the matrix,  $x = ka = 2\pi n_{\text{mat}}(a/\lambda)$  is the size parameter and ('') denotes derivative respect to the argument of the spherical Bessel or Hankel functions; the size parameter compares the size of the scatterer with the incident wavelength in the matrix: the larger the value of  $x$ , the bigger the scatterer can be considered inside such a matrix. The Equations. (1.30) and (1.31) are simplified when the Riccati-Bessel functions  $\psi_\ell(\rho) = \rho j_\ell(\rho)$  and  $\xi(\rho) = \rho h_\ell^{(1)}(\rho)$  are introduced.

When a non-magnetic particle nor matrix are assumed ( $\mu_p = \mu = \mu_0$ ), the coefficients  $a_\ell$  and  $b_\ell$  are known as the Mie coefficients, whose expression is calculated by inverting Eqs. (1.30) and (1.31), yielding

**Mie Coefficients**

$$a_\ell = \frac{\psi_\ell(x)\psi'_\ell(mx) - m\psi_\ell(mx)\psi'_\ell(x)}{\xi_\ell(x)\psi'_\ell(mx) - m\psi_\ell(mx)\xi'_\ell(x)}, \quad (1.32a)$$

$$b_\ell = \frac{m\psi_\ell(x)\psi'_\ell(mx) - \psi_\ell(mx)\psi'_\ell(x)}{m\xi_\ell(x)\psi'_\ell(mx) - \psi_\ell(mx)\xi'_\ell(x)}. \quad (1.32b)$$

Likewise, the coefficients  $c_\ell$  and  $d_\ell$  are given by

$$c_\ell = \frac{-m\xi'_\ell(x)\psi_\ell(x) + m\xi_\ell(x)\psi'_\ell(x)}{m\xi_\ell(x)\psi'_\ell(mx) - \psi_\ell(mx)\xi'_\ell(x)}, \quad (1.33a)$$

$$d_\ell = \frac{-m\xi'_\ell(x)\psi_\ell(x) + m\psi'_\ell(mx)\psi'_\ell(x)}{\xi_\ell(x)\psi'_\ell(mx) - m\psi_\ell(mx)\xi'_\ell(x)}. \quad (1.33b)$$

Even though the coefficients of the linear combination for the scattered and internal fields were obtained assuming an  $x$ -polarized incident field, due to the spherical symmetry of the problem, by applying the transformation  $\varphi \rightarrow \varphi + \pi/2$  the same procedure is valid for a  $y$ -polarized incident field [4], therefore all quantities related to the scattered and the internal field can be expressed in terms of Eqs. (1.32) and (1.33).

As discussed in Section 1.1, the optical properties of a particle are encoded into the scattering, absorption, and extinction cross sections. These quantities can be calculated by means of the scattering amplitude matrix [Eq. (1.1)] and the Optical Theorem [Eq. (1.12)]. Since the particle is spherical, it is convenient to exploit the symmetry of the problem by decomposing the scattered electric field [Eq. (1.27a)] into components parallel and perpendicular to the scattering plane. To obtain the scattering amplitude matrix expressed in an orthogonal base relative to the scattering plane ( $\hat{\mathbf{e}}_s^s = \hat{\mathbf{e}}_\theta$  and  $\hat{\mathbf{e}}_s^s = -\hat{\mathbf{e}}_\varphi$ ) let us substitute the Mie coefficients [Eqs. (1.32)] into Eq. (1.27a) while rewriting the VSH  $\mathbf{M}_{o1\ell}^{(3)}$  and  $\mathbf{N}_{e1\ell}^{(3)}$  [Eqs. (1.22)] in terms of the Riccati-Bessel function  $\xi$  and its derivative:

$$\mathbf{E}^{sca} \cdot \hat{\mathbf{e}}_r = \frac{\cos \varphi}{(kr)^2} \sum_{\ell=1}^{\infty} E_0 i^\ell (2\ell + 1) i a_\ell \xi(kr) \pi_\ell(\cos \theta) \sin \theta, \quad (1.34a)$$

$$\mathbf{E}^{sca} \cdot \hat{\mathbf{e}}_\parallel^{sca} = \frac{\cos \varphi}{kr} \sum_{\ell=1}^{\infty} E_0 i^\ell \frac{2\ell + 1}{\ell(\ell + 1)} [i a_\ell \xi'_\ell(kr) \tau_\ell(\cos \theta) - b_\ell \xi_\ell(kr) \pi_\ell(\cos \theta)], \quad (1.34b)$$

$$\mathbf{E}^{sca} \cdot \hat{\mathbf{e}}_\perp^{sca} = \frac{\sin \varphi}{-kr} \sum_{\ell=1}^{\infty} E_0 i^\ell \frac{2\ell + 1}{\ell(\ell + 1)} [i a_\ell \xi'_\ell(kr) \pi_\ell(\cos \theta) - b_\ell \xi_\ell(kr) \tau_\ell(\cos \theta)]. \quad (1.34c)$$

Following a similar procedure but substituting Eq. (1.33) into Eq. (1.27b), the internal electric field  $\mathbf{E}^{int}$  can be rewritten also in terms of the Riccati-Bessel functions as

$$\mathbf{E}^{int} \cdot \hat{\mathbf{e}}_r = -\frac{\cos \varphi}{(k_p r)^2} \sum_{\ell=1}^{\infty} E_0 i^\ell (2\ell + 1) i d_\ell \psi(k_p r) \pi_\ell(\cos \theta) \sin \theta, \quad (1.35a)$$

$$\mathbf{E}^{int} \cdot \hat{\mathbf{e}}_\parallel^{sca} = \frac{\cos \varphi}{k_p r} \sum_{\ell=1}^{\infty} E_0 i^\ell \frac{2\ell + 1}{\ell(\ell + 1)} [-i d_\ell \psi'_\ell(k_p r) \tau_\ell(\cos \theta) + c_\ell \psi_\ell(k_p r) \pi_\ell(\cos \theta)], \quad (1.35b)$$

$$\mathbf{E}^{\text{int}} \cdot \hat{\mathbf{e}}_{\perp}^{\text{sca}} = \frac{\sin \varphi}{-k_p r} \sum_{\ell=1}^{\infty} E_0 i^{\ell} \frac{2\ell+1}{\ell(\ell+1)} [-id_{\ell} \psi'_{\ell}(k_p r) \pi_{\ell}(\cos \theta) + c_{\ell} \psi_{\ell}(k_p r) \tau_{\ell}(\cos \theta)]. \quad (1.35c)$$

The scattering amplitude matrix relates the incident electric field to the scattered electric field in the far field regime, that it when  $kr \gg 1$ . Considering that the series of Eqs. (1.34a)-(1.34c) converge uniformly, so all contributions after the sufficiently large term  $\ell_c$  of the sum can be neglected for all values of  $kr$ , the asymptotic expressions for the  $\xi$  Riccati-Bessel function and its derivative can be employed, which are given by [4]

$$\xi(kr) \approx (-i)^{\ell} \frac{\exp(ikr)}{i}, \quad \text{and} \quad \frac{d\xi(kr)}{d(kr)} = (-i)^{\ell} \exp(ikr) \left( \frac{1}{ikr} + 1 \right), \quad \text{when } \ell_c^2 \ll kr. \quad (1.36)$$

Substituting Eq. (1.36) into Eqs. (1.34a)-(1.34c) and neglecting terms proportional to  $(kr)^{-2}$ , it yields a zero radial electric field, while

$$\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}_{\parallel}^{\text{sca}} \approx \frac{\exp(ikr)}{r} \left\{ \frac{i}{k} \sum_{\ell=1}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_{\ell} \tau_{\ell}(\cos \theta) + b_{\ell} \pi_{\ell}(\cos \theta)] \right\} E_0 \cos \varphi, \quad (1.37a)$$

$$\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}_{\perp}^{\text{sca}} \approx \frac{\exp(ikr)}{r} \left\{ \frac{i}{k} \sum_{\ell=1}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_{\ell} \pi_{\ell}(\cos \theta) + b_{\ell} \tau_{\ell}(\cos \theta)] \right\} E_0 (-\sin \varphi), \quad (1.37b)$$

where it can be identified that  $\mathbf{E}^i \cdot \hat{\mathbf{e}}_{\parallel}^i = E_0 \cos \varphi$  and  $\mathbf{E}^i \cdot \hat{\mathbf{e}}_{\perp}^i = -E_0 \sin \varphi$  for  $\mathbf{E}^i$  a plane wave traveling along the  $z$  direction with an arbitrary polarization. Finally, the scattering amplitude matrix for a spherical particle can be obtained by comparing Eqs. (1.37a) and (1.37b) with Eq. (1.1), yielding

### Scattering Amplitude Matrix for Spherical Particles

$$\mathbb{F}(\hat{\mathbf{k}}^{\text{sca}}, \hat{\mathbf{k}}^i) = \begin{pmatrix} \frac{i}{k} S_2(\theta) & 0 \\ 0 & \frac{i}{k} S_1(\theta) \end{pmatrix}, \quad (1.38a)$$

with  $\hat{\mathbf{k}}^{\text{sca}} = \hat{\mathbf{e}}_r$ ,  $\hat{\mathbf{k}}^i = \hat{\mathbf{e}}_z$ ,  $\cos \theta = \hat{\mathbf{k}}^{\text{sca}} \cdot \hat{\mathbf{k}}^i$  and

$$S_1(\theta) = \sum_{\ell=1}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_{\ell} \tau_{\ell}(\cos \theta) + b_{\ell} \pi_{\ell}(\cos \theta)], \quad (1.38b)$$

$$S_2(\theta) = \sum_{\ell=1}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_{\ell} \pi_{\ell}(\cos \theta) + b_{\ell} \tau_{\ell}(\cos \theta)], \quad (1.38c)$$

which depend entirely on the angular functions  $\pi_{\ell}(\cos \theta)$  and  $\tau_{\ell}(\cos \theta)$  modulated by the Mie coefficients  $a_{\ell}$  and  $b_{\ell}$ . The scattering amplitude matrix  $\mathbb{F}$  shows the symmetry of the system when it is written in a base relative to the scattering plane, as stated in Section 1.1. Since the scatterer is a spherical isotropic NP,  $\mathbb{F}$  is a diagonal matrix in the base  $\{\hat{\mathbf{e}}_{\parallel}^{\text{sca}}, \hat{\mathbf{e}}_{\perp}^{\text{sca}}\}$ , that is, that the scattered electric field  $\mathbf{E}^{\text{sca}}$  maintains the same polarization degree relative to the scattering plane than the incident electric field  $\mathbf{E}^i$  that illuminates the spherical particle.

### 1.2.3 Optical Properties of a Single Spherical (Gold) Particle

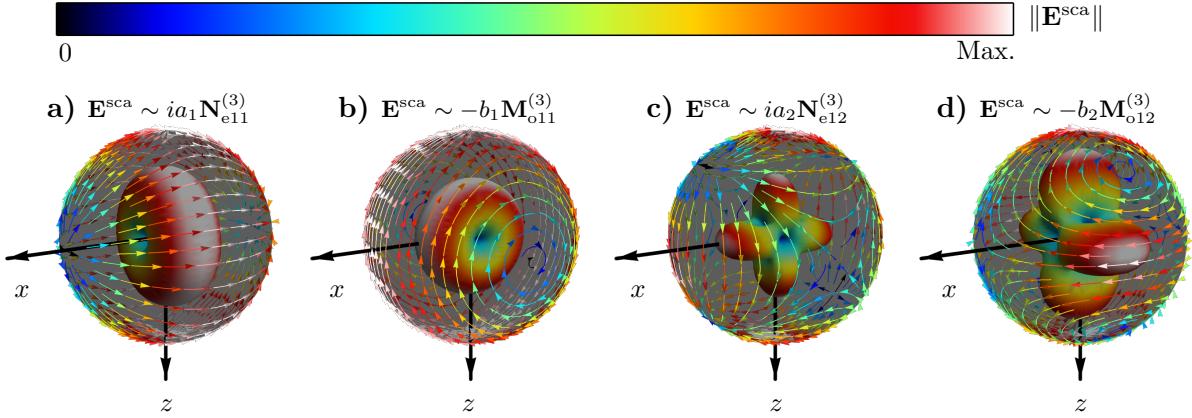
In previous Sections, the general theory for the light scattering was developed, introducing the scattering amplitude matrix  $\mathbb{F}$  [Eq. (1.1)]. Then, the particular problem of a spherical scatterer was addressed and the explicit **expressions for** the scattered electric field [Eq. (1.37)] and for  $\mathbb{F}$  were obtained [Eq. (1.38a)] in terms of the Mie coefficients  $a_\ell$  and  $b_\ell$  [Eqs. (1.32)], as well as the internal electric field inside the scatterer [Eq. (1.35)] in terms of the coefficients  $c_\ell$  and  $d_\ell$  [Eqs. (1.33)]. The optical properties of a particle is related to the electric field outside the scatterer, and can be studied within two different spatial regions: the near field and the far field regimes. The near field **region** consists in the complete analytical solution of the scattered electric field [Eq. (1.27a)], while the far field regime considers only the contributions proportional to  $r^{-1}$ , with  $r$  the distance between the center of the scatterer and the measurement point; the optical properties in the far field regime can be determined by the scattering amplitude matrix  $\mathbb{F}$  itself. In this last Section, the previous results are employed to calculate the optical properties fo a spherical gold nanoparticle (AuNP) with a radius of 12.5 nm, **either** embedded into a matrix of air or into a matrix of glass, when it is illuminated by an incident plane wave with a wavelength  $\lambda$ .

#### 1.2.3.1 Localized Surface Plasmons

The optical properties of a particle, either in the near or the far field regime, are determined by the Mie coefficients  $a_\ell$  and  $b_\ell$  [Eqs. (1.32)] since the exact solution to the scattered electric field  $\mathbf{E}^{\text{sca}}$  [Eq. (1.27a)] is a linear combination of the vector spherical harmonics  $\mathbf{N}_{\text{e}1\ell}^{(3)}$  and  $\mathbf{M}_{\text{o}1\ell}^{(3)}$ , modulated by  $a_\ell$  and  $b_\ell$ , respectively. Thus, the physical interpretation of each term  $\ell$  in the linear combination, as well as of  $\mathbf{N}_{\text{e}1\ell}^{(3)}$  and  $\mathbf{M}_{\text{o}1\ell}^{(3)}$ , can be determined by **plotting each term** independently. By understanding **eacg** contribution, the optical response of a particle illuminated by a plane wave can be studied **both** the near and far regimes.

Figure 1.2 shows the decomposition of the scattered electric field  $\mathbf{E}^{\text{sca}}$  of a spherical particle into its contributions proportional to  $a_1$  [Fig. 1.2a)],  $b_1$  [Fig. 1.2b)],  $a_2$  [Fig. 1.2c)] and  $b_2$  [Fig. 1.2d)], when the particle is illuminated by a  $x$ -polarized plane wave traveling in the  $z$  direction. The vectorial behavior of the  $a_\ell$  contributions to  $\mathbf{E}^{\text{sca}}$  are given by the VSH  $\mathbf{N}_{\text{e}1\ell}^{(3)}$  and by  $\mathbf{M}_{\text{o}1\ell}^{(3)}$  for the  $b_\ell$  contributions. The scattered electric field is evaluated at a spherical surface (gray sphere). The arrow stream on the spherical surface corresponds to the pointing direction of each contribution to  $\mathbf{E}^{\text{sca}}$  parallel to the evaluation sphere, while the color code corresponds to the magnitude of the scattered electric field at each point; the solid shape at the center **of the coordinated system corresponds to** a contour surface  $\|\mathbf{E}^{\text{sca}}\|$ .

The general effect of each contribution to the scattered electric field  $\mathbf{E}^{\text{sca}}$  can be understood by analyzing their behavior around the points where the scattered electric field drops to zero; such points are called nodes and are shown in dark bluish colors in Fig. 1.2. The number of nodes over the evaluation sphere (gray surface) is proportional to the chosen value of  $\ell$ . For example, if  $\ell = 1$  [Figs. 1.2a) and 1.2b)] there is a pair of such nodes and if  $\ell = 2$  [Figs. 1.2c) and 1.2d)] there are two pairs, where each pair consists of two nodes at opposite sides of the evaluation sphere. When comparing the contributions proportional to  $a_1$  and  $a_2$  [Figs. 1.2a) and



**Fig. 1.2:** Decomposition of the scattered electric field  $\mathbf{E}^{sca}$  into its contributions proportional to **a**)  $a_1$ , **b**)  $b_1$ , **c**)  $a_2$  and **d**)  $b_2$  [see Eq. (1.27a)] when a spherical particle (not shown) is illuminated by an  $x$ -polarized plane wave traveling in the  $z$  direction. The scattered electric field  $\mathbf{E}^{sca}$  is evaluated at a sphere larger than the particle: the arrow stream corresponds to the projection parallel to the evaluation sphere of  $\mathbf{E}^{sca}$  and the color code corresponds to the magnitude of  $\mathbf{E}^{sca}$ . A contour surface of the magnitude of  $\mathbf{E}^{sca}$  is located at the center of each .

[1.2c)] with contributions from  $b_1$  and  $b_2$  [Figs. 1.2b) and 1.2d)], one notices a difference in the location of the pairs of nodes for a fixed value of  $\ell$ , which differ spatially by a rotation around the  $z$  axis of an angle  $\varphi = \pi/2$ . Another difference between the contributions of  $a_\ell$  and  $b_\ell$  to  $\mathbf{E}^{sca}$  are the trajectories they performed around each pair of nodes: In the  $a_\ell$  contributions the scattered electric field flows from one node to its pair, thus following an open path, while the scattered electric field for the  $b_\ell$  contributions circulates around the nodes forming a closed path. Taking into account such behaviors, it can be seen that the  $a_\ell$  ( $b_\ell$ ) contribution describes the electric field of an electric (magnetic) dipole when  $\ell = 1$  and of an electric (magnetic) quadrupole when  $\ell = 2$ . Extrapolating such behavior for an arbitrary  $\ell$ , it can be concluded that the  $a_\ell$  contributions to the scattered electric field, described by the VSH  $\mathbf{N}_{e\ell 1}^{(3)}$ , correspond to the electric field of an electric multipole of order  $\ell$ , while the  $b_\ell$  contribution, described by the VSH  $\mathbf{M}_{o\ell 1}^{(3)}$ , correspond to the electric field of a magnetic multipole of order  $\ell$ .

The scattered electric field  $\mathbf{E}^{sca}$  of a spherical particle can be written, according to Eq. (1.27a), as a linear contribution of electric fields associated to electric and magnetic multipoles, as shown in Fig. 1.2, modulated by the Mie coefficients  $a_\ell$  and  $b_\ell$ , respectively. Thus, the field  $\mathbf{E}^{sca}$  reproduces the pattern of a pure electric or magnetic multipole of order  $\ell$  if  $a_\ell$  or  $b_\ell$  are maximized, accordingly. Since the Mie coefficients [Eqs. (1.32)] depend on the material and size of the spherical scatter, on the wavelength and traveling media of the incident plane wave, and on the order  $\ell$ , the values of  $a_\ell$  and  $b_\ell$  are maximized when there is a coupling between the scatterer and the plane wave for a fixed  $\ell$ , which yields a Localized Surface Plasmon Resonance (LSPR). The condition to obtain a LSPR is given by the limit when the denominators of the Eqs. (1.32) tend to zero, that is

$$\xi_\ell(x)\psi'_\ell(mx) - m\psi_\ell(mx)\xi'_\ell(x) \rightarrow 0, \quad (\text{Electric LSPR}), \quad (1.39)$$

$$m\xi_\ell(x)\psi'_\ell(mx) - \psi_\ell(mx)\xi'_\ell(x) \rightarrow 0, \quad (\text{Magnetic LSPR}), \quad (1.40)$$

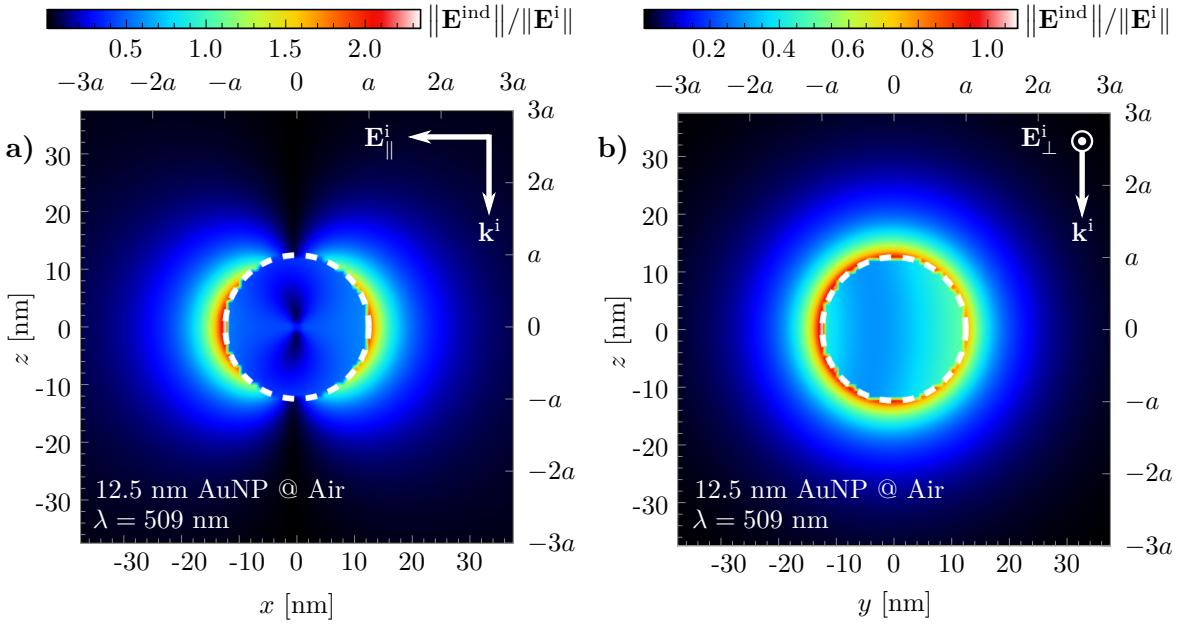
where  $\psi_\ell(\rho) = \rho j_\ell(\rho)$  and  $\xi(\rho) = \rho h_\ell^{(1)}(\rho)$  are the Riccati-Bessel functions, the operator  $(')$  denotes the derivative respect to their argument,  $x = 2\pi n_m(a/\lambda)$  is the size parameter, with  $a$  the radius of the particle and  $\lambda$  the wavelength of the incident plane wave, and  $m = n_p/n_{\text{mat}}$  is the contrast between the refractive indices of the particle ( $n_p$ ) and the matrix ( $n_m$ ), both of which are in general wavelength dependent. A simplified condition for the LSPR can be obtained by employing the Drude Model —see Eq. (B.1) in Appendix B— for the refractive index of the particle [14]. Nevertheless, the roots in Eqs. (1.39) and (1.40) can be found numerically and yield, in general, different solutions.

The system of interest in this work consists of a spherical gold nanoparticle (AuNP) of radius  $a = 12.5$  nm, using dielectric function reported by Johnson and Christy [15]. However, this experimental data corresponds to a bulk sample, meaning that it may not reproduce the optical behavior of a NP since surface effects cannot to be neglected due to its size [16]. In order to study the optical properties of AuNP, for example to determine the conditions for its LSPRs from Eqs. (1.39) and (1.40), while considering surface effects, a size correction to the dielectric function of the AuNP was performed as described in Appendix B. A more detailed discussion on such size effects is performed by analyzing the far field regime in the next section.

The induced electric field  $\mathbf{E}^{\text{ind}}$ , inside the NP (internal electric field) and outside of it (scattered electric field), of a spherical AuNP of radius  $a = 12.5$  nm were calculated at the wavelength of the dipolar ( $\ell = 1$ ) LSPR when the AuNP is embedded into an air matrix ( $n_{\text{mat}} = 1$ ) and when it is illuminated by an  $x$ -polarized electric field  $\mathbf{E}^i$  traveling in the  $z$  direction. In Fig. 1.3 the normalized magnitude of  $\mathbf{E}^{\text{ind}}$  is evaluated at the plane  $y = 0$  [Fig. 1.3a)] where the incident electric field is parallel ( $\parallel$ ) to the scattering plane, and at the plane  $x = 0$  [Fig. 1.3b)] where the incident electric field is perpendicular ( $\perp$ ) to the scattering plane; in both figures the dashed lines corresponds to the surface of the AuNP. The excitation wavelength  $\lambda$  of the LSPR for the described system was calculated by employing the size corrected dielectric function for the AuNP in Eq. (1.39).

By comparing the magnitude of the induced electric  $\mathbf{E}^{\text{ind}}$  field in Fig. 1.3 outside the AuNP, which was calculated up to the multipolar contribution of  $\ell = 7$  accordingly with the Wacombe criteria for convergence [4], with the electric dipolar contribution of the scattered electric field in Fig. 1.2a), the same contour pattern is found. The norm of  $\mathbf{E}^{\text{ind}}$  evaluated at a plane parallel to the scattering plane ( $y = 0$ ) shows a contour pattern of two lobes, which is characteristic of an electric dipole. When the induced electric field is evaluated at a perpendicular plane relative to the scattering plane ( $x = 0$ ), the pattern observed corresponds to the azimuthal symmetry of the dipolar electric field. Lastly, it can be seen that there is an enhancement of twofold the induced electric field relative to the incident electric field at the surface of the AuNP in the direction parallel to the incident electric field [reddish zones in Fig. 1.3a)]; such enhancement corresponds to the LSPR.

From the analysis of the electric field scattered by the particle in the near field regime, the LSPR can be visualized on the surface of the particle at the conditions imposed by Eq. (1.39) for the electric multipoles. The conditions to excite the LSPR are dictated by the Mie coefficients, therefore the LSPR can also be identified in the far field regime since the amplitude scattering matrix, from which any optical properties in the far field regime can be calculated, is written according to Eq. (1.38a) in terms of  $a_\ell$  and  $b_\ell$ . In the following section, the optical properties in the far field regime are calculated and their relation to the LSPR is established, yielding to the



**Fig. 1.3:** Induced electric field  $\mathbf{E}^{\text{int}}$  evaluated at the planes **a)**  $y = 0$  and **b)**  $x = 0$  of a 12.5 nm Au spherical NP (dashed lines) embedded into air ( $n_{\text{mat}} = 1$ ) when illuminated by an incident plane wave with an  $x$ -polarized electric field  $\mathbf{E}^i$  traveling in the direction  $\mathbf{k}^i$  along the  $z$  axis with an excitation wavelength  $\lambda = 509$  nm of the LSPR. At the plane  $x = 0$ , the incident electric field is parallel to the scattering plane, while it is perpendicular to it at  $x = 0$ . The optical response of the 12.5 nm AuNP was modeled using a size correction to the experimental data reported by Johnson and Christy [15].

observation of the LSPR in the far field.

### 1.2.3.2 Far Field Optical Properties

The Localized Surface Plasmon Resonance (LSPR) occurs when the scattered electric field of a particle illuminated by a plane wave is described by a stationary wave on the surface of a particle, meaning that it can be observed in the near field regime. For a spherical particle, the LSPR occurs when the conditions in Eqs. (1.39) and (1.40) are met, which maximize the Mie coefficients  $a_\ell$  and  $b_\ell$  [Eq. (1.32)], respectively. There are optical properties in the far field regime, that is where only the radiative contributions to the electromagnetic fields are non-negligible, that depend on  $a_\ell$  and  $b_\ell$ , for example, the scattering amplitude matrix  $\mathbb{F}$  [Eq. (1.38a)]. Therefore, the LSPR can also be identified by analyzing experimental or theoretical results of optical properties such as the scattering  $C_{\text{sca}}$  and extinction cross sections  $C_{\text{ext}}$ , which are related to  $\mathbb{F}$ . Hereby, explicit expressions for the optical properties in the far field regime, for a scattering sphere, are obtained.

By substituting the scattering amplitude matrix for a spherical particle [Eq. (1.38a)] into Eqs. (1.8) and (1.12) the scattering  $C_{\text{sca}}$  and extinction  $C_{\text{ext}}$  cross sections are obtained; the absorption cross section  $C_{\text{abs}}$  can be calculated by calculating  $C_{\text{ext}} - C_{\text{sca}}$ . Assuming an incident plane wave with an  $x$ -polarized electric field  $\mathbf{E}^i$ , and evaluating the scattering amplitude matrix in the forward direction  $\theta = 0$ , equivalent to  $\cos \theta = 1$ , the extinction cross section  $C_{\text{ext}}$  is given

by

$$C_{\text{ext}} = \frac{4\pi}{k\|\mathbf{E}^i\|^2} \text{Im}\left[\frac{i}{k} S_2(\theta=0) \mathbf{E}^i \cdot \mathbf{E}^{i*}\right] = \frac{2\pi}{k^2} \sum_{\ell=1}^{\infty} (2\ell+1) \text{Re}(a_\ell + b_\ell), \quad (1.41)$$

where the Eq. (A.16) in Appendix A was employed to evaluate the angular functions  $\pi_\ell(\cos\theta)$  and  $\tau_\ell(\cos\theta)$ . In a similar manner, the scattering cross section  $C_{\text{sca}}$  can be written as

$$C_{\text{sca}} = \int_0^{2\pi} \int_0^\pi \frac{(iS_2(\theta)\mathbf{E}^i)^*(iS_2(\theta)\mathbf{E}^i)}{k^2 \mathbf{E}^i} \sin\theta d\varphi d\theta = \frac{2\pi}{k^2} \sum_{\ell=1}^{\infty} (2\ell+1)(|a_\ell|^2 + |b_\ell|^2), \quad (1.42)$$

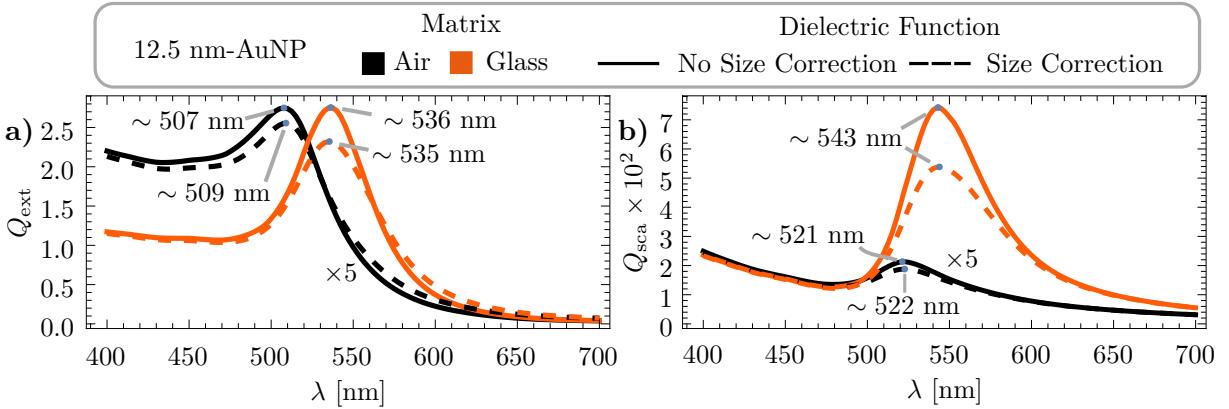
where the orthogonality relations of  $\pi_\ell(\cos\theta) \pm \tau_\ell(\cos\theta)$  [Eq. (A.20) in Appendix A] were used. In order to compare the absorption, scattering or extinction of light by a spherical particle, independently of its radius  $a$  or embedding media (matrix), it is convenient to define the efficiencies of absorption  $Q_{\text{abs}}$ , scattering  $Q_{\text{sca}}$  and extinction  $Q_{\text{ext}}$  by normalizing the absorption, scattering and extinction cross sections by the geometrical cross section of the spherical particle, yielding the dimensionless expressions

$$\frac{C_{\text{ext}}}{\pi a^2} = \frac{C_{\text{abs}}}{\pi a^2} + \frac{C_{\text{sca}}}{\pi a^2} \quad \rightarrow \quad Q_{\text{ext}} = Q_{\text{abs}} + Q_{\text{sca}}. \quad (1.43)$$

The Eq. (1.43), along with optical theorem [Eq. (1.11)], states that the extinction of light considers the combination of both absorption and scattering mechanisms. Since the analytical expression of  $C_{\text{ext}}$  for a spherical particle [Eq. (1.41) is proportional to the real parts of the Mie coefficients  $a_\ell$  and  $b_\ell$ , then it is also maximized at the LSPR. Therefore, the LSPR can be observed in the far field by calculating or measuring the extinction cross section.

In order to study the LSPR of a spherical AuNP of radius  $a = 12.5$  nm, the extinction  $Q_{\text{ext}}$  and the scattering  $Q_{\text{sca}}$  efficiencies are shown in Fig. 1.4, as function of the wavelength  $\lambda$  of the incident plane wave illuminating the NP. Two different matrices were considered: a matrix of air with a refractive index of  $n_{\text{mat}} = 1$  (black lines) and of glass with  $n_{\text{mat}} = 1.5$  (orange lines). The optical response of the AuNP was modeled by a dielectric function considering the raw data (solid lines) from Johnson and Christy [15], and a size correction to it (dashed lines). In all cases, the LSPR wavelength is indicated in the figure at the maximum of the extinction efficiencies and the wavelength of maximum scattering is also indicated.

By comparing Figs. 1.4a) and 1.4b), it is determined that the main loss mechanism in the system is absorption since  $Q_{\text{sca}}$  is two orders of magnitude smaller than  $Q_{\text{ext}}$  for all  $\lambda$  in the visible spectrum. Yet, another difference between  $Q_{\text{sca}}$  and  $Q_{\text{ext}}$  is the value of  $\lambda$  that maximizes them: for the chosen system the  $\lambda$  of maximum scattering is red shifted  $\sim 12$  nm from LSPR excitation wavelength in all cases. On the other side, an effect common for both the scattering and the extinction efficiencies is an overall enhancement when the refractive index of the matrix increases, as well as a redshift of  $\sim 25$  nm of the LSPR excitation wavelength and the wavelength of maximum scattering —compare the black curves ( $n_{\text{mat}} = 1$ , air) with the orange ones ( $n_{\text{mat}} = 1.5$ , glass)—, which can be understood by analyzing the size parameter  $x = (2\pi/\lambda)an_{\text{mat}}$ . Since  $x$  is a linear function of  $n_{\text{mat}}$ , the AuNP embedded into glass optically responds like a larger NP than what it is in air, thus having a more significant contribution from the scattering to the light extinction mechanism inside glass, as well as an increase in the



**Fig. 1.4:** a) Extinction  $Q_{\text{ext}}$  and b) scattering  $Q_{\text{sca}}$  efficiencies of a 12.5 nm Au spherical NP embedded into air (black,  $n_{\text{mat}} = 1$ ) and into glass (orange,  $n_{\text{mat}} = 1.33$ ), as function of the wavelength  $\lambda$  of the incident plane wave. The solid curves were calculated by considering no size effects on the dielectric function of the AuNP, while the dashed curves consider a size correction to it; the experimental data of Johnson and Christy [15] was employed.

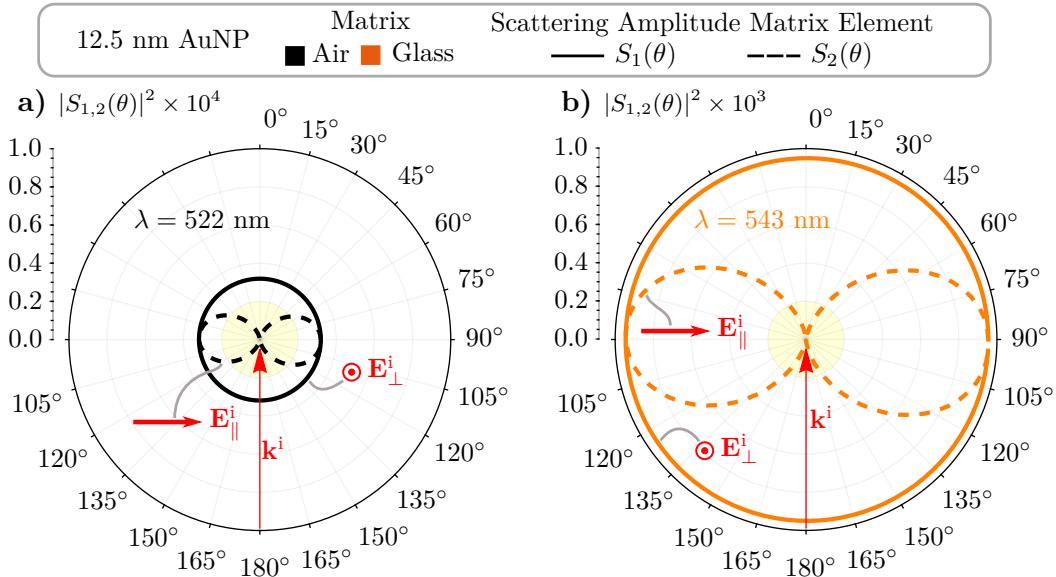
absorption.

The effect of the size correction to the dielectric function of the AuNP can be understood by comparing the solid and dashed lines. On the one hand, there is a spectral shift of the LSPR excitation wavelength of  $\sim 2$  nm. On the other hand, the value of the efficiencies around the wavelength where the extinction and the scattering is maximized decreases in all cases shown if Fig. 1.4. This behavior can be explained by how the size correction is performed: as explained in Appendix B, the surface effects are taken into account by introducing a smaller mean free path for the free electrons inside the AuNP, therefore increasing the value of the damping constant and thus leading to a larger imaginary part for the dielectric functions employed, which is related to the absorption mechanisms [17]. The decrease in the efficiencies due to a size corrected dielectric function is more evident for a matrix of glass than of air, since the AuNP is optically bigger in such matrix as explained above. From this analysis it can be concluded that the most notable effect of a size correction to the dielectric function of a NP is the decrease in the extinction and scattering efficiencies, while there is still a spectral shift of the LSPR, whose effect is less relevant the larger the size parameter is.

While the scattering efficiency  $Q_{\text{sca}}$  is an integral quantity, that is, it describes the scattering in all directions of a plane wave traveling in the direction  $\mathbf{k}^i$  due to the interaction with a NP, the scattering amplitude matrix elements  $S_1(\theta)$ , given for a spherical NP by Eq. (1.38b), and  $S_2(\theta)$ , by Eq. (1.38c), depict the electric field  $\mathbf{E}^s$ , at a measurement angle  $\theta$ , scattered by a NP polarized in a direction perpendicular ( $\perp$ ) to the scattering plane and parallel ( $\parallel$ ) to it, respectively. A radiation pattern helps to visualize the behavior of  $S_{1,2}(\theta)$ , a dimensionless parameter such as the scattering efficiency, by plotting their squared modulus as function of  $\theta$ , as it is shown in for a 12.5 nm AuNP in Fig. 1.5, where  $|S_1(\theta)|^2$  (solid lines) and  $|S_2(\theta)|^2$  (dashed lines) are shown for two different scenarios: a AuNP embedded into air [Fig. 1.5a), black curves] illuminated at a wavelength  $\lambda = 522$  nm and a AuNP embedded into glass [Fig. 1.5b), orange curves] illuminated at  $\lambda = 543$  nm. The wavelengths of the incident plane wave corresponds to the value of  $\lambda$  where  $Q_{\text{sca}}$  is maximized for each matrix as seen in Fig. 1.4.

The quantities  $|S_{1,2}(\theta)|^2$  for a 12.5 nm AuNP embedded into air ( $n_{\text{mat}} = 1$ , black curves)

## 1. SCATTERING THEORY OF A SINGLE SPHERICAL PARTICLE



**Fig. 1.5:** Radiation pattern of a 12.5 nm Au spherical NP embedded into a) air illuminated by a plane wave at a wavelength of  $\lambda = 522 \text{ nm}$  and b) glass illuminated at  $\lambda = 543 \text{ nm}$ ; the wavelength in each case corresponds to the wavelength of maximum scattering (see Fig. 1.4). The solid (dashed) lines corresponds to the scattering matrix element  $S_1$  ( $S_2$ ) related to an incident electric field  $\mathbf{E}^i$  traveling in the  $\mathbf{k}^i$  direction and polarized perpendicularly (parallel) to the page. It was considered for both matrices a size correction to the experimental data of Johnson and Christy [15] for the electromagnetic response of the AuNP.

are one order of magnitude smaller than into glass ( $n_{\text{mat}} = 1.5$ , orange curves), meaning that the AuNP scatters light less efficiently in air than in glass, which is consistent with the obtained values for the scattering efficiency  $Q_{\text{sca}}$  in Fig. 1.4. On the angular dependency, the radiation pattern of the AuNP in both matrices follow the same tendencies: an homogeneous scattered electric field when the AuNP scatters the perpendicularly polarized incident electric field  $\mathbf{E}_{\perp}^i$  (continuous lines), and a two-lobes pattern when illuminated with a parallel polarized  $\mathbf{E}^i$ . The observed radiation pattern can be identify in the near field regime, see Fig. 1.3, nevertheless within the radiation pattern analysis, the presence of the LSPR is lost, unlike within an analysis of the extinction cross section.

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## Chapter 2

# The Finite Element Method

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Several physical problems are described by systems of partial differential equations (PDE) alongside boundary or initial conditions, whose analytical solution can be achieved only in some cases. For example, the scattering of light due to an arbitrary spherical particle, described by the vectorial Helmholtz equation [Eq. (1.13)] with the boundary conditions at the surface of the spherical particle given by Eq. (1.26), is one of the few physical problem with an analytical solution. Nevertheless, it is set in an ideal scenario where the particle is a perfect sphere, it is isolated and embedded into a non-absorbing matrix. Any of these conditions on the geometry and physical properties of the described system were to change, the scattering problem may not have an analytical solution; for such cases one alternative is to employ a numerical approach to find an approximated solution. Among the numerical methods employed in electrodynamics, one of them is the Finite Element Method (FEM).

In this chapter the theory behind the FEM is presented with its implementation on the light scattering problem. In section 2.1 fundamentals of the FEM are explained: the Galerkin Method and the concept of the finite element. In section 2.2, the light scattering problem is revisited so it can be approached through an integral formulation, allowing the use of the FEM since a generalization of the concepts seen in section 2.1 into vectorial quantities is needed, as well as the introduction of boundary conditions in open regions so an infinite medium problem, such as the light scattering, can be approached numerically. In the last section, the scattering problem of an isolated spherical particle, addressed in chapter 1, is solved analytically and numerically—employing the commercial software *COMSOL Multiphysics* Ver. 5.4—and their results are contrasted.

## 2.1 Fundamentals

Any system of PDE describing a physical system in either equilibrium or in a steady-state, with a set of boundary conditions, can be described by [18]

$$\mathcal{L}[\mathbf{u}(\mathbf{r})] - \mathbf{f}_\Omega = 0, \quad \mathcal{C}[\mathbf{u}(\mathbf{r})] = \mathbf{f}_{\partial\Omega}, \quad (2.1)$$

where  $\mathcal{L}$  and  $\mathcal{C}$  are differential operators applied on the unknown functions  $\mathbf{u}$ —a  $D$  dimensional quantity—evaluated at a point  $\mathbf{r}$  in a domain  $\Omega$  and its boundary  $\partial\Omega$ , respectively;  $\mathbf{f}_\Omega$  and  $\mathbf{f}_{\partial\Omega}$

are known functions related to the sources of  $\mathbf{u}$  and to its boundary conditions. The description of the physical system as stated by Eq. (2.1) is known as its strong formulation since  $u$  must be  $m$ -times differentiable on  $\Omega$  if  $\mathcal{L}$  is a differential operator of order  $m$  [18, 19]. It is possible to relax such differentiability condition on  $\mathbf{u}$  by employing the weak formulation of the PDE system, which in an integral representation of Eq. (2.1) obtained by multiplying it by a trial function  $\psi$  and integrating on  $\Omega$  [18–20]

$$W(u) = \int_{\Omega} \psi(\mathbf{r}) \{ \mathcal{L}[\mathbf{u}(\mathbf{r})] - \mathbf{f}_{\Omega} \} d\Omega = \mathbf{0}. \quad (2.2)$$

The weak formulation of the PDE system yields a weak solution to  $\mathbf{u}$  since Eq. (2.2) can be rewritten by performing  $s$ -fold integration by parts and then employing Gauss's Theorem or by employing Green's first identity [19]:

$$\int_{\Omega} \psi \nabla \cdot \mathbf{u} d\Omega = - \int_{\Omega} \nabla \psi \cdot \mathbf{u} d\Omega + \oint_{\partial\Omega} \psi \mathbf{u} \cdot \hat{\mathbf{n}} d(\partial\Omega), \quad (\text{with Gauss's Theorem}), \quad (2.3)$$

$$\int_{\Omega} \mathbf{u} \cdot \nabla \psi d\Omega = - \int_{\Omega} \psi \nabla \cdot \mathbf{u} d\Omega + \int_{\partial\Omega} \psi \mathbf{u} \cdot \hat{\mathbf{n}} d(\partial\Omega), \quad (\text{Green's first identity}). \quad (2.4)$$

If Eqs. (2.3) or (2.4) are used  $s$ -fold on Eq. (2.2) then  $\mathbf{u}$  must be differentiable  $m-s$  times instead of  $m$ , while  $\psi$  must be  $s$  times differentiable. More over, the boundary conditions imposed to  $u$  must be satisfied only if they contain derivatives up to the order  $m-s-1$  since the conditions with derivatives of order bigger than  $m-s$  are taken into account in the integrals of Eqs. (2.3) and (2.4)—and on such boundary conditions  $\psi$  must equal zero—. Thus, any solution  $\mathbf{u}$  to Eq. (2.2) is known as a weak solution since it does not holds the differentiability condition as they are required by the equivalent strong formulation [18].

Among the several methods to find an approximated solution to Eq. (2.2), the Galerkin method is one of the most common and implemented methods alongside the finite element approximation, which together form the finite element method. To ease the key ideas of the Galerkin and the finite element approximation, the unknown function  $\mathbf{u}$  is assumed to be a scalar quantity  $u$  in the following section.

### 2.1.1 The Galerkin Method

To find an approximated solution to  $u$ , one option is to employ the weighted residual method, which changes the PDE system to an algebraic equation system by proposing an approximation  $\tilde{u}$  as a linear combination of  $N$  known functions  $\phi_i$ , which differs from the exact solution  $u$  by an error  $e_u$ , that is [18–20]

$$u(\mathbf{r}) = \tilde{u}(\mathbf{r}) + e_u(\mathbf{r}), \quad \text{with} \quad \tilde{u}(\mathbf{r}) = \sum_{i=1}^N a_i \phi_i(\mathbf{r}), \quad (2.5)$$

where  $\tilde{u}$  follows the same boundary conditions as  $u$  at  $\partial\Omega$  and  $a_i$  are  $N$  parameters to be determined<sup>1</sup>. The values of  $a_i$  are chosen so that  $e_u \ll \tilde{u}$ , which may be achieved by increasing

<sup>1</sup>The  $N$  parameters  $a_i$  are constant for equilibrium and steady-state problems while they may depend on time for transport problems [18].

$N$  or by choosing  $a_i$  that match the exact value of  $u$  at determined points.

One particular form to the approximated solution  $\tilde{u}$  in Eq. (2.5) is known as the nodal approximation [18, 20]:

$$\tilde{u}(\mathbf{r}) = \sum_{i=1}^N u_i \phi_i(\mathbf{r}), \quad \text{with} \quad u_i = u(\mathbf{r}_i), \quad (2.6)$$

where  $\phi_i$  are the so called interpolating—or shape—functions and  $u_i$  are coefficients that equals the exact value of the function  $u$  at  $N$  points  $\mathbf{r}_j \in \Omega$ , called the nodal points. From Eq. (2.6) it can be seen that the error  $e_u$  between the exact and the approximated solutions vanishes at the nodes  $\mathbf{r}_j$  and thus  $\phi_i(\mathbf{r}_j) = \delta_{ij}$ , with  $\delta_{ij}$  the Kronecker delta.

Since  $\tilde{u}$  is an approximated solution, the evaluation fo Eq. (2.6) into Eq. (2.1) equals to a residual  $R_{\tilde{u}}(\mathbf{r}, \{u_i\}_{i \leq N})$  which in general is different to zero [19, 20], that is,

$$\mathcal{L}[\tilde{u}(\mathbf{r})] - f_\Omega = R_{\tilde{u}}(\mathbf{r}, \{u_i\}_{i \leq N}) \neq 0. \quad (2.7)$$

To determine the coefficients  $u_i$ , the residual  $R_{\tilde{u}}$  is multiplied by a weighting—or trial—function  $\psi_j$  and integrated over  $\Omega$  imposing that the integral goes to zero, that is

$$W(\tilde{u}) = \int_{\Omega} \psi_j(\mathbf{r}) R_{\tilde{u}}(\mathbf{r}, \{u_i\}_{i \leq N}) d\Omega = \mathbf{0}. \quad \text{with} \quad \psi_j \in \{\psi_j\}_{j \leq N}, \quad (2.8)$$

which is a set of  $N$  independent algebraic equations with  $N$  variables. It is worth noting that Eq. (2.8) equals Eq. (2.2), and thus  $u = \tilde{u}$ , if the trail functions are elements of an infinite set, that is,  $N \rightarrow \infty$  [18].

The weighted residual method is a family of numerical methods defined by the election of the trial functions set  $\{\psi_j\}_{j \leq N}$ . Some of the most common election for the trial functions set yield the collocation method, the least-squares method ant the method of moments, and the Galerkin method, all given by [18, 20]:

$$\{\psi_j\}_{j \leq N} = \{\delta(\mathbf{r} - \mathbf{r}_j)\}_{j \leq N}, \quad (\text{Collocation method}), \quad (2.9a)$$

$$\{\psi_j\}_{j \leq N} = \{\partial R_{\tilde{u}} / \partial u_j\}_{j \leq N}, \quad (\text{Least-squares method}), \quad (2.9b)$$

$$\{\psi_j\}_{j \leq N} = \{x^j\}_{j \leq N}, \quad (\text{Moments method}), \quad (2.9c)$$

$$\{\psi_j\}_{j \leq N} = \{\phi_j\}_{j \leq N}, \quad (\text{Galerkin method}), \quad (2.9d)$$

where the Galerkin method sets the trial functions equal to the interpolating functions. Comparing the methods shown in Eqs. (2.9), the Galerkin method returns an approximated solution with the highest accuracy while having a moderated ease to implementation [20]. Yet, another advantage of the Galerkin method is that, for a eigenvalue problem, it guarantees real eigenvalues if the PDE system in Eq. (2.1) describes a self-adjoint operator [18, 21]. By substituting Eq. (2.9d) into Eq. (2.8), and exploiting the linearity of the differential operator  $\mathcal{L}$ , the PDE system is transformed into an algebraic problem as follows:

**The Galerkin Method**

$$\mathbb{A}\mathbf{u} = \mathbf{f} \quad (2.10a)$$

where the entries of the matrix  $\mathbb{A}$ , and vectors  $\mathbf{u}$  and  $\mathbf{f}$  are

$$A_{ij} = \int \phi_i(\mathbf{r}) \mathcal{L}[\phi_j(\mathbf{r})] d\Omega, \quad u_i = u(\mathbf{r}_i), \quad \text{and} \quad f_j = \int f_\Omega \phi_j(\mathbf{r}) d\Omega. \quad (2.10b)$$

The Galerkin method is defined by the election of trial functions according to Eq. (2.9d), which are assumed to be linear independent so Eq. (2.10) is a solvable system of algebraic equations for the nodes  $u_j$  [20]. Additionally, due to a better performance, it is recommended to choose the set of trial functions as the first  $N$  elements of a complete set of functions in the domain  $\Omega$  and to meet the boundary conditions on Eq. (2.1) as exactly as possible [20]. It is also recommended for the functions  $\phi_i$  to increase their polynomial order as the size of  $\Omega$  grows since the integral in Eq. (2.10b) can be calculated with higher accuracy if methods as quadrature are employed [20].

The Galerkin method returns an approximated solution  $\tilde{u}$  to  $u$ , in the weak sense, as a linear combination of the interpolating functions  $\{\phi_i\}_{i \leq N}$  so long the error  $e_u$  can be depreciated for all points in the domain  $\Omega$ . Such solution is determined by inverting the matrix  $\mathbb{A}$  in Eq. (2.10) thus, a crucial step is to find the set  $\{\phi_i\}_{i \leq N}$  of functions to solve the problem in  $\Omega$  that follows the boundary conditions on  $\partial\Omega$ . From a computational approach, the required computing time and resources increase as  $\Omega$  does, therefore requiring the cardinality of the sets  $\{\psi_j\}_{j \leq N}$  and  $\{\phi_i\}_{i \leq N}$  to increase as well [18]. To overcome such problem, one alternative is to divide  $\Omega$  into  $M$  smaller subdomains allowing for low cardinality interpolating functions to solve Eq. (2.8) in each subdomain. This method is known as the finite element approximation and it is discussed in the following section.

### 2.1.2 The Finite Element

The finite element approximation allows the use of low order interpolating functions by defining the subdomains  $\Omega_k$  such that

$$\bigcup_{k=1}^M \Omega_k = \Omega, \quad \text{and} \quad \bigcap_{k=1}^M \Omega_k = \emptyset, \quad (2.11)$$

that is that, all  $\Omega_k$  together represent the original domain  $\Omega$  and that they do not overlap nevertheless, the boundaries of the finite elements are shared by neighboring elements [18]. Then, the finite element approximation restricts  $\tilde{u}_k$  —the nodal approximation on each subdomain— to depend only on the nodal points on  $\Omega_k$  and on its boundary  $\partial\Omega_k$ , while all  $\tilde{u}_k$  must be continuous across  $\partial\Omega_k$  and obey the differentiability condition they are bound to, whether the strong or weak formulation is employed [18].

A finite element  $\Omega_k$  is a subdomain of  $\Omega$  following Eq. (2.11) [18] but its formal definition requires  $\Omega_k$  to be a manifold embedded into  $\Omega$ , as well as to chose a polynomial function space

on  $\Omega_k$ , and to define a collection of  $N_k$  linear functionals  $\mathcal{F}_{\ell_k}$  on  $\Omega_k$  [19]. The description of  $\Omega_k$  as a manifold determines its geometrical properties such as dimensionality, shape and curvature, while the polynomials function space sets the order of the interpolating functions  $\{\phi_{i_k}\}_{i_k \leq N_k}$ . By applying  $\phi_{i_k}$  into  $\mathcal{F}_{\ell_k}$ , a system of  $N_k$  algebraic equations is obtained:

$$\mathcal{F}_{\ell_k}[\phi_{i_k}] = \delta_{\ell_k i_k}, \quad (2.12)$$

from which the interpolating functions are determined. Since the  $N_k$  linear functional imposes conditions on the interpolating functions, the  $N_k$  corresponds to the number of degrees of freedom of the finite element [19].

The finite element corresponds to a particular way of discretization of the domain  $\Omega$  and thus it is convenient to define the manifold  $\Omega_k$  by its geometrical nodes  $\mathbf{r}_{m_k}$ , which are a finite collection of points in  $\Omega_k$ . In Fig. 2.1 some examples<sup>2</sup> of common finite elements in one, two and three dimensions are shown: a straight line segment, a triangular surface and a tetrahedron [18]. The markers corresponds to the geometrical nodes in  $\Omega_k$ , from which the red markers corresponds to the geometrical nodes that define the shape of  $\Omega_k$ , since the lines joining two of them are the edges of the finite elements in two and three dimensions. The finite element in Fig. 2.1a) are known as reference elements since they have boundaries with no curvature and their geometrical nodes on its edges are equally spaced [18, 19]. Even so, the finite elements are, in general, of curvilinear shape, as shown in Fig. 2.1b), which may be preferred over the reference elements for  $\Omega$  with no Cartesian symmetries. It is possible to perform a transformation  $T : T(\xi) \rightarrow \mathbf{r}$  on the reference elements ( $\xi$ ) to reshape it into the so-called real-space element ( $\mathbf{r}$ ), which corresponds to the physical space where the Eq. (2.8) is to be solve [18, 20]. Let us recall that the choice of finite elements with straight or curvilinear boundaries is related to the discretization method of the domain  $\Omega$ . For example, were  $\Omega$  a cylinder in 3D, the use of finite elements with straight boundaries arises an error due to truncation of  $\Omega$  at its boundary, which can be minimized by increasing the number of finite elements, while curvilinear finite elements may fill such space without increasing the number of finite elements.

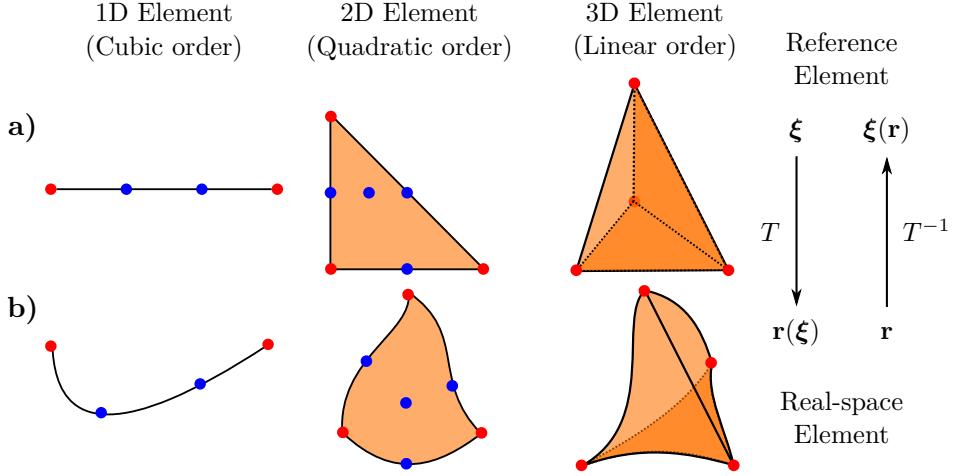
The transformation  $T$  is a change of coordinates from the coordinate system  $\xi$  of the reference finite element into the real-space system  $\mathbf{r}$ . The use of Eq. (2.12) in the reference elements yield the different kind of interpolating functions, which can be employed to solve the weak formulation of a PDE system [Eq. (2.8)] by transforming the derivatives in the real space coordinate system by means of the Jacobian matrix  $\mathbb{J}$ , whose elements are  $J_{ij} = \partial \xi_i / \partial r_j$ , and its determinant, the Jacobian, that is [18, 20]:

$$\frac{\partial}{\partial r_i} = \frac{\partial \xi_i}{\partial r_j} \frac{\partial}{\partial \xi_j}, \quad \text{and} \quad d\Omega_k \rightarrow \det[\mathbb{J}] d\xi_k. \quad (2.13)$$

The Eq. (2.13) sets a constriction into the discretization of the original domain  $\Omega$  and its partition into finite elements, since the Jacobian must be non singular—different from zero—in all points in  $\Omega_k$ , meaning that the transformation  $T$  of the reference element into the real-space finite element is bijective [18, 20]. To avoid singular points in  $\Omega_k$ , the real-space finite element must not be deformed considerably when transformed into the reference element [18].

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<sup>2</sup>Even though the elements shown in Fig. 2.1 are triangles (2D) and triangular pyramids (3D), their shapes can also be composed by squares and prisms; see [18] for a more detailed list.



**Fig. 2.1:** **a)** Reference and **b)** real-space finite elements for one (line segment), two (triangular surface) and three (tetrahedron) dimensional domains. The geometrical nodes on each element are signalized by the blue markers and their edges corresponds to the lines between the red markers; the number of nodes along each edge defines the order of the element. The transformation  $T$  reshapes the reference finite element from its coordinate system  $\xi$  into a real-space element  $r$ .

In order to build the interpolating functions  $\phi_{i_k}(\xi)$  in the reference finite element, the polynomial functions space on  $\Omega_k$  must be chosen by selecting the number of geometrical nodes found along the edges [19], so that the boundary conditions are met. For example, if there are  $m$  geometrical nodes on each edge, the finite element is said to be of order  $m - 1$  since a polynomial of order  $m - 1$  is guaranteed to pass through the values given to  $m$  nodes. For example, the reference finite elements in Fig. 2.1a) are a cubic order 1D finite element (three geometrical nodes along the edges), a quadratic order triangular finite element (2D shape with three node along the edges), and a linear tetrahedral finite element (3D volume with four triangular faces and two nodes at each edge).

Once the polynomial functions space on the manifold  $\Omega_k$  is set, this can be spanned by the set of interpolating functions  $\phi_{i_k}(\xi)$ , that are determined by means of the  $N_k$  linear functionals  $\mathcal{F}_\ell$  [19]. The election of the linear functionals give rise to different sets of interpolating functions and thus different families of finite elements. For example, the linear functional given by

$$\mathcal{F}_{\ell_k}^L[f(\xi)] = f(\xi_{\ell_k}), \quad (2.14)$$

with  $\xi_{\ell_k}$  the  $\ell_k$ -th geometrical nodes, from a collection of  $n_k$ , in the reference finite element, defines the Lagrange finite element family since the interpolating functions obtained by employing Eqs. (2.12) and (2.14) are the Lagrange polynomials [18–20]. The functional  $\mathcal{F}_{\ell_k}^L$  is a point evaluation in the  $N_k = n_k$  geometrical nodes, which imposes no condition on the derivatives of  $\phi_{i_k}$  at the boundary of  $\Omega_k$ , therefore the Lagrange finite element family returns a set of  $N_k = n_k$  interpolating functions with no continuous first derivative between finite elements. One linear functional which does return interpolating functions with continuous first derivatives is the following:

$$\mathcal{F}_\ell^H[f(\xi)] = f(\xi_{\ell_k}), \quad \text{and} \quad \mathcal{F}_{\ell'_k}^H[f(\xi)] = \hat{\mathbf{t}} \cdot \nabla f(\xi_{\ell'_k}) = 0, \quad (2.15)$$

## 2.2 Numerical Approach to the Light Scattering Problem

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**Fig. 2.2:** Interpolating functions of **a)** a Lagrange cubic 1D reference finite element and **b)** a serendipity Lagrange quadratic 2D triangular reference element. The markers corresponds to the evaluation of the linear functionals [Eqs. (2.12) and (2.14)] on the interpolating functions on each case.

with  $\xi_{\ell_k}$  one of the  $n_k$  geometric nodes in  $\Omega_k$ ,  $\xi_{\ell'_k}$  one of the  $n'_k$  geometric nodes at vertices of  $\Omega_k$ , and  $\hat{\mathbf{t}}$  is a unit vector parallel to its edges [19]. The functional in Eq. (2.15) give rise to the Hermite finite element family since the resulting interpolating functions are the Hermite polynomials, which allows for a solution on  $\Omega$  1-differentiable due to its  $N_k = n_k + n'_k$  degrees of freedom [18, 19]. The Lagrange and the Hermite finite element families are two of the most common and simple nevertheless, one can build yet another family known as the serendipity finite element family if the geometrical nodes outside the boundary of  $\Omega_k$  are not considered in Eq. (2.14) [20]. In Fig. 2.2 the interpolating functions for a one and two dimensional finite elements under the Lagrange linear functional [Eq. (2.14)] are shown: a one dimensional cubic finite element [Fig. 2.2a)] and a serendipity triangular reference finite element of quadratic order.

## 2.2 Numerical Approach to the Light Scattering Problem

In chapter 1 the general theory of isolated scatterers in a non-absorbing media was developed and the particular case of spherical scatterers was approached analytically. In order to solve

the light scattering problem through numerical methods and thus allowing for more complex geometries, the fundamentals of the Finite Element Method (FEM) were introduced in section 2.1. Hereby, it is discussed the implementation of the FEM into the light scattering problem to find numerical approximations, in the weak sense, to the electric field  $\mathbf{E}(\mathbf{r})$  in finite domain  $\Omega$ . Due to the vectorial nature of the electric field, the interpolating—and trial—functions employed in the Galerkin method [Eq. (2.10)] are chosen to be vectorial functions instead of scalar, since a family of vectorial finite element can be chosen so the boundary conditions of the electric fields are easily met. In this section, the strong and weak formulation of the scattering of light are developed by employing such vectorial interpolating functions, and the corresponding finite elements are introduced, as well as the matrix representation of the light scattering problem. Lastly, additional conditions are imposed into the light scattering problem in order to solve it numerically through the FEM.

### 2.2.1 Strong and Weak Formulation

The scattering light problem addressed in chapter 1 corresponds to a steady-state problem in a domain  $\Omega$  whose optical properties are characterized by its electric permittivity  $\varepsilon$  and magnetic permeability  $\mu$ , which in general are functions of the angular frequency  $\omega$ . To obtain the strong formulation of the light scattering, let us assume harmonic time dependent electric  $\mathcal{E}(\mathbf{r}, t)$  and magnetic fields  $\mathcal{H}(\mathbf{r}, t)$ :

$$\mathcal{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) \exp(-i\omega t), \quad \text{and} \quad \mathcal{H}(\mathbf{r}, t) = \mathbf{H}(\mathbf{r}) \exp(-i\omega t), \quad (2.16)$$

with  $\mathbf{E}(\mathbf{r})$  and  $\mathbf{H}(\mathbf{r})$  complex valued vectors. For harmonic time dependent EM fields, the Maxwell's equation are rewritten as [19, 21]

$$\nabla \cdot (\varepsilon \mathbf{E}) = \rho_{\text{ext}}, \quad \text{(Electric Gauss's law)}, \quad (2.17a)$$

$$\nabla \cdot \mathbf{B} = 0, \quad \text{(Magnetic Gauss's law)}, \quad (2.17b)$$

$$\nabla \times \mathbf{E} = i\omega \mu \mathbf{H}, \quad \text{(Faraday-Lenz's law)}, \quad (2.17c)$$

$$\nabla \times (\mu \mathbf{H}) = \mathbf{J} - i\omega \varepsilon \mathbf{E}, \quad \text{(Ampère-Maxwell's law)}, \quad (2.17d)$$

where  $\rho_{\text{ext}}$  is the external volumetric charge density,  $\mathbf{J}$  is the volumetric current density and  $\mathbf{B} = \mu \mathbf{H}$ . The volumetric current density is given by [19]

$$\mathbf{J}(\mathbf{r}, t) = \mathbf{J}_{\text{ext}}(\mathbf{r}) \exp(-i\omega t) + \sigma \mathbf{E}(\mathbf{r}) \exp(-i\omega t). \quad (2.18)$$

where the  $\mathbf{J}_{\text{ext}}$  corresponds to external current density,  $\sigma$  is the frequency dependent conductivity of the domain  $\Omega$  and the term  $\sigma \mathbf{E}(\mathbf{r}) \exp(-i\omega t)$  arises from a ohmic response of the domain  $\Omega$ .

The Maxwell's equations can be decouple to avoid working with two unknown functions, yielding [19, 21, 22]

$$\nabla \times [\mu^{-1} \nabla \times \mathbf{E}] - (i\omega \sigma + \omega^2 \varepsilon) \mathbf{E} = i\omega \mathbf{J}_{\text{ext}}. \quad (2.19)$$

which is another formulation of the vectorial Helmholtz equation [Eq. (1.13)]. The Eq. (2.19) is obtained by isolating  $\mathbf{H}$  in the Faraday-Lenz's law, calculating its curl and, then, substituting

with the Ampère-Maxwell's law and the Eq. (2.18). In the absence of an external current and charge densities, Eq. (2.19) becomes the Maxwell eigenvalue problem [19], which corresponds to the strong formulation of the light scattering problem alongside the boundary conditions stated by Maxwell's equations [Eqs. (2.17)]. Therefore, the strong formulation of the light scattering problem is given by [19, 21, 22]

### Maxwell's Eigenvalue Problem and Boundary Conditions (Strong Formulation)

$$\nabla \times [\mu^{-1} \nabla \times \mathbf{E}] - \kappa^2 \mathbf{E} = 0, \quad \text{with } \kappa^2 = (i\omega\sigma + \omega^2\varepsilon), \quad (2.20a)$$

$$\hat{\mathbf{n}} \times \mathbf{E}(\mathbf{r}) \Big|_{\partial\Omega} = \mathbf{E}_D, \quad (\text{Dirichlet Boundary Condition}), \quad (2.20b)$$

$$\mu^{-1} \nabla \times \mathbf{E} \times \hat{\mathbf{n}} \Big|_{\partial\Omega} = \mathbf{E}_N, \quad (\text{Neumann Boundary Condition}), \quad (2.20c)$$

with  $\partial\Omega$  the boundary of  $\Omega$  and  $\hat{\mathbf{n}}$  a normal vector to  $\partial\Omega$ . A Dirichlet type boundary condition is described in Eq. (2.20b) while the Eq. (2.20c) corresponds to Neumann type boundary condition. Both of such boundary condition are equivalent to Eq. (1.26) in section 1.2.2 when  $\mathbf{E}_D = \mathbf{E}_N = \mathbf{0}$ .

In order to build the weak formulation of the light scattering problem let us choose a set of  $N$  linearly independent vectorial interpolating functions  $\{\boldsymbol{\eta}_j\}_{j \leq N}$ . If the Eq. (2.20a) is projected onto one interpolating function  $\boldsymbol{\eta}_j$  and the resulting is integrated in the domain  $\Omega$ , one obtains

$$\int_{\Omega} \boldsymbol{\eta}_j \cdot \nabla \times [\mu^{-1} \nabla \times \mathbf{E}] d\Omega = \int_{\Omega} \kappa^2 \boldsymbol{\eta}_j \cdot \mathbf{E} d\Omega. \quad (2.21)$$

The left-hand side of Eq. (2.21) can be simplified by employing the vectorial identity  $\nabla \cdot (\mathbf{A} \times \mathbf{B}) = \mathbf{B} \cdot \nabla \times \mathbf{A} - \mathbf{A} \cdot \nabla \times \mathbf{B}$ , with  $\mathbf{A} = \boldsymbol{\eta}_j$  and  $\mathbf{B} = \mu^{-1} \nabla \times \mathbf{E}$ , and performing a one-fold integration by parts, yielding

$$\begin{aligned} \int_{\Omega} \boldsymbol{\eta}_j \cdot \nabla \times [\mu^{-1} \nabla \times \mathbf{E}] d\Omega &= \int_{\Omega} (\mu^{-1} \nabla \times \mathbf{E}) \cdot (\nabla \times \boldsymbol{\eta}_j) d\Omega + \\ &\quad - \oint_{\partial\Omega} [\boldsymbol{\eta}_j \times (\mu^{-1} \nabla \times \mathbf{E})] \cdot \hat{\mathbf{n}} d(\partial\Omega), \end{aligned} \quad (2.22)$$

where the last term in the right-hand side is obtained by the Gauss's Theorem. Substituting Eq. (2.21) into Eq. (2.22) and applying the boundary condition given by Eq. (2.20c), the Maxwell's eigenvalue problem in its weak formulation is obtained:

### Maxwell's Eigenvalue Problem and Boundary Conditions (Weak Formulation)

$$\int_{\Omega} \{ (\mu^{-1} \nabla \times \mathbf{E}) \cdot (\nabla \times \boldsymbol{\eta}_j) - \kappa^2 \cdot \mathbf{E} \cdot \boldsymbol{\eta}_j \} d\Omega - \oint_{\partial\Omega} (\boldsymbol{\eta}_j \times \mathbf{E}_N) \cdot \hat{\mathbf{n}} d(\partial\Omega) = 0, \quad (2.23a)$$

$$\hat{\mathbf{n}} \times \mathbf{E}(\mathbf{r}) \Big|_{\partial\Omega} = \mathbf{E}_D. \quad (2.23b)$$

The weak formulation problem of light scattering [Eq. (2.23a)] in the finite element approximation is reduced to the algebraic system of equations given by the Galerkin Method in

each one of the  $M$  subdomains  $\Omega_k$  of  $\Omega$  given by [19, 21]

$$\mathbb{A}\mathbf{e} = \mathbf{0}, \quad (2.24a)$$

with

$$A_{ij} = \int_{\Omega_k} \left\{ (\mu^{-1} \nabla \times \boldsymbol{\eta}_i) \cdot (\nabla \times \boldsymbol{\eta}_j) - \kappa^2 \cdot \boldsymbol{\eta}_i \cdot \boldsymbol{\eta}_j \right\} d\Omega_k - \oint_{\partial\Omega} (\boldsymbol{\eta}_j \times \mathbf{E}_N) \cdot \hat{\mathbf{n}} d(\partial\Omega), \quad (2.24b)$$

where  $A_{ij}$  are the matrix element of  $\mathbb{A}$  and  $\mathbf{e}$  is the vector containing the  $N$  coefficients of the linear combination of the interpolating function  $\boldsymbol{\eta}_j$  that results into an approximated solution  $\tilde{\mathbf{E}}(\mathbf{r}) = \sum_i e_i \boldsymbol{\eta}_j(\mathbf{r})$  to the electric field. The election of the coefficients  $e_i$ , its physical interpretation, and the set of the vectorial interpolating functions is discussed in the next section.

### 2.2.2 The Nédélec Finite Element Family

In order to perform the vectorial finite element approximation in Eq. (2.24) equivalently to the scalar method in Eq. (2.10b), an approximation  $\tilde{\mathbf{E}}$  to the electric field  $\mathbf{E}$  is proposed as linear combination of the vectorial interpolating functions  $\boldsymbol{\eta}_j$  with scalar coefficients  $e_i$ . If the nodal approximation [Eq. (2.6)] were used for linear combination setting the coefficients  $e_i$  as the exact solution of each component of electric field at some nodal points into the finite element  $\Omega_k$ , not only the boundary condition in Eq. (2.23b) might be difficult to meet [19, 21], but also some non-physical solutions may arise [22]. Therefore, instead of employing the nodal approximation, the expression of  $\tilde{\mathbf{E}}$  in a finite element  $\Omega_k$  of  $\Omega$  is given by [19]

$$\tilde{\mathbf{E}}(\mathbf{r}) = \sum_{i_k} e_{i_k} \boldsymbol{\eta}_{i_k}(\mathbf{r}), \quad \text{with} \quad e_i = \hat{\mathbf{t}}_{i_k} \cdot \mathbf{E}(\mathbf{r} \in E_{i_k}), \quad (2.25)$$

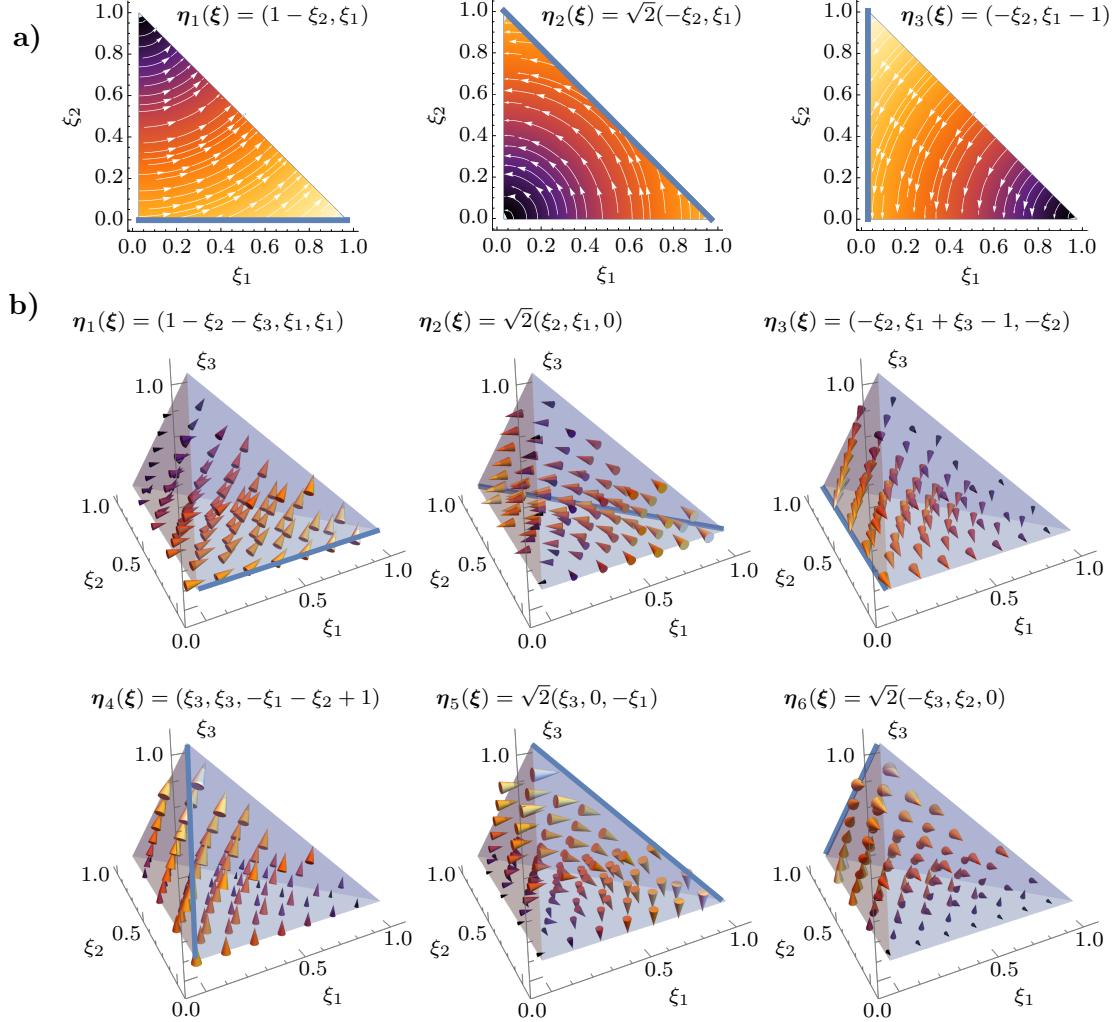
where  $E_{i_k}$  is the  $i_k$ -th edge in  $\Omega_k$ ,  $\hat{\mathbf{t}}_{i_k}$  a unitary vector parallel to  $E_{i_k}$  and  $e_{i_k}$  is the exact value of the tangential component of the electric field on it. If the interpolating functions  $\boldsymbol{\eta}_{i_k}$  in the element  $\Omega_k$  are to follow Eq. (2.20b), they must have a continuous tangential components across  $\partial\Omega_k$ , while no special requirement is asked for their normal component on  $\partial\Omega_k$ . A special family of vectorial—or edge—reference finite elements are given by the linear functional [19]

$$\mathcal{F}_{i_k}^N[\boldsymbol{\eta}_{\ell_k}(\xi)] = \frac{1}{|E_{i_k}|} \left( \int_{E_{i_k}} \hat{\mathbf{t}}_{i_k} \cdot \boldsymbol{\eta}_{\ell_k}(\xi) d(\partial\Omega_k) \right)^{1/2} = \delta_{i_k \ell_k} \quad (2.26)$$

which is the square-root mean value of the interpolating function along the edge  $E_{i_k}$ . The reference finite elements obtained from Eq. (2.26) are known as the Nédélec finite element of lowest order since their only degree of freedom is on the edges of the finite element [23]. For triangular and tetrahedral finite elements, a closed formula for  $\boldsymbol{\eta}_{i_k}$  is given by [19, 21, 22]

$$\boldsymbol{\eta}_{i_k} = |E_{i_k}| (\phi_{j_k} \nabla \phi_{\ell_k} - \phi_{\ell_k} \nabla \phi_{j_k}), \quad (2.27)$$

with cyclic permutation of the indices  $\{i_k, j_k, \ell_k\}$ , corresponding to the vertices of triangular surfaces forming the edges of the reference element. The scalar functions  $\phi_{j_k}$  in Eq. (2.27) are the interpolating functions obtained with the Lagrange linear operator [Eq. (2.14)] applied on  $\Omega_k$  at the vertices. Nédélec finite elements of higher orders can be obtained if, additionally, more degrees



**Fig. 2.3:** Interpolating functions for the lowest order Nédélec **a)** pyramidal (2D) and **b)** tetrahedral (3D) reference finite elements. The thick blue lines correspond to the edges where the linear functional of the Nédélec family [Eq. (2.26)] is evaluated.

of freedom are set to the faces and the volume of  $\Omega_k$  [23] nevertheless, their implementation is of greater difficulty and thus, less common [19, 21]. An example of Nédélec finite elements of lowest order are shown in Fig. 2.3a) for a triangular finite element and in Fig. 2.3b) for a tetrahedral finite element; the edge where Eqs. (2.26) and (2.27) are applied to is shown with a thick blue line in all cases. In all interpolating functions (2D and 3D) it can be seen that all functions  $\eta_i$  are divergentless inside the finite elements and their components parallel to the edges are zero except at the associated  $i_k$ -th edge. Therefore, the Nédélec finite elements are suited to solve Eq. (2.23) by following an exact evaluation for a given boundary condition, and by following the electric Gauss's law with no sources.

### 2.2.3 Open Boundary Conditions

In the previous sections the theory behind the FEM and how it is implemented into the light scattering problem [Eqs. (2.23)] was discussed. A special kind of boundary conditions, known as the Absorbing Boundary Conditions (ABC) are introduced in this section since numerical methods, such as the FEM, require the domain  $\Omega$ , where the electromagnetic fields are to be solved, to be of finite size [21, 22] while, in the scattering problem an infinite—or open—boundary is considered. The ABCs are required since they simulate an open domain with a finite domain  $\Omega$  by imposing that there are no reflections back into the domain due to the interaction between its boundary  $\partial\Omega$  and the scattered electric field [21, 22, 24]. Two of the most common ABCs are the Sommerfeld’s radiation condition—which describes the behavior of the electric field in the far field at  $\partial\Omega$ —and the Perfectly Matching Layer (PML)—which is a thin layer that covers  $\Omega$  and acts as a non-reflective material due to its geometry—[21]. Both of the previous ABCs are preferred over other kinds of ABC since they do not need the domain  $\Omega$  to grow considerably and thus are optimized for the FEM while its implementation faces no extra difficulties [21].

#### 2.2.3.1 Sommerfeld’s Radiation Condition

In 1912 Arnold Sommerfeld first stated its radiation condition in order to guarantee the uniqueness of the solution to the scalar Helmholtz equation [Eq. (1.15)] applied to the scalar potential  $\phi = \phi(\mathbf{r})$  [25]. Its condition for uniqueness can be found by substituting the scalar potential, generated by bounded sources, and the Green’s function to the scalar Helmholtz equation in a 3D domain  $\Omega$ , given by [6, 11]

$$(\nabla^2 + k^2)g(\mathbf{r}|\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \iff g(\mathbf{r}|\mathbf{r}') = \frac{\exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')]}}{\|\mathbf{r} - \mathbf{r}'\|}, \quad (2.28)$$

into Green’s second identity<sup>3</sup> leading to

$$4\pi\phi(\mathbf{r}) = \oint_{\partial\Omega} \frac{\exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')]}}{\|\mathbf{r} - \mathbf{r}'\|^2} \phi(\mathbf{r}') d^2r \oint_{\partial\Omega} \frac{d^2r}{\|\mathbf{r} - \mathbf{r}'\|^2} \left[ \|\mathbf{r} - \mathbf{r}'\| \left( \frac{\partial\phi(\mathbf{r})}{\partial r} - ik \cdot \hat{\mathbf{e}}_r \phi(\mathbf{r}) \right) \right]. \quad (2.29)$$

The boundary condition that the potential  $\phi$  must decay to zero as  $r \rightarrow \infty$  sets Eq. (2.29) equal to zero, which is hold immediately by its left hand side. The first integral in the right hand side of Eq. (2.29) equals zero since  $\phi(r \rightarrow 0) = 0$  while  $d^2r / \|\mathbf{r} - \mathbf{r}'\| \approx d^2r / r^2$  remains bounded, thus the term between brackets in the second integral must equal zero [25], that is

$$\lim_{r \rightarrow \infty} r \left( \frac{\partial\phi(\mathbf{r})}{\partial r} - ik\phi(\mathbf{r}) \right) = 0, \quad (2.30)$$

where it was assumed that  $\|\mathbf{r} - \mathbf{r}'\| \approx r$  and  $\mathbf{k} = k\hat{\mathbf{e}}_r$ . The Eq. (2.30) is known as the Sommerfeld’s radiation condition since it states that in the far field there can only be outgoing waves that decay uniformly in all directions [21, 22, 25].

<sup>3</sup>Let  $\psi$  and  $\phi$  be  $C^2$  in  $\Omega$ , then  $\int_{\Omega} (\psi \nabla^2 \psi - \phi \nabla^2 \psi) d^3r = \oint_{\partial\Omega} \hat{\mathbf{n}} \cdot (\psi \nabla \phi - \phi \nabla \psi) d^2r$ , with  $\hat{\mathbf{n}}$  a normal vector to the boundary  $\partial\Omega$  [11].

A generalization of the Eq. (2.30) to the electric field  $\mathbf{E}$  and the  $\mathbf{H}$  field, both of which are solution to the vectorial Helmholtz equation [Eq. (1.13)], can be obtained as follows: Substitution of  $\mathbf{E}$  —or  $\mathbf{H}$ — and the vectorial Green's function into the generalization for vector fields of Green's second identity<sup>4</sup> [25–27]. Yet, an equivalent derivation is achieved by separating the electromagnetic fields into two contributions and introducing two vectorial potentials according to the origin of their sources: magnetic and electric charges and currents induced into a bounded volume [21, 22]. Under such considerations, the electromagnetic fields can be written as:

$$\mathbf{E} = \mathbf{E}_e + \mathbf{E}_m, \quad \text{and} \quad \mathbf{H} = \mathbf{H}_e + \mathbf{H}_m, \quad (2.31)$$

where the subscript 'e' ('m') stands for the electric (magnetic) sources[21]. Substitution of Eqs. (2.31) into the time harmonic Maxwell's equations [Eqs. (2.17)] leads to

$$\nabla \cdot (\varepsilon \mathbf{E}_e) = \rho_{\text{ext}}, \quad (2.32a)$$

$$\nabla \cdot (\mu \mathbf{H}_e) = 0, \quad (2.32b)$$

$$\nabla \times \mathbf{E}_e = i\omega \mu \mathbf{H}_e, \quad (2.32c)$$

$$\nabla \times \mathbf{H}_e = \mathbf{J}_{\text{ext}} - i\omega \varepsilon \mathbf{E}_e, \quad (2.32d)$$

where  $\rho_m$  and  $\mathbf{J}_m$  are induced charge and current densities due to the magnetization of the sources [21]. From the magnetic Gauss's law applied on  $\mu \mathbf{H}_e$ , it is defined the vector potential  $\mathbf{A}$  and, analogously, the vector potential  $\mathbf{F}$  arises from the electric Gauss's law on  $\varepsilon \mathbf{E}_e$  [21]. Then, scalar potentials  $\phi_e$  and  $\phi_m$  for  $\mathbf{E}_e$  and  $\mathbf{H}_m$  are obtained from the Faraday-Lenz's law and the Ampère-Maxwell's law applied on them, accordingly [21]. If the electric scalar and vector potentials are chosen so that they follow the Lorenz gauge, and the same is imposed for the magnetic scalar and vector potential, that is  $\nabla \cdot \mathbf{A} = -i\omega \mu \varepsilon \phi_e$  and  $\nabla \cdot \mathbf{F} = -i\omega \mu \varepsilon \phi_m$  [11], then the EM fields are given by

$$\mathbf{E} = -\frac{\nabla[\nabla \cdot \mathbf{A}]}{i\omega \varepsilon \mu} + i\omega \mathbf{A} + \frac{1}{\varepsilon} \nabla \times \mathbf{F}, \quad \text{and} \quad \mathbf{H} = -\frac{\nabla[\nabla \cdot \mathbf{F}]}{i\omega \varepsilon \mu} + i\omega \mathbf{F} + \frac{1}{\mu} \nabla \times \mathbf{A}, \quad (2.33)$$

where the vectorial potentials  $\mathbf{A}$  and  $\mathbf{F}$  are also solution to Helmholtz equation on each component and thus can be expressed as [21]

$$\mathbf{A} = \frac{\mu}{4\pi} \int_{\Omega} \mathbf{J}_{\text{ext}} \frac{\exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')]}{\|\mathbf{r} - \mathbf{r}'\|} d\Omega', \quad \text{and} \quad \mathbf{F} = \frac{\varepsilon}{4\pi} \int_{\Omega} \mathbf{J}_m \frac{\exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')]}{\|\mathbf{r} - \mathbf{r}'\|} d\Omega', \quad (2.34)$$

In the far field regime it follows that  $\|\mathbf{r} - \mathbf{r}'\|^{-1} \approx r^{-1}$  and  $\mathbf{k} \cdot \mathbf{r} = kr$  [6, 11], therefore

$$\mathbf{A} = \frac{\mu \exp(ikr)}{4\pi r} \mathbf{N}, \quad \text{with} \quad \mathbf{N} = \int_{\Omega} \mathbf{J}_{\text{ext}} \exp(-i\mathbf{k} \cdot \mathbf{r}') d\Omega' \quad (2.35a)$$

$$\mathbf{F} = \frac{\varepsilon \exp(ikr)}{4\pi r} \mathbf{L}, \quad \text{with} \quad \mathbf{L} = \int_{\Omega} \mathbf{J}_m \exp(-i\mathbf{k} \cdot \mathbf{r}') d\Omega' \quad (2.35b)$$

and that also the nabla operator  $\nabla$  acts as  $\nabla \rightarrow i\mathbf{k} = ik\mathbf{e}_r$  since the electric field can be written as a plane traveling in the  $\mathbf{k}$  direction [6, 21]. Substituting Eqs. (2.35) into Eq. (2.33) leads to

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<sup>4</sup>This can be obtained if Eq. (2.19) is subtracted by itself interchanging  $\boldsymbol{\eta}_j$  and  $\mathbf{E}$  and setting  $\boldsymbol{\eta}_i(\mathbf{r}) = \mathbf{n}g(\mathbf{r}|\mathbf{r}')$  as explained in [11]

the following expressions for the electromagnetic field in the far field regime [21]:

$$\lim_{r \rightarrow \infty} \mathbf{E} = -ik \frac{\exp(ikr)}{4\pi r} \left[ \hat{\mathbf{e}}_r \times \mathbf{L} - \sqrt{\frac{\mu}{\varepsilon}} (\mathbf{N} - (\hat{\mathbf{e}}_r \cdot \mathbf{N}) \hat{\mathbf{e}}_r) \right] \quad (2.36a)$$

$$\lim_{r \rightarrow \infty} \mathbf{H} = ik \frac{\exp(ikr)}{4\pi r} \left[ \sqrt{\frac{\varepsilon}{\mu}} (\mathbf{L} - (\hat{\mathbf{e}}_r \cdot \mathbf{L}) \hat{\mathbf{e}}_r + \hat{\mathbf{e}}_r \times \mathbf{N}) \right] \quad (2.36b)$$

where the dispersion relation  $k^2 = \omega^2 \mu \varepsilon$  was employed. From Eq. (??) it can be seen that the EM fields in the far field regime have no radial components and, by calculating the cross product  $\hat{\mathbf{e}}_r \times \mathbf{E}$  in the far field, an comparing with Eq. (2.36b), one obtains

$$\lim_{r \rightarrow \infty} \left( \hat{\mathbf{e}}_r \times \mathbf{E} - \sqrt{\frac{\mu}{\varepsilon}} \mathbf{H} \right) = 0, \quad (2.37)$$

which states that the electric field is perpendicular to the direction of propagation and to the  $\mathbf{H}$  field in the far field and that their amplitudes have a fixed ratio of  $\sqrt{\mu/\varepsilon}$ , known as the impedance of the medium [21, 25]. Lastly, Eq. (2.37) can be rewritten in terms of only  $\mathbf{E}$  with aide of the Faraday-Lenz's law and relation of dispersion for a plane wave, which yield to the generalization of the Eq. (2.30),

#### Generalized Sommerfeld or Silver-Müller Radiation Condition

$$\lim_{r \rightarrow \infty} r(\nabla \times \mathbf{E} - ik\hat{\mathbf{e}}_r \times \mathbf{E}) = 0 \quad (2.38)$$

which is also known as the Silver-Müller radiation condition [26, 27].

The implementation of the light scattering problem [Eq. (2.23)] into numerical methods, such as the FEM, has the disadvantage that it is a problem solved in an unbounded, or an open, domain. Nevertheless, the evaluation of Eq. (2.38) into  $\partial\Omega$  guarantees that the obtained solution reproduces that of the light scattering [21, 22]. Since the Sommerfeld's radiation condition is a non-homogeneous Neumann boundary condition, it requires Eq. (2.38) to be evaluated at a surface, with a normal vector  $\hat{\mathbf{n}}$ . Due to its integration on  $\partial\Omega$ , Sommerfeld's radiation condition is mostly used when the scatterer into  $\Omega$  is small relative to itself and when the scattered electric field normally illuminates the boundary [21, 22]. Were any of these conditions are not met, another ABC be implemented.

#### 2.2.3.2 Perfectly Matching Layer

The PML is a ABC described by a mathematical domain  $\Omega_{\text{PML}}$  [21] that surrounds  $\Omega$ , where Eq. (2.23) is to be solved, which has the property that any reflection on its boundary is damped [21, 22, 24]. The PML was originally developed by Berenger [28] in 1994 as a highly absorbing media for finite differences time domain simulations and then it was porposed as a *complex coordinate stretching* viewpoint [24], thus attributing the non-reflectivity of the PML to its geometric properties. The FEM solution to the scattering problem with time harmonic dependency, such as described in Eq. (2.23), exploits the later approach since the introduction of the PML do not modifies the methof [21].

In order to determine which conditions are needed for the PML to damp all reflections in  $\Omega$ , let us use stretched coordinates on the PML domain  $\Omega_{\text{PML}}$  where it is assumed that the far field approximation of the electromagnetic fields is valid. Thus, the gradient in such coordinate system can be written as

$$\nabla_s \equiv \left( \frac{\hat{\mathbf{e}}_x}{s_x} \frac{\partial}{\partial x} + \frac{\hat{\mathbf{e}}_y}{s_y} \frac{\partial}{\partial y} + \frac{\hat{\mathbf{e}}_z}{s_z} \frac{\partial}{\partial z} \right) \rightarrow \mathbf{k} = \frac{k_x}{s_x} \hat{\mathbf{e}}_x + \frac{k_y}{s_y} \hat{\mathbf{e}}_y + \frac{k_z}{s_z} \hat{\mathbf{e}}_z, \quad (2.39a)$$

where the subscript 's' stands for stretched and  $\mathbf{k}$  is the wave vector of the traveling electric plane wave in the far field. The stretching factors  $s_{x_i}$ , with  $x_i \in \{x, y, z\}$ , depend only on the coordinate of its stretching direction, that is,  $s_{x_i} = s_{x_i}(x_i)$  and are, in general, complex quantities [21, 24]; on the domain  $\Omega$ , outside the PML, the scale factors are equal to one. Additionally, the divergence and curl operators in the stretched coordinate system are [29]:

$$\nabla_s \cdot \mathbf{v} = \frac{1}{s_x s_y s_z} \nabla \cdot [\text{diag}(s_y s_z, s_x s_z, s_x s_y) \mathbf{v}], \quad (2.39b)$$

$$\nabla_s \times \mathbf{v} = \text{diag} \left( \frac{1}{s_y s_z}, \frac{1}{s_x s_z}, \frac{1}{s_x s_y} \right) \nabla \times [\text{diag}(s_x, s_y, s_z) \mathbf{v}], \quad (2.39c)$$

where  $\mathbf{v} = v_x \hat{\mathbf{e}}_x + v_y \hat{\mathbf{e}}_y + v_z \hat{\mathbf{e}}_z$  is an arbitrary vector and  $\text{diag}(a, b, c)$  is a matrix whose only non-zero elements are its arguments placed along its diagonal. From Eq. (2.39a), the dispersion relation of a plane wave is

$$\mathbf{k} \cdot \mathbf{k} = k^2 = \mu \epsilon \omega^2 = \left( \frac{k_x}{s_x} \right)^2 + \left( \frac{k_y}{s_y} \right)^2 + \left( \frac{k_z}{s_z} \right)^2 \quad (2.40)$$

whose solution is given by [21, 24]

$$k_x = k s_x \sin \theta \cos \varphi, \quad k_y = k s_y \sin \theta \sin \varphi, \quad \text{and} \quad k_z = k s_z \cos \theta. \quad (2.41)$$

with  $\varphi$  and  $\theta$  the azimuthal and polar angles. If any of the stretching factors are chosen so that  $\text{Im}[s_{x_i}] < 0$ , then the EM fields in the PML decay exponentially in the  $x_i$ -direction.

In between the domains  $\Omega$  and  $\Omega_{\text{PML}}$  there is a boundary, which can be locally considered as a plane interface. The Fresnel's reflection amplitude coefficients—for s- and p-polarization relative to the boundary between the domains—can be defined as usual since the ratio of the incident and the reflected electric field in the stretched coordinate system does not depend on any stretching coefficient  $s_{x_i}$  [21, 24]. From the continuity of the tangential component of the electric field, the reflection amplitude coefficients for both polarization states are [6]

$$r_s = \frac{k_z^{(\text{PML})} s_z^{(\text{PML})} \mu_{\text{PML}} - k_z^{(\Omega)} s_z^{(\Omega)} \mu_{\Omega}}{k_z^{(\text{PML})} s_z^{(\text{PML})} \mu_{\text{PML}} + k_z^{(\Omega)} s_z^{(\Omega)} \mu_{\Omega}}, \quad \text{and} \quad r_p = \frac{k_z^{(\text{PML})} s_z^{(\text{PML})} \epsilon_{\text{PML}} - k_z^{(\Omega)} s_z^{(\Omega)} \epsilon_{\Omega}}{k_z^{(\text{PML})} s_z^{(\text{PML})} \epsilon_{\text{PML}} + k_z^{(\Omega)} s_z^{(\Omega)} \epsilon_{\Omega}}. \quad (2.42)$$

where the  $z$  component of the wave vector  $\mathbf{k}$  is perpendicular to the locally plane interface, and the superscripts denote whether the function are evaluated at  $\Omega$  or  $\Omega_{\text{PML}}$ . In a similar manner, the phase matching condition of the reflected and incident wave at the interface between  $\Omega$  and

$\Omega_k$  states that [21]

$$k^{(\text{PML})} s_x^{(\text{PML})} \sin \theta_{\text{PML}} \cos \varphi_{\text{PML}} = k^{(\Omega)} s_x^{(\Omega)} \sin \theta_{\Omega} \cos \varphi_{\Omega}, \quad (2.43a)$$

$$k^{(\text{PML})} s_y^{(\text{PML})} \sin \theta_{\text{PML}} \sin \varphi_{\text{PML}} = k^{(\Omega)} s_y^{(\Omega)} \sin \theta_{\Omega} \sin \varphi_{\Omega}. \quad (2.43b)$$

From Eqs. (2.40)–(2.43) it can be seen that the reflection amplitude coefficient for both polarization states vanish if the magnetic permeability and the electric permittivity, as well as the stretch coefficient  $s_x$  and  $s_y$ , of the PML matches those of the domain  $\Omega$  since such conditions leads to  $\varphi_{\text{PML}} = \varphi_{\Omega}$  and  $\theta_{\text{PML}} = \theta_{\Omega}$  [21]. Therefore, a prefect matching layer can be described as a thin film  $\Omega_{\text{PML}}$ , surrounding  $\Omega$ , with the following specifications

### Perfectly Matching Layer Conditions

$$\left. \begin{aligned} \varepsilon_{\Omega} &= \varepsilon_{\text{PML}}, & \mu_{\Omega} &= \mu_{\text{PML}} \\ s_x^{(\Omega)} &= s_x^{(\text{PML})}, & s_y^{(\Omega)} &= s_y^{(\text{PML})} \end{aligned} \right\} \implies r_s = r_p = 0, \quad (2.44)$$

Let us note that no condition have been established to the stretching coefficient  $s_z$  and that Eq. (2.44) is valid for any frequency  $\omega$ , any angle of incidence, and any value of the stretched coordinates in the parallel directions to the interface [21, 22]. The PML conditions allows non-zero transmission coefficients, thus incoming waves can arise due to the finite size of  $\Omega_{\text{PML}}$ ; to avoid such non-physical incoming waves,  $s_z$  is chosen as a complex quantity with a negative imaginary part, so the waves vanish exponentially after entering the PML domain [21, 24].

In order to employ the PML conditions [Eq. (2.44)] in the domain  $\Omega$  where the FEM is employed to solve the scattering problem [Eq. (2.23)], let us write the Maxwell's equation in the PML—with the complex stretched coordinate system [Eq. (2.39)]—in the stretched coordinate system employed in  $\Omega$ . To do so, let us relate the EM fields in the PML,  $\mathbf{E}^{(\text{PML})}$  and  $\mathbf{H}^{(\text{PML})}$ , to the EM fields in the domain  $\Omega$ ,  $\mathbf{E}^{(\Omega)}$  and  $\mathbf{H}^{(\Omega)}$ , as [21]

$$\mathbf{E}^{(\Omega)} = \text{diag}(s_x, s_y, s_z) \mathbf{E}^{(\text{PML})}, \quad \iff \quad \mathbf{E}^{(\text{PML})} = \text{diag}\left(\frac{1}{s_x}, \frac{1}{s_y}, \frac{1}{s_z}\right) \mathbf{E}^{(\Omega)}, \quad (2.45a)$$

$$\mathbf{H}^{(\Omega)} = \text{diag}(s_x, s_y, s_z) \mathbf{H}^{(\text{PML})}, \quad \iff \quad \mathbf{H}^{(\text{PML})} = \text{diag}\left(\frac{1}{s_x}, \frac{1}{s_y}, \frac{1}{s_z}\right) \mathbf{H}^{(\Omega)}. \quad (2.45b)$$

The Maxwell's equations in the domain  $\Omega_{\text{PML}}$  are written as in Eq. (2.17)—with no external sources—with the operators defined in Eq. (2.39) applied to  $\mathbf{E}^{(\text{PML})}$  and  $\mathbf{H}^{(\text{PML})}$  but they can be rewritten in the  $\Omega$  domain by substituting Eqs. (2.45) into them and isolating the operators in the non-stretched coordinates applied to  $\mathbf{E}^{(\Omega)}$  and  $\mathbf{H}^{(\Omega)}$ . This procedure yields [21]

$$\nabla_s \cdot (\varepsilon \mathbf{E}^{(\text{PML})}) = 0 \quad \implies \quad \nabla \cdot [\varepsilon \mathcal{A} \mathbf{E}^{(\Omega)}] = 0, \quad (2.46a)$$

$$\nabla_s \cdot (\mu \mathbf{H}^{(\text{PML})}) = 0 \quad \implies \quad \nabla \cdot [\mu \mathcal{A} \mathbf{H}^{(\Omega)}] = 0, \quad (2.46b)$$

$$\nabla_s \times \mathbf{E}^{(\text{PML})} = i\omega \mu \mathbf{H}^{(\text{PML})} \quad \implies \quad \nabla \times (\mathbf{E}^{(\Omega)}) = i\omega (\mu \mathcal{A}) \mathbf{H}^{(\Omega)}, \quad (2.46c)$$

$$\nabla_s \times (\mu \mathbf{H}^{(\text{PML})}) = -i\omega \varepsilon \mathbf{E}^{(\text{PML})} \quad \implies \quad \nabla \times [\mu \mathcal{A} \mathbf{E}^{(\Omega)}] = -i\omega (\varepsilon \mathcal{A}) \mathbf{E}^{(\Omega)}. \quad (2.46d)$$

where  $\Lambda$  is given by

$$\Lambda = \text{diag}\left(\frac{s_y s_z}{s_x}, \frac{s_x s_z}{s_y}, \frac{s_x s_y}{s_z}\right). \quad (2.47)$$

Within the approach in Eqs. (2.46), the PML can be implemented into the weak formulation of the scattering problem by introducing a homogeneous, but anisotropic, optical response to the material that embeds the scatterers, and thus, simulate an infinite embedding media [21, 22, 24]. Comparing the Maxwell's equations representation in Eqs. (2.17) and (2.46), the anisotropy of the media is introduced into the weak formulation of the scattering problem [Eq. (2.23)] by replacing  $\mathbf{E}$  by  $\Lambda\mathbf{E}$  [21].

As stated in the PML conditions [Eq. (2.44)], the scalar values of  $\varepsilon$  and  $\mu$ , and of  $s_x$  and  $s_y$ , must match in the medium surrounding the scatterers and in the PML domain. The anisotropy of the dielectric function sets  $s_x = s_y = s_z = 1$  in  $\Omega$  so the scattering problem is described exactly as in Eq. (2.23). In order to guarantee no incoming waves in the domain  $\Omega$  due to the finite size of  $\Omega_{\text{PML}}$ , let us choose  $s_z$  with a negative imaginary part in  $\Omega_{\text{PML}}$ . Lastly, anisotropy is introduced into the finite element formulation of the scattering problem [Eqs. (2.24)] by including the matrix  $\Lambda$  as discussed above. Therefore, the PML implementation into the FEM is summarized as follows

#### Perfectly Matching Layer Implementation into Finite Element Method

$$\Lambda\mathbf{e} = \mathbf{0} \quad \text{with} \quad \Lambda \text{ and } \mathbf{e} \text{ as in Eqs. (2.24)}, \quad (2.48a)$$

$$\Lambda = \text{diag}\left(s_z, s_z, s_z^{-1}\right), \quad \text{with} \quad s_z = 1 \text{ in } \Omega \text{ and } \text{Im}[s_z] < 0 \text{ in } \Omega_{\text{PML}}, \quad (2.48b)$$

$$(\mu^{-1}\nabla \times \boldsymbol{\eta}_i) \cdot (\nabla \times \boldsymbol{\eta}_j) \rightarrow (\Lambda^{-1}\mu^{-1}\nabla \times \boldsymbol{\eta}_i) \cdot (\nabla \times \boldsymbol{\eta}_j), \quad (2.48c)$$

$$\boldsymbol{\eta}_i \cdot \boldsymbol{\eta}_j \rightarrow \boldsymbol{\eta}_i \cdot \Lambda \boldsymbol{\eta}_j, \quad (2.48d)$$

which is valid for any angular frequency  $\omega$ . As a last comment, Eq. (2.48) solves the scattering problem within the domain  $\Omega$  but the obtained values of the scattered EM fields in  $\Omega_{\text{PML}}$  have no physical meaning and are of no concern [21].

## 2.3 Finite Element Method and Analytical Solutions

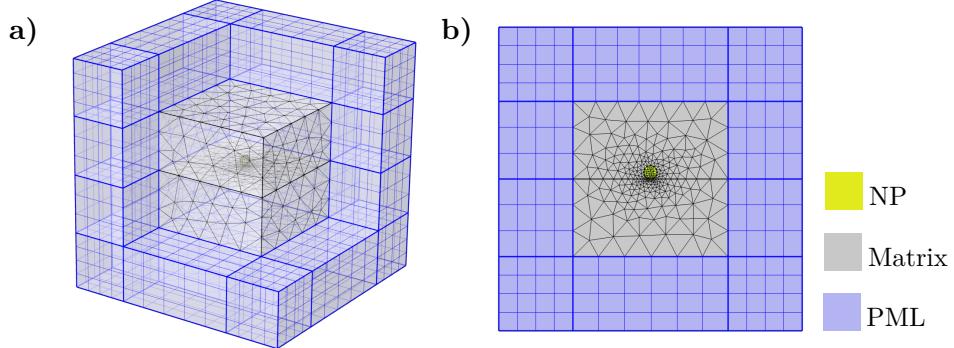
The light scattering problem in its weak formulation, and assuming harmonic time dependency [Eqs. (2.23)], can be solved by means of the so-called FEM in the frequency domain, given by Eqs. (2.24). There are several software that allow the user to introduce the desired geometry, physical properties of the system, and boundary conditions in order to calculate the scattered electric field through the FEM. Examples of commercial FEM software with the capability to solve Eqs. (2.23) are Altair HyperWorks and CTS StudioSuite as well as open-source alternatives, such as Elmer and OpenFOAM. Nevertheless in this work, the commercial software COMSOL Multiphysics™ Ver. 5.4 (COMSOL) was employed; for a more technical description of the performed COMSOL simulation see Appendix C.

## 2. THE FINITE ELEMENT METHOD

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The FEM implemented within COMSOL is based on the Galerkin Method [Eq. (2.10)] with a variety of finite element families, including, but not limited to, the Lagrange [Ec. (2.14)], the Hermite [Ec. (2.15)] and the lowest order Nédélec<sup>5</sup> families [Ec. (2.26)] [30]; such finite element families are built within COMSOL for different shapes in 2D and 3D geometries: triangles, rectangles, pyramids, prisms, tetrahedrons, and more [30]. The core of COMSOL allows the user to set the desired geometry of the PDE problem to be solved, as well as the discretization method and the matrix inversion algorithms to solve Eq. (2.10) [30]. Additionally, the COMSOL's package Wave Optics implements the Maxwell's eigenvalue problem —considering harmonic time dependency as in Eqs. (2.23) [30]— alongside the physical characteristics of the system: the optical properties, decoded into the electric permittivity and magnetic permeability, of different materials and the several boundary conditions such like the generalized Sommerfeld's radiation condition [Eq. (2.38)] or the PML [Eq. (2.44)] [31]. The Wave Optics module returns the total electric field and the user can separate it into two contribution: the incident  $\mathbf{E}^i$  and the induced  $\mathbf{E}^{ind}$  electric fields; the later corresponds to the scattered (internal) electric field  $\mathbf{E}^{sca}$  ( $\mathbf{E}^{int}$ ) outside (inside) any scatterers [31].

In order to minimize errors that may arise in simulations performed with COMSOL, the analytical solution given by the Mie Theory for the light scattering due to a spherical particle —introduced in section 1.2— was contrasted against an approximated solution returned by COMSOL. Since COMSOL's Documentation [30] recommends to let the software choose the kind of finite element<sup>6</sup> to be used, the only numerical characteristics analyzed were the size of the domain  $\Omega$ , its discretization into finite elements (mesh size)<sup>7</sup>, the discretization of the spherical scatterer, and the thickness of the PML used to simulate an open boundary. The geometry employed for the FEM approximated solution, built with COMSOL's internal tools, is shown in



**Fig. 2.4:** a) Three dimensional view and b) the cross section of the geometry employed to solve the light scattering due to a spherical NP (yellow) embedded into a non-absorbing matrix (gray) illuminated by a plane wave in COMSOL; the system is totally covered by a PML (blue) with rectangular geometry. The upper layer of the PML in a) is hidden to allow a better view of the setup.

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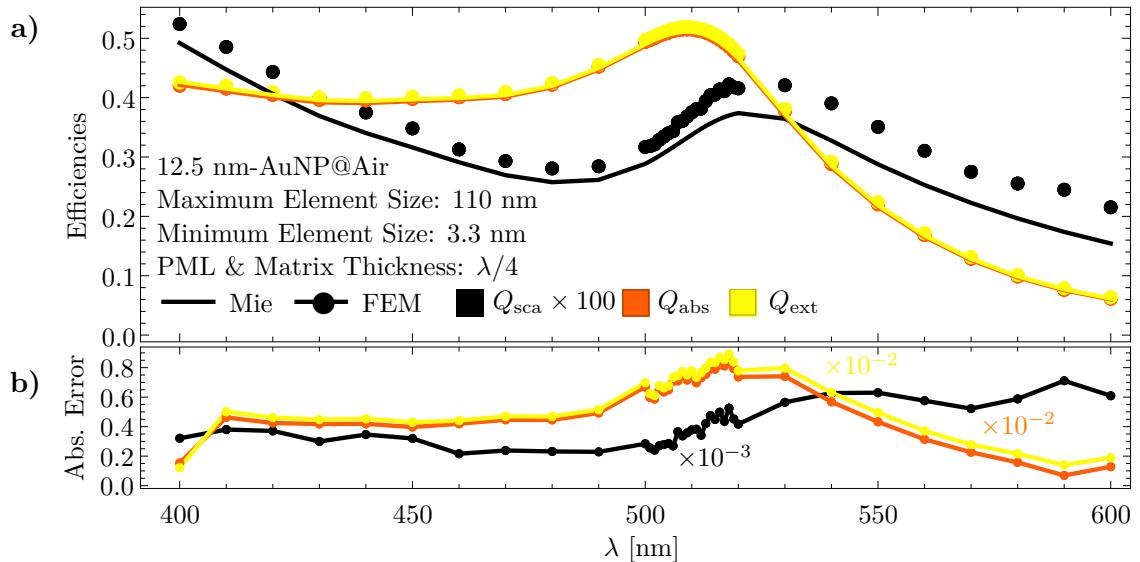
<sup>5</sup>Nédélec Elements of higher order are implemented in COMSOL for particular shapes only [30].

<sup>6</sup>The build geometries within COMSOL may require a transformation from the reference finite elements to the real finite elements but COMSOL's internal tools guarantee a non-vanishing Jacobian for such transformation since they are not highly deformed. See *Mesh Element Quality and size* in [30].

<sup>7</sup>COMSOL allows the user to set a minimum and a maximum size of the employed finite elements and these parameters can be chosen as global or local to specific regions [30].

Fig. 2.4 where a single spherical NP (yellow) is embedded into the middle of the box-shaped<sup>8</sup> matrix (gray) and this last is covered by a PML (blue) which allows the system to be studied as an infinite non-absorbing medium; the generalized Sommerfeld's radiation condition [Eq. (2.38)] was set in addition to the PML since it enhanced the performance of the COMSOL simulation. It is worth noting that COMSOL's internal tools proposes a meshing size by default [30] and that a thickness for the PML of a fourth of the wavelength  $\lambda$  of  $\mathbf{E}^i$  is recommended [31].

To contrast the solutions obtained analytically and through the FEM, the observable optical quantities in the far field regime, that is, the scattering  $Q_{\text{sca}}$ , absorption  $Q_{\text{abs}}$  and extinction  $Q_{\text{ext}}$  efficiencies were calculated with both approaches and contrasted. Since the FEM returns the value of the electric field in the whole domain  $\Omega$ , the Eqs. (1.8), (1.9) and (1.12) are employed to calculate  $Q_{\text{sca}}$ ,  $Q_{\text{sca}}$  and  $Q_{\text{sca}}$ , respectively, while they can be calculated with the Mie Theory through Eqs. (1.41) and (1.42) and the Optical Theorem. In Fig. 2.5a) the efficiencies  $Q_{\text{sca}}$  (black),  $Q_{\text{abs}}$  (orange) and  $Q_{\text{ext}}$  (yellow) are shown as a function of the incident wavelength  $\lambda$ , in the visible light regime, of the incoming electric plane wave  $\mathbf{E}^i$  that illuminates a AuNP of radius  $a = 12.5$  nm (employing the sized corrected dielectric function —see Appendix B— for its optical response) embedded into air (with refractive index  $n_m = 1$ ); the continuous lines corresponds to  $Q^{\text{Mie}}$ , the analytical solution calculated by the Mie Theory, and the markers to  $Q^{\text{FEM}}$  the approximated solution returned by COMSOL with the default values for the meshing size —global parameters applied to the whole domain  $\Omega$  and the PML—, the recommended size for the matrix —the minimum distance between the AuNP and the PML— and the recommended PML thickness; the values of these parameters are shown in Fig. 2.5a) as inset text. The absolute error (Abs. Error) between the analytical and the FEM approximated



**Fig. 2.5:** a) Scattering  $Q_{\text{sca}}$  (black), absorption  $Q_{\text{abs}}$  (orange) and extinction  $Q_{\text{ext}}$  (yellow) efficiencies of a 12.5 nm AuNP embedded into air calculated by means of the Mie Theory (continuous) and the FEM (markers), and b) their absolute error, as function of the wavelength  $\lambda$  of the incident plane wave.

<sup>8</sup>The box-shaped geometry was chosen so that in future work, the reflectance and transmittance of the system can be calculated by the internal functions of COMSOL, which requires a planar interface to act as a sensor.

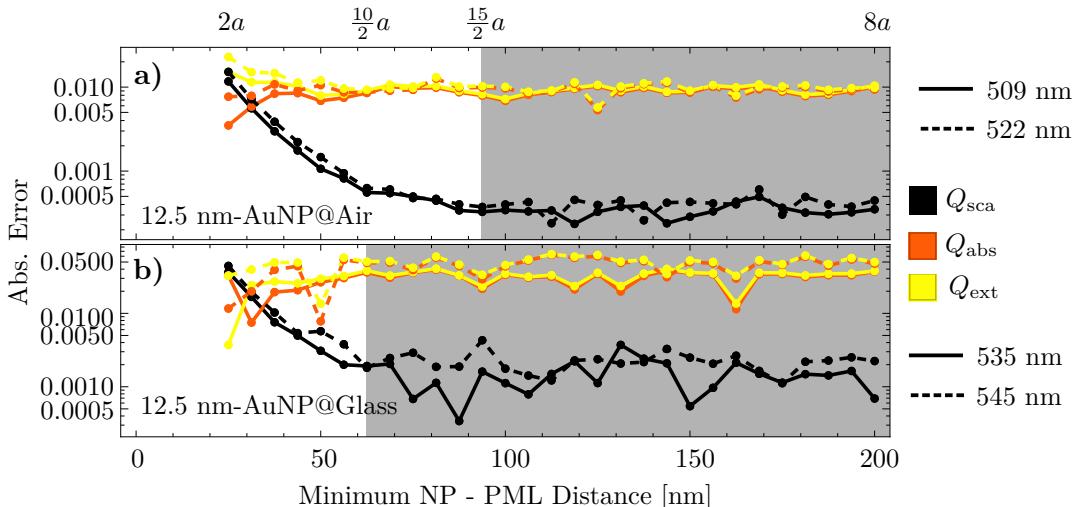
## 2. THE FINITE ELEMENT METHOD

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solution, given by  $|Q^{\text{Mie}} - Q^{\text{FEM}}|$ , is shown in Fig. 2.5b).

The results in Fig. 2.5a) show that the scattering efficiency of a 12.5 nm AuNP is two orders of magnitude smaller than the absorption efficiency, thus making absorption the most important contribution to the light extinction, as discussed in section 1.2.3. This behavior is reproduced by the FEM simulation as the absolute error of the efficiencies [Fig. 2.5b)] shows a discrepancy between the analytical and the approximated solution in the second digit after the decimal point for  $Q_{\text{abs}}$  and  $Q_{\text{ext}}$  and in the third digit after the decimal point for  $Q_{\text{sca}}$ . It is worth noting that the absolute error for the absorption efficiency is maximum at a wavelength  $\lambda \sim 509$  nm, which is the LSPR wavelength, while the absolute error for the scattering efficiency does not change significantly for  $\lambda < 521$  nm, the wavelength of maximum scattering, and it grows linearly with the incident wavelength. On the one hand, the absorption efficiency is calculated numerically by integrating  $\mathbf{E}^{\text{int}}$  in the volume of the AuNP [Eq. (1.9)], thus the associated error arises to the meshing inside the AuNP, which does not resolve  $\mathbf{E}^{\text{int}}$  enough for the value of  $\lambda$  that maximizes it. On the other hand, the scattering efficiency is obtained by integrating  $\mathbf{E}^{\text{sca}}$  on a closed surface outside the AuNP [Eq. (1.8)] —for the FEM simulations the boundary of the AuNP was chosen as the integration surface—, therefore the associated error is related, either to the meshing, or to unappropriated implementation of the boundary conditions to simulate an infinite matrix.

In order to analyze the effect of the size of the matrix on the numerical convergence of the FEM approximated solution, its absolute error against the analytical Mie Theory solution is shown in Fig. 2.6 for  $Q_{\text{sca}}$ ,  $Q_{\text{abs}}$  and  $Q_{\text{ext}}$  for two different systems: a 12.5 nm AuNP embedded in air [Fig. 2.6a)] and in glass [Fig. 2.6b)]. The efficiencies are evaluated at the LSPR wavelength (continuous lines) —507 nm for air and 533 nm for glass— and at the wavelength of maximum scattering (dash lines) —521 nm for air ad 543 for glass— where the error was maximum and where it started to grow, respectively, as seen in Fig. 2.5b). In Fig. 2.6 the efficiencies are plotted

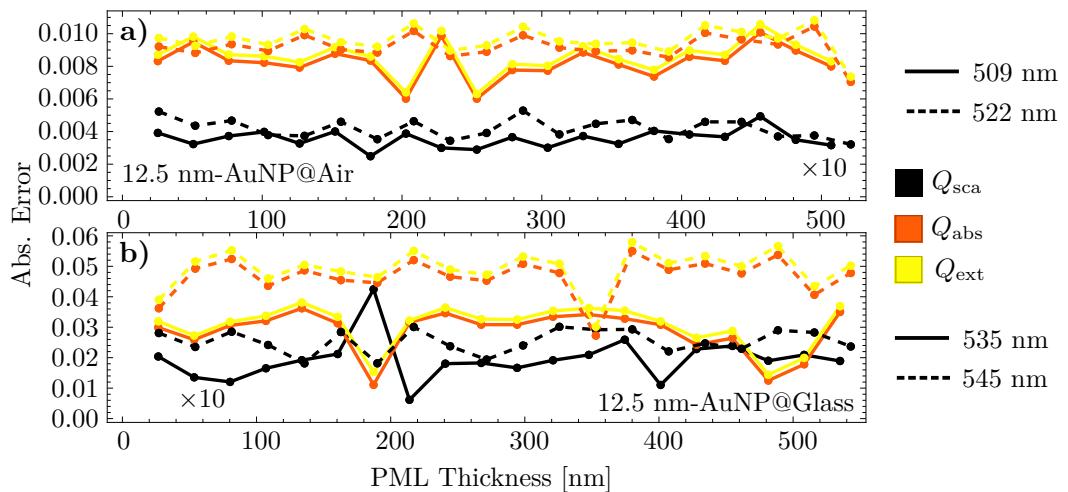


**Fig. 2.6:** Absolute error between the Mie Theory and the FEM approximated solution of the scattering (black), absorption (yellow) and extinction (orange) efficiencies of a 12.5 nm AuNP embedded **a)** in an air matrix ( $n_m = 1$ ) and **b)** in a glass matrix ( $n_m = 1.5$ ) as function of the matrix size. The FEM numerical simulation parameters were the default mesh size —maximum (minimum) element size of 110 nm (3.3 nm) globally— and the recommended  $\lambda/4$  PML thickness.

as functions of the minimum distance between the AuNP's surface and the PML, that is, as function of the size of the matrix; in the upper frame the distance is measured in unites of the AuNP's radius  $a = 12.5$  nm; the same element size and PML thickness as in Fig. 2.5, the default values, were employed.

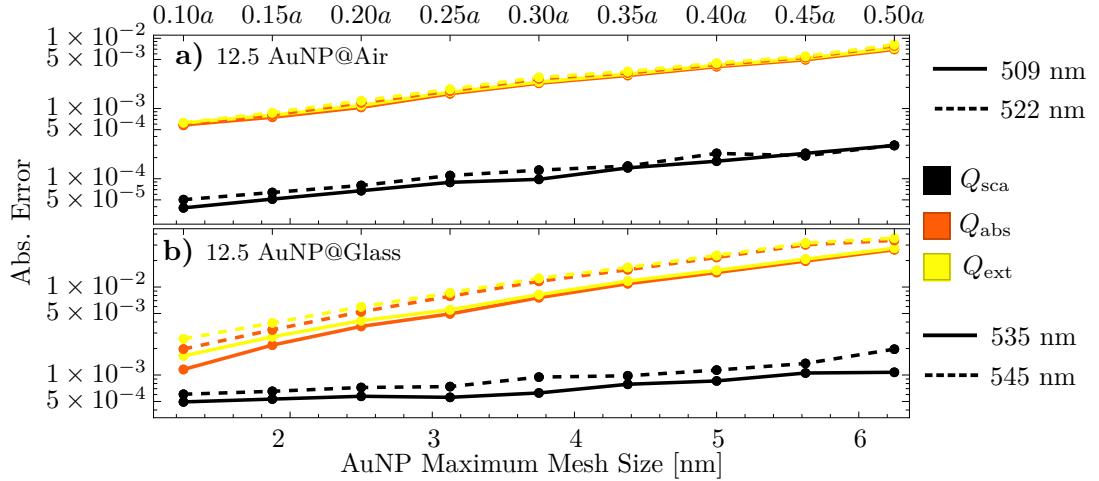
The absolute error on the absorption and extinction efficiency remains in the same order of magnitude independently of the matrix size for any matrix material and chosen wavelength, as it can be seen from the black and yellow lines in Fig. 2.6. However, the scattering efficiency does decrease its absolute error, linearly, as the matrix size grows up to a critical value,  $\sim 15a/2$  and  $\sim 10a/2$  for an air and a glass matrix, respectively, after which the relative error converges. The gray shades in Figs. 2.6a) and 2.6b) corresponds to the converged regime for each matrix material. Since the ratio between the critical value of the matrix size between the air and the glass matrix system is approximately 1.5, the refractive index of glass, a matrix of width  $\sim (15 + 1)an_m$  guarantees a minimum in the scattered electric field  $\mathbf{E}^{sca}$  due to the size of the matrix. This result is only valid for plasmonic NPs, such as the AuNPs, small compared to the incident wavelength, since the scattering is the least important contribution to extinction, as seen in Eq. 2.5a). The convergence of the absolute error on the scattering efficiencies is due to the Sommerfeld's radiation condition [Eq. (2.38)], which is an enough strong criteria to simulate an open boundary if the matrix is sufficiently big; this is supported by the absolute errors shown in Fig. 2.7 where they are plotted as function of the PML thickness considering a default meshing size —see values in Fig. 2.5a)— and a matrix width of  $(15 + 1)an_m$  for both an air [Fig. 2.7a)] and a glass [Fig. 2.7b)] matrix system, where none of the shown absolute errors change considerably.

From the analysis of Figs. 2.6 and 2.7, the absolute error on the scattering efficiency was decreased for a plasmonic NP small compared to the incident wavelength, such as a 12.5 AuNP



**Fig. 2.7:** Absolute error between the Mie Theory and the FEM approximated solution of the scattering (black), absorption (yellow) and extinction (orange) efficiencies of a 12.5 nm AuNP embedded **a)** in an air matrix ( $n_m = 1$ ) and **b)** in a glass matrix ( $n_m = 1.5$ ) as function of the PML thickness. The FEM numerical simulation parameters were the default mesh size —maximum (minimum) element size of 110 nm (3.3 nm) globally— and a matrix width of  $(15 + 1)an_m$ .

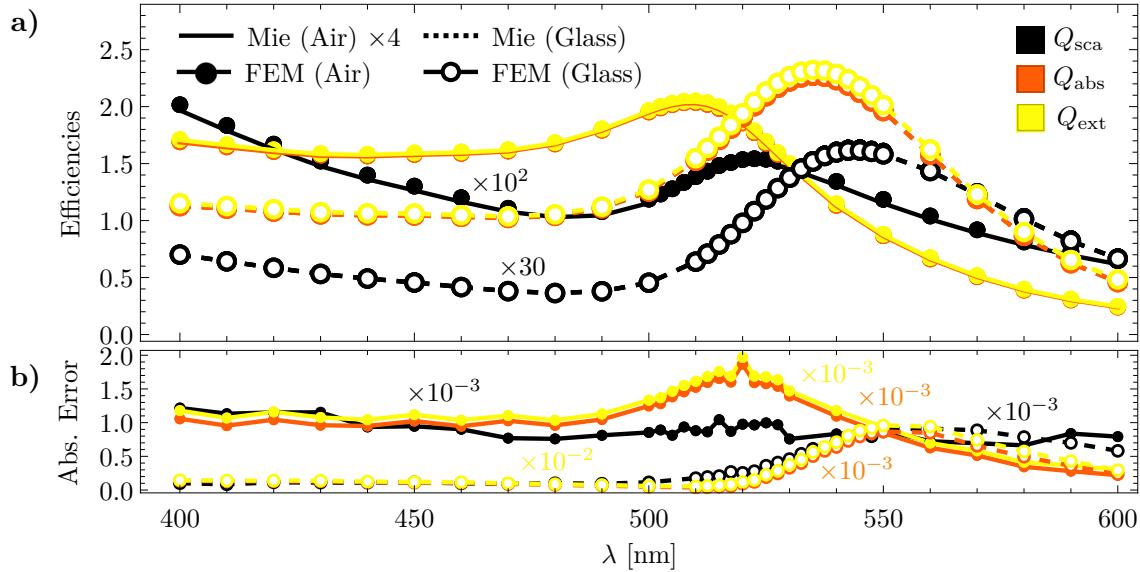
illuminated in the visible range. To diminish the absolute error on the absorption efficiency, and thus the extinction, a variation of the mesh size inside the AuNP was performed, while setting the default mesh size in the matrix but considering a recommended PML thickness of  $\lambda/4$  and a matrix width of  $(15 + 1)an_m$ . In Fig. 2.8 the absolute error of the scattering, absorption and extinction efficiencies are shown as function of the maximum mesh size inside 12.5 AuNP embedded in air [Fig. 2.8a)] and in glass [Fig. 2.8b)] at the wavelength of the LSPR and of the maximum scattering for each system. The variation of the minimum mesh size is shown in nanometers on the lower frame side and in fractions of the AuNP’s radius on the upper frame side.



**Fig. 2.8:** Absolute error between the Mie Theory and the FEM approximated solution of the scattering (black), absorption (yellow) and extinction (orange) efficiencies of a 12.5 AuNP embedded **a)** in an air matrix ( $n_m = 1$ ) and **b)** in a glass matrix ( $n_m = 1.5$ ) as function of the mesh size inside the AuNP. The FEM numerical simulation parameters were the default mesh size in the matrix—maximum (minimum) element size of 110 nm (3.3 nm)—, a matrix width of  $(15 + 1)an_m$  and a PML thickness of  $\lambda/4$ .

In Fig. 2.8, it can be seen that the absolute error of the efficiencies decreases exponentially as the mesh size inside the AuNP becomes finer for all the considered cases: air and glass matrices at two different wavelength each. Such behavior can be explained since the absorption (scattering) efficiency are obtained by integrating the internal (scattered) electric field at the AuNP’s volume (surface). Thus, a finer mesh at the scattered allows the induced electric field to be not only better resolve by the FEM, but also to increase the accuracy of the performed numerical integration. Additionally, the results in Fig. 2.8 show that the decrement of the absolute error on  $Q_{abs}$  has a higher rate than the decrement on the absolute error of  $Q_{sca}$  due to the node quantities in the volume and in the surface of the AuNP. Lastly, the refinement of the mesh size inside the AuNP, alongside with the chosen matrix width and PML thickness, guarantees a difference between the analytical Mie Theory solution and the approximated FEM solution up to the fourth digit after the decimal point both on the scattering and absorption efficiencies. If a refinement in the mesh side inside the matrix were to be done, the absolute error on the efficiencies may diminish even further, but such refinement may not be appreciable for the goals of this thesis. Therefore, the recommended mesh side in the matrix—maximum element size of  $\lambda/(6n_m)$  for first order finite elements [30]—is used as it is smaller than the default mesh size in this region.

Taking into account the results shown of Figs. 2.6–2.8 and the recommended maximum mesh size in the matrix, a converged result of the scattering, absorption and extinction efficiencies by means of the FEM is obtained. In Fig. 2.9 the optical efficiencies of a 12.5 nm AuNP embedded into an air and a glass matrix are shown as function of the incident wavelength  $\lambda$  as well as the relative error between the analytical (lines) and FEM (markers) results: the continuous lines and solid markers corresponds to the air matrix case while the dashed lines and open markers to the glass matrix case.



**Fig. 2.9:** a) Scattering  $Q_{\text{sca}}$  (black), absorption  $Q_{\text{abs}}$  (orange) and extinction  $Q_{\text{ext}}$  (yellow) efficiencies of a 12.5 nm AuNP embedded into air calculated by means of the Mie Theory (continuous lines) and the FEM (solid markers) and embedded into glass (dashed lines and open markers), and b) their absolute error, as function of the wavelength  $\lambda$  of the incident plane wave. The FEM numerical simulation parameters were the recommended mesh side in the matrix —maximum element size of  $\lambda/(6n_m)$ — and a maximum mesh side inside the AuNP of  $a/5$ , a matrix width of  $(15 + 1)a n_m$  and a PML thickness of  $\lambda/4$ .

By comparing the absolute error employing COMSOL's default values for the FEM simulation [Fig. 2.5b)] with optimized the parameters [Fig. 2.9b)] considering an air matrix, it can be seen that the later is an order of magnitud smaller for the absorption and extinction efficiencies in the visible spectrum, while the absolute error of the scattering efficiency between these election of parameters remains the same nevertheless, the FEM simulation with the optimized parameters required less computational resources. Additionally, the absolute errors of the optical efficiencies considering a AuNP embedded into a glass matrix are smaller for all efficiencies in the visible spectrum to those of a AuNP embedded into an air matrix. This behavior is explained by the nominal values of the optical efficiencies [Fig. 2.9a)] since the greater they are, the greater the induced electric field, that is, the induced electric fields are better resolved for more optically dense media and thus their absolute error diminish.



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## Chapter 3

# Results and Discussion

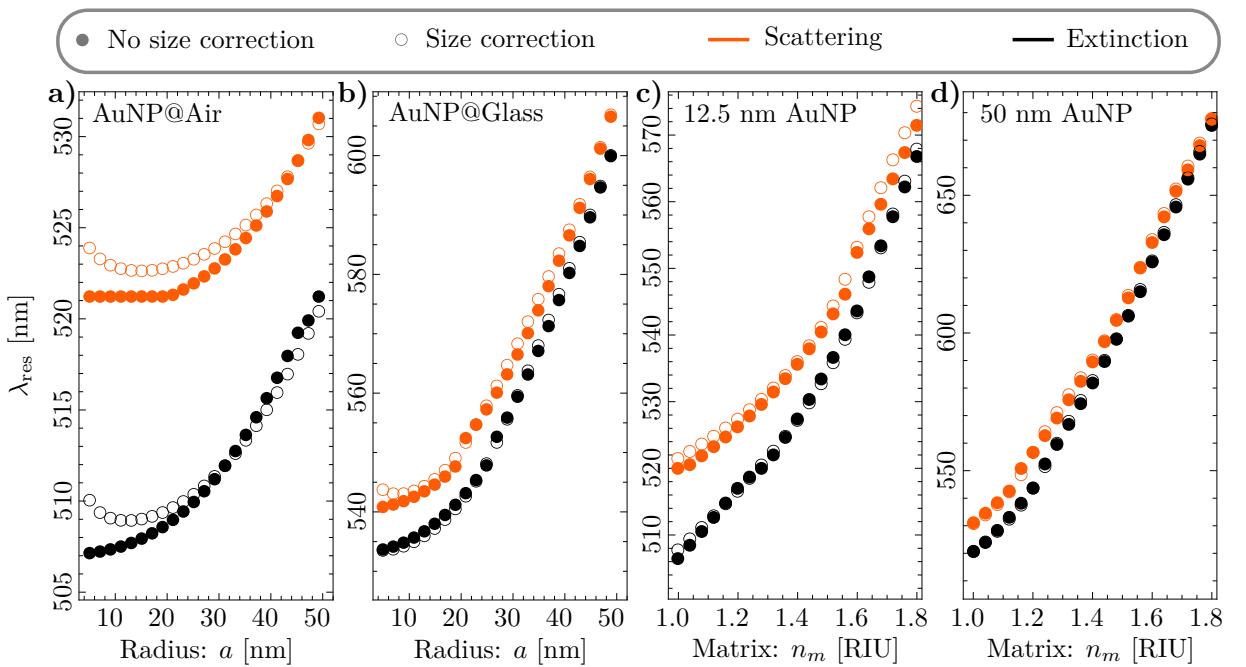
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### **3.1 Incrustation Degree of a Spherical Particle**

### **3.2 Future Work: Application on Metasurfaces**

### 3. RESULTS AND DISCUSSION

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**Fig. 3.1:** Resonance wavelength  $\lambda_{\text{res}}$  of the scattering (orange) and extinction (black) cross sections of a AuNP as function of the NP's radius when embedded **a)** into air ( $n_m = 1$ ) and **b)** into glass ( $n_m = 1.5$ ), and as function of the refractive index of the matrix  $n_m$  for a AuNP of radius equal to **c)** 12.5 nm and **d)** 50 nm, employing the dielectric function for the Au as reported by Johnson and Christy (filled circle) and considering a size correction to it (empty circle).

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Chapter 4

## Conclusions

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## Appendix A

# Mie Theory (Conventions)

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The Vector Spherical Harmonics (VSH) were defined in Sec. 1.2.1 in terms of their generating function  $\psi(r, \theta, \varphi)$  which must satisfy the scalar Helmholtz equation [Eq. (1.15)]. By employing the separation of variables method, it was determined that  $\psi$  is the product of either  $\sin(m\varphi)$  or  $\cos(m\varphi)$ , of the associated Legendre functions  $P_\ell^m(\cos\theta)$  and the spherical Bessel/Hankel functions  $z_\ell(kr)$ , all of which are solutions to Eqs. (1.16)-(1.20). In this section, it is discussed the chosen definitions for  $P_\ell^m$ ,  $z_\ell$  and related functions, as well as how to calculate them. It is also detailed how to code the Mie Theory results employing the Wolfram Language.

### Radial Dependency: Spherical Bessel/Hankel Functions

The radial dependency of the VSH is given by the two linearly independent solutions to Eq. (1.20) which are the spherical Bessel function of first and second kind  $j_\ell(\rho)$  and  $y_\ell(\rho)$ , respectively, related by the regular Bessel function of fractional order  $J_{\ell+1/2}(\rho)$  and  $Y_{\ell+1/2}(\rho)$  by

$$j_\ell(\rho) = \sqrt{\frac{\pi}{2\rho}} J_{\ell+1/2}(\rho), \quad \text{and} \quad y_\ell(\rho) = \sqrt{\frac{\pi}{2\rho}} Y_{\ell+1/2}(\rho). \quad (\text{A.1})$$

Another set of two linear independent solutions to Eq. (1.20) are the spherical Hankel functions of first ( $h_\ell^{(1)}$ ) and second kind ( $h_\ell^{(2)}$ ) given by

$$h_\ell^{(1)}(\rho) = j_\ell(\rho) + iy_\ell(\rho), \quad \text{and} \quad h_\ell^{(2)}(\rho) = j_\ell(\rho) - iy_\ell(\rho). \quad (\text{A.2})$$

Since the spherical Hankel functions are a linear combination of the Bessel spherical functions, they four obey the following recurrence relations

$$\frac{z_\ell(\rho)}{\rho} = \frac{z_{\ell-1}(\rho) + z_{\ell+1}(\rho)}{2\ell + 1}, \quad (\text{A.3})$$

$$\frac{dz_\ell(\rho)}{d\rho} = \frac{\ell z_{\ell-1}(\rho) - (\ell + 1)z_{\ell+1}(\rho)}{2\ell + 1}, \quad (\text{A.4})$$

with  $z_\ell$  any of the functions in Eqs. (A.1) and (A.2).

## Azimuthal Angular Dependency $\varphi$ : Sine, Cosine

Within this text, it was chosen the azimuthal solution to the scalar Helmholtz equation to be sines and cosines, so  $m$  can only take non negative integer values. These functions obey the orthogonality relations

$$\int_0^{2\pi} \sin(m\varphi) \sin(m'\varphi) d\varphi = \delta_{m,m'}(1 - \delta_{0,m})\pi, \quad (\text{A.5})$$

$$\int_0^{2\pi} \cos(m\varphi) \cos(m'\varphi) d\varphi = \delta_{m,m'}(1 + \delta_{0,m})\pi, \quad (\text{A.6})$$

$$\int_0^{2\pi} \cos(m\varphi) \sin(m'\varphi) d\varphi = 0, \quad (\text{A.7})$$

with  $\delta_{m,m'}$  the Kronecker delta.

## Polar Angular Dependence: Associated Legendre Functions and the Angular Functions $\pi_\ell$ and $\tau_\ell$

The solution to the polar angle equation are the associated Legendre functions and in this work they are defined as by Arfken and Weber [29], that is,

$$P_\ell^m(\mu) = (1 - \mu^2)^{m/2} \frac{d^m}{d\mu^m} P_\ell(\mu), \quad \text{with} \quad P_\ell(\mu) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\mu^\ell} (\mu^2 - 1)^\ell, \quad (\text{A.8})$$

where  $\mu = \cos \theta$  and  $P_\ell(\mu)$  are the Legendre polynomials with  $\ell$  a non negative integer. With such definition, the associated Legendre functions follows the orthogonality relation

$$\int_{-1}^1 P_\ell^m(\mu) P_{\ell'}^m(\mu) d\mu = \frac{2\delta_{\ell,\ell'}}{2\ell + 1} \frac{(\ell + m)!}{(\ell - m)!}. \quad (\text{A.9})$$

It was shown in Section 1.2.2 that the a plane wave can be written as a linear combination of the VSH with only  $m = 1$ , which lead to the definition of the angular functions  $\pi_\ell$  and  $\tau_\ell$  given by

$$\pi_\ell(\cos \theta) = \frac{P_\ell^1(\cos \theta)}{\sin \theta}, \quad \text{and} \quad \tau_\ell(\cos \theta) = \frac{dP_\ell^1(\cos \theta)}{d\theta},$$

which can be calculated recursively with Eq. (A.8) and the recurrence relations of the Legendre polynomials

$$(2\ell - 1)\mu P_{\ell-1}(\mu) = (\ell - 1)P_\ell(\mu) + \ell P_{\ell-2}(\mu), \quad (\text{A.10})$$

$$(1 - \mu)^2 \frac{dP_\ell(\mu)}{d\mu} = \ell P_{\ell-1}(\mu) - \ell \mu P_\ell(\mu). \quad (\text{A.11})$$

leading to

$$\pi_\ell(\mu) = \frac{2\ell - 1}{\ell - 1} \mu \pi_{\ell-1}(\mu) - \frac{\ell}{\ell - 1} \pi_{\ell-2}, \quad (\text{A.12})$$


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$$\tau_\ell(\mu) = \ell\mu\pi_\ell(\mu) - (\ell+1)\pi_{\ell-2}(\mu). \quad (\text{A.13})$$

where  $\pi_1(\mu) = 1$  according to Eq. (A.8) and where  $\pi_0(\mu) = 0$  is defined. Another notable result from Eq. (A.8) is that the angular functions  $\pi_\ell(\mu)$  and  $\tau_\ell(\mu)$ , when evaluated at  $\theta = 0$  ( $\mu = 1$ ), follows

$$\pi_\ell(\mu = 1) = \frac{dP_\ell(\mu)}{d\mu} \Big|_{\mu=1}, \quad (\text{A.14})$$

$$\tau_\ell(\mu = 1) = \left[ \frac{dP_\ell^1(\mu)}{d\mu} + (1 - \mu^2)^{1/2} \frac{d^2P_\ell(\mu)}{d\mu^2} \right] \Big|_{\mu=1} = \frac{dP_\ell(\mu)}{d\mu} \Big|_{\mu=1}, \quad (\text{A.15})$$

which can be obtained from the Legendre equation by setting  $m = 1$  and  $\mu = 1$  in Eq. (1.19), leading to

$$\pi_\ell(\mu = 1) = \tau_\ell(\mu = 1) = \frac{\ell(\ell+1)}{2} P_\ell(\mu = 1) = \frac{\ell(\ell+1)}{2}, \quad (\text{A.16})$$

where the last equality arises from the chosen definition of the Legendre polynomial [Eq. (A.8)].

The angular functions  $\pi_\ell$  and  $\tau_\ell$  are not orthogonal in general, nevertheless  $\pi_\ell(\mu) \pm \tau_\ell(\mu)$  are. To prove the orthogonality of  $\pi_\ell \pm \tau_\ell$  let us apply the Legendre equation [Eq. (1.17)] to  $P_\ell^m$  and multiply it by  $P_{\ell'}^m$ ; repeating this procedure inverting  $\ell$  and  $\ell'$  and adding both equations it is obtained that

$$\begin{aligned} & \frac{d}{d\theta} \left( \sin \theta P_{\ell'}^m(\mu) \frac{dP_\ell^m(\mu)}{d\theta} \right) + \frac{d}{d\theta} \left( \sin \theta P_\ell^m(\mu) \frac{dP_{\ell'}^m(\mu)}{d\theta} \right) + \\ & [\ell(\ell+1) + \ell'(\ell'+1)] P_{\ell'}^m(\mu) P_\ell^m(\mu) \sin \theta = 2 \left( \frac{mP_\ell^m(\mu)}{\sin \theta} \frac{mP_{\ell'}^m(\mu)}{\sin \theta} + \frac{dP_\ell^m(\mu)}{d\theta} \frac{dP_{\ell'}^m(\mu)}{d\theta} \right) \sin \theta, \end{aligned} \quad (\text{A.17})$$

where it was added  $2 dP_\ell^m/d\theta dP_{\ell'}^m/d\theta$  on both sides to complete the derivatives. Integrating Eq. (A.17) in the interval  $\theta \in (0, \pi)$ , or  $\mu \in (-1, 1)$ , and employing Eqs. (A.8) and (A.9), one obtains that

$$\int_{-1}^1 \left( \frac{mP_\ell^m(\mu)}{\sin \theta} \frac{mP_{\ell'}^m(\mu)}{\sin \theta} + \frac{dP_\ell^m(\mu)}{d\theta} \frac{dP_{\ell'}^m(\mu)}{d\theta} \right) d\mu = \delta_{\ell,\ell'} \frac{2\ell(\ell+1)}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!}. \quad (\text{A.18})$$

Additionally

$$\int_{-1}^1 \frac{mP_\ell^m(\mu)}{\sin \theta} \frac{dP_{\ell'}^m(\mu)}{d\theta} d\mu = \int_0^\pi mP_\ell^m(\mu) \frac{dP_{\ell'}^m(\mu)}{d\theta} d\theta = - \int_{-1}^1 \frac{mP_{\ell'}^m(\mu)}{\sin \theta} \frac{dP_\ell^m(\mu)}{d\theta} d\mu. \quad (\text{A.19})$$

where Eq. (A.8) was employed along integration by parts. Thus, combining Eqs. (A.18) and (A.19), it leads to

$$\int_{-1}^1 \left( \frac{mP_\ell^m(\mu)}{\sin \theta} \pm \frac{dP_\ell^m(\mu)}{d\theta} \right) \left( \frac{mP_{\ell'}^m(\mu)}{\sin \theta} \pm \frac{dP_{\ell'}^m(\mu)}{d\theta} \right) d\mu = \delta_{\ell,\ell'} \frac{2\ell(\ell+1)}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!}. \quad (\text{A.20})$$

The Eq. (A.20) is the orthogonality of  $\pi_\ell(\mu) \pm \tau_\ell(\mu)$  when  $m = 1$ , which also simplifies the right hand side to  $\delta_{\ell,\ell'} 2\ell^2(\ell+1)^2/(2\ell+1)$ .

## Vector Spherical Harmonics Orthogonality Relations

The VSH follow orthogonality relations inherited from the orthogonality of sine, cosine and the associated Legendre functions. Let us define the inner product as the integral in the solid angle between two vector functions as

$$\langle \mathbf{A}, \mathbf{A}' \rangle_{\Omega} = \int_0^{2\pi} \int_0^{\pi} \mathbf{A} \cdot \mathbf{A}' \sin \theta d\theta d\varphi. \quad (\text{A.21})$$

Under this inner product, all even VSH are orthogonal to the odd VSH, as well as all VSH with  $m \neq m'$ , due to the orthogonality of  $\sin(m\varphi)$  and  $\cos(m'\varphi)$ . The remaining orthogonality relations can be obtained by employing Eq. (A.18), leading to

$$\begin{aligned} \langle \mathbf{L}_{em'\ell}, \mathbf{L}_{em'\ell'} \rangle_{\Omega} &= \langle \mathbf{L}_{om\ell}, \mathbf{L}_{om\ell'} \rangle_{\Omega} \\ &= \delta_{m,m'} \delta_{\ell,\ell'} (1 \pm \delta_{m,0}) \frac{2\pi}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \left[ \left( k \frac{dz_{\ell}(kr)}{d(kr)} \right)^2 + \ell(\ell+1) \left( k \frac{z_{\ell}(kr)}{kr} \right)^2 \right], \end{aligned} \quad (\text{A.22})$$

$$\begin{aligned} \langle \mathbf{M}_{em\ell}, \mathbf{M}_{em\ell'} \rangle_{\Omega} &= \langle \mathbf{M}_{om\ell}, \mathbf{M}_{om\ell'} \rangle_{\Omega} \\ &= \delta_{m,m'} \delta_{\ell,\ell'} (1 \pm \delta_{m,0}) \pi \frac{2\ell(\ell+1)}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} z_{\ell}^2(kr), \end{aligned} \quad (\text{A.23})$$

$$\begin{aligned} \langle \mathbf{N}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_{\Omega} &= \langle \mathbf{N}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_{\Omega} \\ &= \delta_{m,m'} \delta_{\ell,\ell'} (1 \pm \delta_{m,0}) \pi \frac{2\ell(\ell+1)}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \left[ \left( \frac{z_{\ell}}{kr} \right)^2 + \left( \frac{1}{kr} \frac{d[krz_{\ell}(kr)]}{d(kr)} \right)^2 \right]. \end{aligned} \quad (\text{A.24})$$

$$\begin{aligned} \langle \mathbf{L}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_{\Omega} &= \langle \mathbf{L}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_{\Omega} \\ &= \delta_{m,m'} \delta_{\ell,\ell'} (1 \pm \delta_{m,0}) \pi \frac{2\ell(\ell+1)}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \left[ \frac{z_{\ell}}{kr} \frac{dz_{\ell}(kr)}{d(kr)} + \left( \frac{1}{kr} \frac{d[krz_{\ell}(kr)]}{d(kr)} \right)^2 \right] \end{aligned} \quad (\text{A.25})$$

where  $(1 + \delta_{m,0})$  is for odd VSH and  $(1 - \delta_{m,0})$  for even VSH. The orthogonality relations of the VSH can be further simplify by means of the recurrence relations of the spherical Bessel/Hankel functions [Eqs. (A.3) and (A.4)], which imply that

$$\left[ \left( k \frac{dz_{\ell}(kr)}{d(kr)} \right)^2 + \ell(\ell+1) \left( k \frac{z_{\ell}(kr)}{kr} \right)^2 \right] = k^2 [\ell z_{\ell-1}^2(kr) + \ell(\ell+1) z_{\ell+1}^2(kr)], \quad (\text{A.26})$$

$$\left[ \left( \frac{z_{\ell}}{kr} \right)^2 + \left( \frac{1}{kr} \frac{d[krz_{\ell}(kr)]}{d(kr)} \right)^2 \right] = \ell(\ell+1) [(\ell+1) z_{\ell-1}^2(kr) + \ell z_{\ell+1}^2(kr)], \quad (\text{A.27})$$

$$\left[ \frac{z_{\ell}}{kr} \frac{dz_{\ell}(kr)}{d(kr)} + \left( \frac{1}{kr} \frac{d[krz_{\ell}(kr)]}{d(kr)} \right)^2 \right] = \ell(\ell+1) [z_{\ell-1}^2(kr) - z_{\ell+1}^2(kr)]. \quad (\text{A.28})$$

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## Appendix B

# Size Corrected Dielectric Function

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In this work, the optical properties of spherical gold (Au) nanoparticles (NPs) with radius  $a = 12.5$  nm were studied. Even though the optical response of a non magnetic material is codified into the dielectric function  $\varepsilon(\omega)$ , the dielectric function for materials at the nanoscale differs from those in bulk due to surface effects. To perform a size correction to the dielectric function, let us decompose it into two additive contributions arising from intra- and interband electronic transitions [16]. If no spacial dispersion is considered, the intraband contribution of the dielectric function can be described by means of the Drude-Sommerfeld model

$$\frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \quad (\text{B.1})$$

where  $\varepsilon_0$  is the vacuum permittivity, and  $\omega_p$  is the plasma frequency and  $\gamma$  the damping constant. In general, the damping constant is inversely proportional to the average time between collision events of the electrons inside the material and its value depends on the material itself and on its the geometry and dimensions. For example, the damping constant for a material in bulk  $\gamma^{\text{Bulk}}$  equals  $v_F/L$  with  $v_F$  the Fermi velocity and  $L$  the mean free path of the electrons. On the other hand, the damping constant  $\gamma_a^{\text{NP}}$  for a spherical NP of radius  $a$  deviates from  $\gamma^{\text{Bulk}}$  if the mean free path is greater than the size of the NP ( $L > 2a$ ), in which case an effective mean free path replaces  $L$ , leading to the following expression for the damping constant:

$$\gamma_a^{\text{NP}} = \gamma^{\text{Bulk}} + A \frac{v_F}{a}, \quad \text{with} \quad \gamma^{\text{Bulk}} = \frac{v_F}{L}, \quad (\text{B.2})$$

where  $A$  is a theory dependent parameter whose exact value changes according to the approach employed to calculate the effective mean free path; for this work it is considered that  $A = 1$ .

In practice, the experimental data for the dielectric function of a material  $\varepsilon_{\text{Exp}}(\omega)$  corresponds to a material in bulk, so a size correction is performed on  $\varepsilon_{\text{Exp}}(\omega)$  if the optical properties of NPs are studied. The size correction is done by subtracting the intraband contribution that best fits the experimental bulk data and adding an intraband contribution considering Eq. (B.2), that is, the size corrected dielectric function  $\varepsilon_{\text{Size}}(\omega)$  is given by

$$\frac{\varepsilon_{\text{Size}}(\omega)}{\varepsilon_0} = \frac{\varepsilon_{\text{Exp}}(\omega)}{\varepsilon_0} + \left( -\frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \Big|_{\gamma=\gamma^{\text{Bulk}}} + \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \Big|_{\gamma=\gamma_a^{\text{NP}}} \right), \quad (\text{B.3})$$

## B. SIZE CORRECTED DIELECTRIC FUNCTION

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The size correction in Eq. (B.3) considers the size effects on the intraband contribution of the dielectric function while the size corrections due to the interband contributions are neglected since it has been reported that they are relevant for NPs with radii smaller than 2 nm [32].

To employ the size corrected dielectric function [Eq. (B.3)], the parameters  $\omega_p$  and  $\gamma^{\text{Bulk}}$  that best fit  $\varepsilon_{\text{Exp}}(\omega)$  are needed. Let us develop two linear relations involving  $\omega_p$  and  $\gamma^{\text{Bulk}}$  and the real and imaginary parts of  $\varepsilon_{\text{Drude}}(\omega)$  following the method from Mendoza Herrera, Arboleda, Schinca, and Scaffardi. The real and imaginary parts of  $\varepsilon_{\text{Drude}}(\omega)$  are

$$\text{Re} \left[ \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \right] = 1 - \frac{\omega_p^2 \omega^2}{\omega^4 + (\omega \gamma)^2}, \quad \text{and} \quad \text{Im} \left[ \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \right] = \frac{\omega_p^2 (\omega \gamma)}{\omega^4 + (\omega \gamma)^2}. \quad (\text{B.4})$$

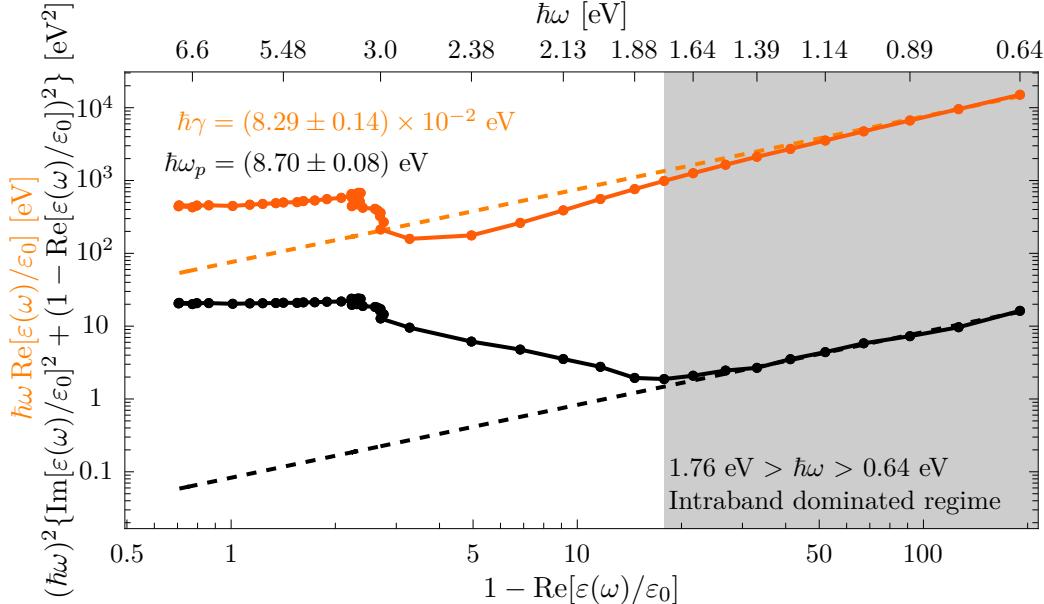
according to Eq. (B.1). By multiplying the imaginary part of  $\varepsilon_{\text{Drude}}(\omega)$  by  $\omega$  and comparing it with its real part, one obtains that

$$\omega \text{Im} \left[ \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \right] = \gamma \left( 1 - \text{Re} \left[ \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \right] \right), \quad (\text{B.5})$$

and in a similar manner it can be verified that

$$\omega^2 \left\{ \text{Im} \left[ \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \right]^2 + \left( 1 - \text{Re} \left[ \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \right] \right)^2 \right\} = \omega_p^2 \left( 1 - \text{Re} \left[ \frac{\varepsilon_{\text{Drude}}(\omega)}{\varepsilon_0} \right] \right). \quad (\text{B.6})$$

By plotting the left hand side of Eqs. (B.5) and (B.6) as a function of  $1 - \text{Re}[\varepsilon_{\text{Drude}}(\omega)/\varepsilon_0]$  and fitting two linear functions, the values for  $\gamma$  and  $\omega_p^2$  can be calculated according to the right

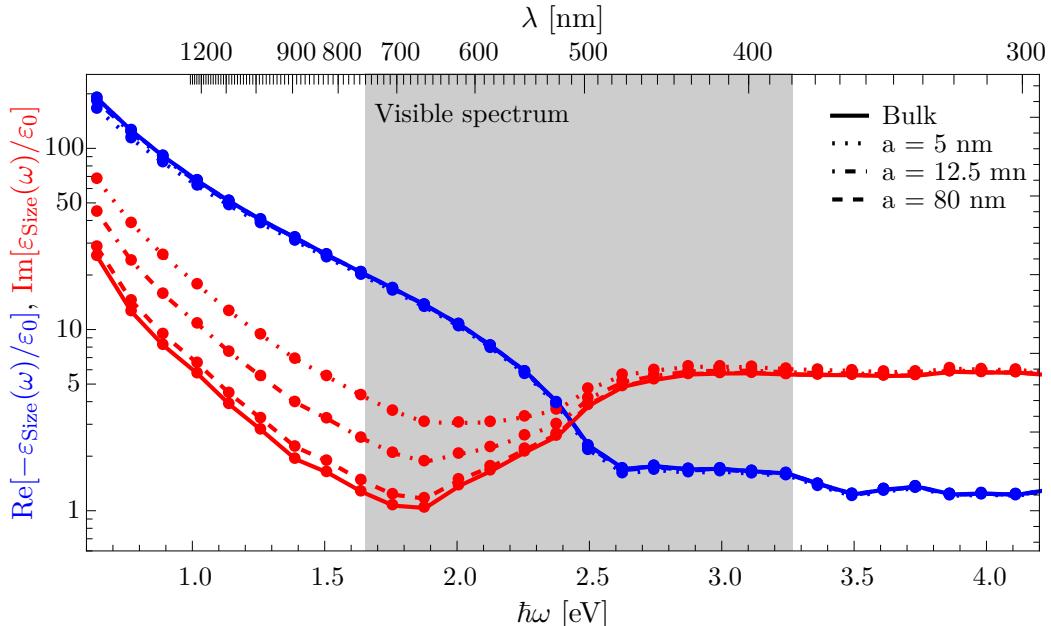


**Fig. B.1:** Plot of Eqs. (B.5) (orange) and (B.6) (black) evaluated with the experimental dielectric function reported by Johnson and Christy [15]. The shaded region corresponds to the frequency window from 0.64 eV to 1.76 eV, which is best described by the Drude-Sommerfeld model and which was considered to perform the linear fits (dashed), determining a plasma frequency of  $\hbar\omega_p = (8.70 \pm 0.08) \text{ eV}$  and a damping constant of  $\hbar\gamma = (8.29 \pm 0.14) \times 10^{-2} \text{ eV}$  for Au.

hand side of Eqs. (B.5) and (B.6), respectively. As a final remark, the experimental dielectric function includes both an intra- and an interband contribution while Eqs. (B.5) and (B.6) are only valid for the intraband contribution of the dielectric function, thus the linear fits should be done within a spectral window into which the interband contributions are negligible compared to the Drude-Sommerfeld model, which best describes the optical properties of a material when  $\omega \rightarrow 0$ . The chose of the spectral window for the experimental data fit of the dielectric function can modify the calculated values of  $\gamma$  and  $\omega_p$ .

In Fig. B.1, the left hand side of Eqs. (B.5) and (B.6) are plotted in orange and black, respectively, as a function of  $1 - \text{Re}[\varepsilon(\omega)/\varepsilon_0]$ , where  $\varepsilon(\omega)$  corresponds to the experimental data of the dielectric function of Au (markers) reported by Johnson and Christy [15]; to ease the read of Fig. B.1, continuous lines between the data were added as a guide to the eye and the photon energy  $\hbar\omega$  of selected points of the experimental data are shown on the top margin. The shaded region in Fig. B.1 is the frequency window  $0.64 \text{ eV} < \hbar\omega < 1.76 \text{ eV}$ , into which the experimental data for Au shows a linear behavior as stated by Eqs.(B.5) and (B.6), that is, within this interval the intraband contribution to the dielectric function is dominant, thus the linear fits (dashed lines) where made with the data in this region, determinating a plasma frequency of  $\hbar\omega_p = (8.70 \pm 0.08) \text{ eV}$  and a damping constant of  $\hbar\gamma = (8.29 \pm 0.14) \times 10^{-2} \text{ eV}$  for Au in bulk. Once the plasma frequency and the damping constant for Au have been obtained, the size corrected dielectric for spheres can be calculated.

The real part (blue) and imaginary part (red) of the size corrected dielectric function for Au, based in the experimental data from Johnson and Christy, is plotted in Fig. B.2 as function of the photon energy  $\hbar\omega$ ; on the top margin it is shown the conversion of the phton energy into



**Fig. B.2:** Real (blue) and imaginary (red) parts of the size corrected dielectric function of Au in bulk (continuous lines) and of spherical Au NPs of radius 5 nm (dotted lines), 12.5 nm (dash dotted lines) and 80 nm (dashed lines), as function of the photon energy  $\hbar\omega$  (wavelength  $\lambda$ ). The size corrected dielectric function was calculated from the experimental data of Johnson and Christy [15].

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## B. SIZE CORRECTED DIELECTRIC FUNCTION

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wavelength  $\lambda$ . The size corrected dielectric function was calculated for several cases: Au in bulk (continuous lines) and spherical Au NPs of radius 5 nm (dotted lines), 12.5 nm (dash dotted lines) and 80 nm (dashed lines); all lines are guides to the eye. The data in Fig. B.2 shows that the need for a size corrected dielectric functions increases as the frequency decreases (wavelength decreases), specifically for the visible spectrum (shaded region) the size correction is appreciated for  $\hbar\omega < 2.5$  eV ( $\lambda > 500$  nm). From Fig. B.2 it can also be seen that the imaginary part of the size corrected dielectric function differs the most from the bulk dielectric function compared to its real part, whose deflection from the bulk optical response are barely visible near  $\hbar\omega \approx 1$  eV.

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## Appendix C

# Brief COMSOL Implementation of the Scattering Problem

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The commercial software COMSOL Multiphysics<sup>TM</sup> Ver. 5.4 (COMSOL) allows the user to set a desired geometry for solving Eqs. (2.23) as well as the physical properties of each component of the geometry including boundary conditions and the discretization of the system into finite elements. Additionally, once the Eqs. (2.23) are solved, the retuned value of the FEM simulation is the total electric field that can be decomposed into an external electric field<sup>1</sup>  $\mathbf{E}^{\text{ext}}$ , which illuminates the system, and the induced electric field<sup>2</sup>  $\mathbf{E}^{\text{ind}}$ , which corresponds to the scattered (internal) electric field if it is evaluated outside (inside) any scatterer of the geometry. In this section a brief summary of the implementation of the scattering problem with a planar interface and a spherical scatterer is described for users familiarized with the COMSOL interface, where the desired geometry is the setup presented in Fig. 2.4 in section 2.3 and the external electric field is a incident electric plane wave and a reflected electric plane wave in the upper half volume of the system and a transmitted electric plane wave in the lower half volume of the system. In order to set up the geometry od the system, the boundary conditions and the physical properties of the system, COMSOL's *Model Builder* is used.

COMSOL's Model Builder is the internal tool where the user sets all the parameters for the FEM simulation and it is divided into four categories: Global Definitions, Components, Study and Results. COMSOL allows for several Components and Studies, since they define the PDE problem to be solved, as well as the desired geometry and physical properties of the system. To build the whole system, geometry and physical properties, one must define the general parameters, then the geometry of the system, afterwards the definition of local variables and operators, later formulation of the PDE and the external electric field, then the boundary conditions and, lastly, the meshing of the system.

The Global Definitions allocate the common parameters of any simulation to be performed with its numerical value. In Table C.1 there are presented the parameters to solve Eq. (2.23) considering a spherical scatterer embedded into a matrix conformed by two semiinfinite non-absorbing media forming a planar interface between them. The parameters in Table C.1 include the properties of the incident electric plane wave —its amplitude ( $E_0$ ), wavelength ( $wlength$ ),

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<sup>1</sup>COMSOL's name for the external electric field is the *background electric field*.

<sup>2</sup>COMSOL's name for the induced electric field is the *relative electric field*.

**Table C.1:** Global definitions for COMSOL simulation: Parameters

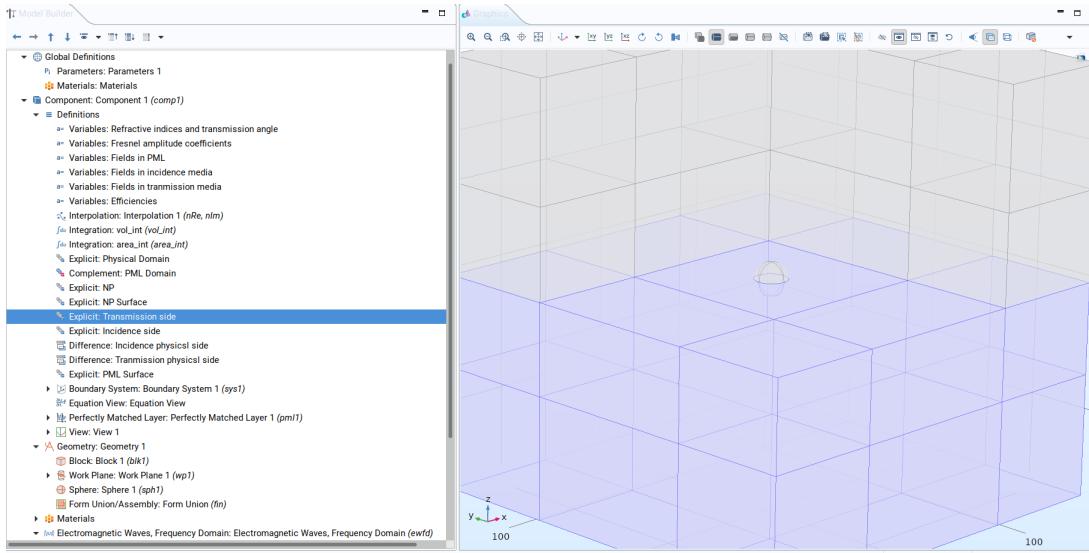
Name	Expression	Description
E_0	1. [V/m]	Incident electric field amplitude
wlength	550. [nm]	Wavelength of incident planewave
theta_i	0. [deg]	(Polar) angle of incidence
phi	0. [deg]	(Azimuthal) angle of incidence
alpha	0. [deg]	Electric field inclination
E_s	E_0 * cos(alpha)	Electric field amplitude (s pol)
E_p	E_0 * sin(alpha)	Electric field amplitude (p pol)
n_i	1.0	Refractive index of the incidence side
n_t	1.5	Refractive index of the transmission side
radius_NP	12.5 [nm]	Radius of the NP
d_matrix	15. * radius_NP / (2 * max(n_i,n_t))	Distance between NP and PML
h_center	radius_NP / 4.	Height of the center of the NP

traveling direction (`theta_i` and `phi`) and its polarization through `alpha`, a parameters which is  $0^\circ$  for s polarization and  $90^\circ$  for p polarization—, the physical properties of the spherical scatterer such as its radius (`radius_NP`) and position in the  $z$ -plane (`h_center`), and the physical properties of the matrices —the refractive indices of the incidence (`n_i`) and transmission (`n_t`) media and its width (`d_matrix`)—.

Once the parameters of Table C.1 are introduced in COMSOL’s Model Builder, the next step is to define the geometry of the system into the Component/Geometry section. The employed geometry consisted in a sphere of radius `radius_NP`, a block of sides equal to `2*d_matrix + radius_NP + wlength/4.` and a layer of `wlength/4.` in all sides—which defines the PML subvolume—, and a working plane of sides `2*d_matrix + radius_NP + wlength/4.,` which corresponds to the planar interface between the two semiinfinite media. All of these elements can be seen in Fig. C.1, where a screenshot of COMSOL’s interface is shown.

After the geometry is built, within section Component/Definitions several subvolumes can be labeled to simplify future calculations. In Fig. C.1 it can be seen that the volume and surface of the scatterer are explicitly selected and labeled as `NP` and `NP Surface`, respectively. Additionally, the subvolumes corresponding to the `Physical Domain` selection are those where the calculated electric field has physical meaning, while the complement of such subvolume, labeled as `PML Domain` corresponds to the region where the PML is defined. Another selection explicitly made are the subvolumes `Incidence side` and `Transmssion side`, both of which are subvolumes of both `Physical Domain` and `PML Domain`. The last volumes to be defined are the intersection of `Physical Domain` with `Incidence side`, and with `Transmssion side`, labeled as `Physical incidence side` and `Physical transmission side`, respectively.

With the made volume and surface definitions, integral operators can be defined. In particular, it can be seen in Fig. C.1 that the volume integral operator of a scalar quantity is defined as `vol_int`, where the the integration volume is `NP` and a surface integral operators in the surface `NP Surface` is defined as `area_int`. Besides integral operators, one can define functions from interpolation of data points, which is the case of the functions `nRe` and `nIm` that corresponds to the real and the imaginary parts of the size corrected refractive index of a gold nanoparticle —see Appendix B—. The PML of the system requires to be set in the Component/Definitions



**Fig. C.1:** Screenshot of a COMSOL Multiphysics™ Ver. 5.4 file showing the Model Builder (left panel) and the Graphics of the built Geometry (right panel). In the Model Builder the Definitions and Geometry sections in Component are expanded to show their contents.

section by choosing this option in its menu and applying it to the **PML Domain** subvolume. Lastly, within Component/Definitions one can define local variables into a subvolume or for the whole system; this COMSOL’s function was used to define the external electric field which corresponds to an incident, a reflected and a transmitted electric plane wave. These three contributions were defined piecewise in three subvolumes: **Physical incidence side**, **Physical transmission side** and **PML Domain**. On the one hand, in Table C.2 there are shown the phase of the incident and reflected electric fields, defined as  $\mathbf{k}_i$  and  $\mathbf{k}_r$ , respectively, as well as their three spatial components — $E_{i_x}$ ,  $E_{i_y}$  and  $E_{i_z}$  for the incident plane wave and  $E_{rt_x}$ ,  $E_{rt_y}$  and  $E_{rt_z}$  for the reflected plane wave —, alongside the Fresnel’s reflection amplitude coefficients for both  $s$  ( $r_s$ ) and  $p$  ( $r_p$ ) polarization. On the other hand, in Table C.3 the three spatial components — $E_{rt_x}$ ,  $E_{rt_y}$  and  $E_{rt_z}$ — and the phase — $\mathbf{k}_t$ — of the transmitted electric field are defined, as well as Fresnel’s transmission amplitude coefficients for both  $s$  ( $t_s$ ) and  $p$  ( $t_p$ ) polarization; the component of the incident electric field are all set equal to zero. Additionally, the external electric field is set to zero in the **PML Domain**, as shown in Table C.4.

Before defining the scattering, absorption and extinction cross sections in the Component/Definitions section, one must choose the PDE problem to be solved in the Electromagnetic Waves, Frequency Domain (**ewfd**) and set its formulation in Scattered Field and choose the external electric field, defined piecewise in Tables C.2–C.4, as the sum of the incident, the reflected and the transmitted plane waves. This can be done in the settings panel of **ewfd** as shown in Fig. C.2, where the Scattering formulation allows the user to use to use the generalized Sommerfeld’s radiation condition [Eq. (2.38)] and to separate the contributions of the total electric field into the external and the induced electric fields, as well as to access to precomputed physical quantities related to the calculated electric field, such as the Poynting vector, for example.

After the Scattering Formulation of the **ewfd** is set, and the external electric field was introduced into COMSOL’s interface, the scattering, absorption and extinction cross sections

**Table C.2:** Local definitions for COMSOL simulation: Component/Definitions/Variables. The below variables are locally defined in the subvolume Physical incidence side.

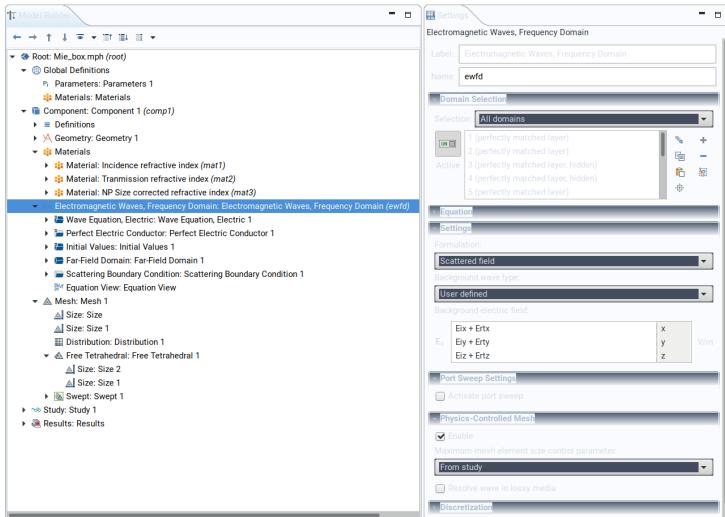
Name	Expression	Description
k_ir	(2*pi/wlength)*n_i*(x*sin(theta_i)*cos(phi)+y*sin(theta_i)*sin(phi)+z*cos(theta_i))	Incident plane wave phase
k_rr	(2*pi/wlength)*n_i*(x*sin(theta_i)*cos(phi)+y*sin(theta_i)*sin(phi)-z*cos(theta_i))	Reflected plane wave phase
Ei_x	(-E_s*sin(phi)+E_p*cos(theta_i))*cos(phi)* exp(-j*k_ir)	Incident plane wave - x component
Ei_y	( E_s*cos(phi)+E_p*cos(theta_i))*sin(phi)* exp(-j*k_ir)	Incident plane wave - y component
Ei_z	E_p*sin(theta_i)* exp(-j*k_ir)	Incident plane wave - z component
r_s	(n_i*cos(theta_i)-n_t*cos(theta_t))/(n_i*cos(theta_i)+n_i*cos(theta_t))	S reflection amplitude coefficient
r_p	(n_t*cos(theta_i)-n_i*cos(theta_t))/(n_t*cos(theta_i)+n_i*cos(theta_t))	P reflection amplitude coefficient
Ert_x	(-E_s*sin(phi)*r_s - E_p*cos(theta_i)*cos(phi)*r_p )* exp(-j*k_rr)	Reflected plane wave - x component
Ert_y	( E_s*cos(phi)*r_s - E_p*cos(theta_i)*sin(phi)*r_p )* exp(-j*k_rr)	Reflected plane wave - y component
Ert_z	E_p*sin(theta_i)*r_p * exp(-j*k_rr)	Reflected plane wave - z component

**Table C.3:** Local definitions for COMSOL simulation: Component/Definitions/Variables. The below variables are locally defined in the subvolume Physical transmission side.

Name	Expression	Description
k_tr	(2*pi/wlength)*n_t*(x*sin(theta_t)*cos(phi)+y*sin(theta_t)*sin(phi)+z*cos(theta_t))	Transmitted plane wave phase
Ei_x	0.	Incident plane wave - x component
Ei_y	0.	Incident plane wave - y component
Ei_z	0.	Incident plane wave - z component
t_s	2*n_i*cos(theta_i)/(n_i*cos(theta_i)+n_t*cos(theta_t))	Incident plane wave - z component
t_p	2*n_i*cos(theta_i)/(n_t*cos(theta_i)+n_i*cos(theta_t))	S amplitude transmission coefficient
Ert_x	(-E_s*sin(phi)*t_s - E_p*cos(theta_t)*cos(phi)*t_p )* exp(-j*k_tr)	P amplitude transmission coefficient
Ert_y	( E_s*cos(phi)*t_s - E_p*cos(theta_t)*sin(phi)*t_p )* exp(-j*k_tr)	Transmitted plane wave - x component
Ert_z	E_p*sin(theta_i)*t_p * exp(-j*k_tr)	Transmitted plane wave - y component
		Transmitted plane wave - z component

**Table C.4:** Local definitions for COMSOL simulation: Component/Definitions/Variables. The below variables are locally defined in the subvolume PML Domain.

Name	Expression	Description
Ei_x	0.	Incident electric plane wave - x component
Ei_y	0.	Incident electric plane wave - y component
Ei_z	0.	Incident electric plane wave - z component
Ert_x	0.	(Reflected) Transmitted plane wave - x component
Ert_y	0.	(Reflected) Transmitted plane wave - y component
Ert_z	0.	(Reflected) Transmitted plane wave - z component



**Fig. C.2:** Screenshot of a COMSOL Multiphysics™ Ver. 5.4 file showing the Model Builder (left panel) and the settings panel of the Electromagnetic Waves, Frequency Domain —ewfd— (right panel). In the Model Builder the Materials and ewfd sections in Components are expanded to show their content, while in the settings planel in ewfd it is shown that the Scattered Field formulation is set and that the external electric field is a user-defined quantity given by the expressions shwon in Tables C.2–C.4.

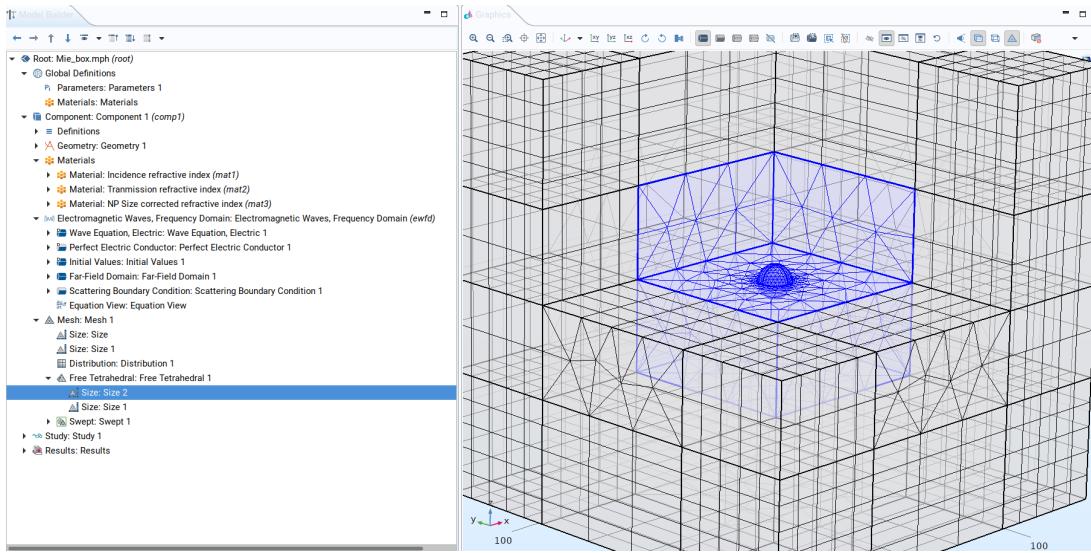
are defined in the Component/Definitions section as a variable in the whole system. Since the scattering cross section is calculated by Eq. (1.8), the time-averaged scattering Poynting vector is projected onto the normal vector to a closed surface and then integrated on such surface. The component of the time-averaged scattering Poynting vector are precalculated by COMSOL and are accessed by the user thought the variables `ewfd.relPoavx`, `ewfd.relPoavy` and `ewfd.relPoavz` [31] and the component of the normal vector to any surface are given by `nx`, `ny` and `nz`. By calculating the dot production of the normal vector and the time-averaged scattering Poynting vector, applying to it the integral operator `area_int` and dividing by the irradiance of the incident plane wave `s_i`, the scattering cross section `c_sca` is obtained. For the absorption cross section `c_abs` the Eq. (1.9) is employed, that is the integral operator `vol_int` is applied to the variable `ewfd.Qh`, which are the heat losses calculated by Joule's law [31]; lastly the extinction cross section `c_ext` is calculated as the sum of the scattering and the absorption cross sections. All the needed definitions are shown

**Table C.5:** Local definitions for COMSOL simulation: Component/Definitions/Variables. The below variables are locally defined in all domains.

Name	Expression	Description
<code>theta_t</code>	<code>arcsin((n_i/n_t)*sin(theta_i))</code>	Transmission angle
<code>S_i</code>	<code>n_i*E0^2/(2*Z0_const)</code>	Incident Irradiance
<code>S_x</code>	<code>nx * ewfd.relPoavx</code>	Average Poynting Vector in the normal x direction
<code>S_y</code>	<code>ny * ewfd.relPoavy</code>	Average Poynting Vector in the normal y direction
<code>S_z</code>	<code>nz * ewfd.relPoavz</code>	Average Poynting Vector in the normal z direction
<code>C_sca</code>	<code>area_int(S_x + S_y + S_z)/(S_i)</code>	Scattering cross section
<code>C_abs</code>	<code>vol_int(ewfd.Qh)/(S_i)</code>	Absorption cross section
<code>C_ext</code>	<code>C_sca + C_abs</code>	Extinction cross section

in Table C.5.

The last step before running the FEM simulation in COMSOL is to define the mesh—or the partition into finite elements—of the system. As discussed in section 2.3, the mesh size can be set for different subvolumes in the system, as also the geometric shape of the finite elements. For this work tetrahedral finite element were chosen for the meshing in the matrix and the spherical scatterer (blue regions in Fig. C.3), where the later had a finer meshing to diminish the absolute error of the obtained approximated solution. This is specified in the Component/Mesh section of the Model Builder by setting two different sizes to each subvolume of interest. Since the PML requires a geometrical transformation to simulate an absorbing media with no reflection, the finite elements in the PML must match the geometrical symmetry of the system to minimize errors [30], which is a rectangular or Cartesian symmetry in the employed geometry, as seen in the gray areas of Fig. C.3. Following the described steps in this section, the geometry and boundary conditions employed in this work can be reproduced. After the system is set up, one can choose any Study and visualize its results in COMSOL’s viewer or export them.



**Fig. C.3:** Screenshot of a COMSOL Multiphysics™ Ver. 5.4 file showing the Model Builder (left panel) and the Graphics of the built geometry with the chosen mesh (right panel). In the Model Builder the Materials, Electromagnetic Waves, Frequency Domain —ewfd— and Mesh sections in Component are expanded to show their contents.

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