SEMI-ANALYTIC APPROACH FOR ELECTROMAGNETIC PROBLEMS OF LARGE ARRAYS STRUCTURES

A Dissertation Presented

by

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Abstract

There are limited electromagnetic problems which have closed form analytic solutions. Most of the real-world electromagnetic problems like electromagnetic scattering, electromagnetic radiation, waveguide modeling, etc., are not analytically calculable, because of the multitude of irregular geometries found in actual devices. Numerical computational techniques can be used as alternative method to overcome the inability of deriving closed form solutions of Maxwell's equations under various constitutive relations of media, and boundary conditions. This makes computational electromagnetics important in microwave, RF and photonic areas. Care must be taken into choosing the right method; otherwise the wrong method can either yield incorrect results, or results which take excessively long or demand great computational resources. Moreover, there are important electromagnetic problems for which numerical method solutions are challenging, if not impossible. Large non-periodic array of dipoles and multilayer spheres are examples of those problems. Some of these problems, because of their specific geometries and characteristics, can be modeled accurately and efficiently by applying Discrete Dipole Approximation (DDA), multipole expansion and translation addition theorem. The usual solution approach is to model the electromagnetic fields, or other unknowns, using multipole expansions, truncate appropriately the infinite summations, apply the boundary conditions, and then solve the resulting matrix problem by numerical methods. Because the approach contains both of analytic methods and numerical matrix solvers, it can be considered as a semi-analytic approach.

The first chapter briefly describes the electromagnetic problems and semi-analytic approaches of this thesis. In the second chapter, a large array of molecular aggregates is investigated with the goal of solving the multiscale problem of a large array of molecules to explore its optical behaviors. Quantum electrodynamics helps us in finding the microscopic characteristics of the structure. Building on the theory that the molecules can be modeled by electric dipoles; a semi-analytic and semi-classical approach is developed to solve the electromagnetic problem of large array of dipoles and simulate the optical response of molecular aggregates. In chapter 3, a double negative (DNG) metamaterial structure is designed by unit cells of multilayer (concentric) spheres. The dispersion diagram is analyzed to find the frequency band with negative group velocity and the losses in DNG region. Basically, the combination of a positive permittivity dielectric and a negative permittivity
plasmonic material can control the resonances of unit cells and therefore the effective permittivity of the 3-D structure. It is also discussed how a novel design of multilayer sphere unit cells leads to the DNG performance at the desired frequency band. In chapter 4, analytical solution to the problem of electromagnetic wave scattering by an arbitrary array of non-concentric spheres is derived. A full wave multipole expansion method is applied to express the electromagnetic fields in terms of the electric and magnetic dipole modes and the higher order moments. Vector spherical wave functions are used as the basis functions of the multipole expansions and the translation addition theorem is implemented to expand fields in desired coordinate systems. The accuracy and computational performance of the model are investigated and some interesting applications are discussed.
I would like to dedicate this dissertation to the most beloved people in my life; my father, *Alimohammad*, who showed me determination and hard work are the most crucial assets for success; my mother, *Mahtab*, who taught me to love unconditionally; my elder brother *Habib*, and two elder sisters *Mahboubeh* and *Samaneh*, whom even when we were continents apart, I always felt their presence beside me with their immense support; and last but not least my lovely wife, *Naghmeh*, who was always there cheering me up and stood by me through the good times and bad.
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Chapter 1

Introduction

The problems containing array structures are an important area in electromagnetics. One can divide these problems into two groups. The first group contains inherently continuous structures approximated and modeled by an array of smaller subsections. One interesting example is modeling bacteria and algae (an aggregate of molecules) by a multiscale approach [1]. The other group contains inherently discrete array structures. Array antennas and metamaterial structures are examples of this group. The computation of large array problems is very challenging. This is due to possibility of having a very large array of different materials and the fact that the coupling may be very large. Therefore, we will have a broad-spectrum eigenvalue problem which makes simulation based on numerical methods very challenging, if not impossible. That explains the importance of finding an analytic solution for these kinds of problems. The analytic solvers are usually more accurate much faster than numerical methods. But to make a computer solver based on an analytic model one has to truncate the summations and solve the matrix equations numerically. Because of these computational approximations we name the models explained in following chapters “semi-analytic” models.

In the second chapter, a large array of molecular aggregates is investigated with the goal of solving the multiscale problem of a large array of molecules to explore its optical behaviors. Green sulfur bacteria are a good example of the organisms which survive because of very high efficiency in the light absorption and energy transfer within the photosynthetic systems. The absorption of light is happening by chlorosome; a very large nanostructure array of bacteriochlorophylls (BChls) which functions as a light absorbing antenna. Quantum Mechanical models cannot be used here due to the large size of the full chlorosome antenna complex. Electrodynamic modeling thus provides a viable alternative. A semi-analytic and semi-classical approach has been used to solve the problem. Hierarchical matrix ($H$-matrix) and parametric $H$-matrix [2] methods are applied for the efficient treatment of multi-frequency problem. To demonstrate the efficiency of the parametric $H$-matrix method, the transient responses of these tubular aggregates are obtained via application of fast Fourier transform (FFT) to a wideband collection of frequency domain solutions. Structural
disorder and dynamical noise are considered to make the problem under investigation more realistic.

The other works presented here are based on multilayer spheres and generalizing Mie theory. Core-shell spheres have attracted significant interests in metamaterial and other communities. Basically combination of a positive permittivity dielectric and a negative permittivity plasmonic material can control the resonances of the structure and therefore the effective material permittivity. This means one can use an array of core-shell spheres where, for instance, each has a different core size and as such tailor a desired material property across the array. While the concept is very promising the computation is very challenging. This is due to the having a large finite array of different core-shells of dispersive materials and the fact that they can be located very close to each other. We need to add to these the cases which core-shells have non-concentric (eccentric) geometries either due to the requirement to in physic or fabrication part of the problem. In Chapter 3, the characteristics of electromagnetic waves supported by three dimensional periodic arrays of multilayer spheres are investigated. The spherical particles have the potential to offer electric and magnetic dipole modes, where their novel arrangements engineer the desired metamaterial performance [3]. A full wave spherical modal formulation is applied to express the electromagnetic fields in terms of the electric and magnetic multipole modes. A 3-D metamaterial constructed from unit-cells of multilayer spheres is designed. It is demonstrated such compositions can exhibit negative-slope dispersion diagram metamaterial properties in frequency spectrum of interest. It is also presented that by adding the third layer to the core-shell structure, due to increased degrees of freedom, the metamaterials operation range will be tunable to the desired frequency. In Chapter 4, the analytical solution is derived to the problem of scattering of electromagnetic wave by an array of non-concentric spheres. Full wave multipole expansion method is applied to express the electromagnetic fields in terms of the electric and magnetic dipole modes and the higher order moments. Vector spherical wave functions are used as the basis functions of the multipole expansion and translation addition theorem has been employed to expand fields in desired coordinate systems. This comprehensive analytic method which is numerically precise and computationally fast can be a useful tool in design and simulation of a wide range of applications. Some interesting applications and examples are explained at the end of Chapter 4.
Chapter 2

Electromagnetic Study of the Large-Scale Molecular Aggregates

Introduction

Companies that make commercial solar cells are happy if they can achieve 20 percent efficiency when converting sunlight to electricity and an improvement of even 1 percent is seen as major progress. But nature, which has had billions of years to fine-tune photosynthesis, can do much better. Micro-Organisms called green sulfur bacteria, which live deep in oceans and hot springs, where the density of photons is extremely low, manage to harvest about 98 percent of the energy in the light that reaches them. Green sulfur bacterium is an iconic example of nature’s adaptation. This bacterium ranks itself amongst the most efficient natural light harvesting organisms. The photosynthetic antenna complex of this bacterium is a self-assembled nano-structure, ~ 60×150nm, made of bacteriochlorophyll molecules.

It has been shown that the main structural component of nano-antennas, Bacteriochlorophylls, can be modeled by a single electric dipole [10]. The microscopic characteristics and quantum mechanics lead us to the macroscopic model of each electric dipole. Then the bio-science problem would be modeled by an electromagnetic problem of very large array of electric dipoles. The electromagnetic problem can be formulated based on an analytic approach. Fast and efficient calculations, of for instance optical responses requires computational acceleration and compression techniques. A hierarchical matrix approach is used for this purpose. In order to model large-scale molecular structures these methods should be applied over wide frequency spectra. A parametric hierarchical matrix method is applied that allows one for a rapid construction of a wideband system representation and enables an efficient wideband solution. We show that the parametric method can provide one with the frequency and time-domain solutions for structures of the size of 100,000 molecules, which is comparable to the size of the whole antenna complex in a bacterium.

Three different nanostructures, built from two molecular packing moieties, are considered: a structure built of concentric cylinders of aggregated bacteriochlorophyll-d monomers, a single
cylinder of bacteriochlorophyll-c monomers and a model for the entire chlorosome. The theoretical model captures both coherent and incoherent components of exciton transfer. The model is employed to extract optical spectra, concentration and depolarization of electromagnetic fields within the chlorosome, and fluxes of energy transfer for the structures. Further, field enhancement is found to be more sensitive to dynamic noise rather than structural disorder. Field depolarization however is similar for all structures. This indicates that the directionality of transfer is robust to structural variations while on the other hand, the intensity of transfer can be tuned by structural variations. The absorption spectrum is also calculated and the significance of electrodynamic retardation effects for relatively large structures, i.e. with respect to the wavelength of light, is studied.

**Green Sulfur Bacteria**

The life cycle of plants, photosynthetic bacteria and algae is based on the harvesting of solar energy. In all of these organisms solar light is absorbed and processed by a photosynthetic system. This unit typically consists of an aggregate of light absorbing molecules, e.g. bacteriochlorophylls (BChls). Photosynthetic systems vary in composition and size, for instance, their dimensions can range from tens to hundreds of nanometers with up to $\sim 2 \times 10^5$ pigment molecules. Solar energy is transferred in these systems through molecular excitations known as excitons. Success in nature’s competition for resources is crucial for the survival of phototrophic organisms. Therefore, optimal efficiency of light absorption and energy transfer within the photosynthetic systems are essential characteristics.

Recently, much scientific effort has been devoted to understanding the microscopic principles which govern the efficiency of photosynthetic systems [4]. Amongst these systems, green sulfur bacteria is one of the most widely studied. The photosynthetic system of green sulfur bacteria consists of three main elements (See Figure 2.1, panel I). The first element is the chlorosome: a large nanostructure array of BChl’s which functions as a light absorbing antenna. The second elements are intermediates (these include the base-plate and the Fenna-Matthews-Olson protein complex) which play the role of exciton bridges connecting the chlorosome to the third and last element, the reaction center, where the exciton energy is employed in the synthesis of metabolic compounds.
The chlorosome nanostructure has dimensions of the order of hundreds of nanometers and works exactly like an antenna; it absorbs photons and transmits them to the next subunits very efficiently. A question naturally arises: can energy transfer principles be deduced from the study of these natural systems and applied to the field of nanoantennas? To begin to answer this question we investigate the electromagnetic properties of the chlorosome antenna complex.

The chlorosome antenna complex is composed of up to tens of thousands of BChls (see Figure 2.1) which makes it the largest of the photosynthetic antenna units known. This nanostructure is thought to be the main element responsible for capturing photons at the extremely low photon densities of the bacteria’s environment [5, 6]. Quantum mechanical models, as employed in some of the recent theoretical work on photosynthetic systems [7, 8], cannot be used here, due to the large size of the full chlorosome antenna complex. Electrodynamic modeling thus provides a viable alternative. This approach can capture, within certain approximations, both coherent and incoherent excitation dynamics are employed in the simple case of a molecular dimer [9].

The chlorosome antenna complexes are composed of different types of BChls, namely BChl-c, BChl-d or BChl-e, with varying chemical composition according to the species in question. Because of the large amount of disorder present in the natural system, the definitive structure for the complex is unknown. However, several models have been proposed [10, 11]. Recently, Ganapathy et al. [10], determined the structure of a synthetic triple mutant chlorosome antennae, generated to mimic natural chlorosomes. This mutant structure replicated various structural signatures of the natural chlorosome while, however, being less efficient in terms of growth rates at different light intensities respect to the wild type chlorosome. Other experimental efforts have been made in this direction using a combination of Nuclear Magnetic Resonance (NMR) and X-Ray diffraction [12-14]. The structure determined by Ganapathy et al. will be considered in this work and their experimental findings inspire the remaining two structures. The first structure comprises a series of concentric cylinders of aggregated BChl-d molecules (Figure 2.1 II-a and III-a). We will consider both the cases of a single cylinder and of two concentric cylinders in this work. The second system is a similar cylindrical array, built of BChl-c molecules rather than BChl-d (See Figure2.1 III-b). This structure is obtained following the findings of Ganapathy et al. [10]. Finally we will consider a model for the entire chlorosome (panel III-c)) consisting of over 70000 BChl-c. More detail on these three structures can be found in the Methods section.
In this chapter, we first describe the physical model of the chlorosome structure. Then we review the derivation of a semi-analytic approach, Discrete Dipole Approximation (DDA). Then a quick introduction to hierarchical matrices is presented and the parametric $H$-matrix representation intended for the efficient treatment of multi-frequency DDA problems. We discuss errors that appear in parametric $H$-matrix representation. The developed method has been used to model optical response of BChl tubular aggregates. The role of different initial excitations, i.e. frequency and polarization of the incoming field, are investigated. The field enhancement and field depolarization as a function of structural disorder and dynamical noise are studied. Fluxes of energy transferred in time to acceptors located around the antenna nanostructures are also determined.

**Physical Model of the Chlorosome Structure**
It is understood that the chlorosome is composed of multiple rolls and curved lamella structures. In this section, we describe the structures employed as models of the chlorosome in more detail. In both of the molecular packing motifs employed to construct the chlorosome structures, BChl molecules are stacked in columns such that the oxygen from the hydroxyl, OH, group of one molecule, see Figure 2.1 panel II-b), binds to the Mg atom of the next molecule [15]. The columns of BChl molecules couple to each other through OH…O hydrogen bonds thus forming two dimensional layers (this is shown in Figure 2.2). These layers are then folded to form cylinders or curved lamellar structures [16].

![Figure 2.2: Two columns of BChl molecules linked together through a network of hydrogen bonds.](image)

Two distinct types of layer folding have been proposed previously. In Ref.10 the authors suggested that BChl layers are folded such that BChl columns form concentric rings. This structure was obtained by fitting the 2D nuclear magnetic resonance (NMR) spectra of mutant Chlorobium tepidum bacteria which produce chlorosomes with BChl-d molecules. This packing motif was also supported by cryo-electron microscopy images [14]. The first structure we consider (III-a in Figure 2.1) comes from these studies. In contrast, in Ref. 15 a different folding pattern has been used, where BChl columns are parallel to the cylinder’s symmetry axis. The latter structure was also supported by 2D NMR studies of different mutant bacteria, which is more similar to wild-type species (the chlorosome was packed with BChl-c). We used this second type of folding to obtain the second structure, i.e. III-b in Figure 2.1. Finally, the layer structures are packed inside of an ellipsoidal shaped body: the chlorosome. While the chlorosome may contain multiple rolls packed in parallel [17], here we use a different model (structure III-c in Figure 2.1) which is composed of concentric rolls [16]. This concentric assembly is in-line with the cryo-EM images [14].

**Quantum Mechanical Modeling**
Measurements on the quantum mechanical energy states show that the lowest electronic excitation in single BChl, $Q_y$ band, is about 1.904 eV (or 460THz) for Bchl-d and 1.881 eV (or 455THz) for Bchl-c. The $Q_y$ band is separated sufficiently from the next transition, $Q_x$ band. Thus, in our modeling only the lowest electronic excitation is considered. In quantum models, a Hamiltonian in the molecule localized basis $|n\rangle$ is often used to describe this type of system

$$\hat{H}_0 = \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} J_{nm} (|n\rangle\langle m| + |m\rangle\langle n|)$$

(2.1)

The energy $\varepsilon_n$ of the $n^{th}$ monomer is typically taken to be the first excited state energy, and as explained, all higher excited states are ignored. $J_{nm}$ indicates the coupling between monomers and $|n\rangle$ is the localized basis in which the $n^{th}$ molecule is excited. When the molecules interact with radiation, an extra interaction term with the field must be added to this expression $V_{\text{field}}$, so that the overall Hamiltonian can be divided into a time independent Hamiltonian $\hat{H}_0$ and a time dependent interaction term $V_{\text{field}}$ ($\hat{H}(t) = \hat{H}_0 + V_{\text{field}}(t)$). One can then write an equation of motion for the system density matrix as a function of the Hamiltonian and solve it perturbatively in orders of interaction with the field. Then, the optical properties can be obtained from the density matrix equation (see optical properties section).

Quantum mechanical models cannot be used here due to the large size of the full chlorosome antenna complex. Electrodynamic modeling thus provides a viable alternative. This approach can capture, within certain approximations, both coherent and incoherent excitation dynamics and has already been described and employed in the simple case of a molecular dimer.

Here we use a multi-scale approach. The microscopic characteristics of main structure components (BChls) are measured and modeled in quantum mechanical parameters. The quantum mechanical properties of the monomers can then be lumped into macroscopic model. The inter- and intra-molecular vibrations, interaction with the solvent, and other environmental fluctuations, generate a source of noise which needs to be taken into account when modeling the system. Generally speaking, we can distinguish between static/structural disorder and dynamic noise based on the time scales of the associated fluctuations. Fluctuations related to structural disorder oscillate on a much longer timescale compared to the dynamics of the system whereas dynamical noise...
fluctuations are more rapid. The noise source is the same for both types of disorder. In this model, one can include noise by introducing a molecular response function,

\[
\langle \chi(\omega) \rangle = \frac{1}{\varepsilon_0 \hbar} \sum_k \frac{2\omega_k}{(\omega + \omega_k + j \frac{\gamma_k}{2})(\omega - \omega_k + j \frac{\gamma_k}{2})} \hat{u}_k \hat{u}_k^* \tag{2.2}
\]

where the sum over \( k \) runs over all excited states of the monomer, \( \omega_k \) is the transition frequency, \( \gamma_k \) is the radiative decay rate, \( \rho_{0,k} \) is the transition dipole moment and \( \hat{u}_k \) is a unit direction vector associated with the transition dipole moment between the ground state and that of the \( k^{th} \) state. The \( \omega_k \) and \( \gamma_k \) are considered to model the monomer as it is in its surrounding environment. The molecules are considered identical. This complex response function is nothing but the response of the monomer to a delta function electric field excitations in the time domain. In equation (2.2), the \( \omega_k \) in the denominator is associated with the monomers' transition energy between the ground and \( k^{th} \) state while \( \gamma_k \) is the so-called dephasing time. The dynamical noise is accounted for by the rate constant, \( \gamma_k \), and structural disorder can be included by introducing noise in the transition frequencies, \( \omega_k \). Usually, \( \omega_k \), is taken from a Gaussian distribution, and structural disorder is characterized by the width of the Gaussian, \( \sigma \). We will only consider the transition between the ground state and the first excited state of each monomer. The dipole moment unit vector \( \hat{u}_i \) coincides with the physical orientation of the dipole \( \hat{s} \) or \( \hat{s}_m \) where \( m \) labels the \( m^{th} \) monomer in the problem. The overall disorder in the localized site basis should be of the same order of magnitude. In this case the linewidth is \( \approx 70 \) meV both for the BChl-c monomeric spectrum and for the Chlorosome spectrum [21].

Now that we could model each monomer with an electric dipole, and the parameters of each dipole are coming from experiments and quantum mechanical modeling, the problem of absorption and transmission of light energy in chlorosome nanostructure is converted to the electromagnetic problem of a large array of small electric dipoles.

According to the model in [18], BChl pigment molecules are arranged in concentric rings and then stacks of these rings form a roll. The molecular transition dipoles are almost orthogonal to the radius and form 35 degrees angle with the plane of the ring. To model the chlorosome response four concentric rolls A, B, C and D with \( N_{A-D} = 60, 80, 100, 120 \) number of molecules per ring.
(Figure 2.3), and $n=36$ rings were constructed and their structure was compared to the structures provided to us by the authors of reference [18]. The molecular structure depicted in Figure 2.1 (panel II-1) corresponds to the innermost roll A. For transient response calculations, we selected six points (and monomers) $a-f$ coinciding some of the monomers in the four-roll structure. Points $a, c (d, f)$ are located on the edges of the inner (outer) rolls, and points $b$ and $e$ belong to the central rings of the same rolls, as shown in Figure 2.3. Clearly, the line shifts associated with the retardation cannot be observed at ambient conditions, where the resonance lines are broadened by about 50meV due to the structural disorder and thermal effects. However, the role of disorder in the intensity redistribution cannot be easily analyzed and should be studied in more detail.

![Figure 2.3: Four-layer chlorosome roll and the location of observation monomers. The letters a, b, c, d, e and f indicate the six monomers used for the observation of the time evolution of their polarization amplitude as depicted in Figure 2.15. The capital letters A, B, C and D correspond to the four layers.](image)

**Semi-classical DDA**

In this work, arbitrary vectors in $\mathbb{R}^3$ are explicitly denoted by the $\vec{\cdot}$ sign and unit vectors in $\mathbb{R}^3$ are denoted by the $\hat{\cdot}$ sign. Moreover, the length of an arbitrary vector $\vec{r}$ is denoted by $r$, dropping the vector sign $\vec{\cdot}$. Also, 3-D tensors, i.e. linear transformations $\mathbb{R}^3 \rightarrow \mathbb{R}^3$, are denoted by the $\overrightarrow{\cdot}$ sign. It is also worth mentioning here that, in the whole of this dissertation, harmonic time dependence $\exp(+j\omega t)$ is assumed. According to Maxwell's equations the electric field at position $\vec{r}$ can be written as
\[ \vec{E}(\vec{r}) = -\eta_0 \Xi_v(\vec{J}^s + \vec{J}^p) \] (2.3)

where \( \eta_0 = \sqrt{\mu_0/\varepsilon_0} \) is the free-space impedance, \( \mu_0 \) and \( \varepsilon_0 \) respectively denote the free-space electrical permittivity and magnetic permeability, \( \vec{J}^s \) represents the independent current density, \( \vec{J}^p \) is the induced current density, and the volumetric electrical field integral operator is [19]

\[ \Xi_v(\vec{J}) = \left\{ -j k_0 \int_{V_J} \vec{G}_e(\vec{r}, \vec{r}') \vec{J}(\vec{r}') dV' + \frac{j}{k_0} \vec{L} \cdot \vec{J}(\vec{r}) \right\} \] (2.4)

In equation (2.4), \( k_0 = \omega \sqrt{\varepsilon_0 \mu_0} \) is the free-space propagation constant and, \( \vec{r} \) and \( \vec{r}' \) are vectors indicating the observation and source points respectively. Moreover, \( V_J \) denotes the volume in which the current is nonzero while \( V_\delta \) is an infinitesimal volume enclosing the observation point. \( \vec{G}_e(\vec{r}, \vec{r}') \) is the generalized dyadic Green's function. The tensor \( \vec{L} \) accounts for the effect of the current that resides at the observation point. As explained in Yanghjian's article [19], \( \vec{L} \) is obtained in the limit where volume approaches zero. In all equations we use \( j \) for imaginary numbers. In the infinitesimal dipole model, polarization sources can be represented by Dirac delta distributions. When observing the field at a point away from the source, the electrical field can be easily obtained using the electrical field representation formula for nonsingular cases

\[ \Xi_v(\vec{J}) = j k_0 \int_{\Omega} \vec{J}(\vec{r}') g(\vec{R}) d\nu' + j \frac{1}{k} \nabla \int_{\Omega} \nabla' \vec{J}(\vec{r}') g(\vec{R}) d\nu' \]

\[ -j \frac{1}{k_0} \nabla \int_{\Omega} \vec{J}(\vec{r}') g(\vec{R}) \vec{n}' d\nu' \] (2.5)

where \( \vec{R} = |\vec{r} - \vec{r}'| \). On the contrary, special care must be practiced when observing the field at points coinciding with the sources. From Yanghjian's derivation [19] the electric field at all points including those coinciding with the location of source currents is obtained via the field operator \( \Xi_v \) of equation (2.4). In Yanghjian's derivation [19], finite current densities are assumed. However, a critical difference here is that Dirac delta distributions must be substituted into the derivation. In order to achieve this effect, one may assume \( V_\delta \) with a uniform current density that is proportional to the inverse of the volume while the limit of the volume is approaching zero. In equation (2.4), the first term on right hand side is a nonsingular integral involving the conventional dyadic \( \vec{G}_e \).
outside the singularity region and the second term is the source dyadic $\bar{L}$ which is determined solely from the geometry of the principal volume chosen to exclude the singularity of $\bar{G}_e$. In our case, the principal volume $V_\delta$ will be described as a circular cylinder in which both the radius and volume go to zero. Therefore, the first term in right hand side of equation (2.4) is zero. On the other hand, it is assumed that $\int_{V_\delta} \bar{J}^r(\bar{r}')dV'$ remains constant while the dimensions of the principal volume $V_\delta$ approach zero. This is equivalent to the assumption of a Dirac delta distribution $\hat{J}^r = J^r \hat{s} \delta(\bar{r})$. Under this assumption it is clear that a finite source dyadic $\bar{L}$ will not be obtained as in the case of Yanghjian's assumption [19]. Now, according to [19], the source dyadic of this principal volume is $\bar{L} = \frac{1}{2} \bar{I}_r$ and only has components orthogonal to the axis of the cylinder. However, despite the infinite value of the field at the source, the orientation of the field will not be changed compared to that of Yanghjian's derivation. Thus, if this field is tested by a vector quantity that is oriented along the axis of the cylindrical dipole, the second term in equation (2.4) will vanish. Hence, in the final discretized (matrix) equation which is due to the testing (collocation) of the field at the location of individual dipoles, the effect of the self term, i.e. the term due to testing of a dipole's field at the dipole itself, will not be present. On the other hand, recall from [20] that for a dipole source $\int J dV = j_0 \hat{p}$ which implies $\bar{J} = j_0 \hat{p} \delta(r)$ for an infinitesimal dipole. Thus, using equation (2.5), the electric field due to a dipole located at points other than the dipole itself is

$$\bar{E}^p(\bar{r}) = \frac{p}{4\pi \varepsilon_0} \left( \frac{1+jkr}{r^2} \left( 3 \hat{r} \hat{s} - \hat{s} \right) - k^2 \hat{s} \times \left( \hat{r} \times \hat{s} \right) \right) g(r)$$

(2.6)

where $p$ is the complex valued polarization intensity, $\hat{s}$ is a unit vector denoting the orientation of the dipole and $g(r) = e^{-jkr}/r$ is the scalar free-space Green's function.

Now, consider a group of dipoles where the electric field of each dipole can be expressed as equation (2.6). Considering a linear regime, the resulting polarization $\bar{p}$ is equal to

$$\bar{p}(\omega) = \varepsilon_0 \bar{Z}(\omega) \bar{E}(\omega)$$

(2.7)
where \( \vec{E} \) is the total electric field on a dipole embedded in a medium of dielectric constant \( \varepsilon_0 \) and \( \vec{p} \) is the polarization of the dipole. Thus, splitting the total electric field into internal (due to dipoles themselves) and incident field components, for the \( m \)th dipole one writes

\[
\vec{p}_m = \varepsilon_0 \bar{\varepsilon}_m \vec{E}^{inc}(r') \bigg|_{r' = r_m} + \varepsilon_0 \bar{\varepsilon}_m \sum_{n=1}^{N} \frac{p_n}{4\pi\varepsilon_0} 
(1 + jkr_{nm}) \left( \hat{r}_{nm} (\hat{r}_{nm} \hat{s}_n) - \hat{s}_n \right) / r_{nm}^2 - k^2 \hat{r}_{nm} \times \left( \hat{r}_{nm} \times \hat{s}_n \right) \bigg) g(r_{nm}) \tag{2.8}
\]

where \( \hat{r}_m \) is the location of the \( m \)th dipole, \( r_{mn} = |\vec{r}_n - \vec{r}_m| \) is the Euclidean distance between the \( m \)th and the \( n \)th dipole, and \( \hat{s}_m \) is the unit vector denoting the orientation of the \( m \)th dipole. Moreover, one observes that the term involving \( r_{nm} \) in equation (2.8) will be infinite. However as discussed earlier, by choosing a vector testing function that is oriented along the \( \hat{s}_m \), the effect of dipole electric field on itself will be dropped from the equation. Here, a testing function of the form \( \vec{E}_t = \delta(\vec{r} - \vec{r}_m)\hat{s}_m \) is used as an electric field testing function where \( \delta(\vec{r}) \) is a 3-D Dirac delta function satisfying

\[
\int_{\Omega} f(\vec{r})\delta(\vec{r} - \vec{r}_0)dV = \begin{cases} f(\vec{r}_0) & \vec{r}_0 \in \Omega \\ 0 & \text{otherwise} \end{cases} \tag{2.9}
\]

Testing, the inner product of, both sides of equation (2.8) by \( \vec{E}_t \) and integrating over the volume, one obtains the final discrete equation:

\[
p_m = \varepsilon_0 \hat{s}_m \bar{\varepsilon}_m \vec{E}^{inc}(r) \bigg|_{r = r_m} + \varepsilon_0 \hat{s}_m \bar{\varepsilon}_m \sum_{n=1, n\neq m}^{N} \frac{p_n}{4\pi\varepsilon_0} 
(1 + jkr_{nm}) \left( \hat{r}_{nm} (\hat{r}_{nm} \hat{s}_n) - \hat{s}_n \right) / r_{nm}^2 - k^2 \hat{r}_{nm} \times \left( \hat{r}_{nm} \times \hat{s}_n \right) \bigg) g(r_{nm}) \tag{2.10}
\]

Equation (2.10) can be written in matrix form \( Z_{N\times N} P_{N \times 1} = E_{N \times 1} \) with the unknown vector \( P = [p_1, p_2, \ldots, p_N]^T \), where \( p_i \) are the complex values of the polarization of the individual dipoles located at \( r_1, r_2, \ldots, r_N \).

\[
Z = [Z_{mn}], Z_{mn} = \begin{cases} 1 & \text{if } m = n \\ Q_{mn} & \text{otherwise} \end{cases} \tag{2.11}
\]
\[ Q_{mn} = -\frac{\varepsilon_0}{4\pi\varepsilon_0} \frac{\hat{s}_m \cdot \vec{E}_m}{g(r_{nm})} \]
\[ \left( 1 + jkr_{nm} \right) \left( 3\hat{r}_{nm} \left( \hat{r}_{nm} \cdot \hat{s}_n \right) - \hat{s}_n \right) - \frac{k^2}{r_{nm}^2} \hat{r}_{nm} \times \left( \hat{r}_{nm} \times \hat{s}_n \right) \]  

\[ (2.12) \]

**Optical properties**

**Linear Absorption**

Using the semi-classical method, an equation for the induced electric dipole \( \vec{p} \) on each monomer can be obtained. In the limit of the dipole approximation, the expression for the molar extinction coefficient is then \([21, 22]\):

\[ \varepsilon_{abs} = -\frac{4\pi\omega}{3000. \log_{10} c} \Lambda_{av} \sum_j \text{Im} A_{ij} \hat{u}_i \hat{u}_j \]  

(2.13)

where \( \hat{u}_i = \frac{\hat{\rho}_i}{|\hat{\rho}_i|} \) is the unit vector corresponding to the direction of the first transition dipole moment of the \( i \)-th monomer. Here the matrix \( A \) is defined as

\[ A_{ij} = \left[ \delta_{ij} + D_{ij} \right]^{-1} \]  

(2.14)

with \( D_{ij} = \hat{u}_i \cdot G_{ij} \cdot \hat{u}_j \), the term which includes dipole-dipole interactions and \( \chi_i \) the molecular response function of \( i \)-th molecule as defined in equation (2.2). In the limit of static dipole interactions, the tensor \( G \) takes the simple form \( G_{ij} = G(\bar{x}_i, \bar{x}_j) = (3\varepsilon\varepsilon_0-1)/r^3 \). To better understand where resonances occur, we can look at the eigenvalues of \( A \). For zero dynamical noise rate \( \Gamma \) and for identical molecules \( (\rho_k = \rho_0, \omega_k = \omega_{mol}) \) we see that resonances are obtained at

\[ \Omega_{agg,k}^2 = \omega_{mol}^2 + 2\frac{|\rho_0|^2}{\hbar} \gamma_k \omega_{mol} \]  

(2.15)
Here, γ_k is the kth eigenvalue of G. We can define \( \frac{1}{\hbar} \gamma_k \equiv \tilde{\gamma}_k \) to get proper units of energy for the coupling. Thus \( \Omega_{agg,k}^2 \equiv \omega_{mol}^2 + 2 \tilde{\gamma}_k \omega_{mol} \). In this expression it is clear that the shift respect to the molecular transition frequency \( \omega_{mol} \) depends on the coupling between monomers. Now, in the quantum case, the simplest approach to obtain the absorption spectrum consists in applying Fermi’s Golden rule:

\[
\varepsilon^{(qv)}_{abs}(\omega) = \frac{4\pi\alpha}{3c} \sum_k |\rho_0|^2 \pi\delta(E_k - \hbar\omega)
\]

with transition frequencies \( \Omega_{agg,k}^2 = E_k^2 / \hbar^2 = (\omega_{mol} + \tilde{\gamma}_k)^2 \). We see that respect to the semi-classical case (equation 2.15), the frequencies are shifted by \( \tilde{\gamma}_k \); this comes from the absence of counter rotating terms in the classical response function [22].

**Circular Dichroism**

Circular Dichroism (CD) is another important optical quantity which can help identify the correct structure of a system. It can also be obtained both classically and quantum mechanically. Following the classical method of the previous section and the approach in [23] one can arrive at the following expression for the molar ellipticity

\[
\theta = -\sum_y C_{ij} \text{Im} A_{ij}
\]

(2.17)

Here we have used the standard definition of CD, as the difference between left polarized and right polarized intensity. The matrix C is defined as

\[
C_{ij} = \frac{6\omega^2\lambda_{av}}{c^2} \left( \hat{u}_i \times \hat{u}_j \right) \cdot (\vec{r}_i - \vec{r}_j)
\]

(2.18)

in the absence of any magnetic dipoles or polarizations. Here, \( \vec{r}_i \) corresponds to the position of the i\(^{th}\) molecule with respect to the origin. Similarly, in the quantum case one finds (see e.g. Ref. [24]) that in the exciton basis, i.e. the basis in which the Hamiltonian of equation (2.1) is diagonal, the rotation strength associated with the exciton level \( J \) is
\[ R_j = -\frac{6\omega^2 \Lambda_{av}}{c^2} \sum_{ik} \sigma_i \sigma_k \left( \hat{u}_i \times \hat{u}_j \right) \left( \vec{r}_i - \vec{r}_j \right) \] (2.19)

The coefficients \( \sigma \) are the coefficients of the matrix \( S \) which diagonalizes the Hamiltonian of the system.

**Hierarchical Matrices**

Hierarchical matrices (\( H \)-matrix) were originally applied to reduce the computational complexity associated with the discretization of elliptic differential equations [25, 26]. It has been shown that for matrices resulting from the discretization of elliptic partial differential equations the \( H \)-matrix method leads to the almost linear complexity of \( O(N \log(N)) \) [25-27] which is clearly advantageous over the \( O(N^2) \) complexity arising from the direct storage of the matrices. Although, the favorable properties of the \( H \)-matrix method will be lost if it is applied to non-elliptic operators, the method still provides very desirable performance in the so-called low frequency regime, i.e. when dimensions of the physical problem are smaller or comparable to the wavelength [28]. Owing to their submicron dimensions, many molecular aggregates give rise to problems that exactly fit in to the low-frequency category.

The details of the \( H \)-matrix method can be found in [25-29] and will not be discussed here. Here it suffices to mention that in the \( H \)-matrix method, matrices are hierarchically reordered and segmented into blocks that are classified into near-field and far-field interaction blocks. The resulting near-field interaction blocks are stored as regular dense matrices while the far-field interaction blocks are stored via low rank representation. In other words, a far-field interaction block \( M_{mn} \) is decomposed into a truncated SVD-like decomposition \( M \approx U \Sigma V^t \) in which singular values below a certain accuracy threshold are discarded. In practice, the low rank representation consists of a left factor \( A_{mk} \) and a right factor \( B_{kn} \) satisfying \( M \approx AB^t \). It is worth mentioning that \( k<< \frac{m}{\sqrt{n}} \) and it guarantees that storage and other operations such as matrix-vector multiplication operations can be handled with a significantly reduced cost compared to that of regular dense matrix representation [25].

The time domain solution of the problem can be obtained by applying FFT to a large collection of frequency dependent solutions. Considering that a small number of \textit{Krylov} iterations are needed
for the problem solution at each frequency, most of the computational cost will be associated with
the construction of the $H$-matrices. Hence, one may naturally think of interpolating the majority of
these frequency dependent $H$-matrices from a limited set generated at a selected frequencies. Note
that here the term ‘interpolation’ is used in its loose sense and shall imply the meaning of any
curve fitting or parameterization technique. In the following section, an efficient parameterization
method for $H$-matrices is proposed that has been applied to the matrix equation of the DDA
approach explained in previous sections.

**Parametric $H$-Matrix Representation**

Let us consider a block of the system matrix $Z_{m \times n}$. We intend to build a frequency dependent
coloration of the complete system matrix. The characteristic to our problem of interest, $Z(f)$,
is a smooth and infinitely differentiable function, except near the frequency points in the vicinity
of the quantum mechanical resonances of individual monomers as discussed before. Due to the
presence of such singularities (poles) in the frequency representation of individual matrix entries,
polynomial interpolation or polynomial least squares curve fitting methods are not applicable.
Nonetheless, a rational function representation can effectively represent the individual matrix
entries. Such a rational function representation can be obtained using the vector fitting method [30,
31]. Thus, if the system matrix is represented in a dense form, the entries can be fitted to rational
functions by means of the abovementioned method. Nevertheless, for large systems the
computational complexity of the dense matrix representation is prohibitive.

Alternatively, in the $H$-matrix representation, two types of blocks are present: (1) dense blocks
in the form of $M$ used for near interactions (2) low rank (compressed) blocks $M = AB^t$. The dense
blocks can be fitted directly into a rational function of frequency using the vector fitting method.
On the other hand, for the low rank blocks, the frequency parameterization cannot be directly
applied to the $A$ and $B^t$ factors. In other words, direct interpolation/parameterization of $A(f)$ and
$B(f)$ for the low rank blocks would result in undesirable results since the smoothness of $A(f)$ and
$B(f)$ is not guaranteed, although the product $M = AB^t$ is known to be sufficiently smooth. This is
because the matrices $A(f)$ and $B(f)$ are not unique, i.e. if $M = AB^t$, so will $M = (AC)(C^{-1}B^t)$ for any
$C \in \mathbb{C}^{k \times k}$, $\det C \neq 0$, $C^t = C^{-1}$. Furthermore, redundancies may exist between the members of the
sets \( \{A_1, A_2, \ldots, A_{n_f}\} \) and \( \{B_1, B_2, \ldots, B_{n_f}\} \) that respectively represent the range and the domain spaces of the frequency dependent matrix \( M \) at a selection of frequencies \( \{f_1, f_2, \ldots, f_{n_f}\} \).

Suppose \( n_f \) sampling frequencies are given as the key data points for the intended parameterization and thus the low rank representation of \( M \) using \( \{A_1, A_2, \ldots, A_{n_f}\} \) and \( \{B_1, B_2, \ldots, B_{n_f}\} \) is given. As one moves from \( f_p \) to \( f_q \), the range space of the operator \( M \) changes from \( A_p \) to \( A_q \). However, due to the finite dimension and the smooth frequency dependence of operator \( M \), it is expected that the range spaces of \( \{A_1, A_2, \ldots, A_{n_f}\} \) share common information. In order to extract the potentially existing redundancies in the set \( \{A_1, A_2, \ldots, A_{n_f}\} \), the SVD can be applied as

\[
\{A_{i,(m \times k_i)}\} \rightarrow [A_1, \ldots, A_n]_{(m \times \Sigma k_i)} = U_{L,(m \times m)} \Sigma_L V_{L,(\Sigma k_i \times k_i)}^t
\]

where \( \{A_{i,(m \times k_i)}\} \) is a set of range-space matrices and the subscript \( L \) denotes its association with left factor \( A \) in the original decomposition of \( M \). With a desired level of accuracy, the above SVD can be truncated and written as

\[
[A_1, \ldots, A_n] \approx \tilde{U}^{L,(m \times k_i)}_{L,(k_i \times \Sigma k_i)} \tilde{V}^t_{L,(\Sigma k_i \times k_i)}
\]

(2.20)

Under the same truncation tolerance, each of the \( A_i \) matrices can be decomposed as

\[
A_{i,(m \times k_i)} = \tilde{U}^{L,(m \times k_i)}_{L,(k_i \times k_i)} \tilde{V}^t_{L,(k_i \times \Sigma k_i)}
\]

where \( V_{L,i} \) represents the portion of row vectors in \( \tilde{V}_L \) that corresponds to the construction of \( A_i \). Applying a similar procedure to the right side factor, \( \{B\}_i \), we get

\[
\begin{bmatrix}
B_1^t \\
\vdots \\
B_{n_f}^t
\end{bmatrix} \approx \tilde{U}^{R,(\Sigma k_i \times k_i)}_{R,(k_i \times \Sigma k_i)} \tilde{V}^t_{R,(\Sigma k_i \times \Sigma k_i)}
\]

(2.21)

Again, each \( B_i \) matrix is written as \( B_{i,(k_i \times k_i)} \approx \tilde{U}^{R,(k_i \times k_i)}_{R,(k_i \times \Sigma k_i)} \tilde{V}^t_{R,(k_i \times \Sigma k_i)} \), where \( \tilde{U}_{R,i} \) represents the collection of row vectors in \( \tilde{U}_R \) corresponding to the construction of \( B_i \). Now, one can state that

\[
M_i \approx \tilde{U}^{L}_{L,i} \tilde{T}^t_{R,i} \tilde{V}^t_{R,i}
\]

(2.22)

where

\[
\tilde{T}_{i,(k_i \times k_i)} = \tilde{V}^t_{L,i,(k_i \times k_i)} \tilde{U}^{R}_{R,i,(k_i \times k_i)}
\]

(2.23)
is the only frequency dependent part in the low rank representation of the block $M_i$. The $\tilde{T}_i$ matrix: 
(1) is unique for each frequency, and (2) it has smaller dimensions compared to the matrices $M_i$, $A_i$ and $B_i$, thus, lending itself to more efficient computational operations.

**Error Control**

Errors in the parametric hierarchical matrix representation can be divided into two main categories: (a) truncation errors and (b) parameterization errors, where the former are associated with the low rank representations used in the $H$-matrix and the latter correspond to the parameterization (interpolation or curve fitting) procedure. There are no truncation errors for dense blocks. Thus, only parameterization errors should be minimized. For low rank blocks, however, some care must be taken to properly control both parameterization and truncation error while imposing minimal computational costs. For this purpose, let us consider the following parametric representation of a low rank block $M(f)$

$$M(f) = U_L\Sigma_L T(f)\Sigma_R V_R^t$$  \hspace{1cm} (2.25)

where we assume that no SVD truncation has been applied to the left and right factors $U_L\Sigma_L$ and $\Sigma_R V_R^t$. In order to model the truncation error, assume that $\Delta\Sigma_L$ and $\Delta\Sigma_R$ represent the part of the singular value spectrum that is eventually removed due to the low rank representation. Also, let's assume that a $\Delta T$ error is introduced to the matrix $T$ due to the parameterization. Then, the parameterized low rank representation is

$$\tilde{M} = U_L (\Sigma_L - \Delta\Sigma_L) (T + \Delta T) (\Sigma_R - \Delta\Sigma_R) V_R^t$$  \hspace{1cm} (2.26)

Assuming that all three sources of error, i.e. $\Delta\Sigma_L$, $\Delta\Sigma_R$ and $\Delta T$ are small relative to their central values, and applying the *Frobenius* norm as an error measure we can write

$$\|e\|_F \approx \|\Delta\Sigma_L T\Sigma_R - \Sigma_L T\Delta\Sigma_R + \Sigma_L \Delta T \Sigma_R\|_F$$  \hspace{1cm} (2.27)

In equation (2.27) only terms linear in the error, i.e. lowest order perturbations, are included and the unitary matrices, $U$ and $V^t$ are discarded due to the invariance of the *Frobenius* norm upon a unitary transformation. The upper bound for the error, equation (2.27), can be derived using the triangle inequality.
\[
\left\| -\Delta \Sigma_L T \Sigma_R - \Sigma_L T \Delta \Sigma_R + \Sigma_L \Delta T \Sigma_R \right\|_F \leq \\
\left\| \Delta \Sigma_L T \Sigma_R \right\|_F + \left\| \Sigma_L T \Delta \Sigma_R \right\|_F + \left\| \Sigma_L \Delta T \Sigma_R \right\|_F \tag{2.28}
\]

The three terms in the above expression indicate that there are three sources of error, two related to the truncation of the left and the right factors and one coming from the error caused by parametrization of matrix entries. The truncation error contributions can be controlled through proper truncation of singular values in the left and right factors, pretty much as it is done for the low rank blocks in non-parametric hierarchical matrices. This bound serves as a convenient measure of the accuracy of the parametric \( H \)-matrix blocks and can be used for assessment of the success of the parametrization.

Moreover, the \( \Sigma_L \Delta T \Sigma_R \) directly reflects how the error due to the parameterization procedure is manipulated by the left and right factors, i.e. \( \Sigma_L \) and \( \Sigma_R \). The immediate consequence, however, is that not all entries in \( T \) need to have the same level parameterization error as these entries are scaled by the singular values in \( \Sigma_L \) and \( \Sigma_R \). Therefore, in order to control the parameterization error in \( T \), one needs not to directly control the error in the individual entries \( T_{ij} \), but rather that of \( \Sigma_{L,ii} \) \( T_{ij} \) \( \Sigma_{R,jj} \). In other words, the error introduced due to the parameterization of the \( T_{ij} \) entries with higher values of \( i \) and \( j \) is less important as it will be multiplied by smaller singular values. In practice, this balances out with the more significant error level that is observed in the parameterization error induced \( T_{ij} \) entries with higher values of \( i \) and \( j \). In this light, the individual entries of the \( T \) matrix can be observed as the modal functions from which the matrix block \( M \) is constructed as a function of frequency. Intuitively, one observes that the modal functions with higher indices have more complicated behavior and thus are more difficult to parameterize.

We apply the discussed parametric \( H \)-matrix to the matrix equation of semi-analytic DDA approach to numerically solve and model the optical responses of BChl roll aggregates, contained in the chlorosome antenna complex of green photosynthetic bacteria [32]. All results presented in this work are obtained using a C++ code compiled with the GNU C++ version 4.6.3 compiler on a Linux based dual 6-core Intel Xeon 5649 workstation although the multi-core features of the machine were not used in our implementation. All reported timings are based on single-thread runs without parallelization.
Antenna Spectra and Resonances

The chlorosome antennae absorb incoming light in the visible range. The resulting spectrum shows resonances determined by the presence of molecular transitions at about 750nm. The chlorosome aggregate resonances are shifted respect to the pigment transitions due to the couplings between monomers. In order to understand which regions are of interest for energy transfer, we calculated the absorption and circular dichroism spectra of the structures. Due to the three-dimensional arrangement of the dipoles in a cylindrical structure, we expect there to be two components in the absorption spectra, a $z$-polarization component, parallel to the main axis of the cylinder, and an in-plane $xy$ component, orthogonal to the main axis. Panel (a) of Figure 2.4 shows the computed absorption spectra for the roll structure III-a) of Figure 2.1. The spectra were obtained using both the explained semi-classical approach and the Fermi-Golden rule quantum approach. The spectra were broadened by adding disorder through the rate $\Gamma = 1$ meV. As remarked previously in the literature (see e.g. Ref.14) the quantum and classical spectra are simply shifted. More importantly, in both approaches we see the expected $z$ and $xy$, components at about $\Delta\omega_z = -280$ meV and $\Delta\omega_{xy} = [-260;-230]$ meV for the classical spectrum. Higher oscillator strength is observed for the $z$ component. The range over which transitions are observed is consistent with experiments [33] though a direct comparison of the components is not possible due to the large amount of noise present in the natural system. The CD spectra in panel (b) also follows the same trend as the experimentally observed CD [16, 33]. The alternating negative and positive peaks in the CD spectra are related to the orientation of the incoming field respect to the helicity of the structure. These spectra were also calculated for structure III-b) of Figure 2.1 and these follow a similar pattern.
As the next step, we compared the resonance spectra of roll D in Figure 2.3 simulated using the hybrid quantum-classical formulation with that of the quantum Hamiltonian model [7] calculated as described in reference [24]. As explained before, the hybrid model of this research, takes the quantum mechanical effects into account via the polarizability factor (complex response function) of individual monomers, while the interaction between molecules is considered within a self-consistent linear response theory. Figure 2.5 shows the spectra computed with both models, where the resonance frequency of isolated monomers 1.8eV was used as a baseline and the linewidth was assumed to be 0.1meV in order to resolve different resonances.

Figure 2.4: Panel a) Absorption spectrum and its components obtained using a classical electrodynamic approach and the quantum Fermi-Golden rule approach. Panel b) Circular Dichroism (CD) spectrum obtained using the classical and quantum approaches. The spectra were broadened with disorder $\Gamma = 1$ meV, and the frequency axis corresponds to the shift in energy respect to the monomer transition frequency. All spectra were computed for structure III-a) in Figure 2.1.
The resonances of the chlorosome aggregates are red-shifted from the monomer frequency in both quantum and hybrid model in agreement with the experimental data [32]. Apart from a frequency shift attributed to the difference between the quantum and the semi-classical model (as discussed on equations 2.15 and 2.16) the structures of the computed spectra are very similar. Please note that the difference in the spectra obtained by means of these models cannot be seen as a perfect red shift since larger shifts are observed at lower frequencies.

Both electrodynamic and electrostatic formulations have been proposed previously to study the interaction of light with molecular aggregates [19, 22, and 23]. Intuitively, when the physical dimension of the structure is much smaller than the wavelength of light, electrodynamic retardation effects are expected to be insignificant. However, as the dimensions of the structure increase and become comparable with the wavelength, those effects can become more pronounced. For this purpose, we constructed a long roll that has the same radius as roll D but length 290 nm, which is comparable to the physical length of a chlorosome [32]. The resulting structure for this ‘extended
roll D’ consists of \( N = 43200 \) molecules. The obtained spectra, Figure 2.6 and Figure 2.7, show that the retardation effects can result in a sufficient redistribution of peak intensities within the aggregate especially for the fields polarized along the roll's symmetry axis.

**Figure 2.6**: Frequency spectrum of the extended roll D in response to \( x \)-polarized initial electric field using both electrostatic and electrodynamic formulation. The numbers on the bottom horizontal axis indicate the relative red shift in meV with respect to the resonant frequency of the individual molecules located at 1.8eV. The vertical axis shows the sum of the squared polarization amplitudes of individual molecules. To enhance the details the vertical axis is in log scale.

**Figure 2.7**: Frequency spectrum of the extended roll D in response to \( z \)-polarized initial electric field using both electrostatic and electrodynamic formulation. The numbers on the bottom horizontal axis indicate the relative red shift in meV with respect to the resonant frequency of the individual molecules located at 1.8eV. The vertical axis shows the sum of the squared polarization amplitudes of individual molecules.
To examine the reliability of the parametric $H$-matrix method two example problems were solved using both the parametric $H$-matrix and the non-parametric $H$-matrix method. As a first example the bacteriochlorophyll roll of Figure 2.3 was excited with a steady state plane wave and polarization intensities were calculated as a function of the excitation frequency. The excitation decay rate was assumed to be the same for all monomers with equal $\gamma = 50$ meV. Figure 2.8 shows a quantitative agreement between the response obtained by means of the $H$-matrix method at 300 frequencies (in the 200 THz to 800 THz band) and twenty five sample points obtained using the parametric $H$-matrix method.

As a second example, see Figure 2.9. A similar comparison was done for the 290 nm long roll which again showed a perfect agreement between the results.
Induced Fields

Within the electromagnetic framework, we can obtain information on the exciton transfer properties from the induced polarizations. Indeed, once the nanostructure interacts with an incoming plane wave, the induced polarizations generate fields and thus transport can be quantified in terms of field enhancement. The directionality of transport can also be determined by computing the field depolarization.

Field concentration and depolarization

Plane wave incoming fields propagating along the $x$ direction (see Figure 2.1 panel II-a), were used to study the electric field enhancement and depolarization from the dipole arrays of the chlorosome. Two different polarizations of the incoming field are considered, along the $y'$ direction and along the $z'$ direction, as shown in Figure 2.1, panel II-a. The roll-A structure (Figure 2.1; III-a), was employed to obtain the field enhancement $\kappa = \frac{|\bar{E}|}{|E_0|}$ plots shown in Figure 2.10. In these plots, we see the values of the scattered field calculated on a grid orthogonal to the structure (panels a and b) and on a grid parallel to the structure (panels c and d). By comparison of panels a) and b) we notice a larger field enhancement when the incoming field is polarized along the $z'$ direction. This is expected due to the more favorable overlap with the dipole orientations in

Figure 2.9: Comparison of the spectral response of extended roll D structure using both $H$-matrix and parametric $H$-matrix method. The response is due to initial field excitation along $z$ direction. The vertical axis shows the sum of the squared polarization amplitudes of individual molecules. To enhance the details the vertical axis is in log scale.
the structure. The field enhancement overall is not very big in this case due to the large value of the noise $\Gamma = 50 \text{ meV}$.

We notice that the field is enhanced homogeneously in the radial direction (panels b and d), for $\gamma'$-polarized incoming field. This trend supports the idea of exciton transfer in the radial direction. This feature is observed even when including structural disorder. For the $\zeta'$-polarized incoming field (panels a and c), we see radial enhancement but also at the edges of the structure (panel c) this suggests that excitons may be transferred between layers and at the edges amongst neighboring substructures. In the next section, we look at how $\kappa$ varies with noise and structural disorder.

In Figure 2.11, we show contour plots of the depolarization $\eta = (|\vec{E}| - |\vec{E}_\parallel|)/|\vec{E}|$ of the electric field on a horizontal grid across the structures. Panel (a) and (b) indicate $\eta$ computed for the roll A structure (Figure 2.1; III-a) while panels (c) and (d) correspond to calculations for the chlorosome model structure with $7 \times 10^4$ molecules (Figure 2.1; III-c). In panels (a) and (c) the depolarization is calculated for a $\zeta'$-polarized incoming field and in panels (b) and (d) for a $\gamma'$-polarized incoming field. The depolarization, $\eta$, was also computed for the wild type roll A structure (Figure 2.1; III-b) and the pattern is analogous to that shown here in panels (a) and (b) for structure III-a. For these two cylindrical structures, the $\zeta'$-polarized incoming field is not significantly depolarized, this is probably due to the fact that the dipoles’ $\zeta$-component is largest.

For the third model chlorosome structure, we see in panel (c) that the field gets depolarized in an interesting pattern which most likely originates from the dipole packing at the edges. For the $\gamma'$-polarized incoming field, the depolarization pattern is similar for all three structures (panels b, d) and the field remains polarized for specific directions, perhaps those corresponding to where other substructures might be found. The observed depolarization patterns ensure that a photon of arbitrary polarization will be transferred to the next layer following the radial direction.
Figure 2.10: Panel a) Base ten logarithm of the electric field enhancement, \( \log_{10} \kappa \), calculated on a grid orthogonal to the roll structure in Figure 2.1, III-a). The dynamical noise rate is \( \Gamma = 50 \text{meV} \); the initial field excitation frequency is shifted by \( \Delta \omega = 0.23 \text{eV} \) (see Figure 2.4). The polarization of the initial field is along the \( z' \)-direction. Panel b), same as panel a) but for external field polarized along the \( y' \)-direction. Panel c) same as panel a) but here field is calculated on a grid parallel to the longest axis of the roll and at a distance of \( r = 80 \text{Å} \) from the origin. Panel d) same as panel c) but for \( y' \)-polarization.
Scaling of field enhancement with disorder

In Figure 2.12 we show the scaling of the field enhancement $\kappa$ as a function of distance from the center of the structure (panel III-a of Figure 2.1) for different values of structural disorder and dynamical noise.

Figure 2.11: Panel a) Depolarization of electric field $\eta$ calculated on a grid orthogonal to the roll structure in Figure 2.1, III-a). The dynamical noise rate is $\Gamma = 50$ meV; the initial field excitation frequency is shifted by $\Delta \omega = \omega_0 - \omega_{\text{ext}} = 0.23 \text{eV}$ (See Figure 2.4). The polarization of the initial field is along the $z$' direction. Panel b), same as panel a) but for $y$'-polarization of the external field. Panels c) and d), same as a) and b) but for the wild type chlorosome model structure III-c) with $\Delta \omega = \omega_0 - \omega_{\text{ext}} = 0.22 \text{eV}$.
In panel a) the field intensity as a function of distance is shown for different values of dynamical noise. We notice that as dynamical noise increases, the field scaling tends to go as $\sim 1/r$, but there are different slopes of the scaling on shorter distances. In panel b), the scaling as a function of structural disorder $\sigma$ is investigated at fixed small $\Gamma$. In this case the trend of the field is $\sim 1/r^3$. It is not immediately clear to us why a different scaling with respect to $r$ is observed in the case of dynamical versus structural disorder; however it is interesting that perhaps nature may tune one or the other type of disorder to modify the intensity of energy transferred through structural variations. The distance amongst substructures has experimentally [10] been determined to be $r_{\text{phys}} \sim 2\text{nm}$. The slope of the fields around this distance is not homogeneous as a function of $\Gamma$. In the case of structural disorder, at about $r_{\text{phys}}$, we notice (Figure 2.12, panel b) that a similar slope is observed with a smaller variation in intensity respect to panel a).

In Figure 2.13, we plot the field enhancement $\kappa$ at the biological distance $r_{\text{phys}}$ for the two cylindrical structures (panels III-a and III-b of Figure 2.1) as a function of dynamical noise (panel a) and structural disorder (panel b). It appears that dynamical noise has the strongest effect. In such large structures it is more likely that the main source of disorder is actually structural disorder however. This means that overall the excitation energy transfer is quite robust to disorder. Further, for all values of $\Gamma$ and $\sigma$, the enhancement is larger for the wild type structure. This suggests that
the dipole arrangement of the wild type structure leads to higher efficiency in terms of field enhancement. This is also observed at the physiological distance, \( r_{\text{phys}} \), relevant for transport.

![Figure 2.13: Panel a) scaling of field enhancement \( \kappa \) with dynamical noise rate \( \Gamma \) for each structure, at a distance of \( r_{\text{phys}} = 2\text{nm} \). Panel b) scaling of field with structural disorder \( \sigma \) for each structure, at a distance of \( r_{\text{phys}} = 2\text{nm} \). The incoming field is polarized along the \( z' \)-direction. Roll-A and Roll-A wild type, correspond to the structures in panels III-a) and b) of Figure 2.1.](image)

**Transient Response of Roll Aggregates**

The main role of the chlorosome is that of transmitting the collected solar energy: it is therefore important to investigate how fast energy is transferred amongst these nanostructures. In our electrodynamic model, the energy flow can be obtained from the induced fields and polarizations. In particular, one defines some acceptor molecules which are not initially excited by the incoming field and some donor molecules which are excited by the incoming field and later interact with the acceptors.

The rates of energy flow absorbed by the acceptors, \( R(t) \), can be obtained from the divergence of the pointing vector as \( R(t) = \sum_{\text{acc}} \mathcal{E}_{\text{acc}}(t) \cdot \frac{d}{dt} \hat{\rho}_{\text{acc}}(t) \) where \( \mathcal{E}_{\text{acc}} \) is the electric field at the acceptor at time \( t \) and \( \hat{\rho}_{\text{acc}} \) is the induced polarization of the acceptor at time \( t \). This approach has been discussed in Ref. 9.

In Figure 2.14, panel a), we show these fluxes of energy as a function of time, \( R(t) \), for transfer from a roll of donors (structure III-a of Figure 2.1) to a dipole acceptor positioned at different distances from the center of the cylinder. The dipole acceptor is oriented vertically along the main
axis of the cylinder and has transition frequency $\omega_{\text{acc}} = 1.51\text{eV}$, in the region where the roll absorbs (see Figure 2.4). The external field which interacts with donors is polarized along the $z'$ direction. The energy flux is normalized by the number of donor molecules squared, $N^2_{\text{donor}}$. In these calculations, the dynamic disorder rate $\Gamma = 50\text{ meV}$. We notice that the energy flux $R(t)$ does not decrease monotonically with distance, in fact there are some distances more favorable for transfer. This can be explained by the fact that the components of the field at each distance are not the same but may rotate. This effect can be thought of as some type of coherence between acceptor and donor.

We also computed the flux of energy transferred between two concentric cylindrical structures (Structure of Figure 2.1, panel II-a) for an external field polarized along the $z'$-direction. The resulting fluxes are shown in Figure 2.14, panel b) for two different values of the dynamic rate constant $\Gamma$. Here, $R_A$ indicates the flux when roll A (the roll with the smaller diameter) is the acceptor and roll B the donor and $R_B$ indicates the opposite case. When $\Gamma = 50\text{meV}$, i.e. the incoherent limit, the fluxes from roll A and B are equivalent, as expected and decay within 300 fs. When the disorder is decreased, the flux is much larger and decays fully only after about 800fs. Further, in this case the fluxes are different in each direction (from roll A to B and from B to A). This model however does not account for relaxation; therefore the estimated fluxes should be considered upper bounds of the actual rates.

![Figure 2.14](image)

**Figure 2.14:** Panel a) Flux of energy transferred from roll A (Figure 2.1, III-a) to a single dipole acceptor, oriented along the $z$ direction and located at various distances $r$ from the outside of the roll along the radial direction, here $\Gamma = 50\text{meV}$. Panel b) Flux of energy transferred from roll A to roll B, $R_B(t)$ and from roll B to roll A, $R_A(t)$ for different values of the dynamic noise constant $\Gamma$. The incoming field is polarized along the $z'$ direction.
As the next investigation, the four-layer chlorosome roll of Figure 2.3 is excited with initial $\hat{z}$ polarized electric field incident on monomers located at the central ring of roll A, i.e. the innermost roll as illustrated in Figure 2.3, and the time evolution of the polarization induced in various monomers at the points $a-f$ in the four-layer roll, see Figure 2.3, is observed. The time domain is constructed from a large number of frequency domain solutions via FFT. Thus it is natural to use the parametric $H$-matrix method to rapidly produce the required frequency response. The results presented in this section were obtained via 350 frequency domain solutions covering the frequency band from 0 THz to 800 THz. The parametric $H$-matrix is produced from 13 $H$-matrices evenly covering the 100 THz to 700 THz band. Generation of each $H$-matrix takes about 172 seconds (2236 seconds total) and the construction of the parametric $H$-matrix takes another 2000 seconds. However, when the parametric $H$-matrix is ready, the construction of each $H$-matrix at a given frequency only requires 7 seconds. At most frequencies, very few (4 to 50) Krylov iterations are needed for the matrix solution process and thus the computational time is mainly determined by the time spent on the construction of the system $H$-matrix. Under this configuration, the parametric $H$-matrix method leads to an overall speedup factor of 8 compared to the direct use of the $H$-matrix method. It is worth mentioning that higher speedup factors will be achieved when a larger number of frequency domain solutions are required or when larger structures need to be solved. Considering the symmetric geometry of the roll and the initial excitation similar time signatures are expected to occur at both (top and bottom) ends of the roll. However, comparing d and e in Figure 2.15 it appears that the polarization dynamics at the two ends of the chlorosome roll is slightly different. This can be linked to the chiral nature of the roll although a more systematic examination of the problem is needed before definitive conclusions can be made. Also as can be seen in Figure 2.15 (b, d and f), the responses on the outmost sub-roll, i.e. sub-roll D, seem to have longer lifetimes which is likely to be consequence of larger radius of sub-roll D compared to sub-roll A. The estimated number of molecules in the whole chlorosome is of the order of $200,000–250,000$ [32], which is about 20 times larger than our four-layered roll model.
In order to examine the performance of the presented parametric $H$-matrix technique for the structures comparable with the size of the chlorosome, we obtain the transient response of a 2 by 4 array of rolls with a lattice spacing of 25.5nm along both $\hat{x}$ and $\hat{y}$ directions. The resulting structure consists of 103680 monomers and thus each frequency solution involves construction and $H$-compression of a $103680 \times 103680$ matrix. Similar to the previous section, a central ring of monomers located in roll1 of the array is exposed to initial electrical field along $\hat{z}$ direction and then the response of the system (polarization) at various monomers is presented in Figure 2.17 and Figure 2.18.

Figure 2.15: Transient response (polarization amplitude) of various monomers in the four-layer roll in response to initial $z$ oriented electrical field of amplitude 1 V/m, imposed on monomers 1049 to 1108 located on a circular ring at the center of the innermost roll. The alphabetical labels in the legend correspond to the probe monomers depicted in Figure 2.3.
Figure 2.16: The 3-D configuration of the 4x2 roll array. The dotted line shows the location of the monomers exposed to initial electrical field.

Figure 2.17: Transient response (polarization amplitude) of various monomers in chlorosome roll number 1 in the array configuration illustrated in Figure 2.16. The labels in the legend refer to observation monomers depicted in Figure 2.3. The response is due to initial $z$ oriented electrical field of amplitude 1 V/m, imposed on monomers 1049 to 1108 located in chlorosome roll number 1.
The statistics presented here correspond to the 2 by 4 array problem of the transient response section. A dense matrix representation in this case will require $10^{3680} \times 10^{3680} \times 16$ bytes (approximately 160 GB) of memory and thus immediately ruled out. In a general scenario, the computational times can be divided into two parts, (1) construction of the system matrix and (2) the iterative solution of the problem. The iterative solution time is equal to the time required for one system matrix-vector multiply operation times the number of iterations needed for the desired accuracy. Thus, the two methods have equal performance in this part. An $H$-matrix representation of the system matrix using an accuracy threshold of $\epsilon = 10^{-4}$ leads to a compressed representation.

**Figure 2.18**: Transient response (polarization amplitude) of various monomers in chlorosome roll number 8 in the array configuration illustrated in Figure 2.16. The labels in the legend refer to the observation monomers depicted in Figure 2.3 shifted into roll number 8. The response is due to initial $z$ oriented electrical field of amplitude 1 V/m, imposed on monomers 1049 to 1108 located in chlorosome roll number 1.

**Computational Statistics**

The statistics presented here correspond to the 2 by 4 array problem of the transient response section. A dense matrix representation in this case will require $10^{3680} \times 10^{3680} \times 16$ bytes (approximately 160 GB) of memory and thus immediately ruled out. In a general scenario, the computational times can be divided into two parts, (1) construction of the system matrix and (2) the iterative solution of the problem. The iterative solution time is equal to the time required for one system matrix-vector multiply operation times the number of iterations needed for the desired accuracy. Thus, the two methods have equal performance in this part. An $H$-matrix representation of the system matrix using an accuracy threshold of $\epsilon = 10^{-4}$ leads to a compressed representation.
of the system that requires about 8GB of memory. However, the construction of the compressed $H$-matrix takes 65 to 70 minutes per frequency. Hence, the construction of the system $H$-matrix at 350 frequency points requires $350 \times 65 \times 60 = 1365000$ seconds. On the other hand, using the parameterized $H$-matrix method, 13 $H$-matrices are constructed at 13 equally spaced frequencies ranging from 100 THz to 700 THz and then the parametric $H$-matrix is constructed from the samples. This process takes $13 \times 65 \times 60$ seconds for the initial $H$-matrices plus another 10 hours for the construction of the parametric $H$-matrix. Thus the parametric $H$-matrix requires a total of 86700 seconds. On top of that, at each frequency point, the $H$-matrix can be constructed from the parametric $H$-matrix in 80 seconds leading to a speed up factor of 12. Figure 2.19 compares the growth of the computational times associated with the construction of the system matrix using both $H$-matrix and parametric $H$-matrix method. The curves depicted in Figure 2.19 are the representation of two linear equations with a considerable difference between their slopes and constant terms. From the figure it can be seen that the parametric $H$-matrix method outperforms the $H$-matrix method when the problem needs to be solved at more than 20 frequencies.

![Figure 2.19: Comparison of the system matrix preparation times between the parametric and non-parametric $H$-matrix methods.](image)

Conclusions

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We have analyzed the chlorosome antenna complex in the green sulfur bacteria Chlorobium tepidum using an electrodynamic model. There are some electrodynamic models for green sulfur bacteria and we have used here the one discussed in [10]. A multiscale analytic approach has been developed which leads to the electromagnetic properties of large array from dipoles. Because of the huge electronic size of chlorosome antenna complex, an $H$-matrix acceleration method is used. The parameterization was used for efficient frequency sweeping. The $H$-matrix and $pH$-matrix solvers, which have been used here, are developed in professor Mosallaei’s group. Numerical experiments conducted in this work verify the validity and robustness of the method. Three structures were considered as models for the natural chlorosome complex. Each antenna structure shows robustness to structural variations. This effect was seen in the values of the field enhancement which is much more sensitive to noise than to structural disorder.

At the physiological distance, the minimum distance observed for packing amongst nanostructures, the field enhancement trend follows different slopes as a function of disorder. Therefore no clear trend regarding variations of induced fields and polarization as a function of disorder can be deduced. However, at this same distance, the wild type nanostructure antenna shows larger field enhancement. This suggests that the molecular packing can be tuned to maximize transport properties. A preferential direction for transfer is observed consistently for all structures for specific polarizations. This suggests that this type of structure acts as a concentrator by enhancing transport for specific photon polarizations. This is also confirmed by the patterns of field depolarization which strongly depend on initial field polarization but not on structural variations. In particular we observe that the field is concentrated in the radial direction and at the edges of the cylinders (depending on the incoming field polarization), which would enable exciton transport to neighboring structures and to other layers. The field depolarization also supports transport to neighboring layers. Finally, transport has been quantified by calculating the flux of electromagnetic energy transferred between the cylindrical structure and a dipole acceptor. In this case there is a specific distance which maximizes transport. One can think of it in terms of coherence amongst the donor field polarization and the acceptor molecule dipole orientation. The timescale for the flux of energy transfer is roughly 300 fs which is an upper bound to the true timescale, in fact the model does not account for relaxation. We also computed these fluxes of energy for transfer amongst cylindrical structures and found that depending on dynamic noise, it
is enhanced in the radial direction. This study opens the road to the possibility of creating antennae that mimic this type of natural system.
Dispersion Diagram Analysis of Arrays of Multishell Multimaterial Nanospheres – A Metamaterial Application

Introduction

Scattering by a spherical scatterer has been studied over many years. The scattering properties of the multilayered scatterer also have been investigated for different types of boundaries [51]. The exact analytic solutions for these problems play an important role not only in developing radar systems and in designing antenna [60] systems and metamaterials [3], but also in estimating the accuracy of solutions obtained by approximate or numerical methods.

A comprehensive fast method which can accurately model interaction of electromagnetic radiation with a system of –not necessarily periodic arrangement of– solid, concentric or eccentric spherical structures is of interest to a wide range of scientific fields and has numerous practical applications. Natural dust particles and atmospheric aerosols are often found to have a fluffy aggregate structure. They often contain small inclusions of insoluble material which can affect their scattering properties. These inclusions can be found anywhere within the host aerosols. Any inclusion or encapsulation can directly affect the optical properties of the aerosol, and hence it’s scattering characteristics. Eccentric spheres, which sometimes are named as spherical crescents, can also be used in design of applied electromagnetic and optical devices.

In this chapter, an analytic solution for the electromagnetic problem of scattering by a periodic array of concentric multilayer spheres is presented. Full wave multipole expansion method is applied to express the electromagnetic fields in terms of electric and magnetic dipole modes and higher order modes. The periodic boundary conditions are applied and the dispersion diagram is calculated. This periodic structure, by assuming unit cells small compared to the wavelength, can be used in designing optical metamaterials. The design procedure, dispersion diagram and properties of designed metamaterials are discussed.

Optical Metamaterials

Metamaterials are formed by embedding inclusions and material components in host media to achieve composite structures with novel phenomena that do not occur or may not be easily
available in nature [34]. There are growing attentions in this area as their electromagnetic properties are considerably different from conventional materials.

Significant amount of research has been performed to realize metamaterials for novel applications. A large variety of the physical effects associated with double and single negative metamaterials and some of their very interesting impacts have been addressed [35]. Among these interesting features are negative index and negative refraction behaviors, usually known as left handed materials (LHMs) [36]. Unique applications have been highlighted, such as phase compensation, electrically small resonators, negative angles of refraction, subwavelength waveguides with lateral dimension below diffraction limits, high-performance focusing, backward-wave media, photon tunneling, and electrically small antennas [34], [36-38].

To obtain an optical metamaterial with the functionality of interest one would need to create appropriate electric and magnetic dipole modes in a building block often regarded as the unit cell [39-41]. As long as isolated plasmonic particles are involved, an analytical circuit-theory based model has been introduced by Alam et al. [42, 43] which allows for the calculation of resonant frequencies and scattering parameters. Furthermore, it has been demonstrated that dielectric spheres have the potential to offer both electric and magnetic dipole modes [41, 44]. Primarily, the electric and magnetic dipole moments are the basic foundations for making metamaterials. Novel arrangements of these dipole moments can lead to desired material properties [41]. Tailoring the appropriate dipole modes allows controlling the performance of the structure.

A unit cell composed of two different spheres with the same radii and different materials or the same dielectric materials and different radii can provide the required electric and magnetic dipole modes [39, 45, and 46]. The low dielectric material of the nanospheres in optical regimes generates some difficulties in tuning optical double negative (DNG) medium. There are also other works where one set of dielectric nanoparticles has been used to accomplish the backward wave behavior in optical spectrum [40]. In such works a 3-D array of dielectric particles are used where the spheres operate in their magnetic modes and their couplings offer electric modes. Bringing the dielectric spheres close to each other, increases their electromagnetic coupling in such a way that both electric and magnetic resonances can be achieved around the same frequency region. Yet, we do not have complete control over the position of the resonances.
In this work, a multilayer sphere is used as the unit cell building block of the structure where a core dielectric sphere is wrapped in a plasmonic material shell. Two different metals (gold and silver) are used for this coating/shell layer. Metals have traditionally been the material of choice for the building blocks of many metamaterials, but they suffer from high resistive losses—even metals with the highest conductivities, silver and gold, exhibit excessive losses at optical frequencies that restrict the development of practical devices at such frequencies. The development of new materials for low loss metamaterial components and telecommunication devices is therefore required [47]. Hence, some new materials (ITO, AZO and GZO) are used as the coating layer to investigate the performance.

It is demonstrated that this arrangement can successfully provide the required electric and magnetic modes at the frequency of interest. First, a two-layer (core-shell) sphere is designed and it is shown that by adjusting the radius of the core and the thickness of the shell the relative position of the resonances with respect to each other can be controlled. Hence, one can use the mentioned configuration to enforce overlapping electric and magnetic resonances. Adding a third layer of coating increases the system flexibility. It is illustrated that by changing the thickness of the third layer the electric and magnetic resonances can be shifted simultaneously into the desired frequency band where negative-slope dispersion behaviors can be synthesized accordingly.

We develop a theoretical approach based on dipole modes to comprehensively characterize the metamaterial performance. The technique is fast and accurate and is aimed to theoretically determine the dispersion diagrams. The proposed approach is based on the recent work by Ghadarghadr et al.[39] while it is extend to the modeling of arrays of multilayer multimaterial spheres (Figure 3.1). To enable this, the problem of multiple scattering of an electromagnetic plane wave by an array of spheres is solved utilizing the multipole expansion method [20, 39, and 48]. This provides an efficient theoretical model for the characterization of the periodically configured bulk of metamaterial.
The Theory and Formulation

This section presents the theoretical formulation of the 3-D array of metamaterial. The building block is constructed from layered spherical particle. A Mie scattering formulation is applied to formulate the problem and solve for dispersion diagram of the periodic configuration.

Scattering Coefficients

Consider a multilayer ($N$ layer) sphere where each layer is characterized by a relative permittivity $\varepsilon_r n$ and a radius $r_n$, $n=1,2,\ldots,N$. We assume the region outside the multilayer sphere is free space and the relative permeability everywhere is assumed to be $\mu_r=1$. A plane wave excitation with $x$-polarized electric field and $y$-polarized magnetic field is considered. The field in each region can be written using the $\vec{M}$ and $\vec{N}$ vector basis functions [49] as:

$$\bar{E}_n = \sum_{m=1}^{\infty} E_m \left[ c_m^{(n)} M_{o1m}^{(1)} + jd_m^{(n)} N_{e1m}^{(1)} - ja_m^{(n)} N_{o1m}^{(3)} - b_m^{(n)} M_{o1m}^{(3)} \right]$$  \hspace{1cm} (3.1a)

$$\bar{H}_n = -\frac{k_n}{\omega \mu_0} \sum_{m=1}^{\infty} E_m \left[ d_m^{(n)} M_{e1m}^{(1)} - ja_m^{(n)} N_{e1m}^{(1)} + jb_m^{(n)} N_{o1m}^{(3)} - a_m^{(n)} M_{e1m}^{(3)} \right]$$  \hspace{1cm} (3.1b)
where \( E_m = (-j)^m E_0 (2m+1)/m(m+1) \), \( \omega \) is the angular frequency and \( k_n \) is the angular wave number of \( n^{th} \) layer. In equations (3.1a) and (3.1b), \( \vec{M}_{olm}^{(s)} \), \( \vec{M}_{elm}^{(s)} \), \( \vec{N}_{olm}^{(s)} \) and \( \vec{N}_{elm}^{(s)} \) are the vector harmonic functions with the radial dependence to spherical Bessel function \( j_m(kr) \) for \( s=1 \) and spherical Hankel function \( h_m^{(1)}(kr) \) for \( s=3 \) [50].

In the region out of the sphere (\( n=N+1 \)), the scattered field can be expanded as:

\[
\vec{E}_{(N+1)} = \sum_{m=1}^{\infty} E_m \left[ -j a_m^{(N+1)} \vec{N}_{elm}^{(3)} - b_m^{(N+1)} \vec{M}_{olm}^{(3)} \right] \quad (3.2a) \\
\vec{H}_{(N+1)} = \frac{k_{(N+1)}}{\omega \mu_0} \sum_{m=1}^{\infty} E_m \left[ a_m^{(N+1)} \vec{M}_{elm}^{(3)} - j b_m^{(N+1)} \vec{N}_{olm}^{(3)} \right] \quad (3.2b)
\]

In the section that follows, the electromagnetic fields and the Mie scattering coefficients \( a_m^{(N+1)} \) and \( b_m^{(N+1)} \) are calculated by means of enforcing the tangential continuity of field components across material interfaces. It is assumed that the dimensions of the nanospheres are sufficiently small compared to free space wavelength and hence higher order modes are neglected. The accuracy of this assumption will be discussed in section 4.1. Therefore, the field due to each particle is modeled with dipole spherical waves. In other words, the first term of the summations (i.e. for \( m=1 \)) in equations (3.2a) and (3.2b) dominates the higher order terms and therefore scattered electric and magnetic fields outside the particle can be approximated as:

\[
\vec{E}_{(N+1)} = \frac{-3}{2} E_0 \left[ a_1^{(N+1)} \vec{N}_{el1}^{(3)} + j b_1^{(N+1)} \vec{M}_{ol1}^{(3)} \right] \quad (3.3a) \\
\vec{H}_{(N+1)} = \frac{3k_{(N+1)}}{2\omega \mu_0} E_0 \left[ ia_1^{(N+1)} \vec{M}_{el1}^{(3)} - b_1^{(N+1)} \vec{N}_{ol1}^{(3)} \right] \quad (3.3b)
\]

It is worthwhile recalling that the spherical vector wave function \( \vec{M} \) has a circular field pattern on the interface, i.e. \( \vec{M} \cdot \hat{r} = 0 \). On the contrary, \( \vec{N} \) includes nonzero radial component. The behavior is graphically depicted in Figure 3.2. Looking at equations (3.3) one observes that controlling the \( a_1^{(N+1)} \) and \( b_1^{(N+1)} \) coefficients, electric and magnetic dipole modes can be excited in the particle. For instance, if \( a_1^{(N+1)} \) has a large value and \( b_1^{(N+1)} \) is small, an electric dipole mode is induced and vice versa.
Electric and Magnetic Mie Scattering Coefficients

In this section the electric and magnetic Mie scattering coefficients of the multilayer sphere are obtained. Using an approach similar to that of [51] one can find the $\hat{\Theta}$ and $\hat{\Phi}$ components of the $m^{th}$ mode of the electric and magnetic field in region $n$ as:

\[
\begin{bmatrix}
E^m_{\theta \
E^m_{\phi}}
\end{bmatrix} = \frac{1}{j\omega \varepsilon_n} \begin{bmatrix}
\frac{\partial}{\partial \theta} P^1_m (\cos \theta) \\
-\frac{j}{\sin \theta} P^1_m (\cos \theta)
\end{bmatrix} \cdot \begin{bmatrix}
\bar{U}_{n,n-1} \frac{1}{r} \frac{\partial}{\partial r} r h^{(1)}_m (k_n r) + \frac{1}{r} \frac{\partial}{\partial r} r j_n (k_n r)
\end{bmatrix}. A_n \tag{3.4a}
\]

\[
\begin{bmatrix}
H^m_{\theta} \\
H^m_{\phi}
\end{bmatrix} = \begin{bmatrix}
-\frac{j}{\sin \theta} P^1_m (\cos \theta) \\
-\frac{\partial}{\partial \theta} P^1_m (\cos \theta)
\end{bmatrix} \cdot \begin{bmatrix}
\bar{U}_{n,n-1} \frac{1}{r} \frac{\partial}{\partial r} r h^{(1)}_m (k_n r) + j_n (k_n r)
\end{bmatrix}. A_n \tag{3.4b}
\]

Here, we have used Debye potentials for characterizing the scalar waves and $e^{j m \phi}$ dependences are suppressed. In the above $\bar{U}_{n,n-1}$ is the reflection from the boundary between regions $n-1$ and $n$ considering the effect of the other inner layers. In spherically layered media, the TM$^r$ and TE$^r$ (transverse to $\hat{e}_r$) waves are decoupled and equations (3.4a) and (3.4b) represent either of the TM$^r$ or
the TE\textsuperscript{r} spherical modes. Now, since a standing wave in region \(n-1\) is a consequence of the standing wave in region \(n\) plus the reflection of the outgoing wave in region \(n-1\), one can write:

\[
A_{n-1} = T_{n,n-1}A_n + R_{n-1,n} \tilde{U}_{n-1,n-2}A_{n-1} \tag{3.5}
\]

In equation (3.5), \(T_{n,n-1}\) is the transmission coefficient of incoming wave travelling from region \(n\) to \(n-1\) while \(R_{n-1,n}\) is the reflection without considering the effect of other layers. Hence,

\[
A_{n-1} = \frac{T_{n-1,n}}{1-R_{n-1,n} \tilde{U}_{n-1,n-2}} A_n \tag{3.6}
\]

Furthermore, the outgoing wave in region \(n\) is just a consequence of the reflection of the standing wave in region \(n\) plus the transmission of the outgoing wave in region \(n-1\), therefore,

\[
\tilde{U}_{n,n-1}A_n = R_{n,n-1}A_n + T_{n-1,n}R_{n-1,n-2}A_{n-1} \tag{3.7}
\]

Substituting \(A_{n-1}\) from equation (3.6) into equation (3.7) yields

\[
\tilde{U}_{n,n-1} = R_{n,n-1} + \frac{T_{n-1,n}}{1-R_{n-1,n} \tilde{U}_{n-1,n-2}} \tilde{U}_{n,n-1} T_{n,n-1} \tag{3.8}
\]

where \(\tilde{U}_{1,0}=0\).

As mentioned earlier, these relations are valid for both TM\textsuperscript{r} and TE\textsuperscript{r} cases. Therefore, by using the general recursive relation (3.8) one can find the coefficients in equations (3.2a) and (3.2b) by using \(a_{m}^{(N+1)}= \tilde{U}_{N+1,N}^{TM}\) and \(b_{m}^{(N+1)}= \tilde{U}_{N+1,N}^{TE}\). For this purpose, TM\textsuperscript{r} and TE\textsuperscript{r} reflection and transmission coefficients need to be obtained without considering the effect of other layers. These parameters can be found by matching the boundary conditions in equations (3.4a) and (3.4b) for a solid sphere. Hence, the TM\textsuperscript{r} reflection and transmission coefficients are found as [51]:

\[
R_{n,n-1}^{TM} = -\frac{\sqrt{\varepsilon_n \mu_n} \hat{J}_{m}^{(s)}(k_{n}r_{n-1}) \hat{Y}_{m}^{(s')}^{*}(k_{n-1}r_{n-1}) - \sqrt{\varepsilon_n \mu_n} \hat{J}_{m}^{(s)}(k_{n}r_{n-1}) \hat{Y}_{m}^{(s')}^{*}(k_{n-1}r_{n-1})}{\sqrt{\varepsilon_n \mu_{n-1}} \hat{J}_{m}^{(s)}(k_{n-1}r_{n-1}) \hat{H}_{m}^{(s')}^{*}(k_{n}r_{n-1}) - \sqrt{\varepsilon_{n-1} \mu_n} \hat{H}_{m}^{(s)}(k_{n-1}r_{n-1}) \hat{J}_{m}^{(s')}^{*}(k_{n}r_{n-1})} \tag{3.9a}
\]

\[
T_{n,n-1}^{TM} = \frac{-j \varepsilon_{n-1} \sqrt{\mu_{n-1}}}{\sqrt{\varepsilon_n \mu_n} \hat{J}_{m}^{(s)}(k_{n}r_{n-1}) \hat{Y}_{m}^{(s')}^{*}(k_{n-1}r_{n-1}) - \sqrt{\varepsilon_{n-1} \mu_n} \hat{H}_{m}^{(s)}(k_{n-1}r_{n-1}) \hat{J}_{m}^{(s')}^{*}(k_{n}r_{n-1})} \tag{3.9b}
\]
where $\hat{J}_m(x)=xj_n(x)$ and $\hat{H}_{m}^{(l)}(x)=xh_{m}^{(l)}(x)$. The relation for $R_{\ell-1,\ell}^{TM}$ can easily be found by replacing the Riccati-Bessel functions $\hat{J}_m(x)$ in the nominator by Riccati-Hankel functions $\hat{H}_{m}^{(l)}(x)$ and also $T_{\ell-1,\ell}^{TM}$ can be found by changing the indices of $n$ and $n-1$ in the nominator [51]. The corresponding relations for the TE case can be obtained by means of electromagnetic duality theorem. Once the complete expression for $a_m^{(N+1)}$ and $b_m^{(N+1)}$ is derived, one can enforce electric and/or magnetic Mie scattering resonances by forcing the denominators of $a_m^{(N+1)}$ and $b_m^{(N+1)}$ to vanish.

For a two-layer sphere the first mode of electric and magnetic Mie scattering coefficients can be found from equation (3.8) as:

$$a_1^3 = U_{3,2}^{TM} = R_{3,2}^{TM} + \frac{T_{2,3}^{TM} R_{2,3}^{TM} T_{3,2}^{TM}}{1 - R_{2,3}^{TM} R_{2,3}^{TM}}$$

(3.10a)

$$b_1^3 = U_{3,2}^{TE} = R_{3,2}^{TE} + \frac{T_{2,3}^{TE} R_{2,3}^{TE} T_{3,2}^{TE}}{1 - R_{2,3}^{TE} R_{2,3}^{TE}}$$

(3.10b)

where one can write the TM reflection and transmission terms from equations (3.9a) and (3.9b) as:

$$R_{2,3}^{TM} = \frac{\sqrt{\varepsilon_2/\varepsilon_0} \hat{J}_1(2\pi r_1) \hat{J}_1(2\pi r_2) - \hat{J}_1(2\pi r_1) \hat{J}_1(2\pi r_2)}{\hat{J}_1(2\pi r_1) \hat{H}_1^{(0)}(2\pi r_2) + \hat{H}_1^{(0)}(2\pi r_2) \hat{J}_1(2\pi r_1)}$$

(3.11a)

$$R_{3,2}^{TM} = \frac{\hat{J}_1(k_2 r_1) \hat{J}_1(k_2 r_2) - \sqrt{\varepsilon_2/\varepsilon_0} \hat{J}_1(k_2 r_1) \hat{J}_1(k_2 r_2)}{\sqrt{\varepsilon_2/\varepsilon_0} \hat{J}_1(k_2 r_1) \hat{H}_1^{(0)}(k_2 r_2) + \hat{H}_1^{(0)}(k_2 r_2) \hat{J}_1(k_2 r_1)}$$

(3.11b)

$$T_{2,3}^{TM} = \frac{\sqrt{\varepsilon_2/\varepsilon_0} \hat{J}_1(2\pi r_1) \hat{H}_1^{(0)}(2\pi r_2) + \hat{H}_1^{(0)}(2\pi r_2) \hat{J}_1(2\pi r_1)}{\hat{J}_1(2\pi r_1) \hat{H}_1^{(0)}(2\pi r_2) + \hat{H}_1^{(0)}(2\pi r_2) \hat{J}_1(2\pi r_1)}$$

(3.11c)

$$T_{3,2}^{TM} = \frac{-j \varepsilon_2/\varepsilon_0}{\sqrt{\varepsilon_2/\varepsilon_0} \hat{J}_1(k_2 r_1) \hat{H}_1^{(0)}(k_2 r_2) + \hat{H}_1^{(0)}(k_2 r_2) \hat{J}_1(k_2 r_1)}$$

(3.11d)

$$T_{2,3}^{TM} = \frac{-j \varepsilon_0/\varepsilon_2}{\hat{J}_1(k_2 r_1) \hat{H}_1^{(0)}(k_2 r_2) + \sqrt{\varepsilon_0/\varepsilon_2} \hat{H}_1^{(0)}(k_2 r_2) \hat{J}_1(k_2 r_1)}$$

(3.11e)
As mentioned, similar relations for TE case can be found by duality theorem. One can also derive easily the coefficients for the three-layer case.

Effective Medium for the Array Structure

From the obtained equations in previous section one can determine the effective medium for a 3-D array made from small scatterers. The assumption is the spheres are small in comparison to the wavelength such that effective constitutive medium properties can be defined.

In a three dimensional array of particles with volume density \( \bar{N} \), the effective permittivity \( \varepsilon_{\text{eff}} \) and permeability \( \mu_{\text{eff}} \) can be obtained from equations (3.12a) and (3.12b) [52]. These relations reflect the first scattered electric and magnetic dipole sources of array particle, i.e. terms with \( a_{\text{1}}^{(N+1)} \) and \( b_{\text{1}}^{(N+1)} \) coefficients, to the constitutive constants of the bulk medium.

\[
\varepsilon_{\text{eff}} = \frac{k_{0}^{3} - j4\pi \bar{N}a_{\text{1}}^{(N+1)}}{k_{0}^{3} + j2\pi \bar{N}a_{\text{1}}^{(N+1)}} \quad (3.12a)
\]

\[
\mu_{\text{eff}} = \frac{k_{0}^{3} - j4\pi \bar{N}b_{\text{1}}^{(N+1)}}{k_{0}^{3} + j2\pi \bar{N}b_{\text{1}}^{(N+1)}} \quad (3.12b)
\]

Therefore, by controlling \( a_{\text{1}}^{(N+1)} \) and \( b_{\text{1}}^{(N+1)} \) a collection of multilayer non-magnetic spheres can be designed to yield almost arbitrary values of \( \varepsilon_{\text{eff}} \) and \( \mu_{\text{eff}} \) (depending on the availability of the required materials for the sphere itself). Furthermore, structures with negative index of refraction can also be realized. This requires both permittivity and permeability coefficients to be negative. Hence, the multilayer spheres must be designed to exhibit simultaneous electric and magnetic resonances, i.e. in the Mie scattering sense, within the same frequency band.

Dispersion Diagram Analysis

Substantial physical knowledge of the material properties of a bulk medium can be extracted from the dispersion diagram, i.e. plot of \( \omega a/2\pi c \) versus \( ka/2\pi \), associated with that medium. The dispersion diagram for 2-D and 3-D arrays of spheres has been previously obtained in [39, 54] and here we follow a similar approach. To obtain the dispersion diagram, a plane wave excitation with \( x \)-polarized electric field and \( y \)-polarized magnetic field is considered. The electric and magnetic dipole components of each sphere are oriented in the \( x \) and \( y \) direction respectively. It is assumed
that the array can support an electromagnetic plane wave with the propagation vector $\vec{k}$ which lies in the direction of array axis ($z$). The electric and magnetic dipole modes in the array are coupled through the fields scattered by the spheres. The dispersion relation is obtained by equating the electric (magnetic) field incident on any sphere of the array to the sum of the electric (magnetic) dipole fields scattered from all other spheres in the array. For simplicity it is assumed that the reference sphere is assumed to be centered at (0, 0, 0) of the Cartesian coordinate system. Hence, the field incident on the reference sphere which is due to the field scattered from other spheres can be expressed as:

$$\vec{E}_0 = \sum_{l_z=-\infty}^{\infty} \sum_{l_x=-\infty}^{\infty} \sum_{l_y=-\infty}^{\infty} \vec{E}_{l_x,l_y,l_z}$$ \hspace{1cm} (3.13a)$$

$$\vec{H}_0 = \sum_{l_z=-\infty}^{\infty} \sum_{l_x=-\infty}^{\infty} \sum_{l_y=-\infty}^{\infty} \vec{H}_{l_x,l_y,l_z}$$ \hspace{1cm} (3.13b)$$

Here, $\vec{E}_{l_x,l_y,l_z}$ and $\vec{H}_{l_x,l_y,l_z}$ are the scattered electric and magnetic field from the element located at $(l_x,l_y,l_z)$. Also, from equation (3.3), the scattered field from each sphere is related to the external incident field through the Mie scattering coefficients:

$$\vec{E}_{l_x,l_y,l_z} = \frac{-3}{2} E_0 \left[ a_1^{(N+1)} \vec{N}_{e11}^{(3)} - j b_1^{(N+1)} \vec{M}_{e11}^{(3)} \right]$$ \hspace{1cm} (3.14a)$$

$$\vec{H}_{l_x,l_y,l_z} = \frac{-3k_{(N+1)}}{2\omega\mu_0} E_0 \left[ j a_1^{(N+1)} \vec{M}_{e11}^{(3)} + b_1^{(N+1)} \vec{N}_{o11}^{(3)} \right]$$ \hspace{1cm} (3.14b)$$

The assumption that a dipolar travelling wave with periodic $\exp(-jkz)$ dependence ($\text{real}|k|>0$) can be supported by the array yields a relation for the normalized travelling wave propagation constant $ka$ as a function of radiuses, dielectric functions and $\omega a/c$. Using the above, the desired system of equations for extracting the dispersion relation is determined as done in [39, 53, and 54]:

$$\left(\frac{\omega a}{c}\right)^3 - S_{-\Sigma_1} = \frac{S_{\Sigma_2}}{S_{-\Sigma_1}} S_{\Sigma_1}; \quad \omega a/c < ka$$ \hspace{1cm} (3.15)
Detailed definitions for $S_+ = -j(3/2) a_1^{(N+1)}$, $S_- = -j(3/2) b_1^{(N+1)}$, $\Sigma_1$ and $\Sigma_2$ can be found in [53].

Performance Analysis of Multilayer Spheres

Two-Layer Structure

Two layered spheres with various types of shells are used to engineer the desired metamaterial characteristics. The material choices considered for the shell are gold, silver, ITO, AZO and GZO. In the subsections that follow, each different shell type is briefly discussed in terms of its optical properties and the design procedure aimed at obtaining simultaneous electric and magnetic $Mie$ resonances. Envisioning DNG performance, a core material $\varepsilon_1=20$ is assumed and then the core and the shell radius are engineered to exhibit a dispersion diagram with negative slope. To simplify the design procedure the core material losses are ignored. The design procedure is general and can be applied to other types of materials.

The electric and magnetic resonances coefficients are determined from equations (3.10a) and (3.10b), respectively. By careful look at these equations and equations (3.11a)-(3.11e) one can observe under the condition of small $r_1$ (compared to the wavelength) and low $\varepsilon_2$ (compared to the core material) for the magnetic $Mie$ scattering coefficient in equation (3.10b) $R_{3,2}^{TE}$ goes to zero and the frequency of resonance is dominantly determined by the radius of the core and is almost the frequency which the resonance of $R_{2,1}^{TE}$ occurs. For the electric $Mie$ scattering coefficient in equation (3.10a), because of the mentioned assumptions, $R_{2,1}^{TM}$, the only term which has dependence on $r_1$, is small and almost constant and thus the frequency for the resonance is strongly controlled by the thickness of the shell. Therefore one can say the magnetic resonance is mainly obtained by the core and the electric resonance by the shell.

In this work we design the multilayer spheres so that the dielectric constant of the shell at the resonance frequency is at -0.2. The radius of the core is then found by adjusting the resonance of $R_{2,1}^{TE}$ to the desired simultaneous resonance frequency and the radius of the shell is obtained from electric $Mie$ scattering coefficient in equation (3.10a).

Here, a Drude model for the permittivity of shell is used:
where $\omega_p$ is plasma frequency and $\Gamma$ is characteristic collision frequency. Because the metal thicknesses used in the examples here are a few nanometers, the parameters in the Drude model should be modified by considering some important effects at such length scale. The parameters for different materials used in this paper are shown in Table 3.1 and they are from experimental and curve fitted results of Ref [55]. The real and imaginary parts of the dielectric functions are respectively shown in Figure 3.3(a) and 3.3(b).

![Figure 3.3](image)

**Figure 3.3:** (a) Real and (b) imaginary parts of the Drude dielectric functions of materials used in this work.

### Gold Shell

Gold (Au) has wide applications in almost all different branches of nanotechnology. Gold plays an important role in a myriad of plasmonics-type spectroscopies - such as surface enhanced Raman scattering (SERS) - where it is widely preferred for biological applications over silver for its relatively easier surface chemistry, the possibility of attaching molecules via thiol groups, good biocompatibility, and chemical stability.
As explained before, the core-shell design is achieved for when the shell has $\varepsilon_r=-0.2$, which is where the gold material is at $f=1575\text{THz}$ (see Figure 3.3(a)). Given the design frequency of 1575THz the radius of the core is obtained at 20.7nm and the shell radius is then obtained to be 22nm. This design will ensure the poles of the electric and magnetic Mie resonances to be around the same band (as shown in Figure 3.4).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_x$</th>
<th>$\omega_p$ [THz]</th>
<th>$\Gamma$ [THz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>1.53</td>
<td>2069</td>
<td>17.64</td>
</tr>
<tr>
<td>Silver</td>
<td>5</td>
<td>2175</td>
<td>4.35</td>
</tr>
<tr>
<td>ITO</td>
<td>3.91</td>
<td>418.1</td>
<td>38.1</td>
</tr>
<tr>
<td>AZO</td>
<td>3.3</td>
<td>352.2</td>
<td>30.4</td>
</tr>
</tbody>
</table>

Table 3.1: The Drude model parameters of different materials.

As mentioned earlier, it is assumed here that the spheres are small enough so that the multipole expansion of the electric field can be approximated with the first dipole mode. The first three modes of Mie scattering coefficients for the designed two-layer sphere are presented in Figure 3.5 in which the strong dominance of the first mode is evident, hence validating the assumption that a

Figure 3.4: Normalized electric and magnetic Mie scattering coefficients of a single two-layer sphere for the first mode with core $\varepsilon_1=20$, $r_1=20.7\text{nm}$ and gold shell with $r_2=22\text{nm}$.

As mentioned earlier, it is assumed here that the spheres are small enough so that the multipole expansion of the electric field can be approximated with the first dipole mode. The first three modes of Mie scattering coefficients for the designed two-layer sphere are presented in Figure 3.5 in which the strong dominance of the first mode is evident, hence validating the assumption that a
single dipole mode can effectively model the problem.

Now from equation (3.4) it can be concluded that using this two-layer sphere in an array structure will lead to a DNG material. The lattice constant of the 3-D array structure presented in Figure 3.1 is considered as $a=75\,\text{nm}$. We apply the developed equations in section 3 and obtain the dispersion diagram as plotted in Figure 3.6. In this figure, one observes a frequency band where slope of the real part of the dispersion diagram is negative. As expected from the design, the negative slope frequency band is centered at about $\omega a/(2\pi c)=0.39$ which corresponds 1560THz. Therefore, in this band the group and phase velocities are oriented along opposite directions resulting in a so called backward wave. The obtained lattice constant is not quite in subwavelength region. Using a higher dielectric material for core can overcome this problem (though the availability of material in this frequency band can be a challenge). Also, from Figure 3.6 it is evident that the imaginary part of the propagation vector has close to zero values everywhere except around resonance. The maximum value of tangent loss is $\text{Im}(ka)=1.32$ which clearly shows the lossy behavior of the negative-slope region.
In Figure 3.6, a small feature is observed at about $\omega a/2\pi c = 0.04$ which corresponds to $f \approx 160$THz. A quick glance at the Mie scattering coefficients, as depicted in Figure 3.7, reveals that the tiny feature in Figure 3.6 is due to the small local maxima of the electric Mie scattering coefficient at the proximity of 160THz.

The design procedure discussed in this subsection is almost identically repeated for the other shell types, i.e. silver, ITO, AZO and GZO. Hence, in what follows, it suffices to report the resulting dispersion diagrams and design parameters.
Silver Shell

Silver (Ag) has the highest electrical conductivity among natural elements and the highest thermal conductivity among metals. In fact, silver nanoparticles can have effective extinction (scattering plus absorption) cross sections up to ten times larger than their physical cross section [56]. From Figure 3.3(a) the -0.2 permittivity for silver occurs at frequencies slightly below 960THz. Hence, following the same procedure as in the previous subsection, the radius of the core and the thickness of the shell are respectively determined to be 33.77nm and 1.23nm. Scattering coefficients for this design are presented in Figure 3.8(a).

The designed two-layer sphere is used to construct a 3-D array structure with a lattice constant of $a=100\text{nm}$. The real and imaginary parts of the resultant dispersion diagram are computed and presented in Figure 3.8(b). The range with negative real part slope is found to be centered at around $\omega a/2\pi c=0.32$ which corresponds to frequencies about 960THz (close to resonance frequency in Figure 3.8(a)). The maximum loss occurs in resonance region and is $\text{Im}(ka)=1.445$.

![Figure 3.8:](image)

Comparison of Figure 3.6 and Figure 3.8(b) shows that although the plasma frequencies of silver and gold in their Drude model are close to each other but there is a large difference in resonances frequencies where negative slope occurs. This difference comes from the difference in
the frequency which satisfies the design condition enforced on the permittivity of the shell layer (i.e. $\varepsilon_r = -0.2$). This frequency for gold is about 1575THz while for silver is about 960THz.

As alternatives to conventional metals, new plasmonic materials offer many advantages in fields of plasmonics and metamaterials. These advantages include low intrinsic loss, semiconductor-based design, compatibility with standard nanofabrication processes, and tunability. Transparent conducting oxides such as Al:ZnO (AZO), Ga:ZnO (GZO) and indium-tin-oxide (ITO) enable many high-performance metamaterial devices [57]. In the following subsections these materials are used for shell layer of the two-layer spheres.

**ITO Shell**

ITO is used for various optical coatings, most notably infrared-reflecting coatings (hot mirrors) for automotive, sodium vapor lamp glasses, gas sensors, antireflection, coatings, electrowetting on dielectrics, and Bragg reflectors for VCSEL lasers [58].

Using the $\varepsilon_r=-0.2$ rule of thumb and Figure 3.3(a), the resonant frequency is found to be around 200THz. The radius of dielectric core is found to be 166.6nm and the thickness of the ITO shell is obtained as 34.4nm. The computed Mie scattering coefficients are shown in Figure 3.9(a) where the resonances occur at 196.88THz.

The real and imaginary parts of the dispersion diagram when using the 3-D array with an array constant of $a=450$nm are shown in Figure 3.9(b). The frequency band with negative group velocity is around $\omega a/2\pi c=0.29$. This band is again around the resonance frequency. From the imaginary part, the loss away from the resonance frequency is small but it is not as small as in the cases with metal shell and maximum loss occurs at $Im(ka)=0.94$. The maximum loss in negative slope region is expectedly smaller than the cases with metal shells.
AZO Shell

ZnOs have high transparency in the visible and near-ultraviolet spectral regions, wide conductivity range and conductivity changes under photoreduction/oxidation conditions. It has wide applications in chemical sensors, heterojunction solar cells, electrophotography, surface acoustic wave devices, conductive transparent conductors and many others. Polycrystalline ZnO films doped with group II and group III metal ions such as indium (In), aluminum (Al), gallium (Ga), copper (Cu) and cadmium (Cd) have enhanced structural, optical and electrical properties. Doping is particularly done to get high transparency, stability and high conductivity. Aluminum doping is particularly suitable for this purpose. Aluminum doped ZnO (AZO) thin films have high transmittance in the visible region, and a low resistivity and the optical band gap can be controlled by using the amount of Al doping. As a result, AZOs have potential applications in solar cells, antistatic coatings, solid-state display devices, optical coatings, defrosters, chemical sensors etc. [59].The design of simultaneous resonances two-layer sphere with AZO shell leads to $r_1=181.5\text{nm}$ and $r_2=212\text{nm}$. The computed Mie scattering coefficients for this two-layer sphere are presented in Figure 3.10(a) where the resonances occur at $180.4\text{THz}$.
Corresponding dispersion diagrams when using this two-layer sphere in the 3-D array structure with lattice constant of $a=500\,\text{nm}$ are plotted in Figure 3.10(b). From the real part, it is determined that the negative group velocity band is centered at $\omega a/2\pi c=0.3$. Furthermore, from the imaginary part, the losses are found to be small when operated at frequencies far from the resonance frequency. The maximum loss occurs at $\text{Im}(ka)=0.85$ which (as expected) is smaller than that of the ITO shell case.

GZO Shell

Gallium doped ZnO (GZO) is another family of materials that has many applications in electronics and optics. GZO shells have applications in organic light emitting diodes, solar cells, solid-state display devices mainly because of their high transparency, stability and high conductivity.

The simultaneous resonances with the GZO shell is achieved with $r_1=160\,\text{nm}$ and $r_2=194\,\text{nm}$. The computed Mie scattering coefficients are presented in Figure 3.11(a). The resonances occur at 205.2THz. Dispersion diagrams for the resulting 3-D array structure with an array constant of 450nm are plotted in Figure 3.11(b). The range with negative group velocity is centered on about $\omega a/2\pi c=0.3$. The loss away from the resonance frequency is small and maximum loss occurs at $\text{Im}(ka)=0.9$ which is happening close to the resonances frequency.
Three Layer Structure

As discussed in previous sections, two-layer spheres can be designed for obtaining simultaneous resonances, i.e. electric and magnetic resonances occurring at the same frequency. It is obvious from the design procedure that we do not have much control over the resonant frequency of the two-layer structure. In other words, it is hard to transfer the resonance to a frequency of choice. Hence, another dielectric layer is added to the system to increase the degrees of freedom in the location of the resonance. The third layer is made from the same dielectric material as the core ($\varepsilon_r^1 = \varepsilon_r^3 = 20$). It is found that increasing the thickness of the third dielectric layer will result in a red shift for both electric and magnetic Mie resonances. Unfortunately, though, the electric and the magnetic resonances do not experience the same shifts when the third (dielectric) layer is added to the unit cell. This mismatch is, however, easily compensated by a fractional change in the radius of the core and/or the thickness of the shell.

Here a three layer case of dielectric-gold-dielectric is explored. Recall for the two layer design that the resonances occurred at 1575THz. Suppose a resonance frequency band around 900THz is desired. Then, adding the coating dielectric layer and adjusting its thickness, the resonance frequency can be transferred to the desired band. The objective can be achieved with $r_1 = 25\text{nm}$, $r_2 = 29\text{nm}$ and $r_3 = 39.9\text{nm}$ for which the resonances occur at 898.1THz. Mie coefficients for this

![Figure 3.11: (a) Normalized electric and magnetic Mie scattering coefficients of a single two-layer sphere with GZO shell, and (b) real and imaginary parts of dispersion diagram for the element used in the array structure with unit cell $a = 450\text{nm}$ ($r_1 = 160\text{nm}$ and $r_2 = 194\text{nm}$).](image)
sphere are plotted in Figure 3.12(a).

This three layer unit cell is integrated into the 3-D array of Figure 3.1 and the resulting dispersion diagram is depicted in Figure 3.12(b). Here, an array constant of $a=120\text{nm}$ is considered. The negative group velocity is found to occur at frequency close to $\frac{\omega a}{2\pi c}=0.36$. Similar to the two layer case with metal shells, the loss is negligible when operating at frequency away from the resonance. Maximum loss occurs at $\text{Im}(ka)=2.07$ which is larger than the losses for the 3-D consisting of two-layer sphere unit cells.

In the end, all of the designs are summarized in Table 3.2. Two-layer spheres with different shell materials can be compared for their characteristic parameters, i.e. the radius of the core ($r_1$), the radius of the shell ($r_2$), the lattice constant of the 3-D array ($a$), the resonance frequency ($\omega_r$) and the maximum value of $\text{Im}(ka)$. The parameters for the designed three-layer sphere are also added to the table. Using Table 3.2, a resonance frequency of 1500THz can be achieved with the two-layer core-shell with gold used for the shell layer. On the other hand, if a resonance at 900THz is desired, one option can be using silver as the shell of a two-layer sphere and the other option is using a three-layer sphere with gold as the second layer. The advantage of using the three-layer sphere lies in the controllability of the resonance frequency such that the resonance can be tuned exactly at the desired frequency at the expense of slight increase in the losses when compared to the two-layer spheres.
If the desired frequency band is about 200THz, depending on the application, each of the ITO, AZO or GZO shell two-layer spheres can be used. For instance, in applications like precisely etching, which the resolution is important, ITO can be used but if a lower control is enough AZO can be used instead.

It must be mentioned that the focus of this work has been on theoretical-computational analysis, and the fabrication challenges will be obviously of importance too. This will include availability of the core dielectric material and the feasibility of the required shell thickness for realization. Also, to have a metamaterial performance a smaller lattice constant is preferable which can be achieved using higher dielectric material for the core (that can be more difficult to realize). The lattice constants used in the presented results in this work fall in the $0.3\lambda$ to $0.4\lambda$ range. Hence, from the view point of homogenization, we may consider them more like negative slope media than DNG materials.

<table>
<thead>
<tr>
<th>Shell</th>
<th>$r_1$ [nm]</th>
<th>$r_2$ [nm]</th>
<th>$a$ [nm]</th>
<th>$\omega_r$ [THz]</th>
<th>$Max{Im(ka)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>20.7</td>
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<td>75</td>
<td>1575</td>
<td>1.32</td>
</tr>
<tr>
<td>Silver</td>
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<td>35</td>
<td>100</td>
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<td>0.94</td>
</tr>
<tr>
<td>AZO</td>
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<td>212</td>
<td>500</td>
<td>180.4</td>
<td>0.85</td>
</tr>
<tr>
<td>GZO</td>
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<td>194</td>
<td>450</td>
<td>205.2</td>
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<td>3 layer</td>
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<td>20</td>
<td>120</td>
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<td>2.07</td>
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</table>
Conclusions

In this Chapter, electromagnetic characteristics of periodic arrays of multilayer multimaterial spheres are theoretically investigated. The focus is on two aspects; first on how to design multilayer spheres that exhibit electric and magnetic Mie scattering resonances around the same frequency, and second to integrate the designed unit cells into a 3-D array configuration to achieve DNG metamaterial with negative-slope dispersion characteristic. A full wave spherical modal analysis is applied to express the electromagnetic fields in terms of the electric and magnetic multipole modes. The dispersion diagrams are obtained using a method that characterizes the interactions of electromagnetic waves with the 3-D arrays of spheres. It is assumed that the spheres are sufficiently small compared to the operating wavelength such that only the first order vector spherical waves, i.e. the dipolar modes, can sufficiently characterize the scattering effects. The dispersion diagrams for 3-D array configurations consisting of various two-layer spheres are fully characterized. It is illustrated that in an array of multilayer spheres one can combine the electric and magnetic modes properly and creates negative slope dispersion diagrams. Different metal and plasmonic materials are used for the shell layer to control the location of the DNG region and the loss performance of the resulting material. Smaller loss characteristics are achieved using ITO, AZO and GZO nonmetallic plasmonic materials. Also, it is shown the resonance frequency can be further controlled by means of replacing the two layer spherical structure with that of an alternative three layer structure. Although three layer structure led to a design of metamaterial with DNG region at the desired frequency band but, at the expense, the losses around the resonance frequency is larger than two layer structure (without the third dielectric layer).
Chapter 4

Semi-Analytic Solution of Non-Concentric Spheres Array

Introduction

The periodic array of concentric spheres, discussed in chapter 3, is very useful in designing metamaterials, photonic bandgaps, lenses and filters. Now, in this chapter, we are going to discuss on solving electromagnetic problem of non-periodic (random) array of spheres. While the concept is very promising the computation is very challenging. This is due to the having a large finite array of different core-shells of dispersive materials and the fact that they can be located very close to each other. This will face us a broad-spectrum eigenvalue problem which makes simulation based on numerical methods very challenging, if not impossible. We need to add to these the cases which core-shells have non-concentric (eccentric) geometries either due to the requirement to achieve a physic of interest or the fabrication practicality.

In the present work, an analytical solution for the problem of scattering by a cluster of non-concentric spheres is presented. Full wave multipole expansion method is applied to express the electromagnetic fields in terms of the electric and magnetic dipole modes and the higher order moments. Addition theorems are needed when it is necessary to expand fields in more than one system of coordinates. The first derivations of the translational addition theorems for the spherical vector wave functions were due to Stein [61] and Cruzan [62]. They derived the vector translation coefficients from the scalar translation coefficients and through a tedious algebraic manipulations. Chew [51] derived the coefficients quite similarly as in [61] and [62]; Chew and Wang [63] also presented recurrence formulas. Here, we use the vector translation coefficients, similar to Cruzan’s original theorem [62] but with some modifications. Modifications are in the \((-1)^n\) coefficient of Legendre polynomial definition. Then one can apply the boundary conditions at the surface of each sphere, to obtain a system of equation which its unknowns are the expansion coefficients of scattered and internal fields. As this method generalizes the Mie solver of one solid sphere we have named it Generalized Mie Method (GMM). Clearly, Mie solid sphere, cluster of concentric spheres and periodic arrangements of spheres are the especial cases of GMM. Geometry of the problem is
presented in Figure 4.1. This system contains $N$ different non-concentric spheres. We consider each non-concentric sphere as an “Inclusion” sphere located inside a “Host” sphere.

![Figure 4.1: Geometry of scattering problem from a cluster of eccentric spheres.](image)

**Multipole Expansion and Boundary Conditions**

To solve scattering problems, it is desirable to express electromagnetic fields in terms of infinite series expansions at all points in space. For spherical structures, choosing spherical wave vectors as the basis functions make the calculations easier and the translation coefficients applicable. Spherical wave functions are basic solutions to the Maxwell’s equations and the Helmholtz equation in the spherical system of coordinates and they form the basis for the expansion of any field satisfying these equations. In spherical polar coordinates, the linear independent vector field solutions of the vector wave equations are the vector spherical wave functions $\mathbf{M}_{nm}^{(l)}$ and $\mathbf{N}_{nm}^{(l)}$ [64].

In expansion of equation (4.1), appropriate radial dependency for $\mathbf{M}_{nm}^{(l)}$ and $\mathbf{N}_{nm}^{(l)}$ functions ($z^{(l)}$) has to be selected from any of the four spherical functions: the spherical Bessel functions of the first kind $j_n$, the second kind $y_n$, or the spherical Hankel functions of the first kind $h_n^{(1)}$ and the second kind $h_n^{(2)}$ denoted by $\rho=1,2,3,4$ respectively; $P_n^m(\cos \theta)$ is the associates Legendre function of the first kind and degree $n$ and order $m$. The electric and magnetic fields at any point can be expressed by infinite summations with the proper spherical wave functions and weighting
coefficients. It is worth mentioning here that electromagnetic fields inside or outside of each inclusion or host spheres are expanded by spherical wave functions at the center of that sphere. In the notation of this work, subscript $q$ means that wave vectors are defined based on a coordinate system at the center of $q^{th}$ sphere.

\[
\hat{M}_{nm,q}^{(r)} = \hat{\theta}_q \left[ \frac{-jm}{\sin \theta_q} z_n^{(r)}(kr_q) P_n^m(\cos \theta_q) e^{-jm\phi} \right] - \hat{\phi}_q \left[ z_n^{(r)}(kr_q) \frac{d}{d\theta_q} P_n^m(\cos \theta_q) e^{-jm\phi} \right], \quad (4.1a)
\]

\[
\hat{N}_{nm,q}^{(r)} = \hat{\rho}_q \left[ \frac{1}{kr_q} z_n^{(r)}(kr_q) n(n+1) P_n^m(\cos \theta_q) e^{-jm\phi} \right] + \hat{\phi}_q \left[ \frac{1}{kr_q} \frac{d}{d\theta_q} (r_n z_n^{(r)}(kr_q)) \frac{d}{d\theta_q} P_n^m(\cos \theta_q) e^{-jm\phi} \right] + \hat{\theta}_q \left[ -\frac{1}{kr_q} \frac{d}{d\theta_q} (r_n z_n^{(r)}(kr_q)) \frac{jm}{\sin \theta_q} P_n^m(\cos \theta_q) e^{-jm\phi} \right], \quad (4.1b)
\]

We are assuming $q^{th}$ sphere is in general a two layer non-concentric sphere. Solid and concentric spheres are clearly special cases of our general problem. We consider that the $q^{th}$ sphere has a Host, and an Inclusion which is located completely inside the Host sphere. Now, one can argue on the electric fields corresponding to the $q^{th}$ sphere by working on its Host and Inclusion separately and then enforcing the boundary conditions.

**Host Sphere:**

For the Host sphere we need to calculate two fields: The field out of the sphere and the field between Host and Inclusion spheres. The field out of the sphere can be divided into the external incident field (the excitation) and the scattered field from the sphere. The external incident field can be expanded by the spherical wave functions with Bessel functions of the first kind:

\[
\vec{E}_{\text{incident}}^{q,\text{Host}} = \sum_{n=0}^\infty \sum_{m=-n}^n a_{nm}^{q,\text{Host}} \vec{M}_{nm,q}^{(1)} + b_{nm}^{q,\text{Host}} \vec{N}_{nm,q}^{(1)} \quad (4.2)
\]

In this work, two kinds of excitation has been considered: plane wave (PW) and the field radiated by a circular aperture. The second one is a model closer to the reality when working with a large structure. The expansion coefficients of the PW incident field for different polarizations (TE,
TM and TEM) can be found in other works [50, 65]. The expansion coefficients for the field from a circular aperture have been calculated analytically in [66].

On the other hand, the scattered electric field can be expanded using the spherical Bessel functions of the third kind:

$$E_{\text{scattered}}^{q\text{Host}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} c_{nm}^{q} \tilde{M}_{nm, q\text{Host}}^{(3)} + d_{nm}^{q} \tilde{N}_{nm, q\text{Host}}^{(3)} \quad (4.3)$$

The fields inside the Host sphere, and outside the Inclusion, may be expanded by incoming and outgoing spherical waves using spherical Bessel functions of the third and fourth kinds:

$$E_{\text{qph}}^{q\text{Host}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} c_{nm}^{q} \tilde{M}_{nm, q\text{Host}}^{(3)} + f_{nm}^{q} \tilde{N}_{nm, q\text{Host}}^{(3)} + g_{nm}^{q} \tilde{M}_{nm, q\text{Host}}^{(4)} + h_{nm}^{q} \tilde{N}_{nm, q\text{Host}}^{(4)} \quad (4.4)$$

The magnetic fields expansions can be written respectively and applying the boundary conditions at the Host sphere surface yields:

$$a_{nm}^{q} k_{q\text{Host}} \psi_{n}^{q}(k_{q\text{Host}}) + c_{nm}^{q} k_{q\text{Host}} \zeta_{n}^{(1)}(k_{q\text{Host}}) = e_{nm}^{q} k_{q\text{Host}} \xi_{n}^{(1)}(k_{q\text{Host}}) a_{q\text{Host}} + g_{nm}^{q} k_{q\text{Host}} \zeta_{n}^{(2)}(k_{q\text{Host}}) a_{q\text{Host}} \quad (4.5)$$

$$a_{nm}^{q} \psi_{n}'(k_{q\text{Host}}) + c_{nm}^{q} \zeta_{n}'^{(1)}(k_{q\text{Host}}) = e_{nm}^{q} \zeta_{n}(k_{q\text{Host}}) a_{q\text{Host}} + g_{nm}^{q} \zeta_{n}'^{(2)}(k_{q\text{Host}}) a_{q\text{Host}} \quad (4.6)$$

$$b_{nm}^{q} \psi_{n}(k_{q\text{Host}}) + d_{nm}^{q} k_{q\text{Host}} \zeta_{n}^{(1)}(k_{q\text{Host}}) = f_{nm}^{q} \zeta_{n}(k_{q\text{Host}}) a_{q\text{Host}} + h_{nm}^{q} \zeta_{n}'^{(2)}(k_{q\text{Host}}) a_{q\text{Host}} \quad (4.7)$$

$$b_{nm}^{q} k_{q\text{Host}} \psi_{n}'(k_{q\text{Host}}) + d_{nm}^{q} k_{q\text{Host}} \zeta_{n}'(k_{q\text{Host}}) = f_{nm}^{q} k_{q\text{Host}} \zeta_{n}(k_{q\text{Host}}) a_{q\text{Host}} + h_{nm}^{q} k_{q\text{Host}} \zeta_{n}'(k_{q\text{Host}}) a_{q\text{Host}} \quad (4.8)$$

where $k$ and $k_{q\text{Host}}$ are the wave number of the background and the Host, $a_{q\text{Host}}$ is the radius of the Host and $\psi_{n}(r)$ and $\zeta_{n}^{(s)}(r)$ ($s=1,2$) are the Riccati-Bessel functions defined by

$$\psi_{n}(r) = r j_{n}(r)$$

$$\zeta_{n}^{(s)}(r) = r h_{n}^{(s)}(r) \quad (4.9)$$

and the primes denote derivatives with respect to the argument.

Inclusion Sphere:
The fields inside the *Inclusion* sphere may be expressed using spherical Bessel functions of the first kind

\[ \vec{E}_{in}^{q_{\text{inc}}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} v_{nm}^{q} \tilde{M}_{nm,q_{\text{inc}}}^{(1)} + w_{nm}^{q} \tilde{N}_{nm,q_{\text{inc}}}^{(1)} \quad (4.10) \]

The fields near the boundary and outside the *Inclusion* sphere may be expressed into incoming and outgoing spherical waves using spherical Bessel functions of the fourth and third kind.

\[ \vec{E}_{ext}^{q_{\text{inc}}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} r_{nm}^{q} \tilde{M}_{nm,q_{\text{inc}}}^{(3)} + s_{nm}^{q} \tilde{N}_{nm,q_{\text{inc}}}^{(3)} + t_{nm}^{q} \tilde{M}_{nm,q_{\text{inc}}}^{(4)} + u_{nm}^{q} \tilde{N}_{nm,q_{\text{inc}}}^{(4)} \quad (4.11) \]

It is worth mentioning that, although both of equations (4.4) and (4.11) describe the electric field in the area between *Host* and *Inclusion* spheres, the coefficients in two relations are not equal. That is because equation (4.4) is expanded by basis functions defined by coordinate system located at the center of *Host* but in (4.11) basis functions are different and they are defined at the center of *Inclusion*. Applying boundary conditions at the *Inclusion* sphere surface yields:

\[ v_{nm}^{q} k_{q_{\text{Host}}} \psi_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) = t_{nm}^{q} k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) + r_{nm}^{q} k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \quad (4.12) \]

\[ v_{nm}^{q} \psi'_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) = s_{nm}^{q} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) + t_{nm}^{q} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \quad (4.13) \]

\[ w_{nm}^{q} \psi_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) = s_{nm}^{q} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) + u_{nm}^{q} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \quad (4.14) \]

\[ w_{nm}^{q} k_{q_{\text{Host}}} \psi'_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) = s_{nm}^{q} k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) + u_{nm}^{q} k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \quad (4.15) \]

One can eliminate the interior field coefficients \( (v_{nm} \text{ and } w_{nm}) \) to find relationships for the exterior field coefficients. Then we have:

\[ r_{nm}^{q} = \frac{t_{nm}^{q} k_{q_{\text{Host}}} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) - k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi'_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}})}{k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) - k_{q_{\text{Host}}} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi'_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}})} = Q_{n,q}^{r} t_{nm}^{q} \quad (4.16) \]

\[ s_{nm}^{q} = \frac{u_{nm}^{q} k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) - k_{q_{\text{Host}}} \tilde{\psi}_{n}^{(2)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi'_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}})}{k_{q_{\text{inc}}} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}}) - k_{q_{\text{Host}}} \tilde{\psi}_{n}^{(1)}(k_{q_{\text{Host}}} a_{q_{\text{inc}}}) \psi'_{n}(k_{q_{\text{inc}}} a_{q_{\text{inc}}})} = Q_{n,q}^{s} u_{nm}^{q} \quad (4.17) \]

where \( Q_{n,q}^{r} \) and \( Q_{n,q}^{s} \) are the \( Q \)-factors which contain information about the *Inclusion* sphere such as its size and reflective index.
**Translation Addition Theorem**

Addition theorems are needed when it is necessary to expand fields in more than one system of coordinates. This can happen, in the case of multiple scattering from a collection of spheres [67], scattering from one non-concentric sphere [68] and therefore in evaluation of a field in a collection of non-concentric spheres. Recently, there has been a renewed interest in the addition theorems because of their important role in Fast Multipole Methods (FMM) [69-72]. The addition theorem used in FMM is translation of the scalar green function but, here in this work, it is translation of the vector spherical wave functions. As mentioned before, here we use the vector translation coefficients, based on the Cruzan’s original theorem [62]. It is worth mentioning that the Legendre polynomial’s used in Cruzan’s translation coefficients are defined without $(-1)^n$ coefficient. The extraction of equations for the translation of the vector spherical wave functions from a coordinate system $S_p$ with origin $O_p$ and spherical polar coordinates $(r_p, \theta_p, \phi_p)$ into a coordinate system $S_q$ with origin $O_q$ and coordinates $(r_q, \theta_q, \phi_q)$ has been discussed in [73]. The translation coefficients can be defined for two different cases depending on relative position between the origins $O_p$ and $O_q$: $r_q > R_{pq}$ and $r_q < R_{pq}$ that $\vec{R}_{pq} = \vec{r}_p - \vec{r}_q$ is the vector that connects the origins $O_p$ and $O_q$.

The fields in the interior of the host sphere are expressed by equation (4.4) while the field exterior to the inclusion sphere is expressed by equation (4.11). As mentioned before, the vector spherical harmonics expressed by these equations are centered about two different coordinate systems. The addition theorem can be applied to express the coefficients of $e_{nm}$, $f_{nm}$, $g_{nm}$, and $h_{nm}$ in terms of the coefficients $r_{nm}$, $s_{nm}$, $t_{nm}$, and $u_{nm}$. The translation of the vector spherical wave functions from the $p^{th}$ to the $q^{th}$ coordinate system takes the form

\begin{equation}
\tilde{M}_{nm,q}^{(s_1)} = \sum_{v=0}^{\infty} \sum_{\mu=0}^{v} A_{\mu v}^{mn}(q, p) \tilde{M}_{v,p}^{(s_2)} + B_{\mu v}^{mn}(q, p) \tilde{N}_{v,p}^{(s_2)} \tag{4.18}
\end{equation}

\begin{equation}
\tilde{N}_{nm,q}^{(s_1)} = \sum_{v=0}^{\infty} \sum_{\mu=0}^{v} B_{\mu v}^{mn}(q, p) \tilde{M}_{v,p}^{(s_2)} + A_{\mu v}^{mn}(q, p) \tilde{N}_{v,p}^{(s_2)} \tag{4.19}
\end{equation}

where $s_1, s_2 = 1, 2, 3, 4$. For a given $s_1$, it is important to choose the correct type of Bessel function for the right hand side ($s_2$) [73].

The addition theorem relations of equation (4.18) and (4.19) can be used in equation (4.11) to transfer the spherical wave functions from the origin of the inclusion to the host sphere. In this case...
the radial dependency of translation coefficients are *Hankel* function of the first kind. Considering
\[ \vec{R}_q = \vec{r}_{qHost} - \vec{r}_{qInc} \] then we have:
\[
E_{ext}^{qInc} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ r_{nm} \left[ \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} A_{mn}^{\nu}(\vec{R}_q) \vec{M}_{\nu \nu, qHost}(3) + B_{mn}^{\nu}(\vec{R}_q) \vec{N}_{\nu \nu, qHost}(3) \right] \\
+ s_{nm} \left[ \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} B_{mn}^{\nu}(\vec{R}_q) \vec{M}_{\nu \nu, qHost}(3) + A_{mn}^{\nu}(\vec{R}_q) \vec{N}_{\nu \nu, qHost}(3) \right] \\
+ t_{nm} \left[ \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} A_{mn}^{\nu}(\vec{R}_q) \vec{M}_{\nu \nu, qHost}(4) + B_{mn}^{\nu}(\vec{R}_q) \vec{N}_{\nu \nu, qHost}(4) \right] \\
+ u_{nm} \left[ \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} B_{mn}^{\nu}(\vec{R}_q) \vec{M}_{\nu \nu, qHost}(4) + A_{mn}^{\nu}(\vec{R}_q) \vec{N}_{\nu \nu, qHost}(4) \right] \}
\]

After interchanging \((n,m)\) with \((\nu,\mu)\), rearranging the expansion coefficients, and comparing to
equation (4.4) one can find:
\[
\begin{align*}
\varepsilon_{nm} &= \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} r_{\nu \nu} A_{mn}^{\nu}(\vec{R}_q) + s_{\nu \nu} B_{mn}^{\nu}(\vec{R}_q) \\
f_{nm} &= \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} r_{\nu \nu} B_{mn}^{\nu}(\vec{R}_q) + s_{\nu \nu} A_{mn}^{\nu}(\vec{R}_q) \\
g_{nm} &= \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} t_{\nu \nu} A_{mn}^{\nu}(\vec{R}_q) + u_{\nu \nu} B_{mn}^{\nu}(\vec{R}_q) \\
h_{nm} &= \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} t_{\nu \nu} B_{mn}^{\nu}(\vec{R}_q) + u_{\nu \nu} A_{mn}^{\nu}(\vec{R}_q)
\end{align*}
\]  

(4.21)

Now, one can find a system of four equations and four unknowns by using equations (4.16),
(4.17) and (4.21) in equations (4.5)-(4.8):
\[
a_{nm}^{q} \psi_{n}(k_{qHost}) + c_{nm}^{q} \varepsilon_{n}^{(1)}(k_{qHost}) = \\
\frac{k}{k_{qHost}} \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} t_{\nu \nu} \left( \varepsilon_{n}^{(1)}(k_{qHost} a_{qHost}) \mathcal{Q}_{\nu}^{\nu} A_{mn}^{\nu}(\vec{R}_q) + \varepsilon_{n}^{(2)}(k_{qHost} a_{qHost}) A_{mn}^{\nu}(\vec{R}_q) \right) \\
+ u_{\nu \nu} \left( \varepsilon_{n}^{(1)}(k_{qHost} a_{qHost}) \mathcal{Q}_{\nu}^{\nu} B_{mn}^{\nu}(\vec{R}_q) + \varepsilon_{n}^{(2)}(k_{qHost} a_{qHost}) B_{mn}^{\nu}(\vec{R}_q) \right)
\]

(4.22)
\[ a_{nm}^q \psi_{nm}^q (ka_{qHost}) + c_{nm}^q \varphi_{n}^{(1)} (ka_{qHost}) = \]
\[ \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} \left[ t_{\nu \mu} \left( \varphi_{n}^{(1)} (k_{qHost} a_{qHost}) Q_{n}^{0} A_{nm}^{\mu} (\vec{R}_q) + \varphi_{n}^{(2)} (k_{qHost} a_{qHost}) A_{nm}^{\mu} (\vec{R}_q) \right) \right. \]
\[ + \left. u_{\nu \mu} \left( \varphi_{n}^{(1)} (k_{qHost} a_{qHost}) Q_{n}^{1} B_{mn}^{\mu} (\vec{R}_q) + \varphi_{n}^{(2)} (k_{qHost} a_{qHost}) B_{mn}^{\mu} (\vec{R}_q) \right) \right] \]
\[ (4.23) \]
\[ b_{nm}^q \psi_{n}^q (ka_{qHost}) + d_{nm}^q \varphi_{n}^{(1)} (ka_{qHost}) = \]
\[ \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} \left[ t_{\nu \mu} \left( \varphi_{n}^{(1)} (k_{qHost} a_{qHost}) Q_{n}^{0} B_{mn}^{\mu} (\vec{R}_q) + \varphi_{n}^{(2)} (k_{qHost} a_{qHost}) B_{mn}^{\mu} (\vec{R}_q) \right) \right. \]
\[ + \left. u_{\nu \mu} \left( \varphi_{n}^{(1)} (k_{qHost} a_{qHost}) Q_{n}^{1} A_{mn}^{\mu} (\vec{R}_q) + \varphi_{n}^{(2)} (k_{qHost} a_{qHost}) A_{mn}^{\mu} (\vec{R}_q) \right) \right] \]
\[ (4.24) \]
\[ b_{nm}^q \psi_{n}^q (ka_{qHost}) + d_{nm}^q \varphi_{n}^{(1)} (ka_{qHost}) = \]
\[ \frac{k}{k_{qHost}} \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} \left[ t_{\nu \mu} \left( \varphi_{n}^{(1)} (k_{qHost} a_{qHost}) Q_{n}^{0} B_{mn}^{\mu} (\vec{R}_q) + \varphi_{n}^{(2)} (k_{qHost} a_{qHost}) B_{mn}^{\mu} (\vec{R}_q) \right) \right. \]
\[ + \left. u_{\nu \mu} \left( \varphi_{n}^{(1)} (k_{qHost} a_{qHost}) Q_{n}^{1} A_{mn}^{\mu} (\vec{R}_q) + \varphi_{n}^{(2)} (k_{qHost} a_{qHost}) A_{mn}^{\mu} (\vec{R}_q) \right) \right] \]
\[ (4.25) \]

If the system under investigation was only one non-concentric sphere, the incident field in equation (4.2) was the external excitation on the sphere and one could solve system of equations (4.22)-(4.25) expansion coefficients.

On the other hand, in case of an array of non-concentric spheres, the electromagnetic field that is incident upon the surface of the \( q \)-th sphere consists of two parts: (1) the original external incident field and (2) the scattered fields of all the other spheres in the array. It means that

\[ \vec{E}_{\text{incident}}^q = \vec{E}_{0}^q + \sum_{p \neq q} \vec{E}_{\text{scattered}}^{p \text{Host}} \]
\[ (4.26) \]

The original excitation can be expanded by spherical wave vectors with \textit{Bessel} functions of first kind.

\[ \vec{E}_{0}^q = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \alpha_{nm}^q \vec{M}_{n,m,q \text{Host}}^{(1)} + \beta_{nm}^q \vec{N}_{n,m,q \text{Host}}^{(1)} \]
\[ (4.27) \]

For the second sentence in right hand side of equation (4.26), which is the effect of other spheres in array, from equation (4.3) we have:
\[ \vec{E}_{\text{scattered}}^{p_{\text{Host}}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} c_{nm}^{p} \vec{M}_{nm, p_{\text{Host}}}^{(3)} + d_{nm}^{p} \vec{N}_{nm, p_{\text{Host}}}^{(3)} \] (4.28)

In equation (4.26) we would like spherical wave functions of all fields on right hand side and left hand side be defined at the same coordinate system. We use again the translation addition theorem to transfer the spherical wave vectors in equation (4.28) from the origin of the \( p^\text{th} \) to \( q^\text{th} \) sphere. The addition theorem relations are the same as equations (4.18) and (4.19); except the radial dependency of translation coefficients which is Bessel functions of the first kind. Considering 
\[ \vec{R}_{qp} = \vec{r}_{q_{\text{Host}}} - \vec{r}_{p_{\text{Host}}} \] and using equations (4.18) and (4.19) in equation (4.28) we have:

\[ \vec{E}_{\text{scattered}}^{p_{\text{Host}}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} c_{nm}^{p} \left[ \sum_{v=0}^{\infty} \sum_{\mu=-v}^{\nu} A_{\mu v}^{mn} (\vec{R}_{qp}) \vec{M}_{\nu v, q_{\text{Host}}}^{(3)} + B_{\mu v}^{mn} (\vec{R}_{qp}) \vec{N}_{\nu v, q_{\text{Host}}}^{(3)} \right] + \sum_{v=0}^{\infty} \sum_{\mu=-v}^{\nu} D_{\mu v}^{mn} (\vec{R}_{qp}) \vec{M}_{\nu v, q_{\text{Host}}}^{(3)} + A_{\mu v}^{mn} (\vec{R}_{qp}) \vec{N}_{\nu v, q_{\text{Host}}}^{(3)} \] (4.29)

Similar relations can be found for the magnetic fields. Substituting equations (4.27) and (4.29) inside (4.26) and comparing to (4.2) leads to:

\[ a_{nm}^{q} = a_{nm}^{p} - \sum_{l=p+q}^{\infty} \sum_{v=0}^{\infty} \sum_{\mu=-v}^{\nu} \left[ c_{\nu v}^{l} A_{\mu v}^{mn} (\vec{R}_{qp}) + d_{\nu v}^{l} B_{\mu v}^{mn} (\vec{R}_{qp}) \right] \] (4.30)

\[ b_{nm}^{q} = b_{nm}^{p} - \sum_{l=p+q}^{\infty} \sum_{v=0}^{\infty} \sum_{\mu=-v}^{\nu} \left[ d_{\nu v}^{l} A_{\mu v}^{mn} (\vec{R}_{qp}) + c_{\nu v}^{l} B_{\mu v}^{mn} (\vec{R}_{qp}) \right] \] (4.31)

Substituting \( a_{nm}^{q} \) and \( b_{nm}^{q} \) from equations (4.30) and (4.31) into (4.22)-(4.25) gives a system of equations which can be solved for the expansion coefficients of field scattered and inside the spheres of the array. Then the electric field, and magnetic field, at any point can be calculated.

**Total Fields**

Once all the scattering coefficients of spheres in the array, \( c_{nm}^{q} \) and \( d_{nm}^{q} \), are found, the total scattered field of the entire cluster in the primary coordinate system (defined with subscript \( q_{0} \)) can be expressed as:
\[
\vec{E}_{\text{scattered}}^{\text{total}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} c_{nm}^{\text{total}} \vec{M}_{nm,qd}^{(3)} + d_{nm}^{\text{total}} N_{nm,qd}^{(3)}
\]  
(4.32)

where
\[
c_{nm}^{\text{total}} = \sum_{l=1}^{L} \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} \left[ c_{\nu\mu}^{l} A_{\mu\nu}^{mn} \left( \vec{R}_{qd} \right) + d_{\nu\mu}^{l} B_{\mu\nu}^{mn} \left( \vec{R}_{qd} \right) \right]
\]  
(4.33)

\[
da_{nm}^{\text{total}} = \sum_{l=1}^{L} \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\nu} \left[ c_{\nu\mu}^{l} B_{\mu\nu}^{mn} \left( \vec{R}_{qd} \right) + d_{\nu\mu}^{l} A_{\mu\nu}^{mn} \left( \vec{R}_{qd} \right) \right]
\]  
(4.34)

**Scattering Properties**

When electromagnetic waves illuminate a collection of particles, the electromagnetic energy of the incident radiation is usually not only scattered but also absorbed by the particles. The presence of the particles results in extinction of the incident waves. The approach used by Xu [74] to derive the expressions for cross sections of a cluster of solid spheres, can be developed here for the case of the cluster of non-concentric spheres. Cross sections relations are extracted by calculating the net rate at which electromagnetic energy crosses the surface of an imaginary sphere enclosing the whole cluster. Here we consider only the case in which the surrounding medium is non-absorbing. The generalized transmission and reflection coefficients are also defined in [66] as functions of total, scattered and incident fields.

The Müller matrix and the amplitude scattering matrix are other parameters which can be used in exploring the scattering properties of the system. These matrices describe the relation between the incident and the scattered fields. The elements of the matrices can be found from the expansion coefficients of the incident and scattered fields. For instance, a derivation of analytical expressions for the four elements of the amplitude scattering matrix for a cluster of solid spheres is given in [64].

**Results and Discussion**

We used the method discussed in the previous sections (GMM) and developed a C++ code which would be useful in finding the electromagnetic properties of a cluster of non-concentric spheres. There is no limitation or assumption on the size, the material type and the relative location of the spheres. The only computational limitation is the number of modes. In the discussed method the number of modes in all of multipole expansions is infinity but to do the computations we need to
truncate it with a proper number $N$. Because of this truncation one can consider the explained method as a semi-analytic method. We know from Mie theory that by choosing a proper $N$ the effect of modes higher than $N$ is negligible. The proper value of $N$ is dependent to $kd$; $k$ is the wave number, which is a function of material properties of the structure at the operation frequency, and $d$ is representation of distances, which can be the radius of spheres and the distance between spheres or the position of the inclusion related to host origin (displacement).

Usually, exploring the properties of one eccentric sphere would be useful in engineering the cluster for a specific application. The electromagnetic properties, such as resonances, cross sections and far field, are tunable by the size and material of the Host and Inclusion spheres, displacement and other parameters like the angle of incident field with the displacement vector.

In the following, to verify the developed method, a few simple examples are solved and the results are compared to the results from commercial or verified simulators. For the first example, one solid dielectric sphere with relative permittivity $\varepsilon=4$ and radius $a=1$ m is excited by a plane wave $(E_x, k_z)$ at frequency $f=900$ MHz. The intensity of the scattered electric field in far field region as a function of $\theta$ when $\varphi=90$ is presented in Figure 4.2. The accuracy of the result is verified by the result from a Method of Moment (MoM) code developed in professor Mosallaei’s group.

![Figure 4.2: Intensity of scattered far field in dB as a function of $\theta$ for one solid dielectric sphere ($\varepsilon=4$ and radius $a=1$ m), excitation is a plane wave $(E_x, k_z)$ at frequency $f=900$ MHz](image)
As the next example, one non-concentric sphere is considered and the intensity of the scattered field in far field region as a function of $\theta$ and at $\varphi=90$ is plotted in Figure 4.3. The Host sphere is considered to be a dielectric with relative permittivity $\varepsilon=4$, and radius $a_H=2m$ and the Inclusion sphere is a dielectric $\varepsilon=2$ and radius $a_I=0.5m$. The displacement (in $+z$ direction) between the origin of the Host and Inclusion spheres is $d=1m$. The excitation is the same as previous example; a plane wave ($E_x$, $k_z$) but here the frequency is $f=400MHz$. The comparison between the results from the GMM and MoM simulations is presented in Figure 4.3.

![Figure 4.3: Intensity of scattered far field in dB as a function of $\theta$ for one non-concentric sphere. For the Host sphere ($\varepsilon=4$ and radius $a_H=2m$) and for the Inclusion ($\varepsilon=2$ and radius $a_I=0.5m$) displacement $d_z=1m$, excitation is a plane wave ($E_x$, $k_z$) at frequency $f=400MHz$](image)

To find the resonances frequencies one need to solve the problem in a frequency band. This has been done in the next example. An eccentric sphere has been considered. The Inclusion sphere is a dielectric with $\varepsilon=3$ and radius $a_I=12nm$. The Host has been considered to be made by silver and radius $a_H=22.5nm$. The Inclusion is displaced from the origin of the Host sphere in $+z$ direction by displacement value $d$. The excitation is again a plane wave ($E_x$, $k_z$). The observation point is in far-field region and located at $\theta=0$ and $\varphi=0$. The normalized electric field as a function of frequency when $d=0$, $d=3nm$ and $d=6nm$ is computed and the results are compared to the results from HFSS software in Figures 4.4, 4.5 and 4.6 respectively. Clearly GMM is leading to accurate results about the resonances frequencies while it is much faster and needs less memory compared to HFSS.
Figure 4.4: Normalized amplitude of the electric field in far field region as a function of frequency when the Host and Inclusion spheres are concentric ($d=0$)

Figure 4.5: Normalized amplitude of the electric field in far-field as a function of frequency when $d=3$nm
Other examples can be solved to explore the accuracy and compare computational statics of GMM to other methods. Different excitations can be considered; near field, far field, extinction coefficients and other parameters can be calculated as well. At this point, we can claim that GMM is a comprehensive and fast method which can accurately model interaction of electromagnetic radiation with a system of—not necessarily periodic arrangement of—solid, concentric or eccentric spheres. Certainly this solver would be of interest to a wide range of scientific fields and has numerous practical applications. For instance, as discussed in chapter 3, by using a concentric core/shell sphere and choosing appropriate materials and sizes for different layers, one can design a Double Negative (DNG) metamaterial [3]. Using non-concentric spheres instead of concentric ones can lead to more control on the location of electric and magnetic scattering coefficients and therefore a wider band DNG structure. On the other hand, in practice, sometimes the fabricated core/shell would not be perfectly concentrated and a fast method which can precisely model the eccentric particle would be useful. In the next section, some other interesting ideas and examples are discussed which GMM, with some modifications, can be useful and applicable.
**Some Interesting Applications**

**Upconverter**

Efficient photonic devices with excitation lights rely on the precise control of light–matter interactions. Whether photons are used for separating charges to produce electricity in solar cells or making electron-hole pairs or excitons in LED or laser applications, the efficiency of all energy conversion processes is regulated by light absorption in the active materials. To improve the interaction of photons with light absorbing media, metallic nanostructures can be used. Illumination of these nanostructures excites coherent oscillations of the conduction electrons, known as surface plasmons. Plasmons not only create substantial near-field intensities, but also modify the absorption and scattering cross-section of the nanostructure beyond its physical size. Coupling of incident light into Surface Plasmon Polaritons (SPP) increases Density of States (DoS) and subsequently increases the absorption. Alternatively, based on the excitation of Localized Surface Plasmon (LSP), metallic nanoparticles can be used to enhance the local electromagnetic field in the active region.

On the other hand, even if the photonic device were able to absorb all above bandgap light, its efficiency would be significantly limited by the transmission of sub-bandgap photons. For example, a solar cell with a bandgap of 1.8eV wastes nearly 54% of the incident solar power due to sub-bandgap transmission. The idea is that an upconverter structure can be designed to transform transmitted low-energy photons to higher-energy, above-bandgap photons, which can then be absorbed by the active region.

A random array of non-concentric spheres can be used as the upconverter structure. Metal shell leads to surface plasmon effects which increases absorption and also intensity of the electric field inside the active region. The non-concentric sphere with dielectric core and plasmonic shell can be designed to have a strong scattered field on a specific frequency band and have a strong internal field (inside the core) in another frequency band. Therefore, one can engineer the non-concentric structure to have a strong scattered field in a frequency band which contains the bandgap of the active region and, on the other hand, have a strong internal field in a frequency band which contains sub-bandgap layers energies. This means that, the upconverter region will increase the intensity of desired fields (with the frequency close to bandgap energy) in the active region.
region and decrease the unpleasant effects of sub-bandgap fields. Upconverter region in a solar cell and Quantum Well (QW), which can be LED or Laser, is presented in the figures 4.7 and 4.8.

**Figure 4.7:** A solar cell with an upconverter region separated by an electrically insulated layer

**Figure 4.8:** A QW (LED/Laser) with an upconverter region separated by an electrically insulated layer
In these designs the electromagnetic properties of layers of QW are very similar. It means that while from quantum mechanics point of view, layers of QW have different band structures but from electromagnetics point of view the permittivities are so similar. But to solve the problem in a general case and precisely one may need to solve the problem of an array of non-concentric spheres in a layered structure.

**Cell Counting**

Since 1978 in vitro fertilization (IVF) procedures have resulted in the birth of over 3 million babies. Till 2005, IVF procedures had a live birth rate of only 34%, with 32% of these births resulting in multiple pregnancies. These multiple pregnancies were directly attributed to the transfer of multiple embryos to increase the probability that a single, healthy embryo was included. The predominantly accepted noninvasive viability markers for embryos created by IVF are (1) number of cells at specific time points during development and (2) overall morphology of the embryo. A nontoxic cell-counting method is reported capable of counting cell numbers ranging from 8 to 26 in live mouse embryos [75]. The method is derived from the fusion of differential interference contrast and optical quadrature microscopy and is verified by epifluorescence images of Hoechst-stained nuclei. The diameter of a mouse embryo is approximately 100 µm, including the zona pellucid, and the diameter of a human embryo is approximately 130 µm. It seems that, having a solver to simulating cells development would be very useful. GMM can be modified to be applicable as the core of such a solver. In GMM, the spheres are completely inside or outside each other. In other words, it is assumed that the boundary of spheres do not have any intersection. The formulations and translation coefficients can be modified to the general case for the position of spheres with and without intersections. Then, many problems, such as the cell structures simulations, can be solved using the modified model. Some pictures from different number of cells are presented in figure 4.9. The results are from reference [75] and show different number of cells in spherical structures and located inside a spherical zona pellucid.
Conclusion

An analytical solution is derived to the problem of scattering of electromagnetic plane wave by an array of non-concentric spheres. The model is named Generalized Mie Method (GMM) because it can be applied to any (periodic or random) array of solid, concentric (core/shell) and non-concentric spheres. There is no restriction on the distance between spheres and their material. The restriction in the current method is that the spheres boundaries cannot have any intersection and the array is located in free space or a homogeneous medium. It is worth mentioning that making the problem more difficult computationally (very close spheres or large permittivities) the required number of modes to have a precise solution increases. This means that higher order modes are getting important in the multipole expansion of electromagnetic fields. The basis functions are vector spherical wave functions. Vector translation addition theorem is applied to transfer the basis functions between different coordinate systems and then the boundary conditions are imposed on the surface of various layers and a system of equations are created which yields to electric and magnetic scattering coefficients and electromagnetic fields in every points of space. This comprehensive analytic method which is numerically precise and computationally fast can be useful in design and simulation of a wide range of applications. Modifications in GMM can make

Figure 4.9: Differential Interference Contrast (DIC) image of live mouse embryos
it a powerful tool in simulation of wide range of applications which two of them are explained in the last section of this chapter.
Chapter 5

References


