Universidad de Cantabria

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

PH.D. THESIS

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Introduction

"El pasado es un prólogo"
—William Shakespeare, 1564-1616, dramaturgo,
poeta y actor inglés

Light has been considered a great mystery for a long time. For centuries, scientists have tried to understand its behavior, in particular when it interacts with matter. From the Greek philosophers as Euclides (300 b.C.) to the modern theories of quantum optics, as those proposed by A. Einstein [30] many aspects of light have been explained.

Following the studies of Claudius Ptolemaeus (100 b.C.), Ibn al-Haytham (965-1040), also known in Europe as Alhazen, was the first scientist who drew ray diagrams, that were the beginning of what we nowadays know as Geometrical Optics. In his work, the concepts of reflection and refraction start to appear. It is not until the $16th$ and $17th$ centuries when systematic studies about these phenomena were made by Galileo Galilei (1564-1642), Johanness Kepler (1571-1630) and René Descartes (1596-1650). Willebrord Snel van Royen (1580-1626), also known as Snellius proposed the refraction and reflection laws, later derived by Descartes.

In the $17th$ century, while Isaac Newton (1643-1727) proposed a corpuscular theory of light, Christian Huygens (1629-1695) was the first who wrote of light as a wave. It was not until the $19th$ century with the experiments by Thomas Young (1773-1829) when the wave theory of light was widely accepted. James Clerk Maxwell (1831-1879) worked deeply in a wave theory that explained several light phenomena, that concluded into the Maxwell equations [91, 90]. Equations that are the basis of the electromagnetism and join the works done by Faraday (1791-1867), Gauss (1777-1855) and Ampère (1775-1863).

Maxwell's works seemed enough to explain light phenomena. However, the debate was reopened in the $20th$ century. A new quantum theory of light was derived from the works done by Max Planck (1858-1947) and Albert Einstein (1879-1955) and the concept of the photon started to appear.

These works have revealed light as being a very useful tool for several applications.

A very important phenomenon, on which we have focused this research, is *light scattering*. This physical phenomenon of scattering, which affects not only light, but also sound waves and moving particles for example, leads to a deviation of the incoming energy due to the presence of a localized inhomogeneity in the medium through which it propagates. Light scattering is quite common and it is responsible of, for instance, the blue color of the sky, explained by Lord Rayleigh [119].

The induced deviation of light, that can affect (inelastic scattering) or not (elastic scattering) its nature, depends strongly on the characteristics of light itself (wavelength, polarization, etc) but also on the medium through which it propagates and its non-uniformities. If we know the main parameters of the system, we can predict how light will be scattered. Or inversely, through the analysis of light scattering we can obtain valuable information about the scatterers. These are known as the *direct* and the *inverse* problem, respectively [88, 136]. Both aspects offer the possibility for several applications based on light scattering. Techniques were adapted for astronomical applications, such as detection of interstellar dust [140], for technological purposes, such as profilometers [113] or particle sizing [25, 103], for meteorological or environmental diagnosis such as the detection of aerosols [117] and recently for renewable energies as described in [149]. The use of light as a way to obtain information about scatterers, constitutes a *non-invasive technique* which is very convenient especially for biological applications such as: imaging [143], tissue diagnosis [104] or even in cancer research [12].

Several theories have been enunciated to analyze and to extract information from light scattering measurements. One of the most important theories, on which this thesis is based, is **Mie theory**. It was developed at the beginning of XX century by Gustav Mie [97]. It constitutes an analytical solution of the Maxwell equations for a spherical, homogeneous and isotropic particle illuminated by a plane wave. It will be discussed later in more detail.

New technological advances are focused on reducing dimensions, reaching the nanometer scale, such that manipulation of genes or the fabrication of high-density integrated circuits on chips will become a reality in a near future. This miniaturization has important technological barriers, mainly related to the manufacture techniques. Light, however, has appeared as a good candidate to overcome the challenges of downsizing. During the last years, researchers have focused their attention on the development of new optical devices with subwavelength dimensions, most of them based on light scattering. Research on those new devices, has found two important dares. First, for small scatterers, the scattered intensity is quite low. This is an important handicap for sensing or communication tools. To get over this limitation, highly confined electromagnetic fields and/or intense resonant behaviors are needed. These intense and highly localized fields can be obtained through the excitation of *Surface Plasmon Resonances (SPRs)* or *Localized Surface Plasmon Resonances (LSPRs)* on metallic nanostructures. This explains the huge interest of researchers in the field of *Plasmonics*, as will be explained. On the other hand, several processes cannot be reproduced using light scattering because they involve material properties not found in Nature. To circumvent this, researchers have developed new engineered materials, called *Metamaterials*, which present non-conventional optical properties giving rise to light propagation phenomena never seen before.

In this introduction, we will briefly discuss these two emerging research areas in which this thesis is based.

1.1. Plasmonics

Due to their optical properties, metallic structures can sustain surface and volume charge oscillations at optical frequencies. These are called *plasmon polaritons*, or just *plasmons*, whose excitation is probably one of the major characteristic of light interacting with metal systems. The collective oscillation of the free electrons at a metal-dielectric interface, associated to a plasmon, gives rise to strongly enhanced surface fields which are spatially confined near the interface.

Both enhancement and confinement of the electromagnetic wave, are used for metal-dielectric interfaces to create sensitive optical interactions on which are based several applications (optical imaging, wave guiding, near-field microscopy).

We can distinguish two types of plasmons. When the electron gas is confined in two dimensions ($2D$), as is the case on a planar substrate, we can then talk about *surface plasmon*

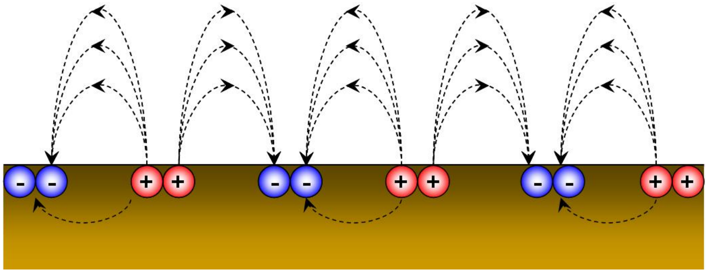

Figure 1.1: Scheme of the excitation of a surface plasmon resonance (SPR) on a metal-air interface.

resonances (SPRs). If the charge distribution is confined in a three dimensional ($3D$) structure, such as in sub-wavelength particles, the interaction with light induces *localized surface plasmon resonances (LSPRs).* Several differences between *SPRs* and *LSPRs*, which will be explained below, justified this classification. In addition, each kind of plasmons gives rise to different applications.

1.1.1. Surface Plasmon Resonances (SPRs). Planar Substrates

Surface plasmon polaritons appear at a metal-dielectric planar interface, if the real part of the dielectric constant of the metal is larger than its imaginary part ($\epsilon'_M \gg \epsilon''_M$), and when the incident light is able to match the surface plasmon wavevector ($\vec{k}_{SP}$) [108]. Thus, a redistribution of the free electrons on the interface generates charge density waves which travel along the substrate as is represented in Figure 1.1.

Unfortunately, $\vec{k}_{SP}$ is always larger than the wavevector of light in free space. Then, a SPR on a planar interface cannot be excited by light of any frequency propagating in free space, unless we are able to increase a wavevector component over its free space value. There are several methods to achieve this. Probably, the most simple and the most commonly used one is by means of evanescent waves which are created at the interface between media of different wave motion properties (a metal and a dielectric, for instance). In Figure 1.2, the two most popular configurations to excite surface plasmon polaritons through evanescent waves are shown: (a) proposed by A. Otto [111] and (b) by E. Kretschmann [76]. In both configurations, a glass prism is used to generate the evanescent field by means of total internal reflection (TIR).

The main manifestation of the excitation of the SPR in those setups is a minimum in the total reflected light. The sensitivity of the angular position of this minimum, due to environmental changes, makes these devices very adequate for surface sensing purposes [55,

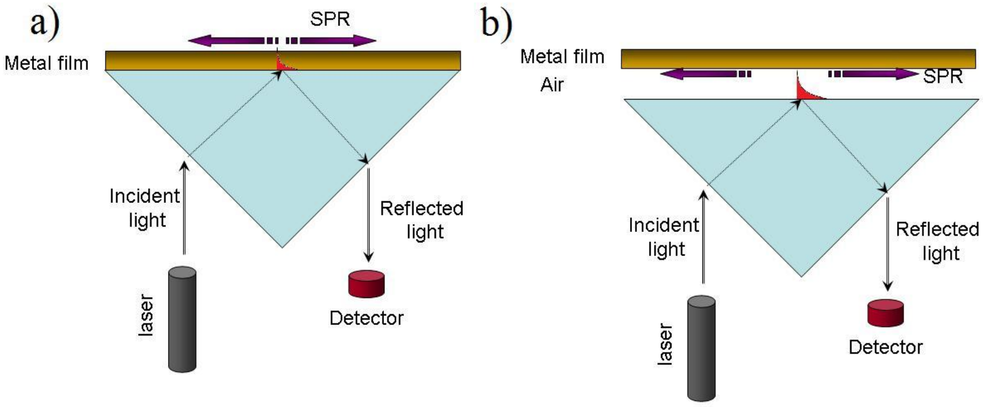

Figure 1.2: (a) Otto configuration and (b) Kretschmann configuration for the excitation of surface plasmons through evanescent waves.

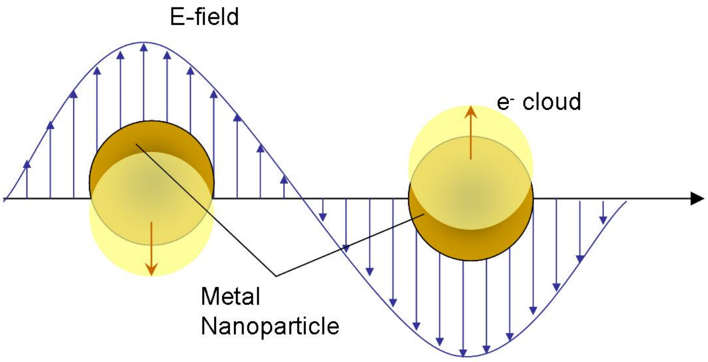

Figure 1.3: Scheme of the excitation of a localized surface plasmon resonance (SPR) on metallic nanoparticles obtained from [118].

116, 78]. In fact, there are already commercial biosensors based on the excitation of SPRs [1, 2]. Besides this and in order to design as smaller geometries as possible of these sensors, new experimental configurations have been developed, for instance, by means of optical fibers [146].

Other ways to excite SPR are by means of, for instance, the near-fields in the vicinity of sub-wavelength apertures for which an extraordinary transmission has been reported [41], metallic particles or even fluorescent molecules that could be important for fluorescence-based arrays in both medical diagnosis and biotechnology [89].

1.1.2. Metallic Nanoparticles. Localized Surface Plasmon Resonances (LSPRs).

Compared with SPRs, localized surface plasmon resonances (LSPRs) generates strongly confined and intense electromagnetic fields in the vicinity of a metallic particle, and consequently very well localized electromagnetic fields. For this reason, LSPRs are not characterized by a wavevector $\vec{k}_{SP}$ and they can be excited by free propagating light [118]. Hence, no special experimental configurations are necessary to excite them. In this case, incident light wave, with a certain frequency may induce an overall displacement of the electron cloud that leads to a restoring force which in turn gives rise to the resonant mode (see Figure 1.3), and a consequent enhancement of the absorption and scattering.

The frequencies of the incident light which produce plasmon oscillations are called plasmon bands. Considering a small metallic sphere ($R << \lambda$) with a frequency-dependent dielectric constant $\epsilon_1(w)$, embedded in a dielectric medium (ϵ_2), the plasmon excitation occurs when $Re(\epsilon_1(w)) = -2\epsilon_2$. This condition is strongly dependent on the shape of the scatterer, among other things [100]. If, for instance, we consider a nanorod, instead of a sphere, two plasmon resonances, with the free electrons oscillating either along or perpendicular to the long axis, are observed when $Re(\epsilon_1(w)) = -\epsilon_2$ [14]. This important shape dependency of localized surface polaritons has been used already to manipulate plasmon resonances by modifying the shape of the nanoparticle [100]. A different way to tune the resonant wavelength is through heterostructured nanoparticles or simply nanoshells. As was demonstrated, a careful control of the core/shell ratio gives the possibility to create a plasmon resonance which covers a broad spectral range [58, 52]. In addition, the resonant frequencies strongly depend on the size of the scatterer through the size dependency of its optical constants [118] and on the refractive index of the surrounding medium. The high confinement of light around resonant particles and the strong enhancement of their absorption and scattering are quite useful for several applications [121]. Nowadays, nanolithography and photofabrication methods employing plasmonic particles are developed following the ideas proposed by H. A. Atwater and co-authors [72]. Improved solar cells have been designed by means of plasmonic nanostructures [19, 112, 130, 6]. The enhancement also affects weak linear and non-linear optical effects in molecules within nanoscopic distances from a metallic nanostructure. Several biological fluorescence-based sensors [92, 73, 124] or SERS (Surface-Enhanced Raman scattering)-based sensors [59, 131, 3] have appeared even for single-molecule detection. For instance, E. Hao and G.C. Schatz reported field enhancements of ~ 11000 times at $520nm$ (dipolar resonance) and ~ 3500 times at $430nm$ (quadrupolar resonance) at the midpoint between a dimer of silver spherical nanoparticles [47].

Several biosensors made with plasmonic nanostructures are also based on the sensitivity of the LSPR spectral position to environmental changes. For this reason, several works have focused on the improvement of the sensitivity of metallic nanostructures. They are chemically modified with interesting properties for food-safety, medical treatments or for biological and environmental research [10, 144, 77, 81, 5]. During the last years, researchers have seen the potential applications of plasmonic nanostructures as an alternative to optical fibers. As is known, optical fibers are limited by the diffraction limit, hence their transversal size must be large. Waveguides based on plasmonics can guide light below the diffraction limit. This was first put forward by S. Maier and co-workers in [85] where they proposed an array of metallic nanoparticles to guide and modulate light with sub-diffraction limit resolution. This kind of optical channels would be very useful for future optical nanocircuits.

1.2. Systems with Magnetic Response

Conventional materials do not have magnetic properties in the visible range. This is expressed by the magnetic permeability being equal to one for optical frequencies. However, materials presenting a response to both the electric and the magnetic part of an incident electromagnetic wave in the visible could be very interesting for future applications. Systems presenting such atypical optical responses have attracted a lot of attention in recent years. Many attempts have been undertaken to obtain negative permittivities and permeabilities, resulting in a negative refractive index ($\epsilon < 0, \mu < 0$ and $n < 0$). Such materials are usually referred to as Left-Handed materials, and were proposed and studied for the first time by V. Veselago [138]. Their non-conventional optical constants induce non-conventional phenomena like negative refraction [51] (see Figure 1.4(a)) or the Poynting vector direction opposite to the propagation of the wave.

Two of their main applications are the theoretical possibility to realize an invisibility cloak [115, 33] (see Figure 1.4(b)) or a perfect lens [114] (see Figure 1.4(c)). Nevertheless, their real possibilities are quite controversial [38].

As these new properties cannot be realized using naturally occurring materials, the only possible way to obtain these, is to manufacture them. These artificial media are structured on a scale smaller than the wavelength of the incident wave (see Figure 1.5), such that they present macroscopic effective optical properties. By changing the composition, density, size or shape of the inner structure, the effective properties can be modified and a wide range of

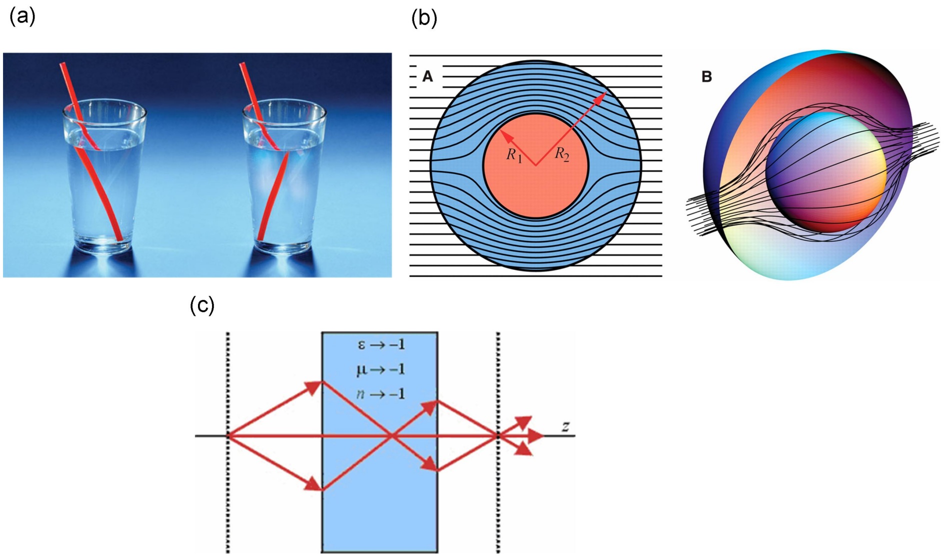

Figure 1.4: Example of three interesting phenomena which can be observed for left-handed materials. (a) Artistic representation of the negative refraction as was described by O. Hess in reference [51], (b) Scheme of the light rays around an invisible particle [115] and (c) Ray scheme for a perfect lens [114].

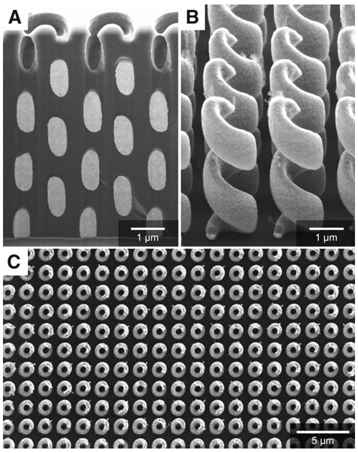

Figure 1.5: Different views of the inner structure of a metamaterial manufactured by J.K. Gansel and co-workers [37].

new optical features can be observed [129]. During the last years, researchers dedicated a lot of attention to the development and the study of these new media [120, 123, 65, 26, 22] which resulted in effective electromagnetic response have been obtained for a wide spectral range covering from the microwave to the visible part of the spectrum [122]. These studies generated an extraordinary swarm of metamaterials, with very different applications. A summary was made by N. Zheludev using an original "metamaterial tree of knowledge" [148], which we reproduce in Figure 1.6. Negative refractive index metamaterials appear in the base of the tree, because they have been demonstrated experimentally and accepted. Other interesting types of metamaterials, designed for specific applications, are also included in this figure. As an example, we give the case of metamaterials which are being developed to improve the sensing characteristics of biosensors. The possibility to control the distribution of the scattered radiation of one of these biosensors by tuning its optical properties, could enhance drastically their sensitivity [62]. In addition, new optical devices based on metamaterials start to appear as solutions for the well-known communication bottleneck in microelectronics [7, 98]. For this task, high-quality and fast responsive devices are needed. Thereto, new switchable and non-linear metamaterials are developed providing the first prototypes of on-chip optical communications, based on metamaterials [42]. In the future, it is even possible that not only communication processes are based on metamaterials, but also the logical gates in chips. Recent studies propose structures using metamaterials which behave as typical electronic devices like a resistance, a capacitor or an inductor [32, 126].

Before this becomes reality, an important challenge must be overcome: the miniaturization of metamaterials. Structures with dimensions in the nanometer scale are the objective of recent research. Several studies have concentrated on the design of nano-metamaterials composed of magnetodielectric nanoparticles forming an array [53, 54]. An important model of these arrangements of particles is the one proposed by Alù et al. [8]. They propose a structure composed of six silver nanoparticles ($R \sim 13.5nm$) and located such that their centers are on the imaginary sphere of $20nm$ in radius (see Figure 1.7). This geometrical configuration implies that the whole system could be considered, for wavelengths in the visible range ($\lambda \sim 500nm$), as isotropic and independent on both the incident direction and the beam polarization. In this case, light sees the structure as an isotropic particle with effective size and optical constants and with an spectral response quite different from that of an isolated silver particle. These differences were demonstrated by the authors [8], where they represent the electric and the magnetic polarizabilities of both the proposed system and an equivalent silver nanoparticle which we reproduce here in Figure 1.8. The proposed structure presents two dipolar resonances, one electric and one magnetic (Figure 1.8(b)), instead

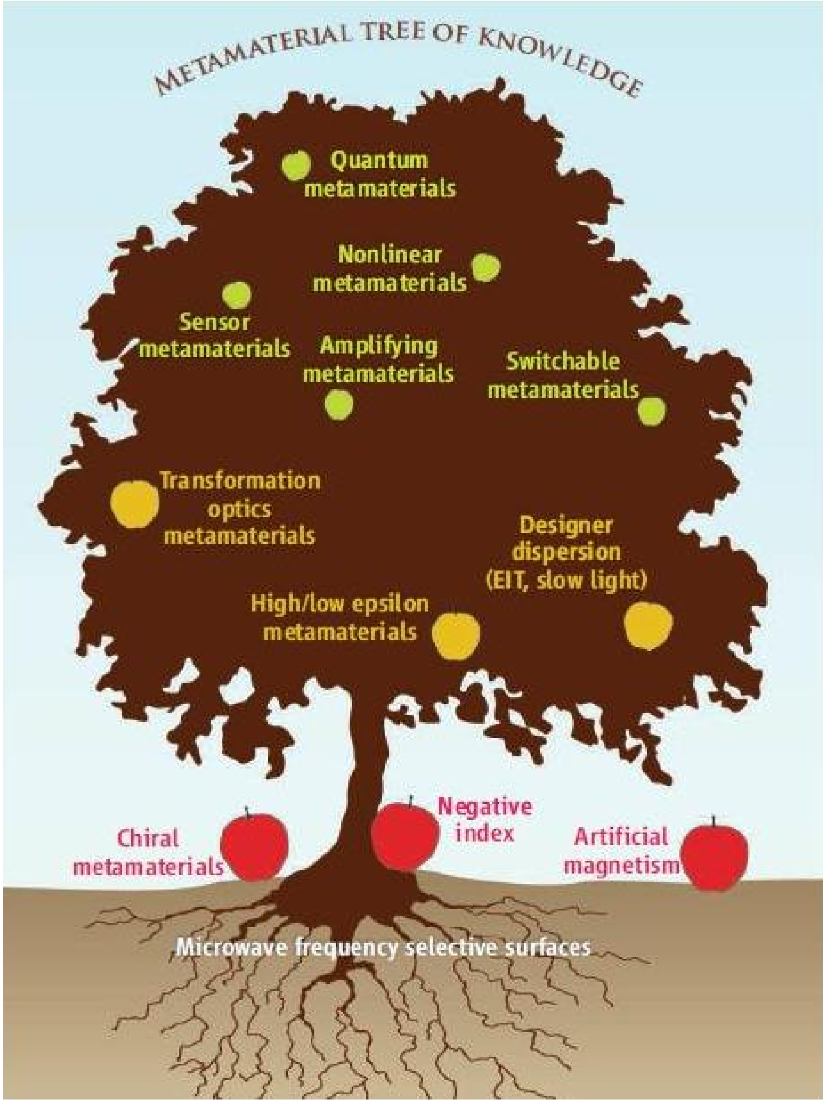

Figure 1.6: Artistic representation of the evolution and future of metamaterials research as was proposed by N. Zheludev in [148]. The base of the tree represent fields in which there is already a solid scientific basis while the top branches still constitute a challenge.

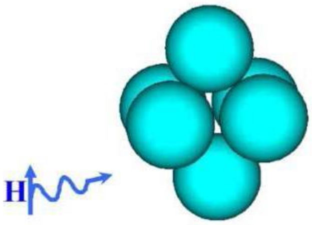

Figure 1.7: Scheme of the nanostructure consisting of six silver nanoparticles, constituting the fundamental magnetic-based plasmonic resonant element proposed by A. Alù and N. Engheta in [8].

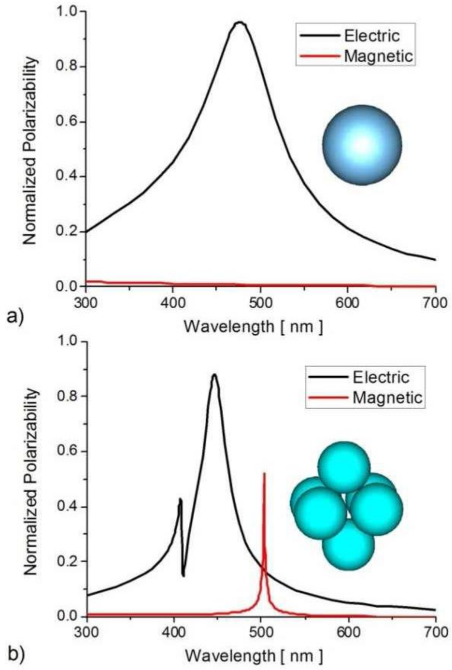

Figure 1.8: Comparison of the electric and magnetic polarizabilities for (a) a single silver nanoparticle with a size equivalent with the proposed arrangement and (b) for the cited configuration [8].

of one electric dipolar resonance for the isolated silver particle (Figure 1.8(a)). Both the interaction between particles and the distribution of the electromagnetic field inside the arrangement, create these spectral properties. Hence, while silver nanoparticles do not present any response to the incident magnetic field, the "nano-metamaterial" does.

Any modification of the geometrical properties of a nanoparticle also modifies its spectrum [100]. An elementary change in the symmetry of a particle can modify drastically its spectrum. It was recently demonstrated that a metallic nanoparticle with a given geometry can present also a dipolar magnetic resonance. Simply stated, an isolated particle made of conventional materials could present magnetic properties only induced by its geometrical properties. This effect was firstly introduced by Mirin et al in [99]. They manufactured gold nanoparticles with diameters around $40 - 80nm$ and a shape similar to a hollow half sphere, called "nanocup" (see Figure 1.9). While the axial mode of this structure corresponds with an electric dipolar resonance (Figure 1.9(a)), the transversal mode is associated with a magnetic dipolar resonance. This is confirmed by an increase of the magnetic field under this mode (Figure 1.9(b)). The system developed by N. Mirin and N. Halas shows a useful and quite interesting feature: while light scattering of these particles depends on the particle

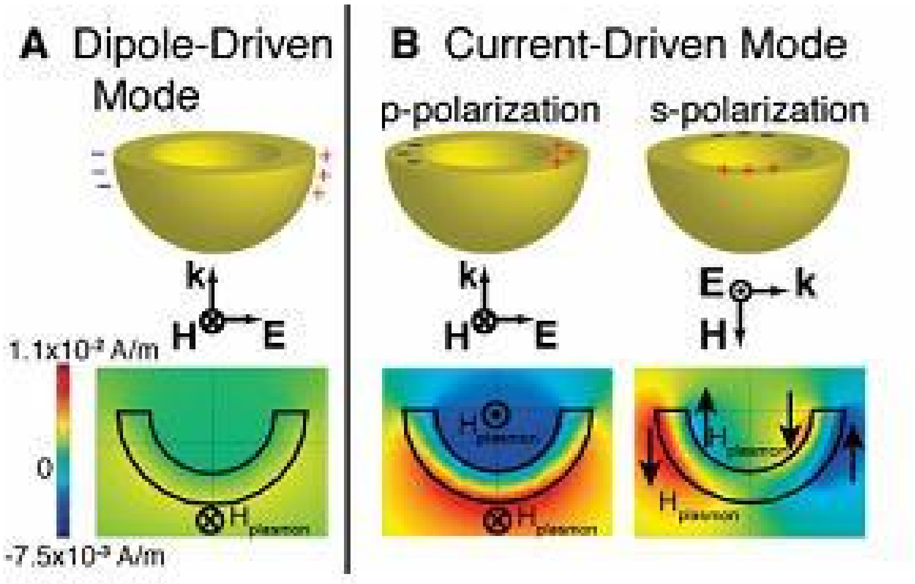

Figure 1.9: (Top) Scheme of the resonances in the gold particles developed by N. Mirin and N. Halas and (down) spatial distribution of the magnetic field around the particle when resonances are excited $(Eo = 1V/m, Ho = 2.7 \cdot 10^{-3} A/m)$.

orientation, it does not depend on the incident direction for a parallel polarization (Figure 1.10). Thus, by controlling the alignment of the particles, we are able to control the angular distribution of the scattered intensity.

These two works, by Alù et al [8] and by Mirin et al [99], have inspired several aspects of this research, although we have not based it on them.

In summary, the new advances in the field of metamaterials can revolutionize photonics and offer a control over light waves never attained with current materials. This is particularly important for the directional control of the scattered light, which has applications in future communication devices.

1.3. Objective and Overview of this Thesis

1.3.1. Objective

Optical effects coming from the electromagnetic interaction of metallic nanoparticles and light have developed new experimental techniques for applications in important fields like Medicine, Biology or Semiconductor Technologies. High-quality optical devices, based on the scattering characteristics of plasmon resonances excited in metallic nanoparticles, have been developed during the last years. In addition, new engineered materials, known as meta-

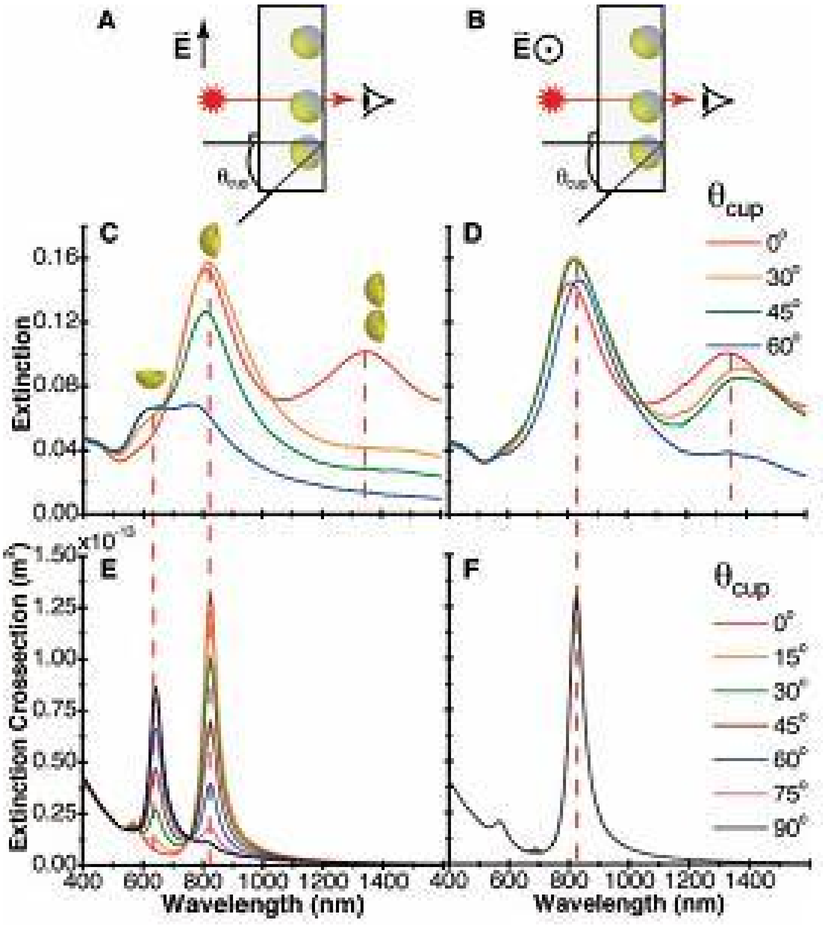

Figure 1.10: Experimental (c and d) and theoretical (e and f) extinction spectra of a sample of nanocups illuminated by an incident beam polarized with the electric field parallel (left column) or perpendicular (right column) to the scattering plane, as is shown in the schemes (a and b). Different particle orientations are considered.

materials, have appeared, presenting new and non-conventional properties, never observed before. These can improve drastically those optical devices and even new optical functionalities could be obtained. These aspects have inspired the present thesis.

We have made a numerical study of the main scattering properties of nanoparticles with non-conventional optical constants, mixing hot topics of both metallic nanoparticles and metamaterials. We will study light scattering by very small particles (with finite size in most of the cases) having arbitrary values for the optical constants (ϵ, μ), including the double-negative range. Directionality consequences will be obtained from the previous analysis applied to isolated and also to aggregates of them as a first step to further applications in optical nanocircuits. In order to analyze in a simple manner the physics involved in the problem, we will consider a simple model. It consists on a spherical particle whose size is much more smaller that the incident wavelength and whose optical constants are arbitrarily chosen.The proposed model can be regarded excessively constrained and quite far from experimental configurations. However, it can give us interesting information about the physics involved in more realistic systems.

In the last part of the thesis, a more realistic situation is considered. We consider metallic nanoparticles located on a planar surface at a certain distance. The objective of this section is to analyze the influence of the surface on the distribution of the scattered intensity of the particle, enhanced by plasmon resonances, and, in particular, the deformation of its dipolar behavior due to the proximity of the surface. As will be seen, the presence of the surface could induce a strong localization and directionality of light scattering which could be useful for certain applications.

1.3.2. Overview of the Thesis

In chapter 2, we explain the main concepts about light scattering by particles and more specifically by nanoparticles. As a part of this, we make a brief review of Mie theory. While many explained concepts have been known for a long time, others have been established only recently. There are useful approximations of Mie theory for point-like particles, such as the dipolar approximation. Nevertheless, these are not accurate for finite-sized particles. In this chapter, we present new analytical approaches for the first four Mie coefficients (a_1, a_2, b_1 and b_2) which have been tested as being valid for particle sizes up to $R \leq 0.1\lambda$.

The results presented in this thesis have been divided into three parts:

1. **Study of the Scattering Properties of an Isolated Particle**

This part is devoted to the analysis of light scattering of one particle whose size is much smaller than the incident wavelength (λ) and which has arbitrary values for both the electric permittivity (ϵ) and the magnetic permeability (μ).

- *Chapter 3* is devoted to the study of Mie resonances. Until now, these modes were studied for conventional materials (dielectric or metallic). In this chapter, we have extended this study giving arbitrary values to the optical constants and analyzed the evolution of resonances as a function of the combinations (ϵ, μ) and of the particle size.
- *Chapter 4* summarizes results about the study of the directionality of light scattering. The directional conditions for scattered light, first proposed by Kerker et al [69], are analyzed showing the influence of a finite size. Under these conditions for the optical constants, light scattering by a small and spherical scatterer presents a minimum in two main directions: the forward ($\theta = 0°$) and the backward one ($\theta = 180°$). However, we show that similar conditions can also be proposed for other interesting scattering angles. In addition, an important exception to the Kerker's proposal is presented.
- *Chapter 5* ends the first part of this work. We discuss the dependence of the directional conditions on the observation distance. Scattering diagrams from the near to the far-field are shown. We consider dipolar particles, either electric or magnetic, since the evolution of their scattered electromagnetic field is well-known. Although this is an approximation, we justify it by showing that, for small particles, there is no difference between the results obtained with the dipolar approximation and those obtained with rigorous Mie calculations.

2. **Study of the Scattering Properties of Agglomerates of Nanoparticles**

Particles tend naturally to form clusters, arrays or aggregates. In those cases, interactions between neighboring particles can be quite important and eventually change the spatial distribution of light scattering. We have extended our former analysis for one particle to a system of interacting ones. As before, the simplest way to analyze this problem, is to consider particles as dipoles following the work of G.W. Mulholland [105].

- *Chapter 6* summarizes our results for the simplest aggregate of particles, a dimer. In this chapter, we go deeper into the control of the spatial distribution of light scattered by particles with convenient optical constants and the influence of the interactions between neighbors. Both the near-field and the far-field regions are considered. However, the interactions and the multipolar contributions in the near-field oblige us to use a more complete analysis than the dipolar approximation. To attain this objective, a method based on surface integral equations (SIE) developed in the Nanophotonics and Metrology Laboratory of the *EPFL* is used.
- *Chapter 7* presents a design of a left-handed system made out of electric and magnetic interacting nanoparticles located on a lattice. Under the proposed geometrical and optical conditions, we demonstrate that this structure shows minimum backward scattering. A complete analysis about the persistence of this minimum as a function of different geometrical parameters (size, distances, particle positions, etc) is also presented, and hereby finishing this part of the thesis.

3. **Study of Light Scattering by a Nanoparticle Above a Substrate**

   The last part of the thesis only contains one chapter, *Chapter 8*, in which we analyze a more realistic situation than the previous ones. In this case, a metallic cylinder (made of either silver or gold), where a plasmon resonance can be excited, is approached to a flat surface, either dielectric or metallic. The presence of the substrate underneath generates a strong modification of the dipolar distribution of the scattered light with high localization of the electric field in the gap between both structures. As will be shown, the distance between scatterer and substrate, the nature of the last one and the incident wavelength (in resonance or out of resonance) affect the spatial distribution of the scattered field in an important manner.

Finally, we conclude the dissertation with a chapter dedicated to a brief summary of the main conclusions and perspectives for future work.

Although the constrained assumptions made in this thesis and the restrictive models used, the results shown here can be quite useful as a first step to the study and the design of new optical devices. These could be applied to the control of light scattering, either for communication or medical applications.