A comparison of techniques used to simulate the scattering of electromagnetic radiation by metallic nanostructures

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ABSTRACT

A comparison is presented of a number of simulation techniques which are used to compute the scattering of electromagnetic radiation by metallic nanostructures. The simulation techniques considered here are Mie theory, the T-Matrix null-field method, the discrete-dipole approximation, the finite-element method and the finite-difference time-domain method. The suitability of each technique is compared in terms of the accuracy, computation time and the range of geometries to which it can be applied. Using each technique, we perform example calculations by simulating the optical response of a 80 nm diameter Au sphere in vacuum. Our main conclusions are summarised in tabulated form, so that the findings presented in this article may serve as a useful reference guide to those looking for suitable numerical tools to model the optical response of metallic nanostructures.

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I. INTRODUCTION

Controlling and manipulating light at the nanoscale is a rapidly expanding field of research, enabled by advances in both fabrication techniques and improved capabilities in numerical simulation. Good simulations are valuable in developing a better understanding, in guiding experiments, and in exploring realms not easily accessed by experiment. For those entering this area and wishing to carry out their own simulations, or better appreciate the simulations of others, there appears to be a wide and rather confusing array of techniques on offer. It is the purpose of the present contribution to give an introduction to the numerical simulation techniques, particularly with reference to the scattering of light by a simple metallic nanostructure, a gold nanosphere in vacuum.

A comprehensive review is beyond the scope of the present contribution. Instead, we focus our attention on five common techniques, these being **Mie Theory**, the Transition Matrix 'null-field' method **(T-Matrix)**, the discrete-dipole approximation **(DDA),** the finite-element method **(FEM)** and the finite-difference time-domain (**FDTD**) method. Our simulations were conducted using a Dell Vostro 200 computer, with a dual-core processor (each having a clock speed of 2.19 GHz) and 2 Gb of RAM.

II. SIMULATION TECHNIQUES

Here we give a very brief outline of the different techniques. References are provided which contain a more detailed description of each approach, and a good comparison is set out by Kahnert [1].

a) Mie Theory

Mie Theory (**Mie**) is a solution of the Maxwell equations applicable to the scattering of an incident plane wave by a spherical, isotropic and non-magnetic particle in a non-absorbing isotropic medium [2,3]. Assuming that in the region of interest there are no sources (charges or currents) then the Maxwell equations can be written as,

$$\nabla \wedge \mathbf{H}(\mathbf{r},t) = \varepsilon(\mathbf{r})\frac{\partial \mathbf{E}(\mathbf{r},t)}{\partial t} \quad (1)$$

$$\nabla \wedge \mathbf{E}(\mathbf{r},t) = -\mu(\mathbf{r})\frac{\partial \mathbf{H}(\mathbf{r},t)}{\partial t} \quad (2)$$

$$\boldsymbol{\nabla} \cdot \mathbf{E}(\mathbf{r},t) = 0 \quad (3)$$

$$\boldsymbol{\nabla} \cdot \mathbf{H}(\mathbf{r},t) = 0 \quad (4)$$

From the Maxwell equations one can in turn show that a time-varying electromagnetic-field (**E**, **H**) in an isotropic medium must satisfy the Helmholtz wave equations (equations 5 and 6).

$$\nabla^2\mathbf{E} + \mathrm{k}^2\mathbf{E} = 0 \quad (5)$$

$$\nabla^2\mathbf{H} + \mathrm{k}^2\mathbf{H} = 0 \quad (6)$$

where

$$k^2(\mathbf{r}) = \omega^2\varepsilon(\mathbf{r})\mu(\mathbf{r})/c^2 \quad (7)$$

The essence of Mie theory is to consider the scattering of light by a spherical object. Taking advantage of the symmetry of the sphere, the scattered fields are expressed in terms of vector spherical harmonics. In this approach the field vectors **E** and **H** are replaced by the vectors $\mathbf{M}_n$ and $\mathbf{N}_n$. The subscript *n* indicates that different vector spherical harmonics are used to describe dipolar (*n* = 1), quadrupolar (*n* = 2) etc. contributions to the scattered field. The scattered fields are related to these vector spherical harmonics through,

$$\mathbf{E}_s = \sum_{n=1}^{\infty} \mathbf{E}_n\left(ia_n\mathbf{N}_{e1n} - b_n\mathbf{M}_{o1n}\right) \quad (8)$$

$$\mathbf{H}_s = \frac{k}{\omega\mu}\sum_{n=1}^{\infty} \mathbf{E}_n\left(ib_n\mathbf{N}_{o1n} + a_n\mathbf{M}_{e1n}\right) \quad (9)$$

In equations 8 and 9, $\mathrm{E}_n = i^n\mathrm{E}_0\frac{(2n+1)}{n(n+1)}$, $\mathbf{E_0}$ being the incident field. In the subscripts of **M** and **N**, '*o*' and '*e*' represent the *odd* and *even* branches of the azimuthal solution to the vector form of the Helmholtz wave-equation, *1* denotes the *m* = *1* terms of the Legendre and Bessel

series. The a_n, and b_n terms are referred to as the Mie coefficients, which determine the relative amplitudes of the vector spherical harmonics when excited with a particular wavelength of light, these are given by:

$$a_n = \frac{\bar{n}^2\, j_n(\bar{n}x)[xj_n(x)]' - \bar{\mu}\, j_n(x)[\bar{n}xj_n(\bar{n}x)]'}{\bar{n}^2\, j_n(\bar{n}x)\left[xh_n^{(1)}(x)\right]' - \bar{\mu}\, h_n^{(1)}(x)[\bar{n}xj_n(\bar{n}x)]'} \tag{10}$$

$$b_n = \frac{\bar{\mu}\, j_n(\bar{n}x)[xj_n(x)]' - j_n(x)[\bar{n}xj_n(\bar{n}x)]'}{\bar{\mu}\, j_n(\bar{n}x)\left[xh_n^{(1)}(x)\right]' - h_n^{(1)}(x)[\bar{n}xj_n(\bar{n}x)]'} \tag{11}$$

where $\bar{n} = n_1 / n_2$ is the relative refractive index (n_1 is the complex refractive index of the particle, n_2 is the refractive index of the surrounding medium), $\bar{\mu} = \mu_1 / \mu_2$ (μ_1 is the complex relative magnetic permeability of the particle, μ_2 is the complex relative magnetic permeability of the surrounding medium), $x = 2\pi n_2 a/\lambda$ is the size parameter (a is the radius of the sphere and λ is the wavelength in vacuum), $j_n$and $h_n$are the spherical Bessel functions and spherical Hankel functions of order n respectively. The primed terms in equations 10 and 11 indicate differentiation of the functions with respect to their argument. It is thus in the a_n, and b_n terms that the size and relative permittivity and permeability of the sphere are included.

When evaluating the electromagnetic scattering response of metallic nanoparticles, the magnitudes of the scattering cross-section, σ_{sca}, and scattering efficiency, Q_{sca}, are often used. The scattering cross-section is defined as the integral of the modulus of the scattered electric-field squared across a spherical surface in the far-field, which is subsequently normalised by the incident irradiance $|\mathbf{E}_i|^2$ (equation 12). The scattering efficiency is equal to the scattering cross-section normalised by the geometrical cross-sectional area of the scatterer (equation 13).

$$\sigma_{sca} = \frac{k}{|\mathbf{E}_i|^2}\int_{dS} |\mathrm{E}_{\mathrm{scattered}}(\boldsymbol{r}').\hat{\boldsymbol{r}}|^2\, dS \tag{12}$$

$$Q_{sca} = \frac{\sigma_{sca}}{\pi a^2} \tag{13}$$

One can easily calculate the a_n and b_n coefficients using computer codes, from which the scattered field can be derived using equations 8 and 9. Mie Theory can also be extended to simulate other spherically symmetric geometries such as dielectric particles with metallic coatings [2,3].

b) The 'T-Matrix' null-field method

As we have previously seen in discussing Mie Theory, the linearity of the Maxwell equations ensures a direct relationship between the coefficients of the vector spherical harmonics of the incident and scattered electric- and magnetic-fields. In the matrix representation (equation 14), the operator which relates the coefficients is termed the Transition Matrix (the **T-Matrix**).

$$\begin{bmatrix} a_n^{scattered} \\ b_n^{scattered} \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} a_n^{incident} \\ b_n^{incident} \end{bmatrix} \tag{14}$$

The 'T' terms in equation 14 correspond to elements of the T-Matrix, ($a_n^{scattered}$, $b_n^{scattered}$) and ($a_n^{incident}$, $b_n^{incident}$) are the coefficients of the scattered- and incident-field respectively. The elements of the T-Matrix depend only on the relative refractive index of the particle $m = n_1 / n_2$ (n_1 is the complex refractive index of the particle, n_2 is the refractive index of the surrounding medium), the size parameter $x = 2\pi n_2 a/\lambda$ (a is the radius of the sphere and λ is the wavelength in vacuum), and the orientation of the particle with respect to the coordinate system] [4-8].

For a spherical scatterer, the a_n and b_n terms in equation 14 are equal to the weighting coefficients of the vector spherical harmonics in equations 10 and 11. A number of techniques may be used to compute the T-Matrix, very often the 'null-field' method is used. Here the incident plane wave is expanded into a series of spherical harmonics, and the coefficients of the incident- and internal-fields are matched at the particle boundary. To simplify the mathematical analysis, the internal polarization currents are described by an equivalent distribution of electric and magnetic currents across the surface of the particle [9].

The surface of the scatterer is discretised into a finite number of point sources, at which both the internal field and surface current density are determined. Each point source radiates a spherical electromagnetic wave which arises from the tangential components of the electric and magnetic currents at the surface of the particle. The scattered-field is the wave-front which is obtained by summing the partial waves from all sources over the particle surface.

There are several T-Matrix codes which are available as open-source applications for use on Unix and Windows operating systems (http://www.t-matrix.de). A rigorous derivation of the T-Matrix 'null field' method can be found in the literature [4]. The key advantage of the T-Matrix technique is that the T-Matrix is the property of a particle. Once it has been determined the scattered fields may be computed for any particle orientation without having to solve the problem from scratch. The T-Matrix method can also be used to model the optical response of arrays of symmetric particles.

c) The discrete-dipole approximation (DDA)

In the discrete-dipole approximation (**DDA**) each particle is modeled as an assembly of finite cubic elements. Each of these elements is considered sufficiently small that only dipole interactions with the incident electric-field and the induced-fields in neighboring elements need to be considered. This reduces the solution of the Maxwell equations to an algebraic problem of many coupled dipoles [10]. Each of the dipoles within a continuous assembly acquires a dipole moment in response to both the external electric-field, and the electric-fields from neighbouring dipoles. The radiated electric-field of an individual dipole may be approximated as [11,12]:

$$\mathbf{E}_{\text{dipole}} = \frac{e^{\frac{i\omega d}{c}}}{4\pi\varepsilon_0}\left[\frac{\omega^2}{c^2 d}\hat{\mathbf{r}}\wedge\mathbf{p}\wedge\hat{\mathbf{r}} + \left(\frac{1}{d^3} - \frac{i\omega}{cd^2}\right)[3(\hat{\mathbf{r}}.\mathbf{p})\hat{\mathbf{r}} - \mathbf{p}]\right] \qquad (15)$$

Here $\hat{\mathbf{r}}$ is a unit vector associated with a vector **r** which is taken from the dipole to the location at which the electric-field is sampled, d is the distance to the sampling point, **p** is the vector associated with the induced dipole moment, ω is the angular frequency of the scattered radiation and ε_0 is the permittivity of free space. In solving for the scattering characteristics of the continuous assembly, each dipole in the cubic array has an induced dipole moment $\mathbf{P}_i = \alpha_i \mathbf{E}_{\text{local}}$. Here α_i is the polarizability of the material associated with the dipole element – it is

through the polarizability of the element that the materials parameters enter the problem. $\mathbf{E}_{\text{local}}$ is the electric-field at $\boldsymbol{r}_i$ due to the incident wave ($\mathbf{E}_{\text{inc},i}$), plus a contribution $\mathbf{E}_j$ from all other dipoles (j), and:

$$\mathbf{E}_{\text{local}} = \mathbf{E}_{\text{inc},i} + \sum_{\substack{j=1 \\ i \neq j}} \mathbf{E}_j \tag{16}$$

The interaction matrix ($\mathbf{A}_{ij}$), shown in equation 17 characterises the sum of the retarded fields from all other dipoles, hence the summation in equations 17 and 18 is performed over all j, with the exception of $i = j$.

$$\mathbf{E}_{\text{local}} = \mathbf{E}_{\text{inc},i} - \sum_{\substack{j=1 \\ i \neq j}}^{N} \mathbf{A}_{ij}\mathbf{p}_j \tag{17}$$

$$\mathbf{A}_{ij}\mathbf{p}_j = k^2 \mathrm{e}^{ikr_{ij}} \left(\frac{\hat{\mathbf{p}}_j \left(\mathbf{r}_{ij\wedge} \left(\mathbf{r}_{ij\wedge} \mathbf{p}_j \right) \right)}{r_{ij}^3} \right) + \mathrm{e}^{ikr_{ij}} \left(1 - ikr_{ij}\right) \left(\frac{r_{ij}{}^2 \mathbf{p}_j - 3\hat{\mathbf{p}}_j \left(\mathbf{r}_{ij} (\mathbf{r}_{ij} \cdot \mathbf{p}_j) \right)}{r_{ij}^5} \right) \tag{18}$$

where $i = 1,2....N$, $j = 1,2....N$ and $i \neq j$.

In equation 18, $\mathbf{r}_{ij}$ and $\mathbf{p}_j$ represent the positions and induced dipole moments of each element within the array. The $\hat{\mathbf{p}}_j$ terms represent the projection along the unit vector of the dipole moment $\mathbf{p}_j$. As previously discussed, once the scattered electric-field associated with the collection of dipoles has been determined, the scattering efficiency (Q_{sca}) may be calculated by performing the integral in equation 12. Very efficient methods for solving the matrix equations have been developed which utilize fast-Fourier-transform and complex-conjugate-gradient methods, and as a result it is possible to employ thousands of dipoles in routine calculations [13]. DDSCAT [14] is an open-source Fortran-based code which uses the DDA to compute the optical response of both metallic and dielectric nanostructures.

d) Finite-element method (FEM)

The finite-element method (**FEM**) is based on solving the scattering problem in the frequency domain by modelling by discretising Helmholtz' equation (equations 5 and 6) in

space and then solving numerically to find fields that satisfy the boundary conditions: these are (i) that the tangential field components are continuous across the surface of the particle, and (ii) (the radiation condition) that fields decay into the far-field no slower than 1/r for large r). Material parameters enter through the wavevector (equation 7). The overall problem space is discretised into many smaller regions, the grid mesh, which very often are tetrahedral. The electric- and magnetic-fields inside each region are described by a local function. Since the tetrahedra have flat faces they cannot exactly represent the surface of a sphere, but by using enough of them a sufficiently accurate polyhedral approximation is possible [15]. A key point in the FEM approach is that one has to avoid the scattered fields being reflected at the boundary of the computational domain (for the case of an isolated particle anyway) – such reflections would provide spurious artefacts in the computation.

It is possible to assess the accuracy of the numerical solution by comparing results from a sequence of successively refined meshes. The solutions often have geometric features such as localized regions of high field-gradient. In this case it is more economical to refine the mesh selectively, (i.e., only where these high gradients occur). Such adaptive refinement procedures generate a sequence of solutions on successively finer meshes, at each stage selecting and refining those elements at which the gradient of **E** or **H** is largest between adjacent elements. In practice, the process is terminated when the gradient of the fields between adjacent tetrahedra falls below a preset limit, or if the total number of elements are such that the computation time for the simulation exceeds a specified duration (both of these constraints are chosen by the user). Ansoft's High Frequency Structure Simulator (HFSS)^{TM}, and Comsol^{TM} are examples of commercial FEM modelling software. The Free Finite-element Package (http://www.ffep.sourceforge.net) is an example of an open-source application.

e) Finite-difference time-domain method (FDTD)

Finite-difference time-domain (**FDTD**) computations involve discretisation of time and space, i.e. all spatial and temporal derivatives in the Maxwell curl equations (equations 1 and 2) are replaced by finite difference quotients. Typically a Cartesian volume element of sides Δx, Δy, Δz, is used for the space discretisation (there are several methods used for discretisation, the most common being the Yee scheme [18-19]), and a time step Δt for the time discretisation [20]. The essence of the FDTD approach is to inject a plane wave at

some initial time and compute new field components from differences calculated using the field components that applied during the previous time interval. In fact the electric field vector components in the volume element are solved at a given instant in time, then the magnetic field vector components in the same volume element are solved at the next instant in time and so on. This process is continued iteratively until the transient solution for the fields has converged to a steady-state solution. The near-field solution that one obtains for the fields inside the computational domain is then Fourier transformed into the frequency domain and subsequently propagated into the far-field, using either a surface integration technique or a volume integration technique. As discussed with the FEM approach, when simulating individual particles using the FDTD method one has to avoid the scattered fields being reflected at the boundary of the computational domain..

Since the FDTD method is solved in the time-domain, dispersion information must be specified over a much wider range of frequencies than simply the range of interest. It is therefore necessary for the permittivity of metallic structures to be approximated using a frequency-dependent permittivity model, as opposed to using experimental values, which may not necessarily cover the required range. FDTD simulations conventionally use a Drude-Lorentz model (equation 19) to represent permittivity values, ω is the angular frequency of the incident radiation and the parameters ε_∞, ω_d, γ_d, Γ_l, Ω_l and $\Delta\epsilon$ are constants which are fitted against experimental relative permittivity values [21-22].

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_d^2}{\omega(\omega + i\gamma_d)} - \frac{\Delta\epsilon.\,\Omega_l^2}{(\omega^2 - \Omega_l^2) + i\Gamma_l\omega} \qquad (19)$$

The optical response in the frequency domain is determined by taking a Fourier transform of the time-domain signal associated with the scattered electric- and magnetic-field distributions. Commerical FDTD software packages include Lumerical FDTD Solutions™ and Remcom Xfdtd™. The MIT Electromagnetic Equation Propagation (http://ab-initio.mit.edu/wiki/index.php/Meep) package is an example of an open-source FDTD application.

III. SUITABILITY OF EACH TECHNIQUE

Mie theory is the preferred option for simulating the optical response of metallic nanospheres since in principle it offers an exact solution for the scattering of electromagnetic radiation by spherical geometries which is limited only by the truncation order of the solution [3]. In contrast to DDA, FEM modeling or the FDTD method, the accuracy of the Mie Theory solution does not depend on resolution-limited parameters such as the inter-dipole spacing or element length. It was previously shown that the scattered-field can be represented as a sum of vector spherical harmonics. If this sum is performed over an infinite number of harmonics (equations 8 and 9) the result would constitute an exact solution for the case of the interaction between an incident plane wave and a spherical scatterer. In practice, however, the sum is truncated at a finite number of terms, and the accuracy of the solution will therefore depend on the truncation order. The T-Matrix method can also be used to simulate spherical particles since for a spherical particle the scattered electric- and magnetic-fields simplify to those obtained using Mie Theory. Both Mie Theory and T-Matrix methods can be used to compute the scattered-field more rapidly in comparison to the other approaches (the DDA, FEM and FDTD methods), with the computation time being proportional to (r / λ), where r is the sphere radius and λ is the incident wavelength [6]. However, for spheres with radii less than 1μm which are simulated at visible frequencies, the computation time is extremely rapid and the dependence on the size of the sphere often goes unnoticed. To evaluate the scattering efficiency (Q_{sca}) for a 80 nm diameter Au sphere at one particular frequency takes approximately 1.0×10^{-3} seconds using both Mie Theory and T-Matrix methods. A comparison between the measured and simulated optical response of a metallic nanosphere is discussed elsewhere [23,24].

If the particle under consideration is non-spherical, but has planar symmetry, or is axially symmetric, it is possible to use the T-Matrix method to compute the scattering characteristics. The majority of T-Matrix codes contain embedded routines which are specifically adapted to match the boundary conditions relating the internal-, incident- and scattered-fields for various geometries such as spheres, cylinders, cones and stratified particles. As with Mie Theory, the computation time also scales according to the ratio between the particle size and the incident wavelength. The truncation of the field expansions can introduce rounding errors, which for the T-Matrix method may be significant for sufficiently elongated or flattened objects.

Mischenko has conducted an extensive study into the effects of particle size on the convergence of the solutions which are derived from the T-Matrix method [4].

The DDA can also be utilised to evaluate the scattering properties of isotropic non-spherical particles which are axially-symmetric or posses other planes of symmetry. The fundamental concept of this approach is that a solid particle is replaced by an array of N point dipoles on a cubic lattice which has a period that is significantly smaller than the wavelength of the incident radiation. The computation time of the simulation is therefore heavily dependent on the inter-dipole spacing and the total number of dipoles which are used to replicate the original scattering object. For example, the time to evaluate the scattering efficiency of a 80 nm diameter Au sphere using an inter-dipole spacing of 3 nm is approximately 48 seconds for one particular frequency of light. This is significantly longer than the Mie Theory solution, which takes only 10^{-3} seconds per frequency. If the inter-dipole spacing is increased to 4 nm the computation time using the DDA is halved to 24 seconds. The limiting factors which affect the computation time of the DDA are the CPU speed and RAM of the workstation used. The RAM requirement, as specified by the program, is given by equation 20 where N_x, N_y, and N_z are the number of dipoles which are distributed across the scattering particle in the x, y and z directions respectively [14].

$$\text{Minimum RAM} = (1690 + 0.764(\ (N_x \times N_y \times N_z))) \times 10^3 \text{ bytes} \qquad (20)$$

From equation 20 one can show that in order to simulate a cuboid with side of length 80 nm using an inter-dipole spacing of 1 nm, a minimum of 0.5 Gb of RAM is required. Whilst the DDA solution converges to the Mie theory result as the inter-dipole spacing approaches zero, there is a compromise between the accuracy of the simulation and the computation time. There is thus a significant disadvantage in terms of computation time associated with using the DDA as opposed to the more rapid T-Matrix method for simulations where the restrictions of the T-Matrix approach are not an issue. Where such restrictions are an issue the DDA is often the preferred approach for evaluating the scattered-field distribution of arbitrarily shaped objects, as one can specify a series of dipole locations in tabulated form.

For some particle or sample geometries, Mie Theory, the T-Matrix method and the DDA are not appropriate techniques for simulating the electromagnetic response. For example, these

techniques cannot be used to simulate the optical response of a two-dimensional periodic array of metallic particles which are not rotationally or axially symmetric. This is because Mie Theory computes the scattered electric- and magnetic-field distributions associated with an individual spherical particle and does not consider the effects of electromagnetic coupling which may occur between particles in a periodic array -. Similarly, the T-Matrix method can become numerically unstable for geometries which are not rotationally or axially symmetric, for reasons discussed previously.

Whilst the DDA may be used to evaluate the optical response of two or more interacting particles of arbitrary shape, it is impractical for simulating periodic arrays of particles. To simulate even a small two-dimensional array of particles using the DDA requires a hardware specification exceeding that which was available here, since the total number of dipoles is directly proportional to the number of particles in the array. By referring to equation 20, one sees that a minimum of 4.5 Gb of RAM is required to simulate the optical response of a 3×3 array (nine) metallic cuboids, each with side of length 80 nm using an inter-dipole spacing of 1 nm.

When such limitations restrict the use of Mie Theory, the T-Matrix method or DDA, it is preferable to use either FEM modelling or the FDTD method. In these techniques, the electromagnetic field distribution is computed within an individual unit cell of the array, and periodic boundary conditions (PBCs) are applied along the edges and faces of the unit cell. The PBCs equate both the magnitude and direction of the electric- and magnetic-fields associated with tetrahedral elements which lie on parallel boundaries across the unit cell. The implementation of PBCs is advantageous, since the scattered electric- and magnetic-field distributions need only be computed for a single unit cell rather than for every lattice site within the array. This significantly reduces both the computation time and the required hardware specification for both FEM modelling and the FDTD method when compared to the DDA.

When using FEM modelling or the FDTD method to compute the optical response of a single particle, PBCs are not required. Instead, perfectly matched layers (PMLs) are used to absorb the radiation which is scattered by the structure. The refractive index of the PML is optimised such that radiation which impinges on the interface of the PML experiences a transmission coefficient which is equal to unity. Beyond the interface, the imaginary component of the complex refractive index is gradually increased as a function of depth into

the PML, so as to absorb the scattered radiation as it propagates into the medium. The range of frequencies and incident angles for which the PML absorbs radiation is specified by the user [20].

When computing the optical cross-sections of individual nanoparticles, Mie Theory, the T-Matrix method and the DDA may be extended in order to consider the effects of a substrate interaction [25-27]. However, it is less straightforward to perform these simulations using FEM modeling or the FDTD method, as these techniques cannot distinguish between the scattered electric- and magnetic-fields which are associated with the individual particle, and those which are associated with the substrate. This inability to distinguish between the scattered-fields leads to the magnitude of the simulated optical cross-sections being scaled according to the size of the unit cell.

Whilst the FEM or FDTD techniques may be used to determine the scattered electric- and magnetic-field distributions of both individual particles and periodic arrays of particles, they are the most time consuming of all the approaches considered. The time to compute the scattering efficiency using FEM modelling for an 80 nm diameter Au sphere at one particular frequency of light is 144 seconds (using a tetrahedral mesh with a minimum element length of 3.11 nm). To compute 100 frequency points across the visible range therefore requires a total simulation time of approximately 4 hours. When using the FDTD method, the time to compute the scattering efficiency across the visible frequency region is approximately 3 hours (using a mesh with a minimum element length of 3 nm).

As was previously discussed in relation to the DDA, when using the FEM and FDTD techniques a compromise has also to be made between the computation time and the level of discretisation. In considering the effects of workstation specification, the required computation time for FEM modelling and the FDTD method is limited in order of importance of CPU speed, RAM and hard drive space. The computation time which is required to solve the matrices for each tetrahedron (FEM) or cubic element (FDTD) is heavily dependent on CPU speed, and a direct correlation exists between the CPU speed and computation time. The software utilises RAM as a temporary storage area for the rapid reading / writing of matrix elements in regions where the vector-field quantities are being solved. Once the field quantities for a particular tetrahedron (FEM) or cubic element (FDTD) have been determined, they are written permanently to disk. Problems can occur if the RAM of the system is

limited, as the hard drive is then used as an alternative storage facility. This considerably lengthens the computation time as the read/write speed of the hard drive is significantly slower than that of the RAM module.

IV. EXAMPLE CALCULATIONS

In this section, each technique is used to simulate the scattering efficiency (Q_{sca}) of a 80 nm diameter gold (Au) sphere in vacuum, which is illuminated with an incident plane wave. In these simulations, we also ignore any non-local contributions to the response [23,28]. For Mie Theory, T-Matrix, DDA and FEM techniques, the Au permittivity values are obtained from data published by Johnson and Christy [22]. The permittivity values used for FDTD simulation are derived from a Drude-Lorentz model using parameters from reference sources [21,22].

Figure 1 shows the real and imaginary components of the permittivity values of gold as a function of wavelength obtained from data published by Johnson and Christy [22] (used for the Mie Theory, T-Matrix, DDA and FEM simulations) and a Drude-Lorentz model with parameters $\varepsilon_\infty = 5.9673$, $\omega_d = 1.32 \times 10^{16}$ Hz, $\gamma_d = 1.00 \times 10^{14}$ Hz, $\Gamma_l = 6.60 \times 10^{14}$ Hz, $\Omega_l = 4.10 \times 10^{15}$ Hz and $\Delta\epsilon = 1.09$ [21,22] (used for the FDTD simulation). In Figure 2 the simulated Q_{sca} values are plotted as a function of wavelength for a 80 nm diameter Au sphere in vacuum using **Mie Theory** (www.iap.unibe.ch/publications/download/201/en/), the **T-Matrix** method (http://www.t-matrix.de), the **DDA** (DDSCAT [14] version 6.1), **FEM** modelling (Ansoft HFSS™ version 11.0) and **FDTD** (Lumerical FDTD Solutions™ version 5.0). The DDA and FDTD methods use a 3.00 nm inter-dipole spacing and element length respectively, whilst the minimum element length for the FEM simulation is 3.11 nm. For each of the simulation techniques considered, the scattering efficiency curves exhibit maxima at a wavelength of 525 nm. These maxima are associated with the excitation of the localized surface-plasmon resonance of the structure [3,9,28].

The Mie Theory and T-Matrix methods both show good agreement across the frequency range studied. These methods in principle offer an exact solution for the scattering of electromagnetic radiation from spherical geometries and are limited only by the truncation order used to obtain the solution. For the structure considered here, the maximum recommended truncation order (n_{max}) is 8 for both Mie Theory and T-Matrix methods [2].

The relative error of the truncated solution is less than 0.001% when compared to the exact solution. It is impractical to continue the summation beyond $n = 8$ as the magnitudes of the field quantities become extremely small, such that they are comparable to the numerical rounding errors which are introduced by the mathematical modelling software. Unlike the other techniques, the errors associated with Mie Theory and the T-Matrix method arise from numerical rounding, and not the level of discretisation used for the calculation.

The scattering efficiency curves in Figure 2 for the DDA, FEM and FDTD methods are for comparable levels of discretisation. Figures 3 and 4 show simulated Q_{sca} obtained using an exact Mie Theory solution compared with those obtained using DDA and FEM approaches respectively. The element length and inter-dipole spacing have been varied so as to determine the relative error in the scattering efficiency when compared to the Mie Theory solution, shown in the inset of each figure. In the limit that either the mesh element length or inter-dipole spacing approach zero, the scattering efficiencies from the DDA, FEM and FDTD are found to approach the Mie theory solution. As has already been discussed, the numerical accuracy of the techniques depends on the resolution of these parameters. However, a compromise has to be made which takes into account the computation time of the simulation and the specification of the available hardware. Simulations were conducted using a Dell Vostro 200 computer, with a dual-core processor (each having a clock speed of 2.19 GHz) and 2 Gb of RAM. The curves shown for each of the techniques in Figure 2 represent the minimum element-length or inter-dipole separation which may be used in order to achieve a computation time which does not exceed 4.5 hours.

From figures 3 and 4 it can be seen that the sources of maximum error when using the DDA and FEM methods occur close to the wavelength associated with excitation of the localized surface-plasmon resonance (LSPR). The scattering behavior at the LSPR wavelength is dominated by the resonant field enhancement that occurs at the surface of the metallic particle. Any resolution-limited factors therefore lead to errors in the field matching conditions at the surface, and to discrepancies when the simulated scattering response is compared against that of the Mie Theory solution. For the DDA there is also a discrepancy at longer wavelengths, away from the resonant frequency. This residual error in the long-wavelength limit has also been observed elsewhere [14], and can be explained through local-field effects which lead to the dipoles near the surface of the sphere having a different effective polarizability from those away from the surface [29]. The error is a lattice effect

which arises as a consequence of using a discrete collection of volume elements with identical polarisabilities to represent a continuous medium. The magnitude of this error decreases significantly as a function of inter-dipole separation, see the inset of figure 3.

The discrepancy between the FDTD method and the other techniques occurs through the use of permittivity values based on a Drude-Lorentz model. In order to investigate just the role of FDTD mesh element size, a different comparison is considered in Figure 5 in which permittivity values based on the Drude-Lorentz model parameters are used for both FDTD and Mie Theory calculations. In Figure 5, simulated scattering efficiency values Q_{sca} for an 80 nm diameter Au sphere in vacuum obtained using the FDTD technique are directly compared against Mie Theory using permittivity values calculated using a Drude-Lorentz model for Au ($\varepsilon_\infty = 5.9673$, $\omega_d = 1.32 \times 10^{16}$ Hz, $\gamma_d = 1.00 \times 10^{14}$ Hz, $\Gamma_l = 6.60 \times 10^{14}$ Hz, $\Omega_l = 4.10 \times 10^{15}$ Hz and $\Delta\epsilon = 1.09$) [21,22]. As the element-length of the mesh is reduced, the simulated values of Q_{sca} from the FDTD method are also shown to approach the equivalent Mie Theory solution. For simulations which use comparable discretisation (~3 nm), it can be seen that the relative error between Mie Theory and the FDTD method at the frequency of the localized surface-plasmon resonance (4.1%) is significantly greater than that which is observed when using FEM modelling (0.4%) and the DDA (1.6%). This is in agreement with previous work [30] and arises from the use of a regular Cartesian mesh for the FDTD simulation, which is not an accurate representation for the surface curvature of the sphere. A sufficient mesh size refinement is required in order to ensure convergence of the solution, particularly in regions close to the surface of the sphere where there is strong confinement of the electric- and magnetic-field. Other studies have also shown that when a cubic mesh is used to simulate spherical geometries, a minimum element length of 0.25 nm is required in order to achieve a relative error of less than 1.0% [30]. Conversely, the use of a non-regular tetrahedral adaptive mesh for the FEM simulation allows for a more accurate approximation of curved surfaces, and a smaller relative error is observed.

V. CONCLUSION

In conclusion, we have compared five techniques used to simulate the scattering of electromagnetic radiation by metallic nanoparticle structures. Using the example of an 80 nm diameter Au sphere in vacuum, the simulated scattering efficiency obtained using a Mie

theory solution has been compared with those obtained using other numerical techniques (the T-Matrix method, DDA, FEM and FDTD methods). We have shown that when parameters which govern the resolution of these alternative methods (such as inter-dipole spacing for the DDA, or element length for FEM and FDTD methods) approach zero, the results of the simulations approach those of the Mie Theory solution. It has also been shown that the use of a non-regular tetrahedral adaptive mesh for the FEM simulation allows for a more accurate approximation of curved surfaces, leading to a smaller relative error between Mie Theory and FEM than the equivalent comparison for the cubic-mesh-based FDTD method.

There are many factors which should be considered when choosing an appropriate simulation technique, and the significant advantages and disadvantages of each approach are summarised in Table 1. It is hoped that the findings presented here may serve as a useful reference guide for future calculations.

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Method	Computation Time for Au sphere with radius << λ	Advantages	Disadvantages
Mie Theory	*Rapid* – a few milliseconds per individual frequency	• Rapid computation time. • Can also be used to compute the optical response of coated spheres.	• Applicable only to spherically symmetric particles. • Not possible to include a substrate interaction, therefore difficult to replicate many experiments.
T-Matrix	*Rapid* – a few milliseconds - per individual frequency.	• Rapid computation time. • Wide range of geometries supported. • Also possible to include a substrate interaction	• Computations are numerically unstable for elongated or flattened objects. (the matrices are truncated during computation– rounding errors become significant and accumulate rapidly)
DDA	*Moderate* – depends on number of dipoles, and separation. Typically 50s per individual frequency.	• Can be used to evaluate any arbitrary shaped particle by specifying a tabulated list of dipole locations	• Convergence criterion: $\lvert n \rvert kd < 1$ n = complex refractive index k = wavevector d = inter-dipole separation (Not possible to solve for high aspect ratio / elongated particles or those having a large refractive index)
FEM	*Lengthy* – typically 150s per individual frequency when using an element length of 3nm. A compromise is made between the computation time and element length.	• Can be used to evaluate the scattered field-distribution of any arbitrary shaped particle. • The use of a non-regular tetrahedral adaptive mesh for the FEM simulation allows for a more accurate approximation of curved surfaces.	• Computation time is lengthy.
FDTD	*Lengthy* – a broadband response is computed across a wide frequency range, typically taking ≈ 3 hours to cover visible frequencies. A compromise is made between the computation time and element length.	• Can be used to evaluate scattering parameters from any arbitrary shaped particle.	• Computation time is lengthy. • Permittivity values have to be specified over much wider frequency range than just the range of interest. The Drude-Lorentz model may not be an accurate representation of experimental data.

Table 1: Comparison of computation time, advantages and disadvantages computational techniques (Mie Theory, the T-Matrix method, the DDA, FEM modelling and the FDTD method) used to simulate the scattering of electromagnetic radiation from metallic

nanostructures. Computations were performed on a Dell Vostro 200 personal computer, having a dual-core processor (each with a clock speed of 2.19 GHz) and 2 Gb of RAM.

List of Figures:

Figure 1: The real and imaginary components of the permittivity values of Au for wavelengths in the range 450 – 750 nm. Curves (a,b) show the real and imaginary components of the experimental permittivity values published by Johnson and Christy [22] (used for the Mie Theory, T-Matrix, DDA and FEM simulations) and (c,d) show those obtained using a Drude-Lorentz model with fitted parameters $\varepsilon_\infty = 5.9673$, $\omega_d = 1.32 \times 10^{16}$ Hz, $\gamma_d = 1.00 \times 10^{14}$ Hz, $\Gamma_l = 6.60 \times 10^{14}$ Hz, $\Omega_l = 4.10 \times 10^{15}$ Hz and $\Delta\epsilon = 1.09$ [21,22], see equation 19 in the main text (used for the FDTD simulation).

Figure 2: Scattering efficiency (Q_{sca}) plotted as a function of wavelength for an 80 nm diameter Au sphere in vacuum, based upon simulation data obtained using **Mie Theory** (www.iap.unibe.ch/publications/download/201/en/) – solid line, the **T-Matrix** method (http://www.t-matrix.de) – open circle, the **DDA** (DDSCAT [14] version 6.1) –open square, **FEM** modelling (Ansoft HFSS™ version 11.0) – cross, and **FDTD** (Lumerical FDTD Solutions™ version 5.0) – open triangle. For Mie Theory, T-Matrix, DDA and FEM techniques, the permittivity values for Au are obtained from data published by Johnson and Christy [22]. The permittivity values used for FDTD simulation are derived from a Drude-Lorentz model with parameters $\varepsilon_\infty = 5.9673$, $\omega_d = 1.32 \times 10^{16}$ Hz, $\gamma_d = 1.00 \times 10^{14}$ Hz, $\Gamma_l = 6.60 \times 10^{14}$ Hz, $\Omega_l = 4.10 \times 10^{15}$ Hz and $\Delta\epsilon = 1.09$ [21,22], see equation 19 in the main text.

Figure 3: DDA vs Mie**:** Simulated Q_{sca} values obtained using Mie Theory for a 80 nm Au sphere in vacuum are compared with those obtained using the DDA (DDSCAT [14] version 6.1). The symbols show the effect of varying the inter-dipole spacing across a 2 nm to 5 nm range. The permittivity values used for Au are obtained from data published by Johnson and Christy [22]. *Inset* - The relative error is plotted as a function of wavelength for inter-dipole separation from 2 nm to 6 nm.

Figure 4: FEM vs Mie: Simulated Q_{sca} values obtained using Mie Theory for a 80 nm Au sphere in vacuum are compared with those obtained using a finite-element method (Ansoft HFSS™ version 11.0). The symbols show the effect of varying the mesh element length.

The permittivity values used for Au are obtained from data published by Johnson and Christy [22]. *Inset* - The relative error is plotted as a function of wavelength for element lengths of 3.1 nm, 4.5 nm and 5.1 nm.

Figure 5: FDTD vs Mie**:** Simulated Q_{sca} values obtained using Mie Theory for a 80 nm Au sphere in vacuum are compared with those obtained using a finite-difference time-domain method (Lumerical FDTD Solutions^{TM} version 5.0). The symbols show the effect of varying the mesh element length. The permittivity values for both techniques are derived from a Drude-Lorentz model with parameters $\varepsilon_\infty = 5.9673$, $\omega_d = 1.32 \times 10^{16}$ Hz, $\gamma_d = 1.00 \times 10^{14}$ Hz, $\Gamma_l = 6.60 \times 10^{14}$ Hz, $\Omega_l = 4.10 \times 10^{15}$ Hz and $\Delta\epsilon = 1.09$ [21,22], see equation 19 in the main text. *Inset* – relative error is plotted as a function of wavelength for different mesh sizes.