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, 2021

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 $\mathbf{E}^{\mathrm{i}} = \mathbf{E}_0^{\mathrm{i}} \exp\big(i\mathbf{k}^{\mathrm{i}} \cdot \mathbf{r}\big)$ 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.

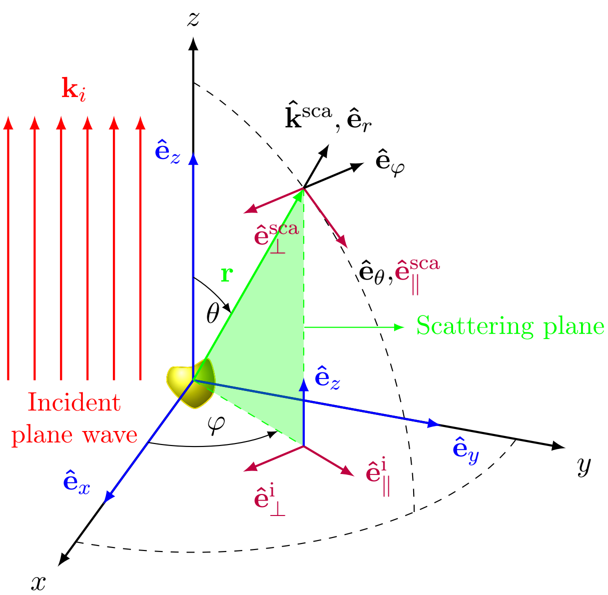

Fig. 1.1: The scattering plane (green) is defined by the vectors $\hat{\mathbf{k}}^{\mathrm{i}}$, direction of the incident plane wave (red), and $\hat{\mathbf{k}}^{\mathrm{sca}}$, direction of the scattered field in a given point $\vec{r}$. If the direction of the incident plane wave is chose to be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

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

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

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

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

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

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

Scattering Cross Section

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

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 $C_{\mathrm{abs}} > 0$ 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

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

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,

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

where the contribution of $\left\langle\mathbf{S}^{\text{i}}\right\rangle_t$ 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

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

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

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

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 Vectorial Spherical Harmonics (SVH). 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 Vectorial 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 wave number in the matrix. 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

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

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:

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

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

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

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

[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 $\boldsymbol{\nabla} \times (\boldsymbol{\nabla}^2\mathbf{F}) = \boldsymbol{\nabla}^2(\boldsymbol{\nabla} \times \mathbf{F})$.

[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 $\mathbf{M}$. As it will be shown, not necessarily $\mathbf{L}$ is orthogonal to $\mathbf{N}$.

decompose in 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 SVH

Even vectorial spherical harmonics

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

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

Odd vectorial spherical harmonics

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

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 in $r=0$, thus it is appropriate for the internal electric field and plane waves. This election of z_ℓ will be denoted in the SVH with the superscript (1). On the other hand, the asymptotic behavior of the Hankel function of first kind $h^{(1)} = j_\ell + iy_\ell$ is an outward spherical wave [2], suited for the scattered field; the VSH with $z_\ell = h^{(1)}\ell$ will be then, denoted with the superscript (3).

The SVH 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 vectorial functions as

$$\langle \mathbf{A}, \mathbf{A}' \rangle_\Omega = \int_0^{2\pi} \int_0^{\pi} \mathbf{A} \cdot \mathbf{A}' \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \,. \tag{1.24}$$

Under this inner product, all even SVH are orthogonal to the odd SVH due to the ortogonallity from the $\sin(m\varphi)$ and $\cos(m'\varphi)$, as well as all SVH with $m \neq m'$. The remaining orthogonality relations are summarized in the following expressions [8]

$$\langle \mathbf{L}_{em\ell}, \mathbf{L}_{em\ell'} \rangle_\Omega = \langle \mathbf{L}_{om\ell}, \mathbf{L}_{om\ell'} \rangle_\Omega = \delta_{\ell,\ell'} \frac{(1+\delta_{m,0})2\pi}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} k^2 \left[\ell z_{\ell-1}^2(kr) + (\ell+1) z_{\ell+1}^2(kr) \right], \tag{1.25}$$

$$\langle \mathbf{M}_{em\ell}, \mathbf{M}_{em\ell'} \rangle_\Omega = \langle \mathbf{M}_{om\ell}, \mathbf{M}_{om\ell'} \rangle_\Omega = \delta_{\ell,\ell'} \frac{(1+\delta_{m,0})2\pi}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \ell(\ell+1) z_\ell^2(kr), \tag{1.26}$$

$$\langle \mathbf{N}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_\Omega = \langle \mathbf{N}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_\Omega = \delta_{\ell,\ell'} \frac{(1+\delta_{m,0})2\pi}{(2\ell+1)^2} \frac{(\ell+m)!}{(\ell-m)!} \ell(\ell+1) \left[(\ell+1) z_{\ell-1}^2(kr) + \ell z_{\ell+1}^2(kr) \right]. \tag{1.27}$$

$$\langle \mathbf{L}_{em\ell}, \mathbf{N}_{em\ell'} \rangle_\Omega = \langle \mathbf{L}_{om\ell}, \mathbf{N}_{om\ell'} \rangle_\Omega = \delta_{\ell,\ell'} \frac{(1+\delta_{m,0})2\pi}{(2\ell+1)^2} \frac{(\ell+m)!}{(\ell-m)!} \ell(\ell+1) k \left[z_{\ell-1}^2(kr) - z_{\ell+1}^2(kr) \right]. \tag{1.28}$$

1.2.2 Incident, Scattered and Internal Electric Field

Let $\mathbf{E}_{0,x}$ be a plane wave traveling in the vertical direction $\mathbf{e}_z$; its representation in the canonical spherical basis is

$$\mathbf{E}_{0,x}(\mathbf{r}) = E_0(\sin\theta\cos\varphi\hat{\mathbf{e}}_r + \cos\theta\cos\varphi\hat{\mathbf{e}}_\theta + -\sin\varphi\hat{\mathbf{e}}_\varphi)\exp(ikr\cos\theta). \tag{1.29}$$

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 $\mathbf{E}_{0,x}$, 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 on $\mathbf{M}_{o1\ell}^{(1)}$. Thus, Eq. (1.30) can be written as the linear combination

$$\mathbf{E}_{0,x}(\mathbf{r}) = \sum_\ell \left(a_\ell \mathbf{M}_{o1\ell}^{(1)} + b_\ell \mathbf{M}_{e1\ell}^{(1)} \right). \tag{1.30}$$

Chapter 2

Results and discussion

2.1 Finite Element Method and Analytical Solutions

2.2 Incrustation Degree of a Spherical Particle

Chapter 3

Conclusions

3.1 Future Work: Application on Metasurfaces

Appendix A

The Finite Element Method

Bibliography

[1] R. S. Moirangthem, M. T. Yaseen, P.-K. Wei, J.-Y. Cheng, and Y.-C. Chang. Enhanced localized plasmonic detections using partially-embedded gold nanoparticles and ellipsometric measurements. *Biomedical Optics Express*, **3**(5):899, May 2012. ISSN: 2156-7085, 2156-7085. DOI: 10.1364/BOE.3.000899. URL: https://www.osapublishing.org/boe/abstract.cfm?uri=boe-3-5-899 (visited on 08/03/2021) (cited on page 3).

[2] C. F. Bohren and D. R. Huffman. *Absorption and Scattering of Light by Small Particles*. English. Wiley Science Paperbak Series. John Wiley & Sons, 1st edition, 1983. ISBN: 0-471-029340-7 (cited on pages 3, 5, 8, 10).

[3] L. Tsang, J. A. Kong, and K.-H. Ding. *Scattering of Electromagnetic Waves: Theories and Applications*. en. John Wiley & Sons, Inc., New York, USA, July 2000. ISBN: 978-0-471-22428-0 978-0-471-38799-2. DOI: 10.1002/0471224286. URL: http://doi.wiley.com/10.1002/0471224286 (visited on 05/17/2020) (cited on pages 3–7).

[4] J. D. Jackson. *Classical electrodynamics*. Wiley, New York, 3rd ed edition, 1999. ISBN: 978-0-471-30932-1 (cited on page 5).

[5] M. Pellarin, C. Bonnet, J. Lermé, F. Perrier, J. Laverdant, M.-A. Lebeault, S. Hermelin, M. Hillenkamp, M. Broyer, and E. Cottancin. Forward and Backward Extinction Measurements on a Single Supported Nanoparticle: Implications of the Generalized Optical Theorem. *The Journal of Physical Chemistry C*, **123**(24):15217–15229, June 2019. ISSN: 1932-7447, 1932-7455. DOI: 10.1021/acs.jpcc.9b03245. URL: https://pubs.acs.org/doi/10.1021/acs.jpcc.9b03245 (visited on 08/03/2021) (cited on page 6).

[6] R. G. Newton. Optical theorem and beyond. en. *American Journal of Physics*, **44**(7):639–642, July 1976. ISSN: 0002-9505, 1943-2909. DOI: 10.1119/1.10324. URL: http://aapt.scitation.org/doi/10.1119/1.10324 (visited on 12/04/2020) (cited on page 6).

[7] A. Zangwill. *Modern Electrodynamics*. Cambridge University Press, Cambridge, 2013. ISBN: 978-0-521-89697-9 (cited on pages 7, 8).

[8] J. A. Stratton. *Electromagnetic theory*. McGraw-Hill, New York, 2012. ISBN: 978-1-4437-3054-9 (cited on pages 8, 10).

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