CHAPTER 2

Theoretical Models and Simulations

2.1 Introduction

For practical applications, it is highly desirable to theoretically understand and predict the optical properties of nanostructures prior to their synthesis that will help the experimentalists to fabricate with the required plasmonic properties for a particular application with less effort, time, and cost. The theoretical developments in studying the plasmonic properties of spherical metal nanoparticles start from the time of Gustav Mie by providing analytical solution of Maxwell’s equations and later on, several extensions to his Mie theory exists for ellipsoidal shape particles and coated nanospheres but along with the advancement in synthesis techniques of arbitrary shape nanoparticles, few numerical approaches are available nowadays to theoretically predict and simulates the optical properties of complex shapes not possible with the analytical methods. The used analytical and numerical techniques in the present work depending on the geometry of the nanostructure in order to calculate the optical properties are discussed.

2.2 Mie theory and its extensions

Mie (1908) developed an analytical solution describing the full calculation of scattering of a plane EM wave from a sphere of arbitrary size and material, known as Mie theory. This theory based on assumptions that the sphere and its surrounding medium are homogeneous in nature and can be described by bulk dielectric functions of the material. However, Mie was able to provide the exact solution for a single spherical nanoparticle of arbitrary size in non-absorbing medium but for other non-spherical geometries, it is not possible to solve the Maxwell’s equations exactly. Therefore, some approximations are needed to be used in order to calculate their optical absorption and
scattering properties. Gans (1912) provided the exact analytical theory to calculate the optical properties of nano-spheroids such as oblate and prolate nanoparticles of arbitrary aspect ratio within the dipolar approximation limit. Later on, Aden and Kerker (1951) were the first to extend the Mie theory for the coated spherical nanoparticles and since then many algorithms have been developed but the code given by Bohren and Huffman (1998) is mostly used for predicting the optical properties of coated nanospheres. In this thesis, the FORTRAN based Mie theory is used for spherical alloy nanoparticles and its approximation called Gans theory for prolate nanoparticles with the inclusion of surface scattering, radiation damping, and dynamic depolarization effects and further, the code given by Bohren and Huffman for coated spheres has been used. The detailed theoretical description of these theories has been described in the next chapters while discussing the results.

Analytically, it is not possible to solve the Maxwell’s equations for complex shape nanoparticles; therefore, their optical properties cannot be described. Moreover, these theories cannot be applied to interacting particles and other complex shape nanostructures. In order to overcome this limitation, various light scattering numerical techniques has been developed, including Discrete Dipole Approximation (DDA), Finite Difference Time Domain Method (FDTD), and Finite Element Method (FEM) (Wriedt & Comberg, 1998; Wriedt, 2012). Among these, the DDA is considered as one of the most powerful and frequently used simulation package (Liz-Marzan, 2006; Jain et al., 2006; Bok et al., 2009; Cho et al., 2009; Alves et al., 2012) for theoretically predicting the optical properties of arbitrary shape isolated nanostructures and their arrays. Therefore, DDA is used in the present studies and its details are discussed below.
2.3 Discrete dipole approximation (DDA)

The DDA was first introduced by Purcell & Pennypacker (1973) that enables to calculate the optical absorption and scattering from the targets of arbitrary shapes (Coronado & Schatz, 2003; Sosa et al., 2008; Ungureanu et al., 2009). Its theory was reviewed and further developed by Draine and collaborators (Draine, 1988; Draine & Flatau, 1994; Draine & Flatau, 2008) which has become an important computational tool nowadays to calculate the absorption and scattering of electromagnetic waves from targets with arbitrary geometries, size, and composition. In this approximation, the whole target is divided into an array of \( N \) polarizable dipoles located on a cubic lattice at vector positions \( r_i \) and these dipoles are characterized by their polarizabilities \( \alpha_i \), where \( i = 1, 2, \ldots N \). This polarizability is due to the local field \( E_{\text{loc},i}(r_i) \) experienced by each dipole which is the sum of the applied external field \( E_{\text{inc},i} \) and the field induced due to the interaction of the \( i^{\text{th}} \) dipole with other \( N-1 \) dipoles i.e. \( E_{\text{dip},i} \). Therefore, the local field at each dipole can be given by: (Brioude et al., 2005)

\[
E_{\text{loc},i}(r_i) = E_{\text{inc},i} + E_{\text{dip},i} = E_0 e^{ikr_i} - \sum_{i \neq j=1}^{N} A_{ij} P_j
\]

(2.1)

where \( k \) and \( E_0 \) represent the wave vector and the amplitude of the incident wave. The second term of the above equation represents the contribution to local EF at position \( r_i \) due to the dipole at a position \( r_j \) which is given as:

\[
A_{ij} P_j = \frac{e^{ikr_{ij}}}{r_{ij}^3} \left\{ k^2 r_{ij} \times (r_{ij} \times P_j) + \frac{(1-ikr_{ij})}{r_{ij}^2} \left[ r_{ij}^2 P_j - 3 r_{ij} (r_{ij} \cdot P_j) \right] \right\}
\]

(2.2)

The induced dipole moment \( P_j \) of the each dipole in the cubic array in the presence of the incident plane wave can be determined as:
\[ P_j = \alpha_j E_{loc,j}(r_j) \]  

(2.3)

where \( A_j \) is an interaction matrix with \( 3N \times 3N \) matrices as elements described by the Equation 2.2. This gives rise to a system of \( 3N \)-complex linear equations given by Equation 2.3, which are solved by using the fast Fourier transform to obtain the induced dipole moments \( P_j \) in terms of which the absorption and extinction cross-sections from the desired target can be obtained as: (Draine, 1988; Duan & Xuan; 2011)

\[
\begin{align*}
C_{abs} &= \frac{4\pi k}{|E_0|^2} \sum_{i=1}^{N} \left\{ \text{Im}[P_i (\alpha_i^{-1})^* \cdot P_i^*] - \frac{2k^3}{3} |P_i|^2 \right\} \\
C_{ext} &= \frac{4\pi k}{|E_0|^2} \sum_{i=1}^{N} \text{Im}(E_{inc,i}^* \cdot P_i) 
\end{align*}
\]

(2.4)

(2.5)

where the superscript asterisk (*) is the complex conjugate symbol and (Im) denotes the imaginary part. For these calculations, more recent version of DDASCAT7.2, a FORTRAN implemented computer code of the DDA that efficiently supports fast calculations of the EF within and near the target adapted by Draine and Flatau (2012) is used. Further, the absorption, extinction, and scattering efficiencies are expressed as:

\[
\begin{align*}
Q_{abs} &= \frac{C_{abs}}{\pi a_{eff}^2} \\
Q_{ext} &= \frac{C_{ext}}{\pi a_{eff}^2} \\
Q_{sca} &= Q_{ext} - Q_{abs}
\end{align*}
\]

(2.6)

(2.7)

(2.8)

where \( a_{eff} \) is the effective radius of the target which is defined as the radius of a sphere having a volume equal to that of the target and can be calculated as \( a_{eff} = \left(\frac{3V}{4\pi}\right)^{\frac{1}{3}} \) with \( V \) as the volume of the target of arbitrary shape as shown in Figure 2.1.
As a matter of fact, the surface dipoles on the cubic lattice are weaker than the inner dipoles which lead to an overestimation in the calculated cross-sections, known as the spurious surface effect. In order to suppress this effect and for precise applicability of the DDA, the DDSCAT authors recommend that the inter dipole separation should be small compared to the dimensions of the target and the wavelength of incident light. For this, a sufficient number of dipoles could be used to accurately represent the target where the results converge. It was suggested that the number of dipoles \( N \geq 10^4 \) for any arbitrary target is a good starting number (Sosa et al., 2003). To ensure the results with good accuracy, the number of dipoles should increase but the problem is increasing in the computational time. Therefore, despite its applicability to different shapes, the DDA has the drawback that there is a tradeoff between computational time and accuracy.

**Figure 2.1:** Schematic of a nanosphere in terms of discrete dipoles located in a cubic lattice.