Resonant Scattering Particles

Morphological characteristics of plasmonic and dielectric resonances on spherical and polyhedral inclusions

Dimitrios C. Tzarouchis
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Morphological characteristics of plasmonic and dielectric resonances on spherical and polyhedral inclusions

Dimitrios C. Tzarouchis
Supervising professor
Prof. Ari Sihvola, Aalto University, Finland

Thesis advisor
Docent Pasi Ylää-Oijala, Aalto University, Finland

Preliminary examiners
Prof. Filiberto Bilotti, ROMA TRE University, Italy
Prof. Boris Lukiyanchuk, Nanyang Technological University, Singapore

Opponent
Prof. Ortwin Hess, Imperial College London, United Kingdom
Abstract

The presented thesis concerns the study of the single particle scattering mechanisms and the corresponding morphological dependencies, specifically targeted for light-matter control applications.

The initial part focuses on aspects regarding the most fundamental electromagnetic scattering problem, i.e., single homogeneous sphere in the small size limit domain. The analytical solutions for the corresponding electrostatic and dynamic problem are implemented with emphasis to the plasmonic and dielectric resonant domains and their corresponding size-dependent dynamic mechanisms. A novel analytic methodological approach is introduced for extracting the resonant pole distribution, the maximum resonant absorption condition, and other scattering features. This part of the thesis summarize the first article trilogy (Publications I-III).

Employed with the intuition that the aforementioned physical results provide, the second part of this thesis explores certain morphological aspects through theory of the superquadric surfaces. These surfaces allow the continuous deformation of a sphere towards other shapes, such as the superquadric hexahedron and octahedron, and the five regular polyhedra i.e., the Platonic solids. The required scattering quantities are numerically extracted via a surface integral equation methodology, and the main results are presented in the second article trilogy presented in Publications IV-VI.

The main contribution of this thesis is the disclosure of a series of resonant effects and peculiarities that can be utilized for the design of resonant nanoparticles with on-demand functionalities. The presented results can be immediately exploited by theoretical and experimental communities, either as reference and benchmarking results, or as stepping stone for further theoretical studies in the field of electromagnetic scattering.

Keywords  Electromagnetic Scattering, Plasmonic Resonances, Dielectric Resonances, Lorenz-Mie Theory, Spheres, Superquadric Surfaces, Platonic Solids

Author
Dimitrios C. Tzarouchis

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Preface

“What is past is prologue” ...
... It means you ain’t heard nothing yet!
Abraham Pais, “Inward Bound”

The present thesis concludes the efforts initiated at the Department of Radioscience and Engineering (RAD) and concluded at the Department of Electronics and Nanoengineering (ELE) in Aalto University. Of course, both names describe essentially the same department, reflecting the rapid changes on the field of electromagnetics, radio science and radio engineering. My work spanned between the period 2015-2018, a fruitful, productive, and exciting period of my life.

The articles included in this thesis acknowledge only a very small number of the people that were involved in the completion of this thesis, resembling very much the structure of an iceberg: most of its volume is well-hidden beneath the sea surface. Therefore, I feel obliged to express my gratitude towards all people that contributed directly or indirectly to the completion of this thesis.

First, I would like to thank my supervisor, mentor, sponsor, colleague, and friend, prof. Ari Sihvola. His devotion into science and people, his all-positive energy, his great teaching abilities, and his exquisite humor – a delicate mixture of Finnish-life philosophy and cosmopolitanism – made my doctoral passage a wonderful journey. His qualities are a constant inspiration for conducting rigorous science with ethos. Moreover, I would like to thank my thesis instructor, Dr. Pasi Ylä-Oijala, for his relentless efforts to my everyday inquiries and concerns. His constant scientific and technical support was (and still is) of paramount importance for my professional life. I am deeply grateful to both of you for all of your support all these years.

Apart from my close colleagues, I would like to acknowledge and thank some of our local collaborators: prof. Tapio Ala-Nissilä, Dr. Henrik Wal-
lén, Dr. Seppo Järvenpää, and Dr. Beibei Kong. Thank you all for your support, patience, and instructive discussions. Additional thanks belong to prof. Keijo Nikoskinen for guiding me into the pedagogical aspects of engineering. Many thanks go also to Dr. Jari Holopainen, for his pedagogical and scientific support, and to prof. Constantin Simovski and prof. Sergei Tretyakov for our nice tea-time discussions.

At this stage I would like to acknowledge some of my Aalto colleagues: prof. Adnane Osmane, Dr. Tommi Rimpiläinen, Dr. Viktar Asadchy, Dr. Younes Ra’di, Mr. Grigorii Ptitcyn, Mr. Xuchen Wang, Dr. Fu Liu, Dr. Mohammad Sajjad Mirmoosa and all the personnel in the ELE Department. Thank you all for the happy times, the interesting discussions, and the wonderful tea-time activities.

Moving towards my international academic circle, I would like to express my gratitude to prof. Nader Engheta for hosting my research visit at the University of Pennsylvania. I am humbled and honored from your support. Many thanks deserve to his team, Dr. Nasim-Mohammadi Estakhri, Dr. Mario (Jr.) Mencagli, and Dr. Yaakov Lumer for creating a nice atmosphere during my stay in Philadelphia. Additionally, many thanks to prof. Mario Silveirinha for hosting my short visit at the University of Lisbon in Portugal. Finally, warm acknowledgments belong to prof. Samel Arslanagic and prof. Richard Ziolkowski for our very nice discussions and happy times during the international conferences that we commonly attended. Indeed, it is my honor and privilege to have met you all.

Apart the “science friends”, warm gratitudes belong to my friends living in Finland: Dr. Osama Khurshid, Dr. Angelos Balatsas-Lekkas, Mr. FranciscoSolano-Eizaguirre, Mr. Pedro Aiboe, Dr. Jussi Alho, prof. Themistoklis Charalampous, prof. Stavros Tripakis, Ms. Evisa Tsolakou, Dr. John Millar, Mrs. Riita-Leena Sihvola, Mrs. Elisavet Rigatou, Dr. Kostantinos Daskalakis, Mr. Stavros Evdoridis, Mr. Antonios Matakos, Mr. Evagoras Makris, and the whole Hellas Helsinki Basketball team. Thank you all for the wonderful times and the positive aura that you shared with me.

Many warm thanks to my music fellows, especially to the Klezmama, Eva Jacobs, and the Helsinki Klezmer Kapelye “family”: Tony, Carolina, Mayim, Philip, Antti, Daniel, Maria Eveliina, Benjamin, Annika, Alevtina, Asta, Mikko, Murat, and Carmela. Thank you all for your warmth, the joy, and brightness that so generously shared with me during the cold and dark winters and the long summer days.
As the radius of this “gratitude circle” increases acknowledgments belong to the “old ’n’ good” friends: Mr. Alexandros–Iakovos Tzenos, Mr. Themistokles Roupakas and Mrs. Yiouli Tsirtoglou and their daughter (my god-daughter!) Rozalia Roupaka, Mr. Apostolos Aspragkathos, Mr. Ioannis Zervas, Dr. Penny Mpouska and Mr. Theodoros Kyrloglou, Mr. Panagiotis and Mrs. Panagiota Geraki, Mr. Orion Afisiadis, Dr. Athanasios and Mrs. Evgenia Margariti, and Mr. Lazaros Theodorakopoulos. Despite being far away, your presence has a huge impact in my well-being, my prosperity, and my personality. Thank you very much for this and I wish you the best in your life.

The center of my existence is close to my parents, Mr. Charalampos and Mrs. Jenny Tzarouchi, for the unconditional love, overwhelming care, and immense support all these years. Many-many hugs and kisses belong to my sister, Dr. Loukia Tzarouchi, her husband, Dr. Alexios Papazotos, and their baby-daughter for all the happy moments that brought into my life. Special thanks go to my grandmothers, Mrs. Loukia Tzarouchi and Mrs. Stasiani Tzouvara, to my cousins, Christos and Dianna Tzouvara, and their parents, Mr. Konstantinos and Mrs. Eleni Tzouvara. May you all be blessed, healthy, happy, and lucky in your life. The most important part of my existence, my heart, belongs to Ms. Dilara Asardag, the brightest, most amazing, and most inspirational person in my life. Thank you, Didi, for your love, your support and your insightful inputs for my life and my work.

The thesis is dedicated to the memory of my first teacher in electromagnetics, prof. Antonios Papagiannakis, a fantastic person, a great tutor, and a good friend that inspired me with the love of electromagnetics research and pedagogy.

Helsinki, February 18, 2019,

Dimitrios Charalampous Tzarouchis
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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Unveiling the scattering behavior of small spheres”

The idea of revisiting the scattering properties of a sphere was proposed and supervised by Prof. Sihvola. The main concept of utilizing for the Padé approximants for extracting the distribution of the magnetic resonances on a homogenous sphere was conceived and developed by the author. All authors discussed the results and reviewed the final manuscript that was written by the author.

Publication II: “Resonant scattering characteristics of homogeneous dielectric sphere”

The author developed further the idea presented in Publication I for studying in detail all the resonant aspects of a homogeneous sphere. Prof. Sihvola supervised the project. The author wrote the manuscript. All authors discussed the results and reviewed the final manuscript.

Publication III: “General scattering characteristics of resonant core–shell spheres”

The author developed further the idea presented in Publication I for re-examining the plasmonic properties of a core-shell sphere and wrote the manuscript. Prof. Sihvola supervised the project. All authors discussed the results and reviewed the final manuscript.
Publication IV: “Shape effects on surface plasmons in spherical, cubic, and rod-shaped silver nanoparticles”

The idea for studying the resonant spectrum of non-analytical particles was proposed by Prof. Sihvola. The author performed the calculations and analyzed the results based on the code provided by Dr. Ylä-Oijala. The author wrote the manuscript. The project was supervised by Prof. Sihvola and co-supervised by Prof. Ala-Nissilä. All authors discussed the results and reviewed the final manuscript.

Publication V: “Plasmonic properties and energy flow in rounded hexahedral and octahedral nanoparticles”

The author developed the idea of studying the mathematical properties and the resonant Poynting distribution of dual superquadric shapes. The calculations were done on numerical codes provided by Dr. Ylä-Oijala. The project was proposed and supervised by Prof. Sihvola and co-supervised by Prof. Ala-Nissilä. The author wrote the manuscript. All authors discussed the results and reviewed the final manuscript.

Publication VI: “Study of plasmonic resonances on Platonic solids”

The author developed the idea and performed the analysis of the plasmonic Platonic solids inspired by a previous work by Prof. Sihvola and Dr. Ylä-Oijala. The calculations performed based on the code provided by Dr. Ylä-Oijala. The project was supervised by Prof. Sihvola. The author wrote the manuscript. All authors discussed the results and reviewed the final manuscript.
List of Abbreviations

abs absorption
BEM boundary element method
EM electromagnetic
e external (subscript)
ext extinction (subscript)
i internal/inside (subscript)
inc incident (subscript)
LSPR localized surface plasmon resonance
PMCHWT Poggio–Miller–Chang–Harrington–Wu–Tsai
RF radio frequencies
RWG Rao–Wilton–Glisson
SEP surface equivalence principle
SIE surface integral equation
sca scattered/scattering (subscript)
TE transverse electric
THz terahertz
TM transverse magnetic
t total (subscript)
UV ultraviolet
3D three dimensions
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>vector potential (A/m)</td>
</tr>
<tr>
<td>$A$</td>
<td>area (m$^2$)</td>
</tr>
<tr>
<td>$A_l$</td>
<td>internal electrostatic coefficient of the $l$-th multipole (V/m$^l$)</td>
</tr>
<tr>
<td>$a$</td>
<td>radius of the sphere (m)</td>
</tr>
<tr>
<td>$a_l$</td>
<td>the $l$-th multipole electric (TE) external Mie coefficient</td>
</tr>
<tr>
<td>$a_l^P$</td>
<td>the Padé expansion of the $a_l$ Mie coefficient</td>
</tr>
<tr>
<td>$a_l^T$</td>
<td>the Taylor expansion of the $a_l$ Mie coefficient</td>
</tr>
<tr>
<td>$B_l$</td>
<td>external electrostatic coefficient of the $l$-th multipole (V m$^{l+1}$)</td>
</tr>
<tr>
<td>$B(x,y)$</td>
<td>beta function with arguments $x$ and $y$</td>
</tr>
<tr>
<td>$b_l$</td>
<td>the $l$-th multipole magnetic (TM) external Mie coefficient</td>
</tr>
<tr>
<td>$b_l^P$</td>
<td>the Padé expansion of the $b_l$ Mie coefficient</td>
</tr>
<tr>
<td>$b_l^T$</td>
<td>the Taylor expansion of the $b_l$ Mie coefficient</td>
</tr>
<tr>
<td>$C_j$</td>
<td>cross section for the $j$ variable (m$^2$)</td>
</tr>
<tr>
<td>$c$</td>
<td>speed of light 299792458 (m/s)</td>
</tr>
<tr>
<td>$c_l$</td>
<td>the $l$-th multipole magnetic (TE) internal Mie coefficient</td>
</tr>
<tr>
<td>$D$</td>
<td>electric flux density (displacement) (As/m$^2$)</td>
</tr>
<tr>
<td>$D_j$</td>
<td>$j$-th domain</td>
</tr>
<tr>
<td>$d$</td>
<td>diameter of the particle (m)</td>
</tr>
<tr>
<td>$d_l$</td>
<td>the $l$-th multipole electric (TM) internal Mie coefficient</td>
</tr>
<tr>
<td>$E_j$</td>
<td>vector electric field on the $j$-th domain (V/m)</td>
</tr>
<tr>
<td>$E_0$</td>
<td>electric field amplitude (V/m)</td>
</tr>
<tr>
<td>$e$</td>
<td>electron charge $1.602 \cdot 10^{-19}$ (As)</td>
</tr>
<tr>
<td>$e$</td>
<td>Euler's constant</td>
</tr>
<tr>
<td>$F_j$</td>
<td>vector field on the $j$ domain</td>
</tr>
<tr>
<td>$f(x,y,z)$</td>
<td>inside-out function of a surface</td>
</tr>
<tr>
<td>$G(kjr)$</td>
<td>free-space Green's function at the $j$-th domain</td>
</tr>
<tr>
<td>$H_j$</td>
<td>vector magnetic field on the $j$-th domain (A/m)</td>
</tr>
<tr>
<td>$H_l(x)$</td>
<td>Riccati–Hankel function of order $l$</td>
</tr>
<tr>
<td>$h_l^{(1)}(x)$</td>
<td>spherical Hankel function of the first kind and order $l$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$I$</td>
<td>dipole moment (Am)</td>
</tr>
<tr>
<td>$J$</td>
<td>electric current density (A/m$^2$)</td>
</tr>
<tr>
<td>$\dot{J}_l(x)$</td>
<td>Riccati–Bessel function of order $l$</td>
</tr>
<tr>
<td>$j_l(x)$</td>
<td>spherical Bessel function of the first kind of order $l$</td>
</tr>
<tr>
<td>$k$</td>
<td>wavenumber (1/m)</td>
</tr>
<tr>
<td>$[L/M]$</td>
<td>Padé approximant of order $L$ (numerator) and $M$ (denominator)</td>
</tr>
<tr>
<td>$l$</td>
<td>multipole order</td>
</tr>
<tr>
<td>$M$</td>
<td>magnetic current (V/m)</td>
</tr>
<tr>
<td>$m_\phi$</td>
<td>azimuthal number</td>
</tr>
<tr>
<td>$m$</td>
<td>material contrast</td>
</tr>
<tr>
<td>$m_e$</td>
<td>electron mass $9.109 \times 10^{-31}$ (kg)</td>
</tr>
<tr>
<td>$n_0$</td>
<td>electron density</td>
</tr>
<tr>
<td>$n$</td>
<td>normal vector</td>
</tr>
<tr>
<td>$P(\phi)$</td>
<td>angular function of $\phi$</td>
</tr>
<tr>
<td>$P_l(x)$</td>
<td>Legendre polynomial of order $l$</td>
</tr>
<tr>
<td>$P^m_l(x)$</td>
<td>Associated Legendre polynomial of degree $l$ and order $m$</td>
</tr>
<tr>
<td>$p$</td>
<td>power or roundness factor of a superquadric surface</td>
</tr>
<tr>
<td>$p_d$</td>
<td>power or roundness factor of a dual superquadric surface</td>
</tr>
<tr>
<td>$p_l$</td>
<td>first root of the $l$-th spherical Bessel function of the first kind</td>
</tr>
<tr>
<td>$Q_j$</td>
<td>efficiency of the j-th quantity</td>
</tr>
<tr>
<td>$R^a_l$</td>
<td>special function for the $a_l$ Mie coefficient</td>
</tr>
<tr>
<td>$R^b_l$</td>
<td>special function for the $b_l$ Mie coefficient</td>
</tr>
<tr>
<td>$R(r)$</td>
<td>radial function</td>
</tr>
<tr>
<td>$r$</td>
<td>radial variable $\in [0, +\infty)$</td>
</tr>
<tr>
<td>$r(\theta, \phi)$</td>
<td>parametric function of a surface</td>
</tr>
<tr>
<td>$S_j$</td>
<td>energy rate density of the j-th quantity (J/sm$^2$)</td>
</tr>
<tr>
<td>$S^a_l$</td>
<td>special function for the $a_l$ Mie coefficient</td>
</tr>
<tr>
<td>$S^b_l$</td>
<td>special function for the $b_l$ Mie coefficient</td>
</tr>
<tr>
<td>$T(\theta)$</td>
<td>angular function $\theta$</td>
</tr>
<tr>
<td>$u_j$</td>
<td>unit vector of the variable j</td>
</tr>
<tr>
<td>$V$</td>
<td>volume (m$^3$)</td>
</tr>
<tr>
<td>$W_j$</td>
<td>energy rate (power) of the j-th quantity (J/s)</td>
</tr>
<tr>
<td>$w$</td>
<td>single scattering albedo</td>
</tr>
<tr>
<td>$x$</td>
<td>size parameter</td>
</tr>
<tr>
<td>$y_l(x)$</td>
<td>spherical Bessel function of the second kind and order $l$</td>
</tr>
<tr>
<td>$\tilde{Y}_l(x)$</td>
<td>Riccati–Neumann function of order $l$</td>
</tr>
<tr>
<td>$Z$</td>
<td>electric vector potential (V)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>polarizability ((\text{As}^2/\text{V}))</td>
</tr>
<tr>
<td>( \alpha_N )</td>
<td>normalized polarizability</td>
</tr>
<tr>
<td>( \gamma_j )</td>
<td>damping term of the ( j )-th oscillator</td>
</tr>
<tr>
<td>( \bar{\varepsilon} )</td>
<td>relative permittivity tensor</td>
</tr>
<tr>
<td>( \varepsilon_0 )</td>
<td>vacuum permittivity, (8.854 \cdot 10^{-12} , (\text{As/Vm}))</td>
</tr>
<tr>
<td>( \varepsilon_\infty )</td>
<td>background permittivity</td>
</tr>
<tr>
<td>( \varepsilon' )</td>
<td>real part of permittivity</td>
</tr>
<tr>
<td>( \varepsilon'' )</td>
<td>imaginary part of permittivity</td>
</tr>
<tr>
<td>( \varepsilon_{bl} )</td>
<td>resonant permittivity for the ( b_l ) resonance</td>
</tr>
<tr>
<td>( \varepsilon_e )</td>
<td>relative permittivity of the host medium (external)</td>
</tr>
<tr>
<td>( \varepsilon_i )</td>
<td>relative permittivity of the internal medium</td>
</tr>
<tr>
<td>( \varepsilon_{\text{diel}} )</td>
<td>resonant permittivity for the ( a_l ) dielectric resonance</td>
</tr>
<tr>
<td>( \varepsilon_{\text{plas}} )</td>
<td>resonant permittivity for the ( a_l ) plasmonic resonance</td>
</tr>
<tr>
<td>( \varepsilon_{i/[L/M]} )</td>
<td>resonant permittivity utilizing the ([L/M]) Padé approximant</td>
</tr>
<tr>
<td>( \eta )</td>
<td>wave impedance (ohm)</td>
</tr>
<tr>
<td>( \theta )</td>
<td>elevation angle variable ( \in [0, \pi] )</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>wavelength (m)</td>
</tr>
<tr>
<td>( \mu_0 )</td>
<td>vacuum permeability, (4\pi \cdot 10^{-7} , (\text{Vs/Am}))</td>
</tr>
<tr>
<td>( \mu )</td>
<td>relative permeability</td>
</tr>
<tr>
<td>( \pi_e )</td>
<td>electric scalar Debye potential (A)</td>
</tr>
<tr>
<td>( \pi_m )</td>
<td>magnetic scalar Debye potential (V)</td>
</tr>
<tr>
<td>( \Phi_j )</td>
<td>electrostatic potential (V) of the ( j )-th quantity</td>
</tr>
<tr>
<td>( \phi )</td>
<td>azimuthal angle variable ( \in [0, 2\pi] )</td>
</tr>
<tr>
<td>( \omega )</td>
<td>angular frequency (1/s)</td>
</tr>
<tr>
<td>( \omega_- )</td>
<td>symmetric resonant frequency (1/s)</td>
</tr>
<tr>
<td>( \omega_+ )</td>
<td>antisymmetric resonant frequency (1/s)</td>
</tr>
<tr>
<td>( \omega_{pj} )</td>
<td>plasma frequency of the ( j )-th oscillator (1/s)</td>
</tr>
</tbody>
</table>
List of Symbols
List of Operators

\[ \partial_{ij} \]  partial derivative with respect to variables \( i \) and \( j \)

\[ \Re\{F\} \]  real part of the complex quantity \( F \)

\[ \Im\{F\} \]  imaginary part of the complex quantity \( F \)
1. Introduction: About resonant particles

Scattering and absorption of light, i.e., electromagnetic (EM) radiation, by a single particle is a long studied basic problem in modern applied and theoretical sciences, such as material and optical physics [1–5], chemistry [6, 7], nanotechnology [5, 8], radio and antenna engineering [9, 10], and applied mathematics [11].

In principle, the study of such problem is usually divided into two domains: the geometrical and material effects. There is an enormous amount of available studies on the subject and the case of a homogenous dielectric sphere is, perhaps, the most useful model for the exploration of both morphological and material effects. Sphere is one of the few three-dimensional bounded geometrical shapes that possess a closed-form analytical solution either in the electrostatic or the electrodynamic domain, thus it can be arguably perceived as an archetypical scatterer. For example, a sphere is commonly used as reference for any kind of EM scattering theory [12] and applications, from the utilization on experimental setups [7] to the benchmarking of computational methods [13, 14] and beyond. A characteristic example is the recent identification of Fano interference line-shapes appearing on the scattering spectrum of a sphere [15–18].

The metamaterial (metasurface) paradigm [19–21] implements basic plasmonic or all-dielectric resonant properties of single inclusions for energy harvesting devices in a vast region of frequencies and sizes, from RF, THz, infrared, and optical regimes to geometrical optics, classical antennas, and size-enabled quantum effects [4, 5, 8, 21–29]. Likewise, the conceptual demonstration and realization of single particle devices, such as sensors [30, 31], EM cloaks [32–36], “super”-scatterers [37], optical force carriers [38], and optical memory devices [39], are all different scattering perspectives of a spherical inclusion. New EM energy control functionalities emerge as the collective effect of a suspension of spherical scat-
Introduction: About resonant particles

It is therefore evident that the spherical scattering particles are in the core of modern EM and optics research.

The sphere, however, is a basic but not the only geometry that can illuminate all the aspects on EM scattering. Actually, manufacturing a perfect sphere can be an extremely challenging task, especially at the nanoscale, and often a spherical inclusion is an approximation that asymptotically emulates the behavior of rather irregular morphologies. In many cases the resulting particles expose intrinsic non-spherical symmetries and irregularities, such as chemically grown silver nanoparticles that exhibit cubic and octahedral symmetries [41]. Naturally occurring particles can exhibit a non-spherical geometry as well [42]. For instance, cubic nanoparticles can deliver promising and unexplored physical features [43–47] and enhanced light–matter interaction functionalities [48–51]. All the above cases, therefore, give a strong motivation for studying the morphological effects on naturally-occurring or artificially-grown non-spherical inclusions, their resonant spectrum characteristics, and their corresponding geometry-related physical properties.

The driving force behind this thesis is to reveal the involved scattering mechanisms and the corresponding morphological dependencies on single particles, specifically targeted to light-matter control applications. To do so, the first objective is to understand and reveal new aspects regarding the most basic case, i.e., a single homogeneous sphere in the small-size limit. The main emphasis here is given towards the plasmonic and dielectric resonant domains and the corresponding dynamic (size-dependent) mechanisms, such as the distribution of the resonances, maximum resonant absorption, directive scattering, and linewidth. For these purposes the Lorenz–Mie theory has been implemented, and novel ways for predicting the aforementioned mechanism have been introduced. The three first publications (Publications I-III) reflect these efforts, by introducing analytical expressions of the resonant distribution of a sphere by approximating the Mie coefficients with Padé expansions. The introduced methodology is applied for all the aforementioned mechanisms.

Employed with the extracted analytical results, we explore further morphological aspects through the perturbation of a sphere towards smooth versions of cubical and octahedral particles. This is the second objective that covers mainly non-spherical particles. In particular, we utilize the generalized theory of superquadric surfaces [52] that allow us to continuously deform a sphere towards a cube and an octahedron. The surface
integral equation (SIE) methodology is utilized for our purposes providing us with the required scattering quantities. The results, presented in Publications IV and V, expose the main morphological mechanism behind the plasmonic spectrum of these shapes, such as the creation of energy vortices and the existence of higher order multipoles with enhanced absorptive characteristics.

Finally, the third objective focused on sharp-edged cases, regular cubes and octahedra, in the context of the family of the five canonical polyhedra, i.e., the Platonic solids. In this case we performed a series of numerical experiments and extracted their resonant plasmonic spectrum (Publication VI). The results indicate a strong correlation between the solid-vertex sharpness and the energy of the corresponding plasmonic resonances.

All three studied cases, i.e., sphere, superquadrics, and Platonic solids, presented in this thesis, show that analytical and numerical modeling can reveal a series of resonant effects and peculiarities, playing a pivotal role for the design of resonant nanoparticles with on-demand functionalities. Therefore, the presented results can be immediately utilized by scientific and applied communities, willing to compare and benchmark similar results, or as a reference for further theoretical studies.

1.1 Why resonant particles? Historical remarks

Before going into further details about the structure of this thesis, we will give a brief retrospective of the main historical contributions on the resonant scattering subject, up to late 1970’s.

The scattering problem can be categorized roughly into three size regimes, relative to the wavelength: (a) The small size limit (Rayleigh or electrostatic region) includes sizes smaller than one tenth of the wavelength (size \(\ll \lambda\)), (b) the medium size regime (or Mie region) where the size is of the order of the wavelength (size \(\approx \lambda\)), and (c) the large limit (geometrical optics limit), i.e., a sphere multiple times larger than the wavelength (size \(\gg \lambda\)). Each regime offers a great variety of phenomena and applications. For example, the geometrical optics regime has been utilized for the design of lenses [53] and the explanations of physical phenomena such as atmospheric halos [54]. On the other hand scattering by small/medium targets has been used for the explanation of fundamental questions on why the sky is blue and the clouds are white, or about the number and direction of a comet’s tail, and the existence of vibrant colors in gold and
Introduction: About resonant particles

other metallic nanocomposites [55].

Table 1.1. Brief timetable of the main contributions in scattering theory up to 1980.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1861</td>
<td>A. Clebsch</td>
<td>Elastic wave scattering</td>
</tr>
<tr>
<td>1871</td>
<td>Lord Rayleigh</td>
<td>“Rayleigh” scattering</td>
</tr>
<tr>
<td>1881</td>
<td>H. Lamb</td>
<td>Elastic wave scattering</td>
</tr>
<tr>
<td>1890</td>
<td>L. V. Lorenz</td>
<td>Exact solution</td>
</tr>
<tr>
<td>1893</td>
<td>J. J. Thomson</td>
<td>Perfectly conducting sphere</td>
</tr>
<tr>
<td>1899</td>
<td>A. E. H. Love</td>
<td>Extension of Thomson’s work</td>
</tr>
<tr>
<td>1900</td>
<td>G. W. Walker</td>
<td>Scattering by a sphere</td>
</tr>
<tr>
<td>1908</td>
<td>G. Mie</td>
<td>Reference solution</td>
</tr>
<tr>
<td>1909</td>
<td>P. Debye</td>
<td>Debye potentials</td>
</tr>
<tr>
<td>1910</td>
<td>J. W. N. Nicholson</td>
<td>Connection with geometrical optics</td>
</tr>
<tr>
<td>1915</td>
<td>H. Bateman</td>
<td>First complete review</td>
</tr>
<tr>
<td>1917</td>
<td>A. J. Proudman</td>
<td>Detail numerical evaluation</td>
</tr>
<tr>
<td>1920</td>
<td>G. N. Watson</td>
<td>Watson transformation</td>
</tr>
<tr>
<td>1919</td>
<td>T. J. Bromwich</td>
<td>Detailed numerical evaluation</td>
</tr>
<tr>
<td>1941</td>
<td>J. A. Stratton</td>
<td>Seminal book</td>
</tr>
<tr>
<td>1951</td>
<td>A. Aden &amp; M. Kerker</td>
<td>Core-shell sphere</td>
</tr>
<tr>
<td>1951</td>
<td>N. Marcuvitz</td>
<td>Spherical field representations [56]</td>
</tr>
<tr>
<td>1959</td>
<td>C. T. Tai</td>
<td>Analytical Luneberg lens [57]</td>
</tr>
<tr>
<td>1953</td>
<td>P. M. Morse &amp; H. Feshbach</td>
<td>Seminal multiphysics book</td>
</tr>
<tr>
<td>1957</td>
<td>H. C. van de Hulst</td>
<td>Seminal scattering book</td>
</tr>
<tr>
<td>1959</td>
<td>M. Born &amp; E. Wolf</td>
<td>Seminal optics book</td>
</tr>
<tr>
<td>1967</td>
<td>M. Kerker</td>
<td>Seminal book</td>
</tr>
<tr>
<td>1973</td>
<td>E. Purcell &amp; C. Pennypacker</td>
<td>Multiple dipole scatterers [58]</td>
</tr>
<tr>
<td>1975</td>
<td>R. Fuchs</td>
<td>Small cubical particles [59]</td>
</tr>
<tr>
<td>1975</td>
<td>R. Ruppin</td>
<td>Non-local effects [60]</td>
</tr>
<tr>
<td>1980</td>
<td>W. J. Wiscombe</td>
<td>Wiscombe’s criterium [61]</td>
</tr>
</tbody>
</table>

1 Historical data from either [62–65] or in-table references.

While physical phenomena drive the scattering studies, the technological developments act as powerful catalyst of these studies. Historically, artificially manufactured large objects have first appeared as optical lenses and other RF components. However, the recent nanotechnological breakthroughs have allowed the construction of micrometer or nanometer objects at the infrared/optical/ultraviolet regime with unprecedented accuracy. This, combined with the nanotechnology advances on smaller, cleaner,
and efficient material and energy technologies can explain why modern studies are very much focused on studying the plasmonic (Rayleigh) and dielectric (Mie) physics as the “new” building blocks for novel energy control (harvesting) applications.

Wave scattering by a spherical object has been studied outside the EM context even before the establishment of Maxwell’s equations. In particular workers such as A. Clebsch in 1861 and L.V. Lorenz in 1890 derived solutions for elastic and EM scattering solving the corresponding, non-Maxwellian derived, boundary value problem. At the same time, workers such as Lord Rayleigh (1871), H. Lamb (1881), J.J. Thomson (1893), and G.W. Walker (1900) delivered solutions for various aspects on the scattering problem, before the reference solution by G. Mie (1908) and P. Debye (1909). A few decades later, several seminal textbooks appeared, such as the one by J. A. Stratton, which introduced a solid pedagogical discussion on the subject. Table 1.1 gives a chronological list on the main contributors and textbooks regarding the subject of scattering by a sphere.

Despite the long history of literature on sphere scattering, studies on non-spherical, non-analytically solvable, particles are a somewhat more recent subject. The main reason is perhaps the development of numerical methods that have undergone an incredible boost in the (post) computer era. Interestingly, the story of a resonant cube has both analytical and computational narratives. The analytical one is connected to its two dimensional corresponding problem, the sharp edge problem, while the computational one has been developed through numerical methods such as the discrete dipole approximation (DDA) [58].

As to the first one, the dielectric wedge in electrostatics has been solved by Dobrzynski and Maradudin [66], showing a rich spectrum of resonances (plasmonic ones). This solution has been further refined by Davis [67], due to the fact that a sharp edge introduces a singularity of infinite energy, i.e., the fields are not integrable at the vicinity (Meixner criterion [68,69]), and a rounded edge is needed, in the negative-permittivity case. The analytical solution of a three-dimensional dielectric case, such as a cube, remains an open “holy-grail” problem.

The early computational studies of the cube can be traced back to 1970’s, where Fuchs in his seminal article revealed its first six (plasmonic) resonances [59]. Since then, more studies verified, refined, and extended these results, revealing, slowly and steadily, several interesting aspects on the scattering by such a particle [44–46, 48, 70, 71].
1.2 Structure of the thesis

In this thesis, some of the fundamental characteristics of a resonant scattering particle are exposed, such as the two most prominent features of a resonant sphere, i.e., the plasmonic and the dielectric resonances, and the morphological effects on plasmonic resonances for non-spherical cases. Therefore, the main contribution of this thesis is twofold. First, aspects of the canonical problem of a sphere are considered, with particular emphasis to the distribution of the resonances. Additionally, several not analytically solvable cases are considered, such as the case of a cube and the family of the Platonic solids.

This thesis consists of six articles published in peer-reviewed journals, and an introductory part that consists of four chapters. Every chapter gives a brief discussion conveying the basic theoretical elements that are used throughout Publications I-VI. The articles can be divided into two “trilogies”, each dedicated for different shape case. Publications I, II, and III discuss the scattering effects of a sphere, forming the “sphere trilogy”, while Publications IV, V, and VI focus on the cubical, superquadric, and polyhedral geometries, defining the “polyhedra trilogy”. The included articles follow both a “smooth-to-sharp” morphological, i.e., from a sphere to the Platonic polyhedra, and an analytical-to-non-analytical transitions.

The introductory part begins with Chapter 2 where we present briefly the necessary mathematical background for three cases: the scattering of a sphere in the electrostatic domain, the scattering by a small Hertzian electric dipole, and the Lorenz–Mie theory. In Chapter 3 we discuss some of the prominent features regarding the resonant conditions of a sphere in the plasmonic and dielectric domains. Finally, Chapter 4 briefly reviews the key elements of the numerical method used and discusses the mathematical background regarding superquadric surfaces, which are essential concepts in the analysis of the extracted morphological scattering effects. Essentially, both Chapter 3 and 4 are a review of the key features found at both trilogies, and the references therein. The last chapter, Chapter 5, includes a brief summary of the aforementioned chapters and an overview of author’s main contributions on the subject of resonant subwavelength scatterers.
2. Electromagnetic scattering preliminaries

Any arbitrary dielectric object under the influence of an EM excitation (primary) field (potential) exerts a perturbation, i.e., the secondary or scattered field. From a physical point of view, this secondary field occurs due to the absorption and re-emission of a part of the incident energy, transferred via the primary field. Actually, a scatterer, no matter how materially and morphologically complex, is a structure microscopically composed of molecules (electrons and protons), i.e., bounded or free charges, that can be polarized by an external excitation field; polarized molecules and atoms radiate. Therefore, the secondary field is an almost unavoidable fact, due to the materiality of the scatterer.\(^1\) In this sense a scatterer is nothing but a system that perturbs the excitation field; a conceptual sketch is illustrated in Fig. 2.1.

The total field is the sum of the excitation and the perturbation fields, viz.

\[
F_t(r) = F_{\text{inc}}(r) + F_{\text{sca}}(r)
\]  

(2.1)

where \(F\) represents either the electric (E) or the magnetic (H) field. This is a fundamental perspective regarding the scattering process. A large part of the current scattering research focuses on the factors that affect the scattered field. This excitation–perturbation causal relation forms the basis for studies where the total (or partial) suppression of the scattered field is required. Obviously a scatterer that is able to produce minimum (or zero) field perturbations is electromagnetically indistinguishable. An

\(^1\)Understanding the physics behind the absorption and re-emission mechanisms by molecules or atoms requires a more thorough quantum mechanical treatment, a subject beyond the scope of this thesis.
everyday example of such is a window glass, almost transparent at the visible frequency range.

**Figure 2.1.** Conceptual representation of the considered scattering problem. A scatterer (internal domain, green), immersed into a host medium (external domain, yellow) exerts a secondary scattered field (perturbation, red lines) due to an excitation field (blue lines).

Let us now consider the fact that any excitation field introduces energy to the overall system (host medium+scatterer). The propagating part of the energy will interact in presence of a finite-size obstacle, the scatterer. Additionally, a part of this interacting energy will be absorbed. Scattering (diffraction) and absorption represent the two main energy channels of the total incident energy. The scattered energy represents the energy that (re-)propagates in the host medium, exhibiting qualitatively different characteristics than its parent source, such as changes in direction (refraction and/or reflection) and in phase (temporal lag). The absorbed energy is the part of the energy that is channeled through the intrinsic loss mechanisms of the particle; in other words, it changes character.

In the EM scattering nomenclature both absorption and scattering are collectively coined as the **extinction.** Extinction represents the total part of the energy of the source that interacts with the scatterer, as it is measured by a fixed observer and his/her measuring apparatus.\(^2\) It depends

\(^2\)There are roughly three big communities that actively study scattering phenomena: earth/radio/space scientists [14, 64, 72], optical/material physicists [53, 73, 74], and RF/antenna engineers [75, 76], all touching theoretical and experimental aspects.
mainly on the material composition of the particles, the morphology (size, shape), the host medium, the number of particles (in the case of multiple scatterers), and the incident wave (polarization, frequency). Here, we examine the case of a single particle, described by a surface that separates space into two domains, the external and the internal domain denoted by the subscript “e” and “i”, hereinafter (see Fig. 2.1). The external domain includes both incident and scattering fields.

From an energy perspective, the total, time-averaged, Poynting vector $S_t$ (energy rate density) at any point of the external domain is

$$S_t = \frac{1}{2} \Re \{E_t \times H_t^*\}$$  \hspace{1cm} (2.2)

and can be seen as a sum of three terms, i.e.,

$$S_t = S_{inc} + S_{sca} + S_{ext}$$  \hspace{1cm} (2.3)

where

$$S_{sca} = \frac{1}{2} \Re \{E_{sca} \times H_{sca}^*\}$$  \hspace{1cm} (2.4)

$$S_{inc} = \frac{1}{2} \Re \{E_{inc} \times H_{inc}^*\}$$  \hspace{1cm} (2.5)

and

$$S_{ext} = \frac{1}{2} \Re \{E_{inc} \times H_{sca}^* + E_{sca} \times H_{inc}^*\}$$  \hspace{1cm} (2.6)

are the incident, scattered, and extinction energy rate densities. For instance, assuming an enclosing surface $A$ and its normal vector $n$ as in Fig. 2.2, the total energy rate is

$$W_{abs} = - \int_A S_t \cdot ndA = - \int_A S_{inc} \cdot ndA - \int_A S_{sca} \cdot ndA + \int_A -S_{ext} \cdot ndA = 0$$

and therefore

$$W_{abs} = W_{ext} - W_{sca}$$  \hspace{1cm} (2.7)

Another important scattering metric is the cross section, defined as the ratio between the energy rate and the energy rate of the incident field, i.e.,

$$C_{ext} = \frac{\int_A S_{ext} \cdot ndA}{|S_{inc}|}$$  \hspace{1cm} (2.9)

$$C_{sca} = \frac{\int_A S_{sca} \cdot ndA}{|S_{inc}|}$$  \hspace{1cm} (2.10)

Therefore, the observer analogy is not a theoretical toy-model but rather an actual experimental fact.
Obviously, absorption cross section is defined as the difference between extinction and scattering cross sections, i.e.,

\[ C_{\text{abs}} = C_{\text{ext}} - C_{\text{abs}} \]  

(2.11)

![Figure 2.2. Conceptual demonstration of the energy balance in a scattering problem. The scattering and extinction Poynting vectors (energy rate density) are defined in an opposite direction. The difference \( W_{\text{abs}} = W_{\text{ext}} - W_{\text{sca}} \) defines the absorbed energy rate.](image)

The formulated scattering problem can be approached in two fundamentally different approaches: the direct and inverse problem approaches [77]. The direct problem approach is formulated once the excitation and morphology/material of the scatterer are known and only the scattered field is unknown. This type of problem is, for example, the EM scattering by a sphere illuminated by a linearly polarized plane wave. The results of this approach create a solid platform for physically intuitive models and interpretations on phenomena and applications.

The second type of approach is the inverse problem for which the scattering field is known (usually measured) while one or both of the morphology-material characteristics and the excitation field are unknown. Plenty of inverse scattering examples can be found mostly in medical imaging, geophysical exploration, and nondestructive testing. The main task in this approach is to find the proper scatterer–excitation combination that causes the observed perturbation. This problem family of problems are a-priori non-linear and most often numerically ill-posed, however being in the forefront of mathematical scattering theory. Actually, the direct
Electromagnetic scattering preliminaries

problem approach, especially the analytically solvable cases, is frequently adopted for the verification of inverse problem results.

In this thesis we discuss problems of the first approach by studying the most fundamental canonical problem, i.e., the scattering by a small sphere in both electrostatic and electrodynamic domains. The following sections introduce the key elements of the mathematical treatment for three distinctive cases. First, scattering by a dielectric sphere in the electrostatic domain is considered, with a brief discussion on the mathematical foundations of the analytical solution. Secondly, the same problem is phenomenologically revisited by assuming the case of scattering by a Hertzian electric dipole as a spherical inclusion. This intermediate link leads to the final section where the main parts of the electrodynamic scattering Lorenz–Mie theory are presented, concluding the chapter with key mathematical features of EM scattering theory.

2.1 Electrostatics: Rayleigh scattering

Let us assume a dielectric sphere of radius $a$ placed inside a linear, homogeneous, isotropic, host medium with relative permittivity $\varepsilon_r$, as illustrated in Fig. 2.3, where

$$\varepsilon_0 \approx 8.854 \cdot 10^{-12} \left( \frac{\text{A} \cdot \text{s}}{\text{V} \cdot \text{m}} \right)$$

is the absolute (vacuum) permittivity. The sphere is immersed in an excitation field $E_{\text{inc}}$.

Following the aforementioned line of argument the sphere exerts a secondary perturbation field, and the total field reads

$$E_t(r) = E_{\text{inc}}(r) + E_{\text{sca}}(r)$$

The electric field is irrotational, i.e., $\nabla \times E = 0$, and hence it can be expressed as the gradient of an electrostatic potential $\Phi(r)$

$$E(r) = -\nabla \Phi(r)$$

which gives an equivalent description of the form

$$\nabla \Phi_t(r) = \nabla \Phi_{\text{inc}}(r) + \nabla \Phi_{\text{sca}}(r)$$

As stated previously, the sphere is a penetrable object that divides the unbounded space into two domains. In the external domain both the excitation ($E_{\text{inc}}$) and the externally scattered field ($E_{\text{sca}}$) are present; at the

---

3The analysis presented here follows closely [78, 79].
internal domain only the internal field $E_i$ exists. The external and internal scattered fields can be treated as the reflected and transmitted fields in a reflection/refraction problem. From a physical perspective, there are two unknown quantities, i.e., $E_{\text{sc}}$ and $E_i$, that need to be determined. Mathematically, the unknown fields require the existence of two, linearly independent equations.

The required set of equations can be rigorously derived through the electric flux density (or displacement) vector $D$. For instance, a sphere, in its most general material description, can be macroscopically considered as a particle consisting of a linear, inhomogeneous, anisotropic, temporally and spatially dispersive medium. In terms of the constitutive relations this medium can be represented as a tensor operator acting upon the electric field, causing a displacement field of the form, i.e.,

$$D = \varepsilon_0 \varepsilon(\omega, k) \cdot E \quad (2.16)$$

Studies on spheres described in a tensorial manner are encountered in many active research fields, such as non-linear optics [80] and atomic scattering physics [81]. Here, we focus our analysis on the cases where a linear, homogeneous and isotropic medium is assumed with a scalar permittivity $\varepsilon_i$. In some cases (see Section 3.2) the electrostatic picture is combined with a realistic model of temporally dispersive permittivity, $\varepsilon(\omega)$ [74]. This combination results in a very good approximative model,
especially for electrically small scatterers. Therefore, studying and analyzing the electrostatic problem offers useful physical insight and intuition regarding the behavior of subwavelength scatterers.

In a charge-free domain, the displacement needs to be divergence-less, i.e.,
\[ \nabla \cdot \mathbf{D} = 0 \] (2.17)
Consequently all excitation, scattered, and internal fields should satisfy this rule. Assuming a homogeneous medium with \( \varepsilon_i \) is constant, any field quantity written in potential form should satisfy the Laplace equation, viz.,
\[ \nabla^2 \Phi(r) = 0 \] (2.18)

Finally, the boundary conditions at the interface require that both tangential electric field and normal displacement should be continuous over the interface between the two domains, \( r = a \). This can be compactly written as
\[ (\mathbf{E}_t - \mathbf{E}_i) \times \mathbf{u}_r = 0 \] (2.19)
and
\[ (\varepsilon_e \mathbf{E}_t - \varepsilon_i \mathbf{E}_i) \cdot \mathbf{u}_r = 0 \] (2.20)
where \( \mathbf{u}_r \) is the radial unit vector in the spherical coordinate system \((r, \theta, \phi)\).

In potential form, Eq. (2.19) and Eq. (2.20) give the three conditions
\[ \frac{\partial \Phi_t(r, \theta, \phi)}{\partial \phi} = \frac{\partial \Phi_i(r, \theta, \phi)}{\partial \phi} \] (2.21)
\[ \frac{\partial \Phi_t(r, \theta, \phi)}{\partial \theta} = \frac{\partial \Phi_i(r, \theta, \phi)}{\partial \theta} \] (2.22)
and
\[ \varepsilon_e \frac{\partial \Phi_t(r, \theta, \phi)}{\partial r} = \varepsilon_i \frac{\partial \Phi_i(r, \theta, \phi)}{\partial r} \] (2.23)

### 2.1.1 Laplace equation in spherical coordinates

To facilitate the analysis, we present some key results regarding the solution of the Laplace equation for the spherical coordinate system. The Laplace equation of the electrostatic potential in spherical coordinates reads
\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \Phi \right) + \frac{\sin \theta}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \partial_{\theta} \Phi \right) + \frac{1}{r^2 \sin^2 \theta} \partial_{\phi \phi} \Phi = 0 \] (2.24)
We separate the potential \( \Phi \) in three independent functions, viz.,
\[ \Phi(r, \theta, \phi) = \frac{R(r)}{r} T(\theta) P(\phi) \] (2.25)
and Eq. (2.24) can be recast to the form
\[
r^2 \sin^2 \theta \left[ \frac{1}{R} \frac{d^2 R}{dr^2} + \frac{1}{T r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dT}{d\theta} \right) \right] + \frac{1}{P} \frac{d^2 P}{d\phi^2} = 0 \tag{2.26}
\]
This equation contains the azimuthal function \(P(\phi)\) for which we assume that
\[
\frac{1}{P(\phi)} \frac{d^2 P(\phi)}{d\phi^2} = -m_\phi^2 \tag{2.27}
\]
with \(m_\phi\) being the azimuthal number. This number is an integer if the full azimuthal range is included. For a sphere the solution of Eq. (2.27) has a form proportional to
\[
P(\phi) = e^{\pm im_\phi \phi} = \cos(m_\phi \phi) \pm i \sin(m_\phi \phi) \tag{2.28}
\]
The azimuthal parameter \(m_\phi\) is dictated by the symmetry of the problem. In problems with azimuthal symmetry (no variation with respect to \(\phi\)) we require that \(m_\phi = 0\).

A few algebraic manipulations on Eq. (2.26) give the following ordinary differential equations for the \(r\) and \(\theta\) variables:
\[
\frac{d^2 R(r)}{dr^2} - \frac{l(l+1)}{r^2} R(r) = 0 \tag{2.29}
\]
and
\[
\frac{1}{\sin \theta} \left[ \frac{d}{d\theta} \left( \sin \theta \frac{dT(\theta)}{d\theta} \right) \right] + \left[l(l+1) - \frac{m_\phi^2}{\sin^2 \theta} \right] T(\theta) = 0 \tag{2.30}
\]
The radial expression (2.29) has the following solution
\[
\frac{R(r)}{r} = A r^l + B r^{-l-1} \tag{2.31}
\]
while Eq. (2.30) is the \textit{Legendre} equation for \(x = \cos \theta\). One solution of Eq. (2.30) for \(m_\phi = 0\) is the Legendre polynomial\textsuperscript{4} i.e.,
\[
P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \tag{2.33}
\]
Finally, by solving the Laplace equation in spherical coordinate system with azimuthal symmetry we get an expression for the potential as a combination of Eq. (2.28), Eq. (2.31), and Eq. (2.33):
\[
\Phi(r,t) = \left( A_l r^l + B_l \frac{r^{-l-1}}{l+1} \right) P_l(\cos \theta) \tag{2.34}
\]
\textsuperscript{4}For azimuthal order \(m_\phi \neq 0\) the solution is the associated Legendre function defined as
\[
P_l^{m_\phi}(x) = (-1)^{m_\phi}(1-x)^{m_\phi/2} \frac{d^{m_\phi}}{dx^{m_\phi}} P_l(x) \tag{2.32}
\]
where $A_l$ and $B_l$ are the unknown scattering amplitude coefficients. Note that the inverse term $(1/r^{l+1})$ represents the potential dependence for a charge ($l = 0$, monopole), a dipole ($l = 1$), a quadrupole ($l = 2$), and so on. Moreover, the $A_l$ term vanishes at the origin ($r = 0$), while it diverges for large distances ($r \to \infty$) when $l > 0$. The $B_l$ term exhibits a complementary behavior, i.e., it converges at $r \to \infty$ and diverges for $r = 0$. The electric field (through Eq. (2.34)) reads

$$E(r, \theta) = -\nabla \Phi(r, \theta) = - \left( A_l l^{l-1} - B_l \frac{l + 1}{r^{l+2}} \right) \frac{P_l(\cos \theta) u_r}{r} - \left( A_l r^{l-1} + B_l \frac{1}{r^{l+2}} \right) \frac{dP_l(\cos \theta)}{d\theta} u_\theta$$

(2.35)

### 2.1.2 The scattering amplitudes

Having assembled all the necessary mathematical pieces we can proceed to the evaluation of the external and internal scattering amplitudes. Here we assume a $z$-polarized, constant amplitude $E_0$ field, i.e.,

$$E_{inc}(r, \theta) = E_0 u_z = E_0 (\cos \theta u_r - \sin \theta u_\theta)$$

(2.36)

which reads in equivalent potential form as

$$\Phi_{inc}(r, \theta) = -E_0 r \cos \theta = -E_0 r P_1(\cos \theta)$$

(2.37)

This type of excitation exhibits an $l = 1$ radial distribution. According to Eq. (2.34) the total potential is $\phi$-independent while the angular distribution follows a Legendre polynomial of order $l$. Since the excitation potential has a $\cos \theta$ angular distribution, the radial order of the scattered field will exhibit the same angular distribution, i.e.,

$$\Phi_t(r, \theta) = -E_0 r \cos \theta + \frac{B_1}{r^2} \cos \theta$$

(2.38)

while the internal potential will be of the form

$$\Phi_i(r, \theta) = -A_1 r \cos \theta$$

(2.39)

Both the internal and external scattered potentials should have a proper behavior (no singularities) at the origin and at infinity, respectively. The particular type of constant excitation of Eq. (2.36) triggers a dipolar field externally and a constant field internally. Indeed, Eq. (2.35) for $l = 1$ gives the scattered and internal fields, i.e.,

$$E_{sca} = \frac{B_1}{r^3} (2 \cos \theta u_r + \sin \theta u_\theta)$$

(2.40)
and
\[ E_i = A_1 (\cos \theta \, u_r - \sin \theta \, u_\theta) \] (2.41)

As a remark, different excitations can excite higher multipoles \( l \neq 1 \). This fact can be particularly useful for studying the multipolar behavior of electrostatic fields beyond the dipolar mode.

Finally, the scattering amplitudes \( A_1 \) and \( B_1 \) can be derived using the boundary conditions given in Eq. (2.22) and Eq. (2.23) combined with the total and internal potential of Eq. (2.38) and Eq. (2.39). The expressions for the amplitudes read
\[ B_1 = -\frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} a^3 E_0 \] (2.42)

and
\[ A_1 = \frac{3\varepsilon_i}{\varepsilon_i + 2\varepsilon_e} E_0 \] (2.43)

In case were \( l \geq 1 \) is allowed by the excitation the scattering amplitudes read
\[ B_l = -\frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + \frac{l+1}{l-1} \varepsilon_e} a^{2l+1} E_0 \] (2.44)

and
\[ A_l = \frac{l(2l+1)\varepsilon_i}{\varepsilon_i + \frac{l+1}{l-1} \varepsilon_e} E_0 \] (2.45)

### 2.2 Scattering by a Hertzian electric dipole

An intermediate connecting link between the electrostatic and the electrodynamic problems is the reasonable assumption that a small sphere illuminated by the aforementioned excitation field (Eq. (2.36)) is, to a very good approximation, an electric Hertzian dipole (Fig. 2.4).\(^5\) Here we focus our efforts towards small dielectric spheres that exhibit strong electric moments, especially around the plasmonic enhancement region \( \varepsilon_i < 0 \) (see Chapter 3).

Assuming an \( e^{-i\omega t} \) time dependence and \( \varepsilon_e = 1 \), the electric and magnetic field distributions of an electric dipole with dipole moment \( I/u_z \) reads

\(^5\)A more general treatment requires the consideration of a magnetic Hertzian dipole as well. Subwavelength structures can induce strong magnetic moments, especially for structures with non-trivial magnetic contrast (permeability) or morphological characteristics that facilitate the development of circulating currents, e.g., loop antennas.
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\[ (\varepsilon_0, \mu_0) \]

Iluz

\[ \mathbf{E}_{\text{inc}} = E_0 \mathbf{u}_z \]

\[ \mathbf{k} \]

\[ \mathbf{E}_{\text{ sca}} \]

\[ \mathbf{u}_y \]

\[ \mathbf{u}_x \]

\[ \mathbf{u}_z \]

**Figure 2.4.** A small sphere represented by an electric Hertzian dipole with moment \( Ilu_z \) interacting with an excitation field \( \mathbf{E}_{\text{inc}} = E_0 \mathbf{u}_z \). The red lines depict the electric field lines \( \mathbf{E}_{\text{ sca}} \).

\[ \mathbf{E}_{\text{ sca}} = -\frac{i\omega\mu_0}{4\pi r} Il \left\{ 2 \cos \theta \left[ \left( \frac{i}{kr} \right)^2 + \frac{i}{kr} \right] \mathbf{u}_r + \sin \theta \left[ \left( \frac{i}{kr} \right)^2 + \frac{i}{kr} + 1 \right] \mathbf{u}_\theta \right\} e^{ikr} \quad (2.46) \]

and

\[ \mathbf{H}_{\text{ sca}} = -\frac{ik}{4\pi r} Il \left( \frac{i}{kr} + 1 \right) \sin \theta \mathbf{u}_\phi e^{ikr} \quad (2.47) \]

where \( \omega \) is the (angular) frequency, \( \mu_0 \) is the permeability of the host medium (here vacuum), \( k = \omega \sqrt{\varepsilon_0 \mu_0} = \frac{\omega}{c} \sqrt{\varepsilon_e} \) is the wavenumber, \( c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} \) is the speed of light and \( Il \) is the dipole moment. The near field expressions \((kr \ll 1)\) are

\[ \mathbf{E}_{\text{near}} = -\frac{i\mu_0}{4\pi r^3} Il \left( 2 \cos \theta \mathbf{u}_r + \sin \theta \mathbf{u}_\theta \right) \quad (2.48) \]

\[ \mathbf{H}_{\text{near}} = \frac{Il}{4\pi r^2} \sin \theta \mathbf{u}_\phi \quad (2.49) \]

where \( \eta = \sqrt{\frac{\mu_0}{2\pi \varepsilon_0}} \) is the wave impedance of the host medium. Actually, Eq. (2.48) is identical with the dipolar field in Eq. (2.40) by proper adjustment of the parameters.

We can derive the expression of the dipole moment following similar arguments as for the electrostatic sphere, i.e., applying the boundary conditions between the total external field and the internal field. Note that
the excitation fields are generally characterized as a small-limit expansion \((ka \ll 1)\) of an \(x\)-propagating, \(z\)-polarized plane wave, i.e.,

\[
E_{\text{inc}} = E_0 u_z e^{i k x} \approx E_0 u_z = E_0 (\cos \theta u_r - \sin \theta u_\theta)
\]  

(2.50)

with the corresponding magnetic field

\[
H_{\text{inc}} = \frac{u_x \times E_{\text{inc}}}{\eta} \approx \frac{-E_0}{\eta} u_y = \frac{-E_0}{\eta} (\sin \theta \sin \phi u_r + \cos \theta \sin \phi u_\theta + \cos \phi u_\phi)
\]  

(2.51)

The dipole moment reads

\[
I_l = -i \frac{4\pi}{\eta k^2} \left( \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} \right) (ka)^3 E_0
\]

(2.52)

The quantity

\[
\alpha = 4\pi \varepsilon_0 a^3 \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e}
\]

(2.53)

is commonly recognized as the polarizability, a proportionality factor between the dipole moment \(I_l\) and the excitation field, \(E_0\). Inversely, the dipole moment can be written as

\[
I_l = -i \omega \alpha E_0
\]

(2.54)

Repeating the above procedure by preserving the first three terms in the Taylor expansion of Eq. (2.46), i.e.,

\[
E_{\text{near}} = \frac{i \eta}{4\pi k r^2} \left[ \left(2 + (kr)^2 + i \frac{2}{3} (kr)^3 \right) \cos \theta u_r + \left(1 - (kr)^2 - i \frac{2}{3} (kr)^3 \right) \sin \theta u_\theta \right]
\]

(2.55)

we obtain a modified dipole moment of the form

\[
I_{l, \text{mod}} = -i \frac{4\pi}{\eta k^2} \frac{\frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} (ka)^3}{1 - \frac{1}{2} \frac{\varepsilon_i - 2\varepsilon_e}{\varepsilon_i + 2\varepsilon_e} (ka)^2 - i \frac{2}{3} \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} (ka)^3} E_0
\]

(2.56)

This modified version of the dipole moment, and the corresponding polarizability, is of particular importance due to the introduction of the imaginary \((ka)^3\) term. As we will see later this term represents the radiative damping/reaction term, i.e., the self-action of the scattered field, necessary for restoring the conservation of energy for lossless systems.

Once the dipole moment is evaluated, we can calculate the scattered field expressions for the far-field \((kr \gg 1)\)

\[
E_{\text{sc}} = \left( \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} \right) k^2 a^2 E_0 \frac{a}{r} e^{i k r} \sin \theta u_\theta
\]

(2.57)

\[
H_{\text{sc}} = \frac{u_r \times E_{\text{sc}}}{\eta}
\]

(2.58)

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The average total power carried by the scattered field is

\[ W_{\text{sca}} = \frac{1}{2} \int_0^{2\pi} \mathbf{E}_{\text{sca}} \times \mathbf{H}_{\text{sca}}^* \, 2\sin \theta \, d\theta \int_0^{2\pi} d\phi = \frac{4\pi}{3\eta} \left( \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} k^2 a^3 E_0^2 \right)^2 \] (2.59)

As in Eq. (2.10) the scattering cross section, reads

\[ C_{\text{sca}} = \frac{W_{\text{sca}}}{\frac{1}{2} |E_0|^2} = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} \right|^2 = \frac{k^4}{6\pi\varepsilon_0^3} |\alpha|^2 \] (2.60)

Equation (2.60) reveals that the total scattered power is proportional to the fourth power of the wavenumber and proportional to the sixth power of the particle radius. This observation, first derived by Rayleigh in 1871 [83], gives a physical interpretation on why the sky is blue coloured; shorter wavelengths (blue) scatter stronger than larger ones (red).

Apart from the scattered power and the corresponding scattering cross section we can evaluate the extinction power near the dipole inclusion. Using the same assumptions as before, i.e., uniform fields in the vicinity of the dipole scatterer, the total near field is the incident field of Eq. (2.50) and Eq. (2.51) plus the scattered field (near zone), Eq. (2.48) and Eq. (2.49). The effect of both incident and scattered fields is reflected into the induced dipole moment. The dipole moment \( I/\sigma_z \) represents the volume average of an equivalent (uniform) volume current density \( J \) induced on the surface of the sphere (or scatterer). Invoking the Poynting theorem [84, 85], the total power extracted (extinction) by a volume current density and the incident field is

\[ W_{\text{ext}} = \frac{1}{2} \Re \left\{ \int_V J^* \cdot E_{\text{inc}} \right\} dV = -\frac{1}{2} \Re \{ i\omega \alpha^* \} |E_0|^2 \] (2.61)

Therefore, the extinction cross section is (via Eq. (2.9))

\[ C_{\text{ext}} = \frac{W_{\text{ext}}}{\frac{1}{2} |E_0|^2} = \frac{k^4}{3\varepsilon_0} |\alpha| \] (2.62)

It is interesting to note that the extinction cross section scales linearly with the frequency, being three orders of magnitude different than the corresponding scattering cross section.\(^6\)

\(^6\)The same expression for the extinction cross section can be alternatively derived by the Poynting vector expression of Eq. (2.6), i.e.,

\[ S_{\text{ext}} = \frac{1}{2} \Re \{ \mathbf{E}_{\text{inc}} \times \mathbf{H}_{\text{sca}}^* + \mathbf{E}_{\text{sca}} \times \mathbf{H}_{\text{inc}}^* \} \] (2.63)

The trick is to avoid the complicated expressions due to exponential terms of the incident field (Eq. (2.50) and Eq. (2.51)). This can be done by taking the Taylor expansion about \( r \to 0 \) or \( k \to 0 \) for all scattered and incident fields (Eq. (2.46), Eq. (2.47), Eq. (2.50), and Eq. (2.51)) up to the \( O(r^3) \) term. The value of this integral at the near field reads

\[ W_{\text{ext}} = \frac{1}{2} \Re \{ H^* \} E_0 = -\frac{1}{2} \omega |\alpha| |E_0|^2 \] (2.64)

resulting in the extinction cross section of Eq. (2.62).
The absorption cross section defined as the difference between extinction and scattering cross sections reads

\[ C_{\text{abs}} = \frac{k_i}{\varepsilon_0} \Im\{\alpha\} - \frac{k^4}{6\pi\varepsilon_0^2} |\alpha|^2 \] (2.65)

In many instances where extremely sub-wavelength particles are considered, such as in optics/atomic physics communities, the scattering effects are usually neglected. Therefore, the absorption cross section expression coincides with the extinction cross section, i.e.,

\[ C_{\text{abs}} \approx C_{\text{ext}} = \frac{k}{\varepsilon_0} \Im\{\alpha\} \] (2.66)

Finally, the ratio between scattering and extinction cross section can be recognized as the single particle albedo [72], i.e.,

\[ w = \frac{C_{\text{sca}}}{C_{\text{ext}}} \] (2.67)

that for a small dipole reads

\[ w = \frac{2}{9} (ka)^3 \left( \frac{\varepsilon' - 1}{\varepsilon''} + (\varepsilon'')^2 \right) \] (2.68)

assuming a lossy material \( \varepsilon_i = \varepsilon' + i\varepsilon'' \). In the lossless case \( C_{\text{ext}} = C_{\text{sca}} \) and the albedo is \( w = 1 \), while for vanishingly small losses the singularity is avoided by introducing the radiation reaction term to the polarizability description.

### 2.3 Electrodynamic scattering: Lorenz–Mie theory

The electrodynamic problem shares a lot of common mathematical background with its static counterpart. The main difference is the fact that this time both electric and magnetic fields are required for the solution, and hence a total of four equations are required for the complete determination of the scattering amplitudes.

#### 2.3.1 Remarks on spherical potentials

We start by giving the solution of the wave equation in spherical coordinates by introducing the vector potentials

\[ A = u_\rho \pi_e \] (2.69)

\[ H_{TM} = \nabla \times A = \frac{1}{\sin \theta \partial \theta} \pi_e u_\theta - \frac{\partial}{\partial \phi} \pi_e u_\phi \] (2.70)
for transverse magnetic (TM) with respect to \( u_r \) waves, and

\[
Z = u_r \pi_m
\]

\[
E_{\text{TE}} = \nabla \times Z = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \pi_m u_\theta - \frac{\partial}{\partial \phi} \pi_m u_\phi
\]

for transverse electric (TE) with respect to \( u_r \) waves. The scalar potentials \( \pi_e \) and \( \pi_m \) are the Debye potentials [82].

Utilizing Maxwell’s equations, the total (TM+TE) fields read in compact form

\[
E = E_{\text{TE}} + i \frac{\nabla \times H_{\text{TM}}}{\omega \varepsilon}
\]

and

\[
H = H_{\text{TM}} - i \frac{\nabla \times E_{\text{TE}}}{\omega \mu}
\]

The Debye potentials satisfy the Helmholtz equation in spherical coordinates. The solution of such potentials is a combination of spherical Bessel and Hankel functions, associated Legendre polynomials, and sinusoidal functions. The complete potential analysis can be found in several classical textbooks [86, 87], hence will be omitted here.

In the following we assume an \( x \)-polarized, \( z \)-propagating plane wave excitation, i.e.,

\[
E_{\text{inc}} = u_x E_0 e^{ikr \cos \theta}
\]

A key step in Lorenz–Mie theory is to express a plane wave in terms of the spherical harmonics. The exponential term of Eq. (2.75) can be expanded as

\[
e^{ikr \cos \theta} = \sum_{l=0}^{\infty} (-i)^{-l} (2l + 1) j_l(kr) P_l(\cos \theta)
\]

where \( j_l(kr) \) is the spherical Bessel function of the first kind. A plane wave can be expressed by the following Debye potentials

\[
\pi_e = -\frac{\cos \phi}{\omega \mu r} \sum_{l=1}^{\infty} E_l \hat{J}_l(kr) P_l(\cos \theta)
\]

\[
\pi_m = \frac{\sin \phi}{kr} \sum_{l=1}^{\infty} E_l \hat{J}_l(kr) P_l(\cos \theta)
\]

where

\[
E_l = (-1)^{-l} \frac{2l + 1}{l(l + 1)} E_0
\]

is the normalized excitation coefficient and

\[
\hat{J}_l(kr) = kr j_l(kr)
\]

can be recognized as the Riccati–Bessel spherical function. Note that the aforementioned results require hard and painstakingly long algebraic manipulations. In their seminal book, Bohren and Huffman [55] describe this
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process as: “... the result of the unwillingness of a plane wave to wear a
guise in which it feels uncomfortable; expanding a planewave in spherical
wave functions is somewhat like trying to force a square peg into a round
hole...”.

Following a similar philosophy, the scattered potentials are

\[
\pi_e = -\frac{\cos \phi}{\omega \mu r} \sum_{l=1}^{\infty} E_l a_l \tilde{H}_l(kr) P_l(\cos \theta) \tag{2.81}
\]

\[
\pi_m = \frac{\sin \phi}{kr} \sum_{l=1}^{\infty} E_l b_l \tilde{H}_l(kr) P_l(\cos \theta) \tag{2.82}
\]

where

\[
\tilde{H}_l(kr) = k r h^{(1)}_l(kr) \tag{2.83}
\]

and \(h^{(1)}_l(kr)\) is the spherical Hankel function of the first kind, representing
an outgoing traveling wave. Finally, the potentials of the internal field are

\[
\pi_e = -\frac{\cos \phi}{\omega \mu r} \sum_{l=1}^{\infty} E_l d_l \tilde{J}_l(kr) P_l(\cos \theta) \tag{2.84}
\]

\[
\pi_m = \frac{\sin \phi}{kr} \sum_{l=1}^{\infty} E_l c_l \tilde{J}_l(kr) P_l(\cos \theta) \tag{2.85}
\]

2.3.2 The Mie coefficients

The last part of the theoretical analysis is dedicated to the values of the
external \((a_l, b_l)\), and the internal \((c_l, d_l)\) amplitudes. All four are
frequently named as Mie coefficients and quantify the scattering behav-
ior of the TM \((a_l, c_l)\) and the TE \((b_l, d_l)\) contributions. Once the
fields are determined at both domains (via their corresponding Debye po-
tentials), the Mie coefficients are evaluated through the corresponding
boundary conditions, i.e.,

\[
(E_{\text{inc}} + E_{\text{scat}} - E_{sc}) \times \mathbf{u}_r = 0 \tag{2.86}
\]

\[
(H_{\text{inc}} + H_{\text{scat}} - H_{sc}) \times \mathbf{u}_r = 0 \tag{2.87}
\]

The resulting coefficients read [82]

\[
a_l = \frac{\sqrt{\varepsilon \mu_h} \tilde{J}_l(ka) \tilde{J}'_l(ka) - \sqrt{\varepsilon \mu_i} \tilde{J}_l(ka) \tilde{J}'_l(ka)}{\sqrt{\varepsilon \mu_i H'_l(ka) \tilde{J}_l(ka) - \sqrt{\varepsilon \mu_i} H'_l(ka) \tilde{J}'_l(ka)}} \tag{2.88}
\]

\[
b_l = \frac{\sqrt{\varepsilon \mu_i} \tilde{J}'_l(ka) \tilde{J}_l(ka) - \sqrt{\varepsilon \mu_i} \tilde{J}'(ka) \tilde{J}_l(ka)}{\sqrt{\varepsilon \mu_i H'_l(ka) \tilde{J}_l(ka) - \sqrt{\varepsilon \mu_i} H'_l(ka) \tilde{J}'_l(ka)}} \tag{2.89}
\]

and

\[
c_l = \frac{i \sqrt{\varepsilon \mu_h}}{\sqrt{\varepsilon \mu_i H'_l(ka) \tilde{J}_l(ka) - \sqrt{\varepsilon \mu_i} H'_l(ka) \tilde{J}'_l(ka)}} \tag{2.90}
\]
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\[ d_l = \frac{-i\sqrt{\varepsilon \mu_i}}{\sqrt{\varepsilon \mu_i}H_l(ka)J_l'(ka) - \sqrt{\varepsilon \mu_i}H_l'(ka)J_l(ka)} \]  

(2.91)

In this thesis, and the articles found hereinafter, we utilize the Mie expressions à la Bohren–Huffman [55]

\[ a_l = \frac{m^2 j_l(mx) [xj_l(x)]' - \mu_l j_l(x) [mxj_l(mx)]'}{m^2 j_l(mx) [xh_l^{(1)}(x)]' - \mu_l h_l^{(1)}(x) [mxj_l(mx)]'} \]  

(2.92)

\[ b_l = \frac{\mu_l j_l(mx) [xj_l(x)]' - j_l(x) [mxj_l(mx)]'}{\mu_l j_l(mx) [xh_l^{(1)}(x)]' - h_l^{(1)}(x) [mxj_l(mx)]'} \]  

(2.93)

where

\[ x = k_e a \]  

(2.94)

is the host medium size parameter, \( m = \frac{k_i}{k_e} = \frac{\sqrt{\varepsilon \mu_i}}{\sqrt{\varepsilon \mu_e}} \) is the material contrast, with \( \varepsilon_i, \mu_i, \varepsilon_e, \) and \( \mu_e \) are the internal and external permittivity and permeability.\(^7\)

These \( a_l \) and \( b_l \) terms are generally complex-valued and demonstrate the electric and magnetic multipole contributions to the overall scattering process [86]. Most of the far-field scattering processes are quantified through these two coefficients. Note that these coefficients can be found in the literature by many names, i.e., TM and TE modes, E-wave and H-wave coefficients etc. [55, 86]. Here we will refer to them as electric \((a_l)\) and magnetic \((b_l)\) multipole terms, having for each value of \( l \) names such as dipole \((l = 1)\), quadrupole \((l = 2)\) and so on. Similarly, the internal fields can be quantified through the \( c_l \) and \( d_l \) coefficients, viz.,

\[ c_l = \frac{\mu_l j_l(x) [xh_l^{(1)}(x)]' - \mu_l h_l^{(1)}(x) [xj_l(x)]'}{\mu_l j_l(mx) [xh_l^{(1)}(x)]' - h_l^{(1)}(x) [mxj_l(mx)]'} \]  

(2.95)

\[ d_l = \frac{\mu_l m j_l(x) [xh_l^{(1)}(x)]' - \mu_l m h_l^{(1)}(x) [xj_l(x)]'}{m^2 j_l(mx) [xh_l^{(1)}(x)]' - \mu_l h_l^{(1)}(x) [mxj_l(mx)]'} \]  

(2.96)

\(^7\)There are at least a dozen of classical and modern textbooks and a huge amount of articles that derive/re-derive partially or fully the Mie coefficients. For example, the most classical textbook include authors such Stratton [86], Van de Hulst [88], Morse–Feshbach [87], Born–Wolf [53], Kerker [64], Jackson [78], Newton [89], Kong [82], Harrington [75], Ishimaru [72], Kreibig–Vollmer [73], and many others. In every case, the expressions are relatively similar, but not entirely identical. This is mostly either due to definitions of the involved functions and the material domains or through the usage of different combinations of the boundary conditions. A comprehensive table comparing different versions encountered in the literature up to the late 1960’s is given by Milton Kerker in [64].
where \( c_l \) and \( d_l \) correspond to the magnetic (TE) and the electric (TM) multipole term, respectively.

Ruppin and Englman were, perhaps, the first to observe \[90\] that the external Mie coefficients can be conveniently recast in the form

\[
a_l = \frac{S_l^a}{S_l^a + iR_l^a} \quad (2.97)
\]

\[
b_l = \frac{S_l^b}{S_l^b + iR_l^b} \quad (2.98)
\]

with

\[
S_l^a = m\hat{J}'_l(x)\hat{J}_l(mx) - \mu_i\hat{J}_l(x)\hat{J}'_l(mx) \quad (2.99)
\]

\[
R_l^a = m\hat{Y}'_l(x)\hat{J}_l(mx) - \mu_i\hat{Y}_l(x)\hat{J}'_l(mx) \quad (2.100)
\]

\[
S_l^b = m\hat{J}'_l(x)\hat{J}_l(mx) - \epsilon_i\hat{J}_l(x)\hat{J}'_l(mx) \quad (2.101)
\]

\[
R_l^b = m\hat{Y}'_l(x)\hat{J}_l(mx) - \epsilon_i\hat{Y}_l(x)\hat{J}'_l(mx) \quad (2.102)
\]

with the Riccati–Bessel functions \( \hat{J}(x) \) and

\[
\hat{Y}_l(z) = zy_l(z) \quad (2.103)
\]

being the Riccati–Neumann function with \( y_n(z) \) to be the spherical Neumann (Bessel function of the 2nd kind) function. All functions (2.99)–(2.102) can be complex for a complex material description (lossy material, i.e., \( \epsilon_i = \epsilon'_i + i\epsilon''_i \)). However, once we assume the material to be lossless \( (\epsilon''_i = 0) \), the coefficients become real, and \( \Re\{a_l\} = |a_l|^2 \) and \( \Re\{b_l\} = |b_l|^2 \). In this case the maximum amplitude of the external Mie coefficients is one.

We conclude this chapter by introducing the expressions for the extinction and scattering cross sections as functions of the Mie coefficients,

\[
C_{\text{sca}} = \frac{2\pi}{k^2} \sum_{l=1}^{\infty} (2l + 1) (|a_l|^2 + |b_l|^2) \quad (2.104)
\]

\[
C_{\text{ext}} = \frac{2\pi}{k^2} \sum_{l=1}^{\infty} (2l + 1) \Re\{a_l + b_l\} \quad (2.105)
\]

and

\[
C_{\text{abs}} = C_{\text{ext}} - C_{\text{sca}} \quad (2.106)
\]
3. Resonant scattering

In this chapter we discuss some characteristic features encountered for the case of a small homogeneous dielectric ($\mu_i = 1$) sphere, immersed in free space ($\varepsilon_e = 1$). We define one figure of merit: the efficiency as the ratio between the cross section and the geometric area of a sphere, i.e.,

$$Q_j = \frac{C_j}{\pi a^2}$$  \hspace{1cm} (3.1)

where the subscript $j$ can be either the scattering ($j=\text{sca}$, Eq. (2.104)), the extinction ($j=\text{ext}$, Eq. (2.105)), or the absorption ($j=\text{abs}$, Eq. (2.106)) cross section. Another central quantity here is the size parameter defined in (2.94), denoting the electric size of the sphere in the host medium.

A closer look at the scattering quantities reveals that there are regions of scattering enhancement in the ($\varepsilon_i, x$) parametric space. The extinction efficiency, $Q_{\text{ext}}$ as plotted in Fig. 3.1, depicts a rich spectrum comprised of a series of scattering maxima and minima. The peaks represent regions for which the scattering amplitude is maximized, exhibiting a resonant behavior, while the valleys (scattering minima) correspond to regions where the coupling between the incident field and the exerted multipole moment is minimum.

We observe two regions in the scattering spectrum. The first region is for negative permittivity values. In this case resonances with sharp characteristics appear even for vanishingly small spheres, i.e., $x \to 0$. The region occurs at the negative permittivity regime, known as the plasmonic region. These resonances are predominantly due to electric multipoles indicated in Fig. 3.2. In other words, the plasmonic region is where the TM Lorenz–Mie coefficients are maximized when $\varepsilon_i < 0$. The surface charge distribution (inset figures on Fig. 3.2) verify the electric multipolar character of the resonances.

The second region is when $\varepsilon_i > 0$ (both Fig. 3.1 and Fig. 3.2), representing resonances with both magnetic and electric multipolar origin. We
Resonant scattering

Figure 3.1. The extinction efficiency of a lossless dielectric sphere, as a function of the material permittivity and the size parameter. There are two visible regions: the plasmonic region for \( \varepsilon_i < 0 \) and the dielectric region \( \varepsilon_i > 0 \). In both regions vibrant resonances occur. The dielectric resonances are geometrically induced resonances, of either magnetic or electric origin. The plasmonic resonances are due to the free oscillating charges, thus characterized as electric. The inset image depicts (only a few of) the main plasmonic resonances residing in region \(-3 < \varepsilon_i < -1\). Picture from [91]; note that here \( \varepsilon(\omega) = \varepsilon_i \).

name this region as the dielectric region and we observe that the main scattering peaks occur for either large size parameters or large permittivity values.

In this thesis we address a basic question regarding the distribution of both plasmonic and dielectric resonances, i.e., how these resonances are affected by the material and size parameters and what is their distribution at the \((\varepsilon_i, x)\) parametric space?

3.1 Distribution of the Mie resonances for small spheres

In order to give a definite answer regarding the material and size dependencies for the Mie resonances (both plasmonic and dielectric) we need to examine the behavior of the Lorenz–Mie coefficients, as expressed in Eq. (2.92) and Eq. (2.93). It is a rather obvious fact that coefficients \(a_l\) and \(b_l\) (Eq. (2.92) and Eq. (2.93)) cannot actually offer any direct physical interpretation on the studied problem, mostly due to their mathematical form;
Figure 3.2. The total scattering efficiency (blue line), in logarithmic (dB/10) scale, as a function of the permittivity (lossless case) for a fixed size parameter $x = 0.75$. Additionally, the lines $a_1$, $a_2$, and $a_3$ (dashed colorful lines) depict the absolute value of the first three electric multipoles, while $b_1$, $b_2$, and $b_3$ (dash-dot colorful lines) illustrate the magnetic dipole, quadrupole, and octupole terms, respectively. The inset figures (left column) depict the corresponding surface charge distributions for the $a_1$, $a_2$, and $a_3$ electric multipoles, while the inset figure (top) the corresponding surface electric current distributions for $b_1$, $b_2$, and $b_3$ magnetic multipoles, respectively. Note that the $a_l$ multipoles resonate at both plasmonic ($\varepsilon_i < 0$) and dielectric ($\varepsilon_i > 0$) regions, exhibiting an identical charge distribution. The amplitude of $a_l$ and $b_l$ coefficients is bounded at the interval $[0, 1]$. Picture from [92]; note that here $\varepsilon(\omega) = \varepsilon_i$.

a complicated fractional expression of spherical Bessel and Riccati–Bessel functions. To circumvent this, several remedies have been proposed based on approximative methods of the Mie coefficients, such as the Taylor expansion [61, 93–99], the Weierstrass approximation [100], and the Padé approximation [91, 101–103]. The main objective here is to review some simple, yet intuitive, expressions regarding the dependencies governing the behavior of the Mie coefficients, by expanding both $a_l$ and $b_l$ through a Taylor (Mie–Taylor) and a Padé (Mie–Padé) approximation.

3.2 Taylor expansion: Electrostatic resonances

We begin by approximating the Mie coefficients (Eq. (2.92) and Eq. (2.93)) with a Taylor series expansion for small spheres, i.e., around $x \approx 0$. A
straightforward application of this expansion for the first two electric and magnetic multipoles gives the following expressions

\[ a_1^T = -i \frac{2}{3} \frac{\varepsilon_1 - \varepsilon_e}{\varepsilon_1 + 2\varepsilon_e} x^3 + ... \]  
(3.2)

\[ b_1^T = -i \frac{1}{45} (\varepsilon_1 - \varepsilon_e) x^5 + ... \]  
(3.3)

\[ a_2^T = -i \frac{1}{15} \frac{\varepsilon_1 - \varepsilon_e}{2\varepsilon_1 + 3\varepsilon_e} x^5 + ... \]  
(3.4)

\[ b_2^T = -i \frac{1}{1575} (\varepsilon_1 - \varepsilon_e) x^7 + ... \]  
(3.5)

as a function of both \( \varepsilon_1 \) and \( x \). Here the superscript \( T \) denotes the Taylor expansion, while the subscript shows the order of the multipole for each TE and TM term. The above expressions reveal that the TM cases (electric multipoles \( a_l \)) have poles when

\[ \varepsilon_1 = -2\varepsilon_e, \quad -\frac{3}{2}\varepsilon_e, ... \]  
(3.6)

This is a special type of resonant enhancement that occurs at each of the electric multipole term. The general form of this condition reads

\[ \varepsilon_1 = -\frac{l + 1}{l} \varepsilon_e \]  
(3.7)

This particular type of resonant condition has been intensively studied by many communities, such as optical physics, RF engineering, and materials sciences. For this reason one can encounter this condition by different names, such as localized surface plasmon resonance (LSPR) [73], polarization enhancement [79, 104], and Mossotti catastrophe [105]. This condition dictates that the amplitude of the multipole term becomes arbitrarily large for a certain negative permittivity value. On the other hand, this resonant condition is obvious also by inspecting the corresponding electrostatic problem (see Eq. (2.44)). Negative permittivity values require certain temporal dispersion, i.e., \( \varepsilon_i(\omega) \). This is why condition (3.7) is often called as “Fröhlich frequency” [55].

The lowest term of Eq. (3.2) is directly proportional to the polarizability in Eq. (2.53). Therefore, by truncating the orders higher than \( x^3 \), we deduce that

\[ a_1^T = -i \frac{2}{9} a_N x^3 \]  
(3.8)

where

\[ a_N = \frac{\alpha}{\varepsilon_0 V} = \frac{3}{4\pi \varepsilon_0 a^3 \alpha} \]  
(3.9)
is the normalized polarizability (where $V$ is the sphere volume). This simple fact implies that the electric Mie coefficients contain the same polarization enhancing character as the electrostatic polarizability. The amplitude of this resonance can be infinite for real permittivity, while it is usually suppressed to a certain value due to the imaginary part of the permittivity.

### 3.2.1 Negative permittivity

The Fröhlich frequencies require the real part of the permittivity to be negative. Physical principles do not prevent the case where the real part is negative, unless it is followed by the appropriate imaginary part. Usually, regions with negative permittivity are regions either close to transitions, i.e., regions where polarized molecules, atoms, etc. oscillate as a collection of Lorentzian oscillators \([73,106]\). This information is commonly condensed into the material description of the form

$$
\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma} + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}
$$

(3.10)

where $\varepsilon_\infty$ is the background permittivity, and $\omega_p$ are the plasma frequencies for each oscillator\(^\dagger\), $\gamma$ and $\gamma_j$ are the damping terms. In our analysis, we use a simple Drude-like material description for silver (Ag). Silver is a standard benchmarking material for exploring basic plasmonic phenomena in nanoparticles, mostly due to its vivid plasmonic resonances at the blue-near UV region \([107, 108]\). The model used here is a curve fit based on Johnson and Christy’s \([109]\) experimental data for bulk silver, i.e.,

$$
\varepsilon_{Ag}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma},
$$

(3.11)

where $\varepsilon_\infty = 5.5$, $\omega_p = 2\pi 2.306 \text{PHz} \approx 9.537 \text{eV}$, and the damping constant $\gamma = 2\pi 9.993 \text{THz} \approx 0.041 \text{eV}$. The main feature of this Drude model is that it describes the free electron (interband) contributions. This model gives accurate results for wavelengths $> 350 \text{nm}$ (photon energy $< 3.54 \text{eV}$) \([110]\).

Note that nonlocal and other inhomogeneous phenomena that modify the material description are here neglected. These effects change slightly the amplitude of the resonances by introducing additional losses into the

\(^\dagger\)In the Lorentz oscillator model, plasma frequency is $\omega_p^2 = \frac{n_0 e^2}{m_e \varepsilon_0}$ where $n_0$ is the electron density, $e$ is the electron charge, $m_e$ is the mass of the electron and $\varepsilon_0$ is the absolute free-space permittivity.
used model being particularly pronounced for deeply subwavelength particles and exposing the quantum mechanical origins of the plasmonic resonances [73]. Our analysis focuses only into the classical scattering effects, hence any size modification of the Drude model is neglected.

Turning to the behavior of the Drude model we observe that for frequencies below the plasma frequency, small real (negative) and imaginary permittivity values are obtained. This is the region where the LSPR occurs, a particular type of resonance at the interface of two media, occurring due to the collective oscillations of the free electrons (plasma gas) in metallic particles, close to optical wavelengths [73].

From an electrical engineering perspective, negative permittivity values denote an inductive behavior. Since a resonating system requires the interplay between at least two different kinds of energy, we schematically adopt a circuit inductive-capacitive behavior for the plasmonic resonances. Given an inductive material behavior (negative permittivity) we argue that the geometrical characteristics (sphere) essentially contribute to the electrostatic (capacitive) stored energy. This simple analogy fits the main phenomenological elements behind LSPR, i.e., free electrons oscillate, contributing a part of a kinetic energy (inductive) on the system that compensates the electrostatic energy (capacitive) stored in the scatterer, hence causing a resonance [111].

3.2.2 Core–shell case: Plasmon hybridization

By inspecting the permittivity of the ideal lossless Drude-like material, i.e,

\[ \varepsilon_1(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2} \]  

the resonant condition for a solid homogeneous sphere is

\[ \omega^2 = \frac{\omega_p^2}{\varepsilon_\infty + 2\varepsilon_e} \]  

and it is often called the symmetric (bonding) resonance of a sphere [1]. A very important feature of this type of resonance is that it can, in principle, occur even for extreme subwavelength particles, as long as the enhancement condition is met. This is actually one reason why plasmonic

A dielectric resonance is a result of the interplay between the electric and magnetic stored energies in an open cavity. In this case, both electric and magnetic energies are of the same order of magnitude due to the electrical size of a scatterer, essentially creating a spherical Fabry–Perot étalon.
Resonant scattering resonances are particularly attractive for applications where localization of energy below the diffraction limit is required \( [2, 6, 13, 74] \). However, this feature comes at a cost; there is no negative permittivity without dissipation, hence the LSPRs are followed by omnipresent losses.

Let us now introduce the case of a complementary structure, i.e., a cavity of material \( \varepsilon_e \) surrounded by a dispersive, silver-like material as in Eq. (3.12), illustrated in Fig. 3.3. The polarizability of this complementary structure, is given by the mutual exchange between \( \varepsilon_e \) and \( \varepsilon_i \) on Eq. (3.2). As a result, the resonant condition now reads

\[
\varepsilon_i = -\frac{1}{2} \varepsilon_e \tag{3.14}
\]

or generalizing to the \( l \) multipole, viz.,

\[
\varepsilon_i = -\frac{l}{l+1} \varepsilon_e \tag{3.15}
\]

Similarly, in terms of a Drude-like material Fröhlich frequency reads

\[
\omega_{\perp}^2 = \frac{2\omega_p^2}{2\varepsilon_\infty + \varepsilon_e} \tag{3.16}
\]

This resonant condition is known the dipole antisymmetric (antibonding) resonance \([1]\) of a cavity. It is interesting to note that all plasmonic resonances occur at the negative permittivity range, which is a necessary condition for the existence of such resonances \([112, 113]\).\(^3\)

\(^3\)Why negative permittivity? Assume a scatterer inside a host medium (electro-
3.2.3 A mathematical remark on the distribution of the plasmonic resonances

Following Eq. (3.7) and Eq. (3.15) both symmetric and antisymmetric plasmonic resonant conditions are compactly generalized for $\varepsilon_\infty = 1$ as

$$\varepsilon_i^− = -\frac{l + 1}{l}$$  \hspace{1cm} (3.17)

$$\varepsilon_i^+ = -\frac{l}{l + 1}$$  \hspace{1cm} (3.18)

where superscripts $-$ and $+$ denote the symmetric and antisymmetric resonances, respectively.

The above conditions illustrate the quantized and hierarchical nature of the resonances. Interestingly, these resonances are quantized at ratios of integer numbers. Actually, Eqs. (3.18) and (3.17) exhibit a complementary distribution. This can be seen by adopting the mediant sum between both symmetric and antisymmetric resonances, viz.,

$$\left( -\frac{l + 1}{l} \right) \oplus \left( -\frac{l}{l + 1} \right) = -\frac{l - 1 - l}{l + l + 1} = -1$$  \hspace{1cm} (3.19)

The mediant sum illustrates the fact that both symmetric and antisymmetric multipole resonances are complementary to each other. This observation suggests that we can depict their geometrical loci as a set of Ford circles [114]. In particular, the symmetric resonances can be depicted as the Ford circles with radius $\frac{1}{2l^2}$ and center at $\left(-\frac{l + 1}{l}, \frac{1}{2l^2}\right)$. Equivalently, the antisymmetric resonances can be thought as circles with radius $\frac{1}{2(l+1)^2}$ and center at $\left(-\frac{l}{l+1}, \frac{1}{2(l+1)^2}\right)$. Both circle distributions are illustrated in Fig. 3.4. It is remarkable to notice that every symmetric and antisymmetric resonance describes a circle that is tangent to a circle with radius 0.5 and center at $(-1, 0.5)$. Each of these circles is tangent to each other which is an intrinsic property of the Ford circles [114]. This representation shows that all higher order resonances converge at the $-1$ value, and provide a simple, yet intuitive, hierarchical view for hybridized plasmonic resonances on a sphere as illustrated in Fig. 3.4. The Ford circles distribution is closely connected with the so-called Farey sequence. The static problem). The irrotational electric field requires zero total stored electrostatic energy, in absence of any source, inside a large volume that includes the scatterer. In principle, this setup can sustain a resonance (for non-zero electric field) only if both the host and particle material exhibit opposite signs, creating the necessary phase difference between the stored energy at the free space and the particle hence allowing the existence of a resonance, given a certain excitation [113].
latter has been observed in many other physical processes, such as the fractional quantum Hall effect [115] and other hierarchical models [116].

![Figure 3.4.](image)

**Figure 3.4.** The distribution of the static resonances for a core-shell sphere illustrated with the Ford circles. The horizontal axis represents the permittivity \( \varepsilon_i \). Green-colored circles denote the symmetric plasmon resonances, while the red circles denote the antisymmetric ones. As the order increases both resonances yield asymptotically to the point \( \varepsilon_i = -1 \). All circles are tangential to the horizontal axis and to a central circle of radius 0.5 centered at (-1,0,5).

### 3.3 Dielectric resonances

Although the Taylor expansion delivers a straightforward connection with the electrostatic problem, and therefore with the plasmonic enhancement, it offers very little insight regarding the dielectric resonances. This can be explained by the fact that the dielectric resonances asymptotically occur at extremely large permittivity contrast values for small spheres, as can be seen in Fig. 3.1. Likewise, the expansions presented in Eqs. (3.2)–(3.5) do not capture any other resonances (poles of the system) beyond the plasmonic case. Therefore, an alternative approach is required in order to get a rigorous view on the subject. Inspecting the form of the Lorenz–Mie coefficients we observe that an approximation capable of describing all features of the modeled system (zeros and poles) for complicated rational functions is required. Such expansion, fulfilling the above requirements, is the Padé expansion.

The Padé approximants are a special type of rational approximations constructed by expressing any function in a rational form and expanding each of the rational terms in power series [117, 118]. Here, the Padé expansion is expressed as a ratio of two polynomials \( \frac{P(x)}{Q(x)} \) of order \( x^L \) and \( x^M \), and denoted simply as \([L/M]\), following the notation of [117]. The Padé approximants have been previously utilized to some extent for the Rayleigh
Resonant scattering regime [101, 102]. Here, however, we introduce a rigorous Padé-based methodology for the study of the resonant conditions and other enabled mechanisms on a dielectric sphere [91, 103, 119, 120].

Let us begin with the \([3/3]\) Padé expansion for \(a_1\), i.e.,

\[
a_1^P \approx -i \frac{2 \varepsilon_1 - 1}{3 \varepsilon_1 + 2} \left( 1 - \frac{3}{5} \frac{\varepsilon_1 - 2}{\varepsilon_1 + 2} x^2 - i \frac{2}{3} \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} x^3 \right)
\]  

(3.20)

where the superscript \(P\) denotes the Padé approximant. We observe the similarities between the modified dipole moment Eq. (2.52) presented in Section 2.2. Actually, Eq. (3.20) can be decomposed into three distinctive parts. First, the term \(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\) is the normalized static polarizability term, similarly with Eq. (3.2). As before, this term contributes a system pole at \(\varepsilon_1 = -2\) only for the static case [121]. The second part is \(\frac{\varepsilon_1 - 2}{\varepsilon_1 + 2} x^2\) that introduces the size effects over the coefficient and to the overall scattering procedure, and thus it is generally recognized as the dynamic depolarization term [122]. Note the difference between the dipole moment coefficient computed in Eq. (3.20) and Eq. (2.56). The Padé approximant gives a coefficient \((3/5 = 0.6)\) larger than the one evaluated by the Hertzian dipole \((1/2 = 0.5)\). This term introduces the first approximation for the dynamic size effects. In a typical plasmonic setup the depolarization \(x^2\) term introduces a red-shift of the dipole resonance towards lower energies, which is a characteristic dynamic effect, as depicted in Fig. 3.5.

The imaginary term of order \(x^3\) in the denominator of (3.20) is recognized as the radiative damping part. For the lossless case, this part prevents the coefficient from infinite growth and represents the intrinsic radiative damping (reaction) mechanism of the scattering process [78, 81, 123]. The effects of this term to the scattering spectrum can be seen in Fig. 3.5, where both a shift and a dampening of the resonance are observed. Ignoring the dynamic depolarization term in (3.20) and utilizing the normalized polarizability expression (3.9) we have

\[
a_1^{\text{rad}} = \frac{a_1^T}{1 + a_1^T} = \frac{-i \frac{2}{3} \alpha N x^3}{1 - i \frac{2}{3} \alpha N x^3}
\]  

(3.21)

This is an expression of the polarizability model that includes the induced radiative reaction on a single subwavelength scatterer, reported by many workers [6, 81, 122–127]. In Fig. 3.5 we observe that such an additional term decreases the amplitude of the resonance for increasing size parameter.

Turning to the pole analysis of the Mie coefficients, the expression (3.20)
Figure 3.5. The scattering efficiency for the first electric multipole term depicting the plasmonic enhancement and the effect of different terms on the overall scattering. (Top-left) The static term (Taylor expansion Eq. (3.2)): a resonance occurs at $\varepsilon_i = -2$, with increasing amplitude for larger size parameters. (Top-right) The $[3/2]$ Padé approximant, i.e., the static and the $x^2$ depolarization term: a shift of the main plasmonic resonance is observed as a function of the size parameter. (Bottom-left) The $[3/3]$ Padé approximant including the static, depolarization and damping term as in Eq. (3.20): Both a shift and a dampening of the resonant amplitude as the size increases (note the scale). (Bottom-right) The static term with the radiative correction term as in Eq. (3.21): we observe a dampening of the resonance as $x$ increases but no shift.

exhibits a pole (resonance) at

$$\varepsilon_i = -2 \frac{15i + 9ix^2 - 5x^3}{15i - 9ix^2 + 10x^3}$$

which for small $x$ gives

$$\varepsilon_i = -2 - \frac{12}{5} x^2 (1 + \frac{3}{5} x^2) - 2i x^3 (1 + \frac{7}{5} x^2) + \ldots$$

The resonant condition contains a static term ($-2$), a dynamic depolarization term ($x^2$), and a radiative damping imaginary term ($x^3$).\footnote{Note that, for an open resonator, the resonant frequencies should be generally complex, known as natural frequencies [86].} Again, the real terms of Eq. (3.23) represent the shift that the position of the
Resonant scattering exhibits with respect to the size. However, the imaginary term dictates both the width of the resonance and the amount of required losses for maximum resonant absorption. The latter can be seen as a form of a conjugate matching between the incident wave and the scatterer [15, 54, 91, 128, 129].

The actual power of the Padé stratagem used above can be seen for the magnetic coefficient $b_l$, where the Taylor expansion does not give any information regarding the pole of the magnetic resonances. The $[5/5]$ Padé expansion of the first magnetic dipole coefficient $b_1$ reads

$$b_1^P \approx -i\varepsilon_1 - \frac{1}{45} \frac{x^5}{(1 + \frac{1}{21}(5 - 2\varepsilon_1)x^2 + [x^4] - i\frac{1}{45}(\varepsilon_1 - 1)x^5)}$$

(3.24)

with the truncated term being

$$[x^4] = -\varepsilon_1^2 + \frac{100\varepsilon_1 - 125}{2205}x^4$$

(3.25)

The expression (3.24) gives a resonant condition that yields the value

$$\varepsilon_1^{[5/5]} = -2.07 + \frac{10.02}{x^2} + 1.42x^2 - 2ix(1.06 - 0.77x^2)$$

(3.26)

where the accuracy was kept up to the second decimal. The condition (3.26) predicts, in contrast to the Taylor–Mie expansion, a pole for the magnetic dipole coefficients, suggesting a clear intuitive picture regarding the nature of the magnetic resonances enabled on a dielectric sphere.

First, the pole condition of Eq. (3.26) suggests an inverse square dependence on the size parameter, showing that the magnetic resonance for small spheres can be reached only for large-contrast materials, making the observation of this kind of resonances for very small spheres practically impossible. Secondly, a constant term appears, regulating slightly the real part of the pole condition. Lastly, the radiative damping process (imaginary part) of a magnetic dipole does not follow the same volume dependence ($x^3$) observed in the previous electric dipole (plasmonic) case (Eq. (3.23)), but rather a linear $x$ dependence [103].

Turning back to the case of the first electric dipole coefficient ($a_1$), we saw that the first $[3/3]$ Padé approximant gives information about the plasmonic resonance. An obvious question occur: how we can extract the dielectric pole condition for the electric coefficients?

The answer to this is to consider higher-order Padé approximants and to analyze their poles. In particular, the $[7/2]$ expansion of the $a_1$ coefficient gives in total four poles, one corresponding to the plasmonic case,
two non-observable double complex roots, and a fourth yielding the following expression

\[ \varepsilon_{1}^{[7/2]} = -14.5 + \frac{22.5}{x^2} + i\frac{77.778}{x} + \ldots \]  

(3.27)

This pole condition demonstrates the same inverse square size dependence observed in Eq. (3.26). Here, the radiative damping term is extremely large, indicating that a more accurate, higher order expansion is needed. To do so we increase the order of the numerator, keeping the denominator order as low as possible.\(^5\) By this, straightforward, and numerically convenient heuristic method, we are able to identify more accurately any of the pole conditions. For example, after several iterations, the \([19/2]\) Padé expansion of \(a_1\) gives a pole at

\[ \varepsilon_{1}^{[19/2]} = -1.99546 + \frac{20.193}{x^2} - 2.05137x^2 + i0.0241962x - i1.91773x^3 + \ldots \]  

(3.28)

### 3.4 Comparison between plasmonic and dielectric resonances

We conclude the analysis of the Mie coefficients by introducing a set of general rules regarding the pole conditions of all three type of resonances and summarizing their particular characteristics. After extensive calculations using the heuristic Padé methodology described above, we obtain a pattern for all three resonances, electric plasmonic, magnetic and electric dielectric. The general form of the pattern is shown in Table 3.1, where formulas for the first five \((l = 1, 2, 3, 4, 5)\) magnetic \(b_l\), and the first four electric \(a_l\) poles are given.

**Table 3.1.** Rules of the resonances on a homogeneous sphere for \(l = 1, 2, 3,\ldots\). The \(p_l\) values can be found in Table 3.2

\[
\begin{align*}
\text{electric plasmonic:} & \quad \varepsilon_{\text{plas}}^{al} = -\frac{l+1}{l+1} + \frac{2(l+1)(l+1)}{l(l+1)(l+2)}x^2 - i\frac{l+1}{l(l+1)^3}x^{2l+1} \\
\text{electric dielectric:} & \quad \varepsilon_{\text{dil}}^{al} = -\frac{2}{l} + \left(\frac{p_{l+1}}{x}\right)^2 - i\frac{2}{l(l+1)^3}x^{2l+1} \\
\text{magnetic:} & \quad \varepsilon_{\text{m}}^{bl} = -\frac{2}{2l-1} + \left(\frac{p_l}{x}\right)^2 - i\frac{2}{[(2l-1)!!]^2}x^{2l-1}
\end{align*}
\]

\(^5\) Trick: We keep the order of the denominator small, e.g., 2 or 3, in order to have always a polynomial with known roots.
Table 3.2. Values of uses parameters for the $b_l$ and $a_l$ pole resonances.

<table>
<thead>
<tr>
<th>$l$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_l$</td>
<td>$\pi$</td>
<td>4.4934</td>
<td>5.7634</td>
<td>6.9879</td>
<td>8.1428</td>
</tr>
</tbody>
</table>

The above generalized conditions give the value of the complex permittivity required for the system to resonate. These expressions can be used as rule-of-thumb design equations. The pole conditions of the electric resonances in Table 3.1 reveal a similar but not identical imaginary part; the $a_1$ (dipole resonance) exhibits the same amplitude of the $x^3$ term compared to the plasmonic case. This difference states that the behavior of the electric resonances in the plasmonic and dielectric regions are close but not completely identical. Similarly, the $b_l$ coefficient possesses a different radiative damping term than the electric ones both in amplitude and in order of $x$. Note that the $p_l$ coefficients correspond to the first root of the $l$-th spherical Bessel function of the first kind ($j_l(p_l) = 0$).

Summarizing, a small homogeneous sphere may exhibit a series of resonances that correspond to the maxima of each of the Mie coefficients. Figures 3.1 and 3.2 depict the existence of electric and magnetic multipole resonances as a function of both permittivity and size parameter. One distinctive category of resonances are the plasmonic resonances; these resonances, with electric multipole character appear in subwavelength spheres [92, 111]. Increasing either the size or the material contrast of the scatterer, a second type of resonances occur, i.e., dielectric resonances, of either magnetic or electric multipole character. Note that the electric resonances are resonances due to the $a_l$ Mie coefficient, siblings to the plasmonic cases, occurring at a different permittivity range.

Therefore an obvious question appears: do the electric multipole resonances exhibit any significant differences on their field distributions? One way to approach this question is to study the electric field distribution near and inside the sphere. In particular, the amplitude of the scattered electric field for the first two plasmonic and dielectric dipole and quadrupole resonances for a relatively large sphere ($x = 0.75$) are depicted in Fig. 3.6. One observes that although the external (scattered) field is identical, the internal field distribution displays a different character, which is an indication of the different origin of each resonance. The main differences lie in the fact that the plasmonic resonances manifest a rather uniform internal field distribution, while their dielectric coun-
terparts exhibit a spatial variation. Dielectric resonances are spatially extended, especially in the inner domain, due to the high permittivity contrast. The same does not hold for the plasmonic case for which the fields are highly localized at the surface of the sphere with small internal field variations.

Figure 3.6. The amplitude of the scattered electric field distribution for a sphere with $x = 0.75$ at: (a) $\varepsilon_i \approx -3.5$; (b) $\varepsilon_i \approx -1.754$; (c) $\varepsilon_i \approx 32.9$; and (d) $\varepsilon_i \approx 57.93$. These resonances correspond to the first two plasmonic and dielectric resonances, i.e., (a,c) dipole and (b,d) quadrupole, respectively. Picture form [92].
4. Morphological effects

But we no longer seek the harmony in static forms
like the regular solids,
but rather in dynamic laws.
Hermann Weyl “Symmetry” [130, p.77]

The main discussion covered in Chapters 2 and 3 focused on the scattering process of the canonical spherical inclusion and its main resonant features. Undoubtedly, such an analytically solvable example offers intuitive physical results: a perfect sphere is an ideal concept in a Platonic (idealistic) sense. Spheres shed their conceptual perfection into our imperfect world. Thus, in reality we encounter mostly, if not always, imperfect versions of the very same perfect sphere studied in the previous chapters. This argument is directly supported by our empirical views. Anyone can be convinced easily that artificially or naturally grown nanoparticles deviate from their ideal siblings. And this is exactly what triggers an everlasting scientific debate regarding the qualities of this deviation.

The very same theoretical curiosity drives the discussion of this chapter, where some “imperfect” versions of spheres are studied. In particular we introduce the family of superquadric surfaces that generalizes the notion of a sphere. These surfaces can model particles like rounded cubes and octahedra, and connect them with the surface of a sphere. In other words, a realistic sphere can be seen as a perturbation of a perfect sphere. Here, we quantify this perturbation with the aid of the superquadric surfaces. In order to treat the corresponding scattering problem we employ a numerical study. Recent developments in computational electromagnetism have delivered a variety numerical methods and treatments for scattering and radiation problems. Here, all the results are extracted using a numerical technique based on a surface integral equation (SIE) approach. A brief summary of the key points behind this methodology is presented in Section 4.1. The next section, Section 4.2, describes some mathemati-
Morphological effects and properties of the superquadric surfaces, such as the area and volume dependence with respect to the rounding factor. Finally, Section 4.3 is dedicated to the study of a set of five regular polyhedra, the Platonic solids, and their resonant plasmonic properties.

4.1 Surface integral equation approach

The scattering quantities, such as the internal and external fields and the corresponding cross sections, for an arbitrary-shaped homogeneous penetrable 3D object require implementation of a robust and efficient numerical technique. One popular approach is the SIE method, commonly known also as Boundary Element Method (BEM) [13, 112, 131, 132].

Let us assume an arbitrary shaped dielectric object with internal material characteristics as $\varepsilon_i$ and $\mu_i$ placed in a host medium with $\varepsilon_e$ and $\mu_e$, as discussed in Chapter 2. We denote $\mathcal{D}_1$ and $\mathcal{D}_2$ the external and internal domains, $A$ the surface of the object and $n$ the exterior unit normal vector on $A$ (as in Chapter 2). The external ($1$) and internal ($2$) fields are

\begin{align}
E_1 &= E_{\text{inc}} + E_{\text{sca}} \quad \text{and} \quad E_2 = E_i \\
H_1 &= H_{\text{inc}} + H_{\text{sca}} \quad \text{and} \quad H_2 = H_i
\end{align}

The free-space Green’s function at each domain reads

\[ G(k_j r) = \frac{e^{i k_j r}}{4\pi R} \]

and $R = |r - r'|$ is the distance between the observer ($r$) and the source ($r'$). The SIE method is based on the surface equivalence principle [75] (SEP), where the scatterer is substituted by the equivalent surface currents

\begin{align}
J &= n \times H \\
M &= -n \times E
\end{align}

being the electric and magnetic current distribution. Utilizing Green’s function, the SEP can be written in a manner known as Stratton–Chu formulas, that allows us to express the fields in terms of $J$ and $M$, and certain surface integral operators. These integral representations can be cast into SIE by applying the interface conditions. The resulting set of equations is the Poggio–Miller–Chang–Harrington–Wu–Tsai (PMCHWT) formulation [133–135].

Having reformulated the original problem as SIE, the surface $A$ is discretized into $N_T$ planar triangles (elements), $N_N$ nodes, and $N_E$ edges.
Each of these edges is associated with the (so-called) Rao–Wilton–Glisson (RWG) function [136]. The unknown currents J and M are approximated as a linear combination of the introduced RWG functions. Finally the RWG functions are used to test the formulated PMCHWT equations using Galerkin’s scheme, a special form of the method of moments. This results a set of linear equations, i.e., a matrix equation. The essential part in this procedure is the numerical evaluation of the matrix elements, since the matrix elements contain singular terms due to the Green’s function. At these singular points, special techniques are required. An efficient solution of the matrix equation is crucial too, as the size of the problem is enlarged.

The main benefit of this method is the discretization only of the surface of scatterer, making it particularly attractive for surface phenomena, such as LSPR, studied in this thesis. Although this is a seemingly mature research field, developments on the SIE methodology and techniques are still an active research area especially, since new physics and applications require constantly the adjustment of these old tools into the current research reality. For instance, SIE is attractive for scattering and radiation problems with homogeneous/piecewise homogeneous targets, and impenetrable targets with boundary conditions. The numerical studies reported here are extracted through an in-house 3D SIE solver, developed by Ylä-Oijala et al. [132]. The singular integrals involved are evaluated with the singularity subtraction technique [137, 138]. Sufficiently accurate evaluation of these integrals is essential in order to maintain low error of the solution, in particular in the near-field region. Once the solution to the matrix equation is available, the scattered and absorbed power can be efficiently evaluated using the associated SIE matrices as explained in [139].

4.2 Superquadric scatterers: Rounded cubes and octahedra

The systematic implementation of the SIE method to an arbitrarily shaped scatterer requires the proper discretization of the scatterer’s surface. In modern computer graphics, computer vision, and pattern recognition sciences there is an important family of parametric surfaces, the so-called superquadric surfaces. Originally, two-dimensional superelliptical curves (Lamé curves) where first described by the mathematician Gabriel Lamé [140, 141]. In 1960’s, Danish scientist Piet Hein introduced the surface
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equivalent of the Lamé curves, for 3D design purposes. He named these surfaces superellipsoids or superspheres [141, 142]. In 1981, Barr generalized the notion of superellipses in a more systematic way to the general family of superquadrics [52, 141].

We start the analysis by assuming the simplest case of an ellipsoidal surface. One mathematically convenient way to describe this surface is by using its parametric description. In our case, the surface of an ellipsoid can be described in the following well-known parametric form

\[ r(\theta, \phi) = \begin{pmatrix} a_1 \sin \theta \cos \phi \\ a_2 \sin \theta \sin \phi \\ a_3 \cos \theta \end{pmatrix} \]  \hspace{1cm} (4.6)

where \( a_1, a_2, \) and \( a_3, \) are the axis scale factors. This equation gives a sphere with radius \( a \) when \( a_1 = a_2 = a_3 = a. \) Alternatively, Eq. (4.6) yields to the known inside-out function,

\[ f(x, y, z) = \left( \frac{x}{a_1} \right)^2 + \left( \frac{y}{a_2} \right)^2 + \left( \frac{z}{a_3} \right)^2 \]  \hspace{1cm} (4.7)

since the conditions \( f(x, y, z) > 1 \) or \( f(x, y, z) < 1 \) define the external and internal domains of the surface.

An obvious generalization can be reached by raising each of the components to an power of \( 1/p, \) i.e.,

\[ r(\theta, \phi) = \begin{pmatrix} a_1 |\sin \theta \cos \phi|^{1/p} \\ a_2 |\sin \theta \sin \phi|^{1/p} \\ a_3 |\cos \theta|^{1/p} \end{pmatrix} \]  \hspace{1cm} (4.9)

\[ f(x, y, z) = \left| \frac{x}{a_1} \right|^{2p} + \left| \frac{y}{a_2} \right|^{2p} + \left| \frac{z}{a_3} \right|^{2p} \]  \hspace{1cm} (4.10)

where \( p \in \mathbb{R}. \) This kind of surface is a special case of a superquadric surface, as defined by Barr in [52], where a complete description can be found. Obviously, Eq. (4.10) describes an ellipsoid (or a sphere for \( a_1 = a_2 = a_3 \)) when \( p = 1. \)
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Figure 4.1. Five cases of a superquadric surfaces. From left to right the value of $p$ increases, sweeping between a perfect octahedron ($p = 0.5$), towards a sphere ($p = 1$), and a rounded cube ($p = 10$).

4.2.1 Geometric properties

Let us focus on the case $a_1 = a_2 = a_3$. For $p = 1$ we obtain a sphere; $p \to \infty$ defines a cube; the range between $p \in (1, +\infty)$ gives a form as illustrated in Fig. 4.1, that resembles the shape of a “rounded cube”. The other limiting case is $p = \frac{1}{2}$, where the surface shapes to an octahedron (Fig. 4.1). From a mathematical perspective, hexahedron and octahedron are dual solids. For dual solids the number of faces and vertices interchange. This duality has been also experimentally observed, since cubes and octahedra can result from the same growth process, as shown by Tao et al. [41]. Actually, the rounding factor connecting both shapes is given by the simple expression

$$p_d = \frac{p}{2p - 1}$$

(4.11)

denoting that any superquadric rounded cube of rounding factor $p$ has a dual counterpart with of $p_d$, and vice versa. Finally, cases with $p < 0.5$ produce star-like shapes while negative power factors produce superquadric

1A more general family that includes the superquadric surfaces are the hyperquadrics, introduced by Hanson in 1988 for computer graphic applications [143].

2The most general inside-out function is

$$f(x, y, z) = \left(\left|\frac{x}{a_1}\right|^{2p_1} + \left|\frac{y}{a_2}\right|^{2p_1} + \left|\frac{z}{a_3}\right|^{2p_2}\right)^{1/p_1} + \frac{z}{a_3}^{2p_2}$$

(4.8)

representing a general superquadric-toroidal surface for $a_4 \neq 0$. The power factors $p_1$ and $p_2$ adjust the “sharpness” of this surface on each $xy$ plane and $z$ axis.
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Another important geometric property of these surfaces is the cross-sectional area and volume, displayed in Fig. 4.2. The expression for the area of a superquadric of diameter \( d \) is

\[
C_g = \frac{d^2}{2p} B\left(\frac{1}{2p}, \frac{1}{2p} + 1\right)
\]

(4.12)

where \( B \) is the beta function. For \( p = 1 \) we have \( C_g = \pi \frac{d^2}{4} \), since \( B(0.5, 1.5) = \frac{\pi}{2} \). Similarly, the volume reads,

\[
V = \frac{d^3}{4p^2} B\left(\frac{1}{p}, \frac{1}{2p} + 1\right) B\left(\frac{1}{2p}, \frac{1}{2p}\right)
\]

(4.13)

Again, \( p = 1 \) gives the volume of a sphere, \( V = \frac{\pi}{6} d^3 \), since \( B(1,1.5) = \frac{2}{3} \) and \( B(0.5, 0.5) = \pi \).

![Figure 4.2](image-url)

**Figure 4.2.** The cross-section, \( C_g \) and volume \( V \) of a superquadric shape for a normalized diameter value \( (d = 1 \text{ m}) \) as a function of \( p \). The diameter of a sphere corresponds to the size of the side of a cube \( (p \to \infty) \).

A more intuitive picture of the \( p \)-dependence for both the area and the volume of the superquadrics can be derived by inspecting the approximative expressions of (4.12) and (4.13). Table 4.1 summarizes the first Taylor expansion terms for the three characteristic cases, i.e., sphere \((p = 1)\), cube \((p \to \infty)\), and octahedron \((p = \frac{1}{2})\).

### 4.2.2 Scattering properties

The expression (4.9) allows us to approach highly symmetric structures, such as cubes and octahedra, by varying continuously the power factor. In other terms, the cube (hexahedron) is a shape that can be seen as the limit of a continuous perturbation of a sphere. Therefore, we can directly
Table 4.1. Asymptotic behavior of the volume and area of a superquadric close to a sphere ($p = 1$), cube ($p \to \infty$), and octahedron ($p = \frac{1}{2}$).

<table>
<thead>
<tr>
<th>Superquadric cases</th>
<th>$V \approx$</th>
<th>$C_k \approx$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p \approx 1$</td>
<td>$\frac{1}{6} \pi d^3 p$</td>
<td>$\frac{\pi d^2}{4} \left(1 + \ln(4/e)p^{-1}\right)$</td>
</tr>
<tr>
<td>$p \to \infty$</td>
<td>$d^3 \left(1 - \frac{\pi^2}{8p^2}\right)$</td>
<td>$d^2 \left(1 - \frac{\pi^2}{24p^2}\right)$</td>
</tr>
<tr>
<td>$p \approx \frac{1}{2}$</td>
<td>$\frac{d^3}{12}(10p - 3)$</td>
<td>$d^2 p$</td>
</tr>
</tbody>
</table>

model numerically a whole family of surfaces, and extract the behavior of their resonant spectrum as a function of the power factor $p$ [144, 145]. Indeed, Fig. 4.3 reveals the evolution of the resonant spectrum for a silver sphere of $d = 25$ nm in diameter as a function of the rounding factor. Changing the power factor we obtain a red shift of main plasmonic curve (electric dipole). Additionally, we observe the development of pronounced higher order resonances, which is a characteristic signature for structures with corners and edges [59]. Actually, the emergent structural properties of the superquadrics (vertices, edges, etc.) beyond the sphere facilitate the existence of collective electron oscillations in higher energies (smaller wavelengths). These higher energy resonances generally couple weakly to the incident plane wave and exhibit increased absorptive characteristics.

Figure 4.3. Shape transformation mappings as a function of the rounding factor $p$ for silver nanoparticles. Left: the extinction efficiency (ratio of the extinction cross section over the geometrical cross section, i.e., $Q_{\text{ext}} = \sigma_{\text{ext}}/C_g$) in the range $0.6 \leq p \leq 5$. The electrical dipole-like (ED) resonance is visible (red line). Right: the plasmonic albedo, i.e., the ratio between the scattered and the extinction cross sections. Notice that the ED resonance exhibits a smooth albedo transition, while lower albedo values for the higher modes are manifested. Picture adopted form [145] with permission.

A measure for the interplay between the scattering and absorptive mech-
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anism is the single particle plasmonic albedo (see Eq. (2.68)) [72], i.e.,

$$w = \frac{C_{\text{sca}}}{C_{\text{sca}} + C_{\text{abs}}}$$

(4.14)

The albedo is a qualitative figure exposing the balance between the absorption and scattering mechanisms, as illustrated in Fig. 4.3 (right). In this case, the maximum albedo level is $w = 0.3$, indicating that absorption is the main extinction mechanism in all cases. This is a common feature for all subwavelength particles where extinction is mainly attributed to materially induced absorption.

### 4.3 The Platonic solids

The cases studied above, cube and octahedra, occur as limiting cases in the superquadric solids. Additionally they belong to another family of solids, the regular polyhedra known as the Platonic solids. These solids are the tetrahedron, octahedron, hexahedron (cube), icosahedron, and dodecahedron, shown in Fig. 4.4. These five solids, known already before the Pythagoreans and other pre-Socratic natural philosophers, borrow their names after Plato, who was the first to use them collectively\(^3\) in his natural philosophies [130].

![Figure 4.4. The five Platonic solids (regular polyhedra) presented in a sv (solid vertex)–hierarchical order (“sharper-to-softer” solids). From left to right (top-to-bottom): tetrahedron, octahedron, hexahedron (cube), icosahedron, and dodecahedron with 4, 8, 6, 20, and 12 edges, respectively. The sv–hierarchy is visible in the increasing smoothness of the shapes from left to right.](image)

\(^3\)At his work Timaeus (or dialogues on Atlantis and Nature, Plato, c. 360 BC), Plato connects the five polyhedra to the five universal components, such as fire (tetrahedron), earth (hexahedron), air (octahedron), water (icosahedron), and fifth element (dodecahedron).
4.3.1 Geometric properties

Platonic solid-shaped structures occur either naturally in organic and inorganic compounds or can be artificially engineered [42]. Some of the most characteristic geometric properties of these solids are given in Table 4.2 where we can find the volume and vertex solid angle for each solid. One interesting property is the duality between these solids. For instance, the hexahedron is dual to octahedron, the dodecahedron dual to icosahedron, while the tertahedron is self-dual. This can be easily deduced by mutually interchanging the hedrae and the vertices (see Fig. 4.4). These duality relations are a key issue in understanding and categorizing the plasmonic behavior of the solids.

Table 4.2. Key features of the Platonic Solids. Note that all solids are adjusted to have equal volume (50\(^3\) nm\(^3\)).

<table>
<thead>
<tr>
<th>Polyhedron</th>
<th>Volume</th>
<th>Vertex angle (sr)</th>
<th>Edge(^1) a [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron</td>
<td>(\frac{\sqrt{2}}{12} a^3)</td>
<td>0.551</td>
<td>101.98</td>
</tr>
<tr>
<td>Octahedron</td>
<td>(\frac{\sqrt{2}}{3} a^3)</td>
<td>1.359</td>
<td>64.245</td>
</tr>
<tr>
<td>Hexahedron</td>
<td>(a^3)</td>
<td>(\pi / 2 = 1.571)</td>
<td>50</td>
</tr>
<tr>
<td>Icosahedron</td>
<td>(\frac{5 + \sqrt{5}}{12} a^3)</td>
<td>2.635</td>
<td>38.55</td>
</tr>
<tr>
<td>Dodecahedron</td>
<td>(\frac{15 + 7\sqrt{5}}{4} a^3)</td>
<td>2.962</td>
<td>25.36</td>
</tr>
</tbody>
</table>

\(^1\) Required edges for equi-volumed particles.

Classically, the preferred order for categorizing the Platonic solids is by the number of the faces, i.e., the order tetra–hexa–octa–dodeca–icosa, implying an ascending hedrae number for each solid. We name this as the hedra-hierarchical order, or h-hierarchy for short. However, instead of the h-hierarchy there is another way of categorization following the sharpness of a solid, i.e., based on its solid angle vertex. This categorization results in the tetra–octa–hexa–icosa–dodeca scheme, and we call it solid vertex hierarchy, or sv-hierarchy for short.

4.3.2 Scattering properties

The most pronounced scattering properties of Platonic solids are summarized in Fig. 4.5 that shows the volume normalized extinction cross section of all treated particles. In particular here we simulate equivolumed Platonic solids \((V = (50)^3 \text{ nm}^3)\), and compare their resonant spectrum, extracted with the SIE computation method discussed above. As can be seen, the evolution of the main scattering features, i.e., the first and sec-
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Resonances and scattering minima, follow the sharpness of the NPs, especially for the three last cases (tetra-, octa-, and hexahedron).

Figure 4.5. Comparative chart depicting the volume normalized extinction cross section of the five equivolumed silver Platonic solids and the sphere. Each line corresponds to one solid. Picture adopted with permission from [146].

The main resonant peaks of the tetra-, octa-, and hexa-hedron occur at $\lambda_{\text{tetra}} = 550\text{nm}$, $\lambda_{\text{octa}} = 431\text{nm}$, and $\lambda_{\text{hexa}} = 423\text{nm}$, respectively. The vertex angles are $0.551$, $1.359$, $\frac{\pi}{2} \approx 1.571$ and the edge lengths are $101.98$, $64.245$, $50$ for the tetra-, octa-, and hexa-hedron, respectively. The statistical correlation between the maximum extinction peak and the vertices is approximately $0.988$ while the wavelength-edge correlation is somewhat smaller, exhibiting roughly a value of $0.977$. Due to the fact that the plasmonic resonances follow an sv-hierarchical order in terms of the lowest to highest resonant energies (lowest resonant wavelength), it stands to reason that the main plasmonic resonance is straightforwardly affected by the sharpness of the vertex. Note that previous experimental work [147] indicate that the edge length (plasmonic length) is the main resonant affecting mechanism. Fixing the type of solid and its volume defines its edge length and its vertex sharpness. However, in our perspective, the vertex categorization is more universal, since it is defined only by the type of solid and not its volume. This categorization follows the same philosophy as with its 2D counterparts, where sharper corners induce resonances at lower energies, as can be found in references [66, 148, 149].

On the other hand, earlier studies on dielectric solids, for example in [70,
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revealed an hedra-hierarchical order regarding the strength of the calculated electrostatic polarizabilities. This difference can be explained by the fact that different physical mechanisms are involved for plasmonic response than in the quasistatically explainable dielectric response. In particular, sharp corners and edges facilitate the accumulation and radiation of the energy carried by free conduction electrons, which is the main radiation enhancement mechanism behind the plasmonic resonances.

Figure 4.6. The scattering albedo for a sphere and the five Platonic solids. A minimum albedo can be identified for the region between the first two resonances for all particles. Picture adopted with permission from [146].

As in Section 4.2, the albedo of almost all solids exhibits a minimum valley close to their second absorptive resonance as can be seen in Fig. 4.6. This is an indication that close to regions of minimum scattering the absorption mechanism prevails. The most interesting case is observed for the tetrahedron since its albedo drops below 0.5 almost for the entire spectrum. Tetrahedron exhibits extremely sharp solid vertices that shift the main dipole resonance towards lower energies. At these energy ranges the losses of the Drude-like model for silver are somewhat larger than in the other cases justifying the low albedo values. This argument can be further supported by the albedo expression of a small dipole (Eq. (2.68)), where larger losses result in smaller albedo values for the same particle volume.
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5. Summaries

5.1 Summary of thesis introduction

The introduction summarized the basic elements regarding the electrostatic and electrodynamic resonant scattering of spheres. The purpose of the introduction was to provide the theory required for following up the included articles. It condenses mainly two aspects of the scattering theory, i.e., the underlying physical mechanism of a small sphere from both static and dynamic perspectives, and the morphological dependencies on the main plasmonic resonances.

The discussion in Chapter 2 opened with the electrostatic perspective, introducing the standard electrostatic perturbation theory, followed by the analysis of the scattering by the fundamental case of a Hertzian dipole. The chapter concluded with the main features of the Lorenz–Mie theory, i.e., electrodynamic scattering by a homogeneous sphere.

In Chapter 3 the main resonant scattering features were summarized. Particular emphasis was given to the heuristic Padé methodology for extracting the distribution of each resonance on a homogeneous sphere. A few illustrative examples clarified the significance of the proposed methodology.

Finally, Chapter 4 exposed the key elements of the numerical method used and the mathematical background regarding the superquadric surfaces, with which the effects of morphology on scattering could be analyzed efficiently.
5.2 Summary of thesis publications

As stated in Chapter 1 the publications can be divided into two subunits: the “sphere trilogy” consisted of Publications I, II, and III, and the “polyhedra trilogy” including Publications IV, V, and V.

Publication I: Unveiling the scattering behavior of small spheres
This is the first article of the “sphere trilogy”. In this work the authors introduced and developed a rigorous idea for extracting analytical expressions of the distribution of magnetic resonances utilizing the Padé approximants. This methodology was first applied for the case of the plasmonic resonances, confirming its validity over known results. Additionally new results regarding the depolarization and radiative damping terms were given for the case of magnetic resonances, predicting the existence of a plateau for the maximum resonant absorption for the magnetic resonances of a dielectric spheres. The distribution of the first five magnetic multipoles was derived.

Publication II: Resonant scattering characteristics of homogeneous dielectric sphere
This is the second part of the first trilogy. In this contribution, the classical problem of EM scattering by a single homogeneous sphere is revisited utilizing the same idea that was presented in Publication I. In this case a full analysis on the potential of the Padé–Mie heuristic methodology was discussed. For example, low-order Padé approximants can give compact and physically insightful expressions for the scattering system and the enabled size-dynamic mechanisms. Higher order approximants were used for predicting accurately the resonant spectrum, and summarized into general pole formulae, up to fifth magnetic and forth electric multipole order. The reported pole distributions were similar, but not identical, with the conditions presented in [54], especially for the higher order radiative damping terms (imaginary part of the resonant permittivity). Moreover, the connection between the radiative damping process and the resonant linewidth was investigated. The results revealed the fundamental connection between the radiative damping mechanism and the maximum width and resonant absorption.
**Publication III: General scattering characteristics of resonant core-shell spheres**

This is the last and concluding part of the first trilogy. Here, the Padé methodology was applied to the core-shell problem following Publications I and II. Initially, the thickness effects on the plasmonic resonances were presented in the electrostatic (Rayleigh) limit, utilizing the MacLaurin expansion of the Mie coefficients of hollow scatterers. Several aspects regarding the core effects were given, illustrating the involved mechanisms of its resonant scattering response at the electrostatic limit. The electrodynamic aspects of the scattering process were revealed through the newly introduced Padé expansion of the Mie coefficients. The key feature of this article was the connection of the core material and the dynamic mechanisms. In particular, a condition was presented for which the two resonances (symmetric and antisymmetric) become degenerate, consequently affecting the resonant width as well as the maximum resonant absorption of the core–shell scatterer.

**Publication IV: Shape effects on surface plasmons in spherical, cubic, and rod-shaped silver nanoparticles**

This first article of the “polyhedra trilogy” presented a simple analysis of the localized surface plasmon resonances on silver nanoparticles via the SIE methodology. In particular, the extinction, albedo, and charge distribution of the first two resonances were calculated for the cases of a spherical, a cubic, and a cylindrical rod-shaped silver nanoparticle.

**Publication V: Plasmonic properties and energy flow in rounded hexahedral and octahedral nanoparticles**

In this second part of the second trilogy, we discussed the resonant plasmonic properties of small, geometrically dual, rounded nanoscatterers. In particular, the scattering properties for the cases of rounded hexahedral and octahedral superquadric solids were studied and compared with a reference spherical particle through the SIE numerical technique. Several mathematical remarks about the superquadric cases were given. Surface, near-field, Poynting field, and stream-line distributions were presented illustrating interesting plasmonic features, especially around vertices of the scatterers.

**Publication VI: Study of plasmonic resonances on Platonic solids**

The third article concludes the “polyhedra trilogy” with a study regarding the plasmonic resonances of five regular polyhedra, that is, the Platonic...
solids. As in Publications IV and V, the resonant spectra of the solids were compared with that of a sphere. The main results indicated that the dipole resonance shifts, following a solid-vertex hierarchical order, i.e., the position of the resonance correlates with the solid angle of the vertex of the given solid. This result was in contrast with a hedra-hierarchy found for the electrostatic dielectric response of the same solids [71].
Bibliography


How a small sphere scatters the incident light? Does the existence of an air bubble inside a sphere affects these resonances and how? Can we transform a sphere into a cube and how this affects the overall scattering? What is the connection between Plato and light scattering?

The thesis discusses the electromagnetic scattering of single subwavelength nanoparticles and nanoantennas and their morphological effects to the overall scattering response. The energy localization via plasmonic or dielectric resonances has been studied for a number of shapes, such as spheres, spherical shells, rounded cubes, and the Platonic polyhedra. Understanding the single-particle response is of paramount importance for applications with enhanced or novel energy control/harvesting functionalities within the areas of RF engineering, material science, applied physics, optics, and photonics.