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OPTICAL RESPONSE OF PARTIALLY EMBEDDED NANOSPHERES

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PRESENTA:

JONATHAN ALEXIS URRUTIA ANGUIANO

TUTOR:

DR. ALEJANDRO REYES CORONADO
FACULTAD DE CIENCIAS, UNAM

MIEMBROS DEL COMITÉ TUTOR

DRA. CITLALI SÁNCHEZ-AKÉ
INSTITUTO DE CIENCIAS APLICADAS Y TECNOLOGÍA, UNAM

DR. GIUSEPPE PIRRCUCCIO
INSTITUTO DE FÍSICA, UNAM

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Abstract/Resumen

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Introduction

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

- Your field: Context about the field your are working
  Plasmonics -> Metameterials -> 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.

Chapter 1

Optical properties of single plasmonic nanoparticles

The problem studied in this thesis corresponds to the theoretical 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 theoretical 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) , nevertheless, to verify the validity of the obtained results, the problem of the absorption and scattering of light by an isolated particle must be addressed. In this chapter, we revisit the general solution of the light absorption and scattering by both an arbitrary particle and by a spherical particle, given by the Mie Theory [2].

1.1 The Optical Theorem: Amplitude Matrix and Cross Sections

Let $\mathbf{E}^{\mathrm{i}} = \mathbf{E}_0^{\mathrm{i}} \exp(i\mathbf{k}^{\mathrm{i}} \cdot \mathbf{r})$ be the electric field of an incident monochromatic plane wave with constant amplitude $\mathbf{E}_0^{\mathrm{i}}$ traveling through a non-dispersive medium with refractive index n_{m}, denominated matrix, in the direction $\mathbf{k}^{\mathrm{i}} = k\hat{\mathbf{k}}^{\mathrm{i}}$, with $k = (\omega/c)n_{\mathrm{m}}$ the wave number of the plane wave into the matrix, and let $\mathbf{E}^{\mathrm{sca}}$ 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 a given point $\mathbf{r} = r\hat{\mathbf{e}}_r$ the traveling direction is defined by the vector $\mathbf{k}^{\mathrm{sca}} = k\hat{\mathbf{k}}^{\mathrm{sca}} = k\hat{\mathbf{e}}_r$. Due to the linearity of the Maxwell's equations, the incident and scattered electric fields in the far field regime are related by the linear relation [3],

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

where $\mathbb{F}(\hat{\mathbf{k}}^{\mathrm{sca}}, \hat{\mathbf{k}}^{\mathrm{i}})$ is the scattering amplitude matrix from direction $\hat{\mathbf{k}}^{\mathrm{i}}$ into $\hat{\mathbf{k}}^{\mathrm{sca}}$. Since only the far field is considered, both the incident and the scattered electric field can be decomposed into two linearly independent components perpendicular to $\mathbf{k}^{\mathrm{i}}$ and $\mathbf{k}^{\mathrm{sca}}$, respectively, each forming a right-hand orthonormal system. If the particle acting as a scatterer has a symmetric shape, it is convenient to define the orthonormal systems relative to the scattering plane, which is the plane containing $\mathbf{k}^{\mathrm{i}}$ and $\mathbf{k}^{\mathrm{sca}}$, since the elements of $\mathbb{F}(\hat{\mathbf{k}}^{\mathrm{sca}}, \hat{\mathbf{k}}^{\mathrm{i}})$ simplify when represented in these bases [3]. By defining the directions perpendicular ($\perp$) and parallel ($\|$) to the scattering plane, the incident and scattered electric fields can be written as

$$\mathbf{E}^{\mathrm{i}} = \left(E^{\mathrm{i}}_{\|}\hat{\mathbf{e}}^{\mathrm{i}}_{\|} + E^{\mathrm{i}}_{\perp}\hat{\mathbf{e}}^{\mathrm{i}}_{\perp}\right)\exp\left(i\mathbf{k}^{\mathrm{i}}\cdot\mathbf{r}\right), \tag{1.2}$$

$$\mathbf{E}^{\mathrm{sca}} = \left(E^{\mathrm{sca}}_{\|}\hat{\mathbf{e}}^{\mathrm{sca}}_{\|} + E^{\mathrm{sca}}_{\perp}\hat{\mathbf{e}}^{\mathrm{sca}}_{\perp}\right)\frac{\exp(i\mathbf{k}^{\mathrm{sca}}\cdot\mathbf{r})}{r}, \tag{1.3}$$

where an harmonic time dependence $\exp(-i\omega t)$ has been suppressed, and where it has been assumed that the scattered field is described by a spherical wave; the superindex 'i' ('sca') denotes the orthonormal system defined by the incident plane wave (scattered fields). Since $\{\hat{\mathbf{e}}^{\mathrm{i}}_{\perp}, \hat{\mathbf{e}}^{\mathrm{i}}_{\|}, \hat{\mathbf{k}}^{\mathrm{i}}\}$ and $\{\hat{\mathbf{e}}^{\mathrm{sca}}_{\perp}, \hat{\mathbf{e}}^{\mathrm{sca}}_{\|}, \hat{\mathbf{k}}^{\mathrm{sca}}\}$ are right-hand orthonormal systems, they are related as follows

$$\hat{\mathbf{e}}^{\mathrm{i}}_{\perp} = \hat{\mathbf{e}}^{\mathrm{sca}}_{\perp} = \hat{\mathbf{k}}^{\mathrm{sca}} \times \hat{\mathbf{k}}^{\mathrm{i}}, \qquad \hat{\mathbf{e}}^{\mathrm{i}}_{\|} = \hat{\mathbf{k}}^{\mathrm{i}} \times \hat{\mathbf{e}}^{\mathrm{i}}_{\perp}, \qquad \text{and} \qquad \hat{\mathbf{e}}^{\mathrm{sca}}_{\|} = \hat{\mathbf{k}}^{\mathrm{sca}} \times \hat{\mathbf{e}}^{\mathrm{sca}}_{\perp}. \tag{1.4}$$

As the 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, then $\hat{\mathbf{k}}^{\mathrm{i}} = \hat{\mathbf{e}}_z$ and $\hat{\mathbf{k}}^{\mathrm{sca}} = \hat{\mathbf{e}}_r$. Thus, according to Eqs. (1.4), the unit vector bases of the systems relative to the scatterig plane are $\hat{\mathbf{e}}^{\mathrm{i}}_{\|} = \cos\varphi\hat{\mathbf{e}}_x + \sin\varphi\hat{\mathbf{e}}_y$, $\hat{\mathbf{e}}^{\mathrm{sca}}_{\|} = \hat{\mathbf{e}}_\theta$ and $\hat{\mathbf{e}}^{\mathrm{i}}_{\perp} = \hat{\mathbf{e}}^{\mathrm{sca}}_{\perp} = -\hat{\mathbf{e}}_\varphi$, with θ the polar angle and φ azimuthal angle. In Fig. 1.1 the unit vector systems (purple) based on the scattering plane (green) defined by the vectors $\hat{\mathbf{k}}^{\mathrm{i}} = \hat{\mathbf{e}}_z$ and $\hat{\mathbf{k}}^{\mathrm{sca}} = \hat{\mathbf{e}}_r$ are shown, along with the Cartesian (blue) and spherical (black) unit vector bases.

After an incident plane wave interacts with a particle with a possible 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

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

where $(*)$ is the complex conjugate operation and where the total Poynting vector is separated into the contribution from the incident field $\langle\mathbf{S}^{\mathrm{i}}\rangle_t$, from the scattered field $\langle\mathbf{S}^{\mathrm{sca}}\rangle_t$ and from their cross product denoted by $\langle\mathbf{S}^{\mathrm{ext}}\rangle_t$. By means of the Faraday-Lenz Law and Eq. (1.1), the contribution to the Poynting vector from the incident and the scattered fields can be rewritten as

$$\left\langle\mathbf{S}^{\mathrm{i}}\right\rangle_t = \frac{\|\mathbf{E}^{\mathrm{i}}_0\|^2}{2Z_{\mathrm{m}}}\hat{\mathbf{k}}^{\mathrm{i}}, \qquad \text{and} \qquad \langle\mathbf{S}^{\mathrm{sca}}\rangle_t = \frac{\|\mathbf{E}^{\mathrm{sca}}\|^2}{2Z_{\mathrm{m}}}\hat{\mathbf{k}}^{\mathrm{sca}} = \frac{\left\|\mathbb{F}(\hat{\mathbf{k}}^{\mathrm{sca}}, \hat{\mathbf{k}}^{\mathrm{i}})\mathbf{E}^{\mathrm{i}}\right\|^2}{2Z_{\mathrm{m}}r^2}\hat{\mathbf{k}}^{\mathrm{sca}}, \tag{1.6}$$

with $Z_{\mathrm{m}} = \sqrt{\mu_{\mathrm{m}}/\varepsilon_{\mathrm{m}}}$, the impedance of the non-dispersive matrix, while the crossed contribution

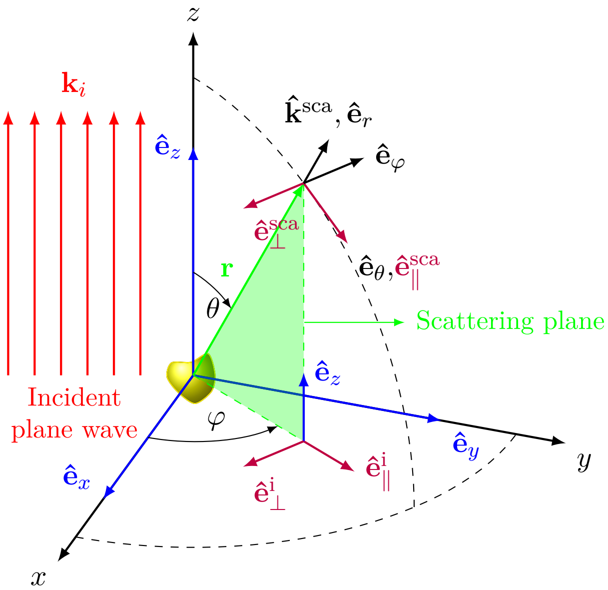

Fig. 1.1: The scattering plane (green) is defined by the vectors $\hat{\mathbf{k}}^{\text{i}}$, direction of the incident plane wave (red), and $\hat{\mathbf{k}}^{\text{sca}}$, direction of the scattered field in a given point $\vec{r}$. If the direction of the incident plane wave is chose to be $\hat{\mathbf{e}}_z$, the parallel and perpendicular components of the incident field relative to the scattering plane are $\hat{\mathbf{e}}_\parallel^{\text{i}} = \cos\varphi\hat{\mathbf{e}}_x + \sin\varphi\hat{\mathbf{e}}_y$ and $\hat{\mathbf{e}}_\perp^{\text{i}} = -\hat{\mathbf{e}}_\varphi$, while the components of the scattering field relative to the scattering plane are $\hat{\mathbf{e}}_\parallel^{\text{sca}} = \hat{\mathbf{e}}_\theta$, $\hat{\mathbf{e}}_\perp^{\text{sca}} = -\hat{\mathbf{e}}_\varphi$. 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.

is given by

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

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

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 $\|\langle \mathbf{S}^{\text{i}} \rangle_t\|$, it is obtained a quantity with units of area known as the scattering cross section C_{sca}, given by

Scattering Cross Section

$$C_{\text{sca}} = \frac{2Z_{\text{m}}}{\|\mathbf{E}_0\|^2} \oint \langle \mathbf{S}^{\text{sca}} \rangle \cdot \mathrm{d}\mathbf{a} = \oint \frac{\left\| \mathbb{F}(\hat{\mathbf{k}}^{\text{sca}}, \hat{\mathbf{k}}^{\text{i}}) \mathbf{E}^{\text{i}} \right\|^2}{\|\mathbf{E}_0^{\text{i}}\|^2} \mathrm{d}\Omega, \tag{1.8}$$

where $\mathrm{d}\Omega$ is the solid angle differential. In a similar manner, an absorption cross section C_{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 [2]. On the other side, if an Ohmic material for the particle with conductivity $\sigma(\omega) = i\omega n_p^2(\omega)$ [4] is assumed, through Joule's Heating Law [3] the absorption cross section can be computed as

Ohmic Particle - Absorption Cross Section

$$C_{\text{abs}} = \frac{1}{2}\int \frac{\text{Re}(\mathbf{j}\cdot\mathbf{E}^{\text{int}*})}{\|\mathbf{E}_0^{\text{i}}\|^2/2Z_{\text{m}}}\,\text{d}V = \int \omega Z_{\text{m}}\,\text{Im}(n_p^2)\frac{\|\mathbf{E}^{\text{int}}\|^2}{\|\mathbf{E}_0^{\text{i}}\|^2}\,\text{d}V\,, \tag{1.9}$$

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 [5], and their relation can be made explicit by performing the surface integral representation of C_{abs} and defining C_{ext}, that is,

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

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

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

where the relations $\hat{\mathbf{k}}^{\text{sca}}\cdot\hat{\mathbf{e}}_r = 1$, $\hat{\mathbf{k}}^{\text{i}}\cdot\hat{\mathbf{e}}_r = \cos\theta$ and $\mathbf{E}^{\text{sca}}\cdot\hat{\mathbf{e}}_r = 0$ were employed. The integrals in Eq. (1.11) can be solved by a two-fold integration by parts on the polar angle θ and by depreciating the terms proportional to r^{-2}. This process leads to a zero contribution from the integrand proportional to $\sin\theta$ of Eq. (1.11), and after arranging the other terms in their real and imaginary parts, it follows that C_{ext} depends only in the forward direction $\hat{\mathbf{k}}^{\text{sac}} = \hat{\mathbf{k}}^{\text{i}}$ ($\theta = 0$). This result is known as the Optical Theorem whose mathematical expression is given by [3, 5, 6]

Optical Theorem - Extinction Cross Section

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

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 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 $\mathbb{F}$ [3]. 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 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 determinated 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 can arise when either the scattering amplitude matrix or extinction cross section is approximated[1]. 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 SVH are defined, they will be used to write a monochromatic plane wave and, lastly, the scattered field by a spherical particle will be calculated by imposing the continuity of the tangential components of the electric and magnetic field.

1.2.1 Vector Spherical Harmonics

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

Vectorial Helmholtz Equation

$$\boldsymbol{\nabla}^2\mathbf{E}(\mathbf{r},\omega) + k^2\mathbf{E}(\mathbf{r},\omega) = \mathbf{0}, \tag{1.13a}$$

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

where the vectorial operator $\boldsymbol{\nabla}^2$ must be understood as $\boldsymbol{\nabla}^2 = \nabla(\nabla\cdot) - \nabla\times\nabla\times$, and k is the

[1] See for example Section 2.4 from Ref. [3] on the Rayleigh Scattering and Section 21.7 from Ref. [7] on Thompson scattering.

wave number in the matrix, which must follow the relation of dispersion $k = (\omega/c)n_{\mathrm{m}}$, with $n_{\mathrm{m}} = \sqrt{\mu_{\mathrm{m}}\varepsilon_{\mathrm{m}}/\mu_0\varepsilon_0}$ the refractive index of the matrix, μ_{m} its magnetic permeability and ε_{m} 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

$$\mathbf{L} = \nabla\psi, \tag{1.14a}$$
$$\mathbf{M} = \nabla \times (\mathbf{r}\psi), \tag{1.14b}$$
$$\mathbf{N} = \frac{1}{k}\nabla \times \mathbf{M}, \tag{1.14c}$$

that are solution to the homogeneous vectorial Helmholtz equation as long as the scalar function ψ is solution to the scalar Helmholtz equation[2]

$$\nabla^2\psi + k^2\psi = 0. \tag{1.15}$$

The triad $\{\mathbf{L}, \mathbf{M}, \mathbf{N}\}$ is a set of vectors[3] that obey Helmholtz equation *i.e.*, they can be directly identify as electric or magnetic fields. The elements of the vector basis from Eq. (1.14) are known as the Vectorial Spherical Harmonics (VSH) as defined by Stratton [8], and Bohren and Huffman [2] and the scalar function ψ 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 $\mathbf{M}$ and $\mathbf{N}$ have only transversal components; specifically $\mathbf{M}$ is tangential to any sphere of radius $\|\mathbf{r}\|$.

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 decouple into three ordinary differential equations:

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\varphi^2} + m^2\Phi = 0, \tag{1.16}$$
$$\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \left[\ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right]\Theta = 0, \tag{1.17}$$
$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \left[(kr)^2 - \ell(\ell+1)\right]R = 0, \tag{1.18}$$

where ℓ can take natural values and zero, and $|m| \le \ell$ so Φ and Θ are univalued and finite on a sphere. Eqs. (1.17) and (1.18) can be rewritten as

$$(1-\mu^2)\frac{\mathrm{d}^2\Theta}{\mathrm{d}\mu^2} - 2\mu\frac{\mathrm{d}\Theta}{\mathrm{d}\mu} + \left[\ell(\ell+1) - \frac{m^2}{1-\mu^2}\right]\Theta = 0, \quad \text{with } \mu = \cos\theta, \tag{1.19}$$
$$\rho\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\rho\frac{\mathrm{d}Z}{\mathrm{d}\rho}\right) + \left[\rho^2 - \left(\ell + \frac{1}{2}\right)^2\right]Z = 0, \quad \text{with } Z = R\sqrt{\rho} \text{ and } \rho = kr. \tag{1.20}$$

[2]This result can be proven 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 $\boldsymbol{\nabla} \times \left(\boldsymbol{\nabla}^2\mathbf{F}\right) = \boldsymbol{\nabla}^2(\boldsymbol{\nabla} \times \mathbf{F})$.

[3]Employing the Einstein sum convention with ϵ_{ijk} the Levi-Civita symbol, Eq. (1.14b) can be the 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, not necessarily $\mathbf{L}$ is orthogonal to $\mathbf{N}$ in a geometrical sense.

The solution to Eq. (1.19) are the associated Legendre functions $P_\ell^m(\mu)$ and to Eq. (1.20) the solution is given by the spherical Bessel functions of the first (j_ℓ) and second (y_ℓ) kind, and 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 literature on Mie Scattering [7], the solution to Eq. (1.16) will be decompose into an odd (o) and an even (e) solution, that is, as sine and cosine functions, thus restricting the values of m to non-negative integers. After this procedure, it is determined that the generating function of the VSH is given by

ψ: Generating function of the vectorial spherical harmonics

$$\psi_{e\ell m}(r,\theta,\varphi) = \cos(m\varphi)P_\ell^m(\cos\theta)z_\ell(kr), \tag{1.21a}$$
$$\psi_{o\ell m}(r,\theta,\varphi) = \sin(m\varphi)P_\ell^m(\cos\theta)z_\ell(kr). \tag{1.21b}$$

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

Even vectorial spherical harmonics

$$\begin{aligned}\mathbf{L}_{em\ell} =& k\cos(m\varphi)P_\ell^m(\cos\theta)\frac{\mathrm{d}z_\ell(kr)}{\mathrm{d}(kr)}\,\hat{\mathbf{e}}_r + k\cos(m\varphi)\frac{z_\ell(kr)}{kr}\frac{\mathrm{d}P_\ell^m(\cos\theta)}{\mathrm{d}\theta}\,\hat{\mathbf{e}}_\theta \\ &- km\sin(m\varphi)\frac{P_\ell^m(\cos\theta)}{\sin\theta}\frac{z_\ell(kr)}{kr}\,\hat{\mathbf{e}}_\varphi \qquad (1.22a)\\ \mathbf{M}_{em\ell} =& -m\sin(m\varphi)z_\ell(kr)\frac{P_\ell^m(\cos\theta)}{\sin\theta}\,\hat{\mathbf{e}}_\theta - \cos(m\theta)z_\ell(kr)\frac{\mathrm{d}P_\ell^m(\cos\theta)}{\mathrm{d}\theta}\,\hat{\mathbf{e}}_\varphi, \qquad (1.22b)\\ \mathbf{N}_{em\ell} =& \cos(m\varphi)\frac{z_\ell(kr)}{kr}\ell(\ell+1)P_\ell^m(\cos\theta)\,\hat{\mathbf{e}}_r + \cos(m\varphi)\frac{1}{kr}\frac{\mathrm{d}[kr\,z_\ell(kr)]}{\mathrm{d}(kr)}\frac{\mathrm{d}P_\ell^m(\cos\theta)}{\mathrm{d}\theta}\,\hat{\mathbf{e}}_\theta \\ &- m\sin(m\varphi)\frac{1}{kr}\frac{\mathrm{d}[kr\,z_\ell(kr)]}{\mathrm{d}(kr)}\frac{P_\ell^m(\cos\theta)}{\sin\theta}\,\hat{\mathbf{e}}_\varphi, \qquad (1.22c)\end{aligned}$$

where the term $\ell(\ell+1)P_\ell^m$ arises since the associated Legendre functions obeys Eq. (1.19). Likewise, the odd VSH are given by

Odd vectorial spherical harmonics

$$\begin{aligned}\mathbf{L}_{om\ell} =& k\sin(m\varphi)P_\ell^m(\cos\theta)\frac{\mathrm{d}z_\ell(kr)}{\mathrm{d}(kr)}\,\hat{\mathbf{e}}_r + k\sin(m\varphi)\frac{z_\ell(kr)}{kr}\frac{\mathrm{d}P_\ell^m(\cos\theta)}{\mathrm{d}\theta}\,\hat{\mathbf{e}}_\theta \\ &+ km\cos(m\varphi)\frac{P_\ell^m(\cos\theta)}{\sin\theta}\frac{z_\ell(kr)}{kr}\,\hat{\mathbf{e}}_\varphi \qquad (1.23a)\\ \mathbf{M}_{om\ell} =& m\cos(m\varphi)z_\ell(kr)\frac{P_\ell^m(\cos\theta)}{\sin\theta}\,\hat{\mathbf{e}}_\theta - \sin(m\theta)z_\ell(kr)\frac{\mathrm{d}P_\ell^m(\cos\theta)}{\mathrm{d}\theta}\,\hat{\mathbf{e}}_\varphi, \qquad (1.23b)\\ \mathbf{N}_{om\ell} =& \sin(m\varphi)\frac{z_\ell(kr)}{kr}\ell(\ell+1)P_\ell^m(\cos\theta)\,\hat{\mathbf{e}}_r + \sin(m\varphi)\frac{1}{kr}\frac{\mathrm{d}[kr\,z_\ell(kr)]}{\mathrm{d}(kr)}\frac{\mathrm{d}P_\ell^m(\cos\theta)}{\mathrm{d}\theta}\,\hat{\mathbf{e}}_\theta \\ &+ m\cos(m\varphi)\frac{1}{kr}\frac{\mathrm{d}[kr\,z_\ell(kr)]}{\mathrm{d}(kr)}\frac{P_\ell^m(\cos\theta)}{\sin\theta}\,\hat{\mathbf{e}}_\varphi. \qquad (1.23c)\end{aligned}$$

The election on z_ℓ in Eqs. (1.22) and (1.23) is due to the physical constrains of the scattering problem. The spherical Bessel function of first kind, unlike the other three proposed solution to the radial equation, is finite at $r = 0$, thus it is appropriate for the internal electric field and plane waves. This election of z_ℓ 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 are outgoing spherical waves [2]

$$h_\ell^{(1)}(\rho) \approx (-i)^\ell \frac{\exp(i\rho)}{i\rho} \quad \text{and} \quad \frac{\mathrm{d}h_\ell^{(1)}(\rho)}{\mathrm{d}\rho} \approx (-i)^\ell \frac{\exp(i\rho)}{\rho} \tag{1.24}$$

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

Within this text, the VSH were define in Eq. (1.14) under the condition of being a solution to the vectorial Helmholtz equation, which lead to the generating function ψ to be a solution to the scalar Helmholtz equation, nevertheless there are other definitions as discussed by Barrera, Estevez, and Giraldo [9]. 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, as it will be shown in the following sections.

1.2.2 Incident, Scattered and Internal Electric Field

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

$$\mathbf{E}^{\mathrm{i}}(\mathbf{r}) = E_0(\sin\theta\cos\varphi\hat{\mathbf{e}}_r + \cos\theta\cos\varphi\hat{\mathbf{e}}_\theta - \sin\varphi\hat{\mathbf{e}}_\varphi)\exp(ikr\cos\theta). \tag{1.25}$$

The monochromatic plane wave is a transversal wave, thus it can be written in terms of only the VSH $\mathbf{M}^{(1)}$ and $\mathbf{N}^{(1)}$, where the radial dependency is given by j_ℓ since the monochromatic plane wave is finite everywhere. Even more, due to the dependency on φ, it is only restricted to values of $m = 1$. By inspection on the radial component of $\mathbf{E}^{\mathrm{i}}$, proportional to $\cos\varphi$ it depends only on $\mathbf{N}_{e1\ell}^{(1)}$, and on the azimuthal component, proportional to $\sin\varphi$, it can depend only on $\mathbf{M}_{o1\ell}^{(1)}$. Thus, Eq. (1.25) can be written as the linear combination of $\mathbf{N}_{e1\ell}^{(1)}$ and $\mathbf{M}_{o1\ell}^{(1)}$. Through the orthogonality relations of the VSH, the x polarized plane wave can be written as [8]

$$\mathbf{E}^{\mathrm{i}}(\mathbf{r}) = E_0 \sum_\ell \frac{i^\ell(2\ell+1)}{\ell(\ell+1)} \left(\mathbf{M}_{o1\ell}^{(1)} - i\mathbf{N}_{e1\ell}^{(1)}\right), \tag{1.26a}$$

$$\mathbf{H}^{\mathrm{i}}(\mathbf{r}) = \frac{-kE_0}{\mu\omega} \sum_\ell \frac{i^\ell(2\ell+1)}{\ell(\ell+1)} \left(\mathbf{M}_{e1\ell}^{(1)} + i\mathbf{N}_{o1\ell}^{(1)}\right). \tag{1.26b}$$

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

$$\left(\mathbf{E}^{\mathrm{i}} + \mathbf{E}^{\mathrm{sca}} - \mathbf{E}^{\mathrm{int}}\right)\Big|_{r=a} \times \hat{\mathbf{e}}_r = \left(\mathbf{H}^{\mathrm{i}} + \mathbf{H}^{\mathrm{sca}} - \mathbf{H}^{\mathrm{int}}\right)\Big|_{r=a} \times \hat{\mathbf{e}}_r = 0, \tag{1.27}$$

with $\mathbf{E}^{\text{sca}}$ ($\mathbf{E}^{\text{int}}$) the scattered (internal) electric field and $\mathbf{H}^{\text{sca}}$ ($\mathbf{H}^{\text{sca}}$) the scattered (internal) magnetic field. If the incident field $\mathbf{E}^{\text{i}}$ is given by a x polarized plane wave [Eq. (1.25)] 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 dependency is given by the function $j_\ell(k_p a)$ with k_p the wave number inside the particle, while it is chosen the spherical Hankel function of first kind $h^{(1)}(ka)$ for the scattered fields due to its asymptotic behavior of a spherical outgoing wave, such election for the radial dependency is denoted by the superscript (3) over the VSH. To simplify the following steps, the scattered and the internal electric files are proposed as

$$\mathbf{E}^{\text{sca}}(\mathbf{r}) = E_0 \sum_\ell \frac{i^\ell(2\ell+1)}{\ell(\ell+1)}\left(ia_\ell \mathbf{N}^{(3)}_{e1\ell} - b_\ell \mathbf{M}^{(3)}_{o1\ell}\right), \tag{1.28a}$$

$$\mathbf{E}^{\text{int}}(\mathbf{r}) = E_0 \sum_\ell \frac{i^\ell(2\ell+1)}{\ell(\ell+1)}\left(c_\ell \mathbf{M}^{(1)}_{o1\ell} - id_\ell \mathbf{N}^{(1)}_{e1\ell}\right), \tag{1.28b}$$

with the respective magnetic fields

$$\mathbf{H}^{\text{sca}}(\mathbf{r}) = \frac{-kE_0}{\mu\omega} \sum_\ell \frac{i^\ell(2\ell+1)}{\ell(\ell+1)}\left(ib_\ell \mathbf{N}^{(3)}_{o1\ell} + a_\ell \mathbf{M}^{(3)}_{e1\ell}\right), \tag{1.29a}$$

$$\mathbf{H}^{\text{int}}(\mathbf{r}) = \frac{-kE_0}{\mu_p\omega} \sum_\ell \frac{i^\ell(2\ell+1)}{\ell(\ell+1)}\left(d_\ell \mathbf{M}^{(1)}_{e1\ell} + ic_\ell \mathbf{N}^{(1)}_{o1\ell}\right). \tag{1.29b}$$

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

$$\pi_\ell(\cos\theta) = \frac{P^1_\ell(\cos\theta)}{\sin\theta}, \quad \text{and} \quad \tau_\ell(\cos\theta) = \frac{\mathrm{d}P^1_\ell(\cos\theta)}{\mathrm{d}\theta}, \tag{1.30}$$

which are not orthogonal but their addition and substraction are, that is $\pi_\ell \pm \tau_\ell$ are orthogonal functions [2]. After substitution of Eqs. (1.26), (1.28) and (1.29) into Eq. (1.27) and considering the orthogonality of the odd and even VSH, of the vectors $\mathbf{M}$ and $\mathbf{N}$, and of $\pi_\ell \pm \tau_\ell$, it is shown that the coefficients a_ℓ, b_ℓ, c_ℓ and d_ℓ are given by two decoupled equation systems

$$\begin{pmatrix} [xh^{(1)}_\ell(x)] & (\mu/\mu_p)[(mx)j_\ell(mx)] \\ m[xh^{(1)}_\ell(x)]' & [(mx)j_\ell(mx)]' \end{pmatrix}\begin{pmatrix} a_\ell \\ d_\ell \end{pmatrix} = \begin{pmatrix} [xj_\ell(x)] \\ m[xj_\ell(x)]' \end{pmatrix}, \tag{1.31}$$

and

$$\begin{pmatrix} m[xh^{(1)}_\ell(x)] & [(mx)j_\ell(mx)] \\ [xh^{(1)}_\ell(x)]' & (\mu/\mu_p)[(mx)j_\ell(mx)]' \end{pmatrix}\begin{pmatrix} b_\ell \\ c_\ell \end{pmatrix} = \begin{pmatrix} m[xj_\ell(x)] \\ [xj_\ell(x)]' \end{pmatrix}, \tag{1.32}$$

where $m = k_p/k = n_p/n_{\text{m}}$ is the contrast between the sphere and the matrix, $x = ka = 2\pi n_{\text{m}}(a/\lambda)$ is the size parameter and $(')$ denotes the derivative respect to the argument of the spherical Bessel or Hankel functions. The Eqs. (1.31) and (1.32) are simplified when the Riccati-Bessel functions $\psi_\ell(\rho) = \rho j_\ell(\rho)$ and $\xi(\rho) = \rho h^{(1)}_\ell(\rho)$ are introduced.

When a no magnetic particle nor matrix are assumed ($\mu_p = \mu = \mu_0$), the coefficients a_ℓ and b_ℓ are known as the Mie Coefficients whose expression is calculated by inverting Eqs. (1.31) and (1.32), leading to

Mie Coefficients

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

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

Likewise, the coefficients c_ℓ and d_ℓ are

$$c_\ell = \frac{-m\xi'_\ell(x)\psi_\ell(x) + m\xi_\ell(x)\psi'_\ell(x)}{m\xi_\ell(x)\psi'_\ell(mx) - \psi_\ell(mx)\xi'_\ell(x)}, \tag{1.34a}$$

$$d_\ell = \frac{-m\xi'_\ell(x)\psi_\ell(x) + m\psi'_\ell(mx)\psi'_\ell(x)}{\xi_\ell(x)\psi'_\ell(mx) - m\psi_\ell(mx)\xi'_\ell(x)}. \tag{1.34b}$$

Even though the coefficients of the linear combination for the scattered and internal fields were obtained by assuming an x polarized incident field, due to the spherical symmetry of the problem, by applying the transformation $\varphi \to \varphi + \pi/2$ the same procedure is valid for a y polarized incident field [2], therefore all quantities related to the scattered and the internal field can be expressed in terms of Eqs. (1.33) and (1.34).

As discussed in Section 1.1, the optical properties of a particle are codified into the scattering, absorption and extinction cross sections, quantities that 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 convinient to exploit the symmetry of the problem by decomposing the scattered electric field [Eq. (1.28a)] 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 ($\hat{\mathbf{e}}^s_\parallel = \hat{\mathbf{e}}_\theta$ and $\hat{\mathbf{e}}^s_\perp = -\hat{\mathbf{e}}_\varphi$) let us substitute the Mie Coefficients [Eq. (1.33)] into Eq. (1.28a) while rewriting the VSH $\mathbf{M}^{(3)}_{o1\ell}$ [Eq. (1.23b)] and $\mathbf{N}^{(3)}_{e1\ell}$ [Eq. (1.22c)] in terms of the Riccati-Bessel function ξ and its derivative:

$$\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}_r = \frac{\cos\varphi}{(kr)^2} \sum_\ell^\infty E_0 i^\ell (2\ell+1) i a_\ell \xi(kr)\pi_\ell(\theta)\sin\theta, \tag{1.35}$$

$$\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}^{\text{sca}}_\parallel = \frac{\cos\varphi}{kr} \sum_\ell^\infty E_0 i^\ell \frac{2\ell+1}{\ell(\ell+1)} [i a_\ell \xi'_\ell(kr)\tau_\ell(\theta) - b_\ell \xi_\ell(kr)\pi_\ell(\theta)], \tag{1.36}$$

$$\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}^{\text{sca}}_\perp = \frac{\sin\varphi}{-kr} \sum_\ell^\infty E_0 i^\ell \frac{2\ell+1}{\ell(\ell+1)} [i a_\ell \xi'_\ell(kr)\pi_\ell(\theta) - b_\ell \xi_\ell(kr)\tau_\ell(\theta)]. \tag{1.37}$$

The scattering amplitude matrix relates the incident electric field to the scattered electric field in the far field regime, that its when $kr \gg 1$. Considering that the series of Eqs. (1.35)-(1.37) converge uniformly, so all contributions after the sufficiently large term ℓ_c of the sum can be neglected for all values of kr, the asymptotic expressions for the ξ Riccati-Bessel function and its derivative can be employed, which are [2]

$$\xi(kr) \approx (-i)^\ell \frac{\exp(ikr)}{i}, \quad \text{and} \quad \frac{\mathrm{d}\xi(kr)}{\mathrm{d}(kr)} = (-i)^\ell \exp(ikr)\left(\frac{1}{ikr} + 1\right), \quad \text{when} \quad \ell_c^2 \ll kr. \tag{1.38}$$

Substituting Eq. (1.38) into Eqs. (1.35)-(1.37) and depreciating all terms proportional to $(kr)^{-2}$ it leads to a zero radial electric field while

$$\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}_{\parallel}^{\text{sca}} \approx \frac{\exp(ikr)}{r} \left\{ \frac{i}{k} \sum_{\ell}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_\ell \tau_\ell(\cos\theta) + b_\ell \pi_\ell(\cos\theta)] \right\} E_0 \cos\varphi, \tag{1.39}$$

$$\mathbf{E}^{\text{sca}} \cdot \hat{\mathbf{e}}_{\perp}^{\text{sca}} \approx \frac{\exp(ikr)}{r} \left\{ \frac{i}{k} \sum_{\ell}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_\ell \pi_\ell(\cos\theta) + b_\ell \tau_\ell(\cos\theta)] \right\} E_0(-\sin\varphi), \tag{1.40}$$

where it can be identified that $\mathbf{E}^{\text{i}} \cdot \hat{\mathbf{e}}_{\parallel}^{\text{i}} = E_0 \cos\varphi$ and $\mathbf{E}^{\text{i}} \cdot \hat{\mathbf{e}}_{\perp}^{\text{i}} = -E_0 \sin\varphi$ for $\mathbf{E}^{\text{i}}$ 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. (1.39) and (1.40) with Eq. (1.1), leading to

Scattering Amplitude Matrix for Spherical Particles

$$\mathbb{F}(\hat{\mathbf{k}}^{\text{sca}}, \hat{\mathbf{k}}^{\text{i}}) = \begin{pmatrix} \frac{i}{k} S_2(\theta) & 0 \\ 0 & \frac{i}{k} S_1(\theta) \end{pmatrix}, \tag{1.41}$$

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

$$S_1(\theta) = \sum_{\ell}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_\ell \tau_\ell(\cos\theta) + b_\ell \pi_\ell(\cos\theta)], \tag{1.42}$$

$$S_2(\theta) = \sum_{\ell}^{\infty} \frac{2\ell+1}{\ell(\ell+1)} [a_\ell \pi_\ell(\cos\theta) + b_\ell \tau_\ell(\cos\theta)]. \tag{1.43}$$

Chapter 2

Results and discussion

2.1 Finite Element Method and Analytical Solutions

2.2 Incrustation Degree of a Spherical Particle

2.3 Future Work: Application on Metasurfaces

Chapter 3

Conclusions

Appendix A

Dielectric Function Size Correction

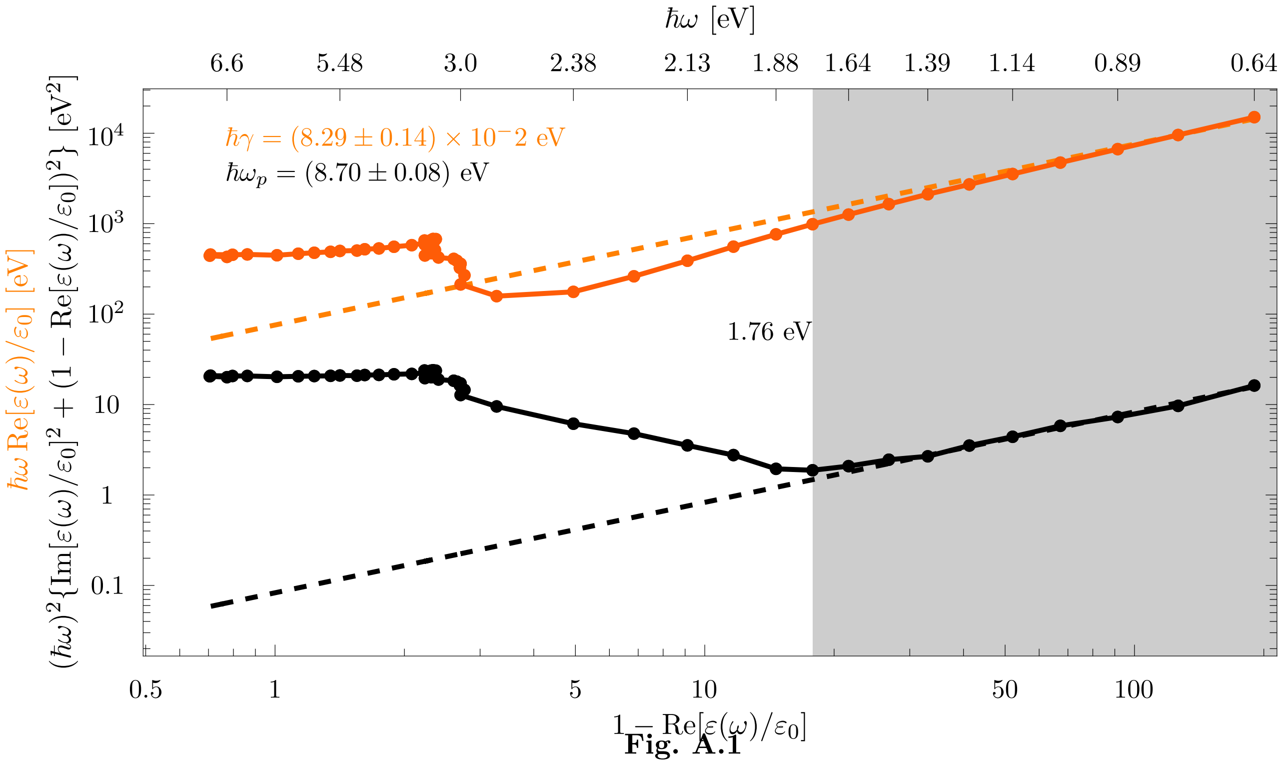
$\hbar\omega$ [eV]
6.6
5.48
3.0
2.38
2.13
1.88
1.64
1.39
1.14
0.89
0.64
$\hbar\gamma = (8.29 \pm 0.14) \times 10^{-2}$ eV
$\hbar\omega_p = (8.70 \pm 0.08)$ eV
1.76 eV
$\hbar\omega$ Re$[\varepsilon(\omega)/\varepsilon_0]$ [eV]
$(\hbar\omega)^2\{\mathrm{Im}[\varepsilon(\omega)/\varepsilon_0]^2 + (1 - \mathrm{Re}[\varepsilon(\omega)/\varepsilon_0])^2\}$ [eV^2]
10^4
10^3
10^2
10
1
0.1
0.5
1
5
10
50
100
$1 - \mathrm{Re}[\varepsilon(\omega)/\varepsilon_0]$

Fig. A.1

Appendix B

Specila Functions, Vector Spherical Harmonics, and Mie Theory Code

The Vector Spherical Harmonics (VSH) where 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 ψ 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_ℓ^m, z_ℓ 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

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

$$j_\ell(kr) = \sqrt{\frac{\pi}{2(kr)}} J_{\ell+1/2}(kr), \quad \text{and} \quad y_\ell(kr) = \sqrt{\frac{\pi}{2(kr)}} JY\ell + 1/2(kr), \tag{B.1}$$

Angular Dependency on θ and φ: Sine, Cosine, Associated Legendre Functions and the Angular Functions π_ℓ and τ_ℓ

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. This functions obey the orthogonality relations

$$\int_0^{2\pi} \sin(m\varphi)\sin(m'\varphi)\,\mathrm{d}\varphi = \int_0^{2\pi} \cos(m\varphi)\cos(m'\varphi)\,\mathrm{d}\varphi = \delta_{m,m'}(1+\delta_{0,m})\pi, \tag{B.2}$$

$$\int_0^{2\pi} \cos(m\varphi)\sin(m'\varphi)\,\mathrm{d}\varphi = 0, \tag{B.3}$$

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

The solution to the polar angle equation are the associated Legendre functions and in this work they are defined as by Arfken and Weber [10], that is,

$$P_\ell^m(\mu) = (1-\mu^2)^{m/2}\frac{\mathrm{d}^m P_\ell(\mu)}{\mathrm{d}\mu^m}, \quad \text{with} \quad P_\ell(\mu) = \frac{1}{2^\ell \ell!}\left(\frac{\mathrm{d}}{\mathrm{d}\mu}\right)^\ell (\mu^2-1)^\ell, \tag{B.4}$$

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

$$\int_{-1}^1 P_\ell^m(\mu)P_{\ell'}^m(\mu)\,\mathrm{d}\mu = \frac{2\delta_{\ell,\ell'}}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}, \tag{B.5}$$

To prove the orthogonality of $\pi_\ell(\mu) \pm \tau_\ell(\mu)$, with π_ℓ and τ_ℓ the angular functions defined in Eq. (1.30), let us apply the Legendre equation [Eq. (1.17)] to P_ℓ^m and multiply it by $P_{\ell'}^m$; repeating this procedure inverting ℓ and ℓ' and adding both equations it is obtained that

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta P_{\ell'}^m(\mu)\frac{\mathrm{d}P_\ell^m(\mu)}{\mathrm{d}\theta}\right) + \frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta P_\ell^m(\mu)\frac{\mathrm{d}P_{\ell'}^m(\mu)}{\mathrm{d}\theta}\right) + \\ &\quad [\ell(\ell+1)+\ell'(\ell'+1)]P_{\ell'}^m(\mu)P_\ell^m(\mu)\sin\theta = 2\left(\frac{mP_\ell^m(\mu)}{\sin\theta}\frac{mP_{\ell'}^m(\mu)}{\sin\theta} + \frac{\mathrm{d}P_\ell^m(\mu)}{\mathrm{d}\theta}\frac{\mathrm{d}P_{\ell'}^m(\mu)}{\mathrm{d}\theta}\right)\sin\theta, \end{aligned} \tag{B.6}$$

where it was added $2\,\mathrm{d}P_\ell^m/\mathrm{d}\theta\ \mathrm{d}P_{\ell'}^m/\mathrm{d}\theta$ on both sides to complete the derivatives. Integrating Eq. (B.6) in th interval $\theta \in (0,\pi)$, or $\mu \in (-1,1)$, and employing Eqs. (B.4) and (B.5), one obtains that

$$\int_{-1}^1 \left(\frac{mP_\ell^m(\mu)}{\sin\theta}\frac{mP_{\ell'}^m(\mu)}{\sin\theta} + \frac{\mathrm{d}P_\ell^m(\mu)}{\mathrm{d}\theta}\frac{\mathrm{d}P_{\ell'}^m(\mu)}{\mathrm{d}\theta}\right)\mathrm{d}\mu = \delta_{\ell,\ell'}\frac{2\ell(\ell+1)}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}. \tag{B.7}$$

Additionally

$$\int_{-1}^1 \frac{mP_\ell^m(\mu)}{\sin\theta}\frac{\mathrm{d}P_{\ell'}^m(\mu)}{\mathrm{d}\theta}\,\mathrm{d}\mu = \int_0^\pi mP_\ell^m(\mu)\frac{\mathrm{d}P_{\ell'}^m(\mu)}{\mathrm{d}\theta}\,\mathrm{d}\theta = -\int_{-1}^1 \frac{mP_{\ell'}^m(\mu)}{\sin\theta}\frac{\mathrm{d}P_\ell^m(\mu)}{\mathrm{d}\theta}\,\mathrm{d}\mu\,. \tag{B.8}$$

where Eq. (B.4) was employed along integration by parts. Thus, combining Eqs. (B.7) and (B.8), it leads to

$$\int_{-1}^1 \left(\frac{mP_\ell^m(\mu)}{\sin\theta} \pm \frac{\mathrm{d}P_\ell^m(\mu)}{\mathrm{d}\theta}\right)\left(\frac{mP_{\ell'}^m(\mu)}{\sin\theta} \pm \frac{\mathrm{d}P_{\ell'}^m(\mu)}{\mathrm{d}\theta}\right)\mathrm{d}\mu = \delta_{\ell,\ell'}\frac{2\ell(\ell+1)}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}. \tag{B.9}$$

The Eq. (B.9) is the orthogonality of $\pi_\ell(\mu) \pm \tau_\ell(\mu)$ when $m = 1$, which also simplifies the right hand side to $\delta_{\ell,\ell'}2\ell^2(l+1)^2/(2\ell+1)$.

The angular functions $\pi_\ell(\tau)$ and $\tau_\ell(\mu)$ can be calculated recursively by taking advantage of the recurrence relations of the Legendre polynomials [10]

$$(2\ell-1)\mu P_{\ell-1}(\mu) =(\ell-1)P_\ell(\mu)+\ell P_{\ell-2}(\mu), \tag{B.10}$$

$$(1-\mu)^2\frac{\mathrm{d}P_\ell(\mu)}{\mathrm{d}\mu} =\ell P_{\ell-1}(\mu)-\ell\mu P_\ell(\mu), \tag{B.11}$$

and Eq. (B.4) with $m=1$, which also implies that $\pi_1(\mu)=1$. By defining $\pi_0(\mu)=0$, then

$$\pi_\ell(\mu) =\frac{2\ell-1}{\ell-1}\mu\pi_{\ell-1}(\mu)-\frac{\ell}{\ell-1}\pi_{\ell-2}, \tag{B.12}$$

$$\tau_\ell(\mu) =\ell\mu\pi_\ell(\mu)-(\ell+1)\pi_{\ell-2}(\mu). \tag{B.13}$$

```
In[1]:= (*Angular functions pi and tau - n-> order - th -> polar angle theta*)
MiePi[n_, th_] := Module[{pi},
   pi[0] = 0; pi[1]= 1;
   pi[i_]:= pi[i] = ((2i-1)/(i-1))*Cos[th]*pi[i-1]-(i/(i-1))*pi[i-2];
  pi[n]]

MieTau[n_, th_] := Module[{pi},
   pi[0] = 0; pi[1]= 1;
   pi[i_]:= pi[i] = ((2i-1)/(i-1))*Cos[th]*pi[i-1]-(i/(i-1))*pi[i-2];
  n*Cos[th]*pi[n]-(n+1)*pi[n - 1]]

SetAttributes[MiePi, Listable]
SetAttributes[MieTau, Listable]
```

Another notable result from Eq. (B.4) is that the angular functions $\pi_\ell(\mu)$ and $\tau_\ell(\mu)$ when evaluated at $\theta=0$ ($\mu=1$) follows

$$\pi_\ell(\mu=1)=\left.\frac{\mathrm{d}P_\ell(\mu)}{\mathrm{d}\mu}\right|_{\mu=1}, \tag{B.14}$$

$$\tau_\ell(\mu=1)=\left.\left[\frac{\mathrm{d}P_\ell^1(\mu)}{\mathrm{d}\mu}+(1-\mu^2)^{1/2}\frac{\mathrm{d}^2P_\ell(\mu)}{\mathrm{d}\mu^2}\right]\right|_{\mu=1}=\left.\frac{\mathrm{d}P_\ell(\mu)}{\mathrm{d}\mu}\right|_{\mu=1}, \tag{B.15}$$

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

$$\pi_\ell(\mu=1)=\tau_\ell(\mu=1)=\frac{\ell(\ell+1)}{2}P_\ell(\mu=1)=\frac{\ell(\ell+1)}{2}, \tag{B.16}$$

where the last equality arises from the chosen definition of the Legendre polynomial [Eq. (B.4)].

Radial functions and Mie Coefficients

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

$$\langle \mathbf{A}, \mathbf{A}' \rangle_\Omega = \int_0^{2\pi} \int_0^{\pi} \mathbf{A} \cdot \mathbf{A}' \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \,. \tag{B.17}$$

Under this inner product, all even VSH are orthogonal to the odd VSH due to the orthogonality of $\sin(m\varphi)$ and $\cos(m'\varphi)$, as well as all VSH with $m \neq m'$ [Eq. (B.2)]. The remaining orthogonality relations can be obtained by considering Eq. (B.7), leading to

$$\begin{aligned}\langle \mathbf{L}_{em'\ell}, \mathbf{L}_{em'\ell'} \rangle_\Omega &= \langle \mathbf{L}_{om\ell}, \mathbf{L}_{om\ell'} \rangle_\Omega \\ &= \delta_{m,m'}\delta_{\ell,\ell'}(1+\delta_{m,0})\frac{2\pi}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}\left[\left(k\frac{\mathrm{d}z_\ell(kr)}{\mathrm{d}(kr)}\right)^2 + \ell(\ell+1)\left(k\frac{z_\ell(kr)}{kr}\right)^2\right],\end{aligned} \tag{B.18}$$

$$\begin{aligned}\langle \mathbf{M}_{em\ell}, \mathbf{M}_{em\ell'} \rangle_\Omega &= \langle \mathbf{M}_{om\ell}, \mathbf{M}_{om\ell'} \rangle_\Omega \\ &= \delta_{m,m'}\delta_{\ell,\ell'}(1+\delta_{m,0})\pi\frac{2\ell(\ell+1)}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}z_\ell^2(kr),\end{aligned} \tag{B.19}$$

$$\begin{aligned}\langle \mathbf{N}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_\Omega &= \langle \mathbf{N}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_\Omega \\ &= \delta_{m,m'}\delta_{\ell,\ell'}(1+\delta_{m,0})\pi\frac{2\ell(\ell+1)}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}\left[\left(\frac{z_\ell}{kr}\right)^2 + \left(\frac{1}{kr}\frac{\mathrm{d}[krz_\ell(kr)]}{\mathrm{d}(kr)}\right)^2\right].\end{aligned} \tag{B.20}$$

$$\begin{aligned}\langle \mathbf{L}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_\Omega &= \langle \mathbf{L}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_\Omega \\ &= \delta_{m,m'}\delta_{\ell,\ell'}(1+\delta_{m,0})\pi\frac{2\ell(\ell+1)}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}\left[\frac{z_\ell}{kr}\frac{\mathrm{d}z_\ell(kr)}{\mathrm{d}(kr)} + \left(\frac{1}{kr}\frac{\mathrm{d}[krz_\ell(kr)]}{\mathrm{d}(kr)}\right)^2\right]\end{aligned} \tag{B.21}$$

$$\langle \mathbf{L}_{em\ell}, \mathbf{L}_{em\ell'} \rangle_\Omega = \langle \mathbf{L}_{om\ell}, \mathbf{L}_{om\ell'} \rangle_\Omega = \delta_{\ell,\ell'}\frac{(1+\delta_{m,0})2\pi}{2\ell+1}\frac{(\ell+m)!}{(\ell-m)!}k^2\Big[\ell z_{\ell-1}^2(kr) + (\ell+1)z_{\ell+1}^2(kr)\Big], \tag{B.22}$$

$$\langle \mathbf{N}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_\Omega = \langle \mathbf{N}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_\Omega = \delta_{\ell,\ell'}\frac{(1+\delta_{m,0})2\pi}{(2\ell+1)^2}\frac{(\ell+m)!}{(\ell-m)!}\ell(\ell+1)\Big[(\ell+1)z_{\ell-1}^2(kr) + \ell z_{\ell+1}^2(kr)\Big]. \tag{B.23}$$

$$\langle \mathbf{L}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_\Omega = \langle \mathbf{L}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_\Omega = \delta_{\ell,\ell'}\frac{(1+\delta_{m,0})2\pi}{(2\ell+1)^2}\frac{(\ell+m)!}{(\ell-m)!}\ell(\ell+1)k\Big[z_{\ell-1}^2(kr) - z_{\ell+1}^2(kr)\Big]. \tag{B.24}$$

Appendix C

The Finite Element Method

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