

ETPMSE2016: Numerical Simulations for Plasmonics

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1 Introduction

This hands-on workshop aims at presenting two different numerical simulation techniques, namely the Discrete Dipole Approximation and the finite-difference time-domain (FDTD) technique. The goal is to provide the basic informations required for starting with these methods. The Discrete Dipole Approximation will be used in the DDSCAT implementation. The FDTD will be used in the MEEP implementation.

2 Freely available ressources for simulations in plasmonics

Thanks to many contributions, a number of useful ressources are freely available on the web.

1. **F. Garcia de Abajo widgets:** a collection of widgets to compute the scattering and absorption from spheres and dimers, Electron Energy Loss Spectra and much more, running online at [this address](#).
2. **Nanohub:** nanoHUB lets you run over 320 simulation tools in a web browser. Your simulations run transparently in a scientific computing cloud at Purdue University and US national grid resources powered by a sophisticated cyberinfrastructure. The gateway to nanohub can be found at <https://nanohub.org/>.
3. **DDSCAT:** The DDSCAT package developed by Draine and Flatau is freely available on the [DDSCAT website](#).
4. **MEEP:** The MEEP FDTD package developed at MIT is freely available on the [MEEP website](#).

5. **MNPBEM:** MNPBEM is a toolbox for the simulation of metallic nanoparticles (MNP), using a boundary element method (BEM) approach developed by F. J. Garcia de Abajo and A. Howie, Phys. Rev. B 65, 115418 (2002). The main purpose of the toolbox is to solve Maxwell's equations for a dielectric environment where bodies with homogeneous and isotropic dielectric functions are separated by abrupt interfaces. Although the approach is in principle suited for arbitrary body sizes and photon energies, it is tested (and probably works best) for metallic nanoparticles with sizes ranging from a few to a few hundreds of nanometers, and for frequencies in the optical and near-infrared regime. MNPBEM can be downloaded on the [MNPBEM website](#).

More specific tools are available for Electron Energy Loss Spectroscopy on plasmonic nanoparticles:

1. **e-DDA:** a package for EELS and CL computations based on DDSCAT which can be found on the [e-DDA website](#).
2. **DDEELS:** Discrete Dipole approximation for Electron Energy Loss Spectroscopy (DDEELS) is a Fortran 90 code for simulating Electron Energy (low) Loss Spectroscopy (EELS) and catholuminescence (CL) performed on irregular particles. It is based on the optical properties of solids and the Discrete Dipole Approximation (DDA). The current version is DDEELsv2.1. It has been developed by N. Geuquet, S.-O. Guillaume and L. Henrard from the University of Namur. The code and its documentation can be found on the [DDEELS website](#).

3 The Discrete Dipole Approximation

3.1 Introduction

DDSCAT 7.3 is a freely available open-source Fortran-90 software package applying the "discrete dipole approximation" (DDA) to calculate scattering and absorption of electromagnetic waves by targets with arbitrary geometries and complex refractive index. The targets may be isolated entities (e.g., metal nanoparticles), but may also be 1-d or 2-d periodic arrays of "target unit cells", which can be used to study absorption, scattering, and electric fields around arrays of nanostructures. The DDA approximates the target by an array of polarizable points. The theory of the DDA and its implementation in DDSCAT is presented in Draine (1988) and Draine & Flatau (1994), and its extension to periodic structures in Draine & Flatau (2008). Efficient near-field calculations are carried out as described in Flatau & Draine (2012).

DDSCAT 7.3 allows accurate calculations of electromagnetic scattering from targets with "size parameters" $2\pi a_{eff}/\lambda \lesssim 25$ provided the refractive index m is not large compared to unity ($|m - 1| \lesssim 2$). DDSCAT 7.3 includes support for MPI, OpenMP, and the IntelR Math Kernel Library (MKL).

DDSCAT supports calculations for a variety of target geometries (e.g., ellipsoids, regular tetrahedra, rectangular solids, finite cylinders, hexagonal prisms, etc.). Target materials may be both inhomogeneous and anisotropic. It is straightforward for the user to "import" arbitrary target geometries into the code. DDSCAT automatically calculates total cross sections for absorption and scattering and selected elements of the Mueller scattering intensity matrix for specified orientation of the target relative to the incident wave, and for specified scattering directions. DDSCAT 7.3 can calculate scattering and absorption by targets that are periodic in one or two dimensions. DDSCAT 7.3 can calculate and store E and B throughout a user-specified rectangular volume containing the target. A Fortran-90 code `ddpostprocess` to support postprocessing of P, and nearfield E and B, is included in the distribution.

3.2 Available distributions and documentation

All necessary information about DDSCAT can be found on the [DDSCAT website](#). DDSCAT 7.3 can run on windows, Linux or Mac Os. To install it, first download the code, examples and user manual of the latest stable release on [the following website](#) (`ddscat7.3.0_160608.tgz` at the time of ETPMSE). Follow the installation procedure described in the user manual section 5.

4 Presentation of DDSCAT

4.1 DDSCAT structure and conventions

In DDSCAT, the geometry of the investigated nano-object can be defined in two ways.

1. **Basic shapes:** DDSCAT comes with several subprograms to generate basic shapes such as spheres, ellipsoids, rectangles, coupled spheres.....
2. **User-Defined shapes:** If the investigated nano-object does not have a "classical" shape, then it is possible to use your own structure file. To do so, it is necessary to select the option 'FROM_FILE' in the `ddscat.par` file and provide a 'shape.dat' file containing the location of all dipoles.

4.2 Geometry in DDSCAT

In DDSCAT, the laboratory frame is (Oxyz). The incident EM wave is coming along (Ox). The first polarization is along (Oy) and the second along (Oz). The investigated nano-object (or "target") has two axis \mathbf{a}_1 and \mathbf{a}_2 . The orientation of these axis with respect to the laboratory frame can be defined using three angles β , Θ and Φ as shown on the figure.

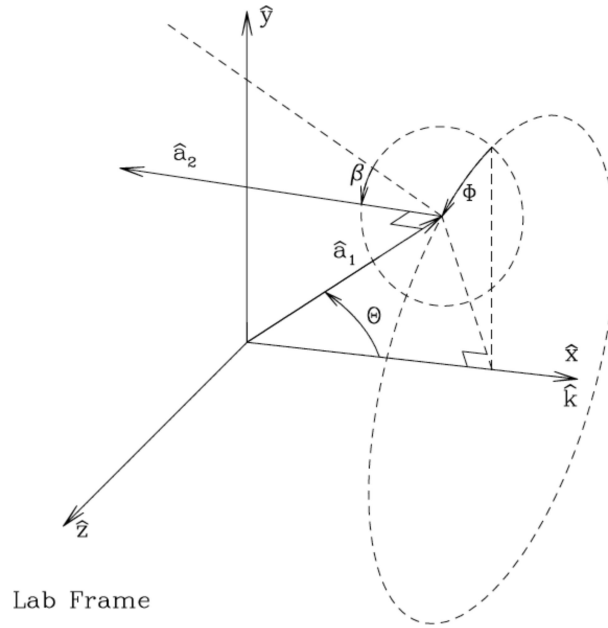


Figure 1: (color online) Target orientation in the Lab Frame. x is the direction of propagation of the incident radiation, and y is the direction of the real component (at $x = 0$, $t = 0$) of the first incident polarization mode. In this coordinate system, the orientation of target axis \mathbf{a}_1 is specified by angles Θ and Φ . With target axis \mathbf{a}_1 fixed, the orientation of target axis \mathbf{a}_2 is then determined by angle β specifying rotation of the target around \mathbf{a}_1 . When $\beta = 0$, \mathbf{a}_2 lies in the (\mathbf{a}_1, x) plane.

4.3 Inputs and outputs

Input

In DDSCAT, all important informations are given in a parameter file called *ddscat.par*. This file contains all required information about:

- **Illumination:** incident wavelength and polarization

- Nano-object geometry

Details on the structure of this file are given below.

Output

DDSCAT can calculate total cross sections for absorption and scattering and selected elements of the Mueller scattering intensity matrix for specified orientation of the target relative to the incident wave, and for specified scattering directions. DDSCAT 7.3 can calculate scattering and absorption by targets that are periodic in one or two dimensions. DDSCAT 7.3 can calculate and store E and B throughout a user-specified rectangular volume containing the target.

In the following, we will only use absorption, scattering and extinction cross-sections provided in the *qtable* file.

4.4 The parameter file *ddscat.par*

A typical *ddscat.par* file looks like this:

```
'===== Parameter file for v7.3 ====='
'**** Preliminaries ****'
'NOTORQ '= CMDTRQ*6 (NOTORQ, DOTORQ) -- either do or skip torque calculations
'PBCGS2'= CMDSOL*6 (PBCGS2, PBCGST, GPBICG, PETRKP, QMRCCG) -- CCG method
'GPF AFT'= CMDFFT*6 (GPF AFT, FFTMKL) -- FFT method
'GKDLDR'= CALPHA*6 (GKDLDR, LATTDR, FLTRCD) -- DDA method
'NOTBIN'= CBINFLAG (NOTBIN, ORIBIN, ALLBIN) -- specify binary output
'**** Initial Memory Allocation ****'
100 100 100 = dimensioning allowance for target generation
'**** Target Geometry and Composition ****'
'RCTGLPRSM'= CSHAPE*9 shape directive
16 32 32 = shape parameters 1 - 3
1 = NCOMP = number of dielectric materials
'../diel/Au_evap'= file with refractive index 1
'**** Additional Nearfield calculation? ****'
0 = NRFLD (=0 to skip nearfield calc., =1 to calculate nearfield E)
0.0 0.0 0.0 0.0 0.0 0.0 (fract. extens. of calc. vol. in -x,+x,-y,+y,-z,+z)
'**** Error Tolerance ****'
1.00e-5 = TOL = MAX ALLOWED (NORM OF |G>=AC|E>-ACA|X>)/(NORM OF AC|E>)
'**** maximum number of iterations allowed ****'
300 = MXITER
```

```

'**** Interaction cutoff parameter for PBC calculations ****'
1.00e-2 = GAMMA (1e-2 is normal, 3e-3 for greater accuracy)
'**** Angular resolution for calculation of <cos>, etc. ****?'
0.5 = ETASCA (number of angles is proportional to  $[(3+x)/ETASCA]^2$ )
'**** Vacuum wavelengths (micron) ****'
0.5000 0.5000 1 'LIN'= wavelengths (first,last,how many,how=LIN,INV,LOG)
'**** Refractive index of ambient medium'
1.000 = NAMBIENT
'**** Effective Radii (micron) **** '
0.246186 0.246186 1 'LIN'= aeff (first,last,how many,how=LIN,INV,LOG)
'**** Define Incident Polarizations **** '
(0,0) (1.,0.) (0.,0.) = Polarization state e01 (k along x axis)
2 = IORTH (=1 to do only pol. state e01; =2 to also do orth. pol. state)
'**** Specify which output files to write ****'
1 = IWRKSC (=0 to suppress, =1 to write ".sca" file for each target orient.
'**** Prescribe Target Rotations **** '
0. 0. 1 = BETAMI, BETAMX, NBETA (beta=rotation around a1)
0. 0. 1 = THETMI, THETMX, NTHETA (theta=angle between a1 and k)
0. 0. 1 = PHIMIN, PHIMAX, NPHI (phi=rotation angle of a1 around k)
'**** Specify first IWAV, IRAD, IORI (normally 0 0 0) ****'
0 0 0 = first IWAV, first IRAD, first IORI (0 0 0 to begin fresh)
'**** Select Elements of  $S_{ij}$  Matrix to Print ****'
6 = NSMELTS = number of elements of  $S_{ij}$  to print (not more than 9)
11 12 21 22 31 41 = indices ij of elements to print
'**** Specify Scattered Directions ****'
'LFRAME'= CMDFRM (LFRAME, TFRAME for Lab Frame or Target Frame)
2 = NPLANES = number of scattering planes
0. 0. 180. 5 = phi, thetan_min, thetan_max,dtheta (deg) for plane 1
90. 0. 180. 5 = phi, thetan_min, thetan_max,dtheta (deg) for plane 2

```

In the following examples, we will only give details and modify the sections highlighted in red which are the most important for basic calculations.

4.4.1 Target Geometry and Composition

This part specifies the **shape and composition** of the nano-object. In this case, it is a rectangular slab of gold. RCTGLPRSM is the name of the built-in subprogram of DDSCAT which will generate the appropriate shape. In this case, it is a homogeneous, isotropic, rectangular solid. The following three numbers are **shape parameters** specific to each target built-in subprogram which give the dimensions of the target (here, the length along the x,y and z

axis respectively). Then comes the number of different materials considered (not including the environment), in the present case it is one as the nano-object is only made of gold.

4.4.2 Vacuum wavelengths (micron)

This section is extremely important as it tells DDSCAT which wavelengths must be computed. The units are microns and it is the wavelength in vacuum which must be given. It is required to provide the minimum and maximum wavelengths, the number of different wavelengths to be computed. It is also possible to specify the type of wavelength scan desired (linear, logarithmic...).

4.4.3 Effective Radii (micron)

The shape is specified in the Target Geometry section but not its dimension. The dimension is provided to DDSCAT using the so-called *effective radius* which reads:

$$a_{eff} = \left(\frac{3V}{4\pi} \right)^{1/3} \quad (1)$$

V is the total volume of the nano-object (in microns).

In the case of a sphere, the effective radius a_{eff} is of course the radius of the sphere.

For a dipole spacing d , the total volume of the nano-object is:

$$V = N d^3 \quad (2)$$

4.4.4 Refractive index of ambient medium

This section sets the refractive index of the environment of the nano-object. In this case, the target is placed in vacuum.

4.4.5 Define Incident Polarizations

This section contains the information about the incident polarization. Polarization state e_{01} refers to an electric field polarized along (Oy). Polarization state e_{02} refers to an electric field polarized along (Oz). To tell DDSCAT that you want both polarization states to be considered in the computation, it is required to set IORTH=2.

4.4.6 Prescribe Target Rotations

This section allows to scan through different orientations (i.e different values of the angles Θ , Φ and β shown in figure 1).

4.4.7 Using your own shapes

To tell DDSCAT that you want to use your own structure file called 'shape.dat', it is necessary to modify the Target Geometry and Composition section in the following way:

```
'**** Target Geometry and Composition ****'  
'FROM_FILE'= CSHAPE*9 shape directive  
'shape.dat'  
1 = NCOMP = number of dielectric materials  
'Au_evap'= file with refractive index 1
```

4.5 The *qtable* file

The results of the computation of absorption, scattering and extinction cross-sections are summarized for the different values of the effective radius and incident wavelength in the *qtable* file. This file looks like :

```
DDSCAT --- DDSCAT 7.3.0 [13.05.03]  
TARGET --- Ellipsoid, 1032 dipoles, 1.000 1.000 1.000=x,y,z lattice spacing  
GPFAFT --- method of solution  
GKDLDR --- prescription for polarizabilities  
ELLIPSOID --- shape  
1032 = NATO = number of dipoles  
Au_evap  
0.000 0.000 = beta_min, beta_max ; NBETA = 1  
0.000 0.000 = theta_min, theta_max; NTHETA= 1  
0.000 0.000 = phi_min, phi_max ; NPFI = 1  
0.5000 = ETASCA (param. controlling # of scatt. dirs used to calculate  
<cos> etc.  
Results averaged over 1 target orientations  
and 2 incident polarizations  
aeff wave Q_ext Q_abs Q_sca g(1)=<cos> <cos2> Q_bk Nsca  
1.0000E-02 4.0000E-01 8.5472E-01 8.4761E-01 7.1285E-03 3.4649E-03 4.0281E-01 8.4662E-04 214  
1.0000E-02 4.0847E-01 8.3987E-01 8.3327E-01 6.6081E-03 3.3155E-03 4.0279E-01 7.8497E-04 214
```



```

1.0000E-02 4.1695E-01 8.2351E-01 8.1743E-01 6.0995E-03 3.1828E-03 4.0276E-01 7.2467E-04 214
1.0000E-02 4.2542E-01 8.0644E-01 8.0084E-01 5.6109E-03 3.0614E-03 4.0274E-01 6.6671E-04 214
1.0000E-02 4.3390E-01 7.9249E-01 7.8733E-01 5.1762E-03 2.9366E-03 4.0272E-01 6.1516E-04 214
...

```

The first lines (in red) are a summary of the parameters used for the computation and given by the parameter file `ddscat.par`. Then, the data given in the file are reminded (line in blue) before the complete list of computed data. The quantities Q_{ext} , Q_{abs} and Q_{sca} which are computed by DDSCAT are the extinction, absorption and scattering efficiency factors respectively. For instance, the extinction efficiency factor Q_{ext} is defined by:

$$Q_{ext} = \frac{C_{ext}}{\pi a_{eff}^2} \quad (3)$$

in which C_{ext} is the extinction cross-section and a_{eff} is the effective radius.

5 Basic computations with DDSCAT

Now, we will use DDSCAT on several basic calculations. First, you need to:

- Start the computer and choose the session **OPENSUSE**
- launch the application **KONSOLE**. If required you can increase the font size pressing 'ctrl' and '+' simultaneously.
- Go to the directory: [/home/etudiant/ETPMSE2016/TPddscat](#). You should find all necessary files in this directory.

To launch a simulation with DDSCAT, , it is necessary:

1. Edit the DDSCAT parameter file `ddscat.par`

This can be done in command line using the application *vi*. To do so, simply type `vi ddscat.par` and then type *i* to enter edit mode. To exit edit mode and save the file, type `esc` and then `:wq`. To exit without saving the file, type `esc` and then `:q!`

2. Run DDSCAT

To launch the simulation, just type:

```
./ddscat >& ddscat.out
```

This will not display the runtime informations on the screen (and therefore save a lot of time). These informations will be saved in a file called `ddscat.out`. This file must be examined carefully in case of runtime error.

3. Plot the extinction cross section using gnuplot

To plot the computation results contained in the file *qtable*, we launch gnuplot by typing *gnuplot* in the command line. Then, we type:

```
plot "qtable" every ::13 using 2:3
```

This tells gnuplot to skip the first 13 lines (file header) and plot the third column (extinction efficiency factor) as a function of the second column i.e the incident wavelength.

In the following, we will first consider the optical response of spheres and ellipsoids. To do so, we will use the built-in function 'ELLIPSOID' instead of 'RCTGLPRSM' in the *ddscat.par* file. 'ELLIPSOID' takes three shape parameters which are the dimensions of the semi-axes along respectively (Ox), (Oy) and (Oz). Therefore, to define a sphere we take them equal.

To start, open the *ddscat.par* in the [/home/etudiant/ETPMSE2016/TPddscat](#) folder. This file should have all parameters set properly. **It is recommended that you copy the simulation results file *qtable* for each simulation with explicit names so that you can reuse them later and compare different results.**

To do so, you can type for instance:

```
cp qtable qtable-sphereA
```

5.1 Sphere - Influence of discretization

In all computations using DDSCAT, it is extremely important to check the convergence of the results. To confirm that the computation converged, the same structure must be computed with different numbers of dipoles and the results must agree. Here, we compute the optical response of the same nano-object (a 10 nm nanosphere) with two discretizations.

Sphere of radius 10 nm

- Target generation program: 'ELLIPSOID'
- Shape parameters: Shape1 = 10, SHAPE 2 = 10 SHAPE3 = 10
- Wavelength: initial = 400 nm, Final = 900 nm, Number = 20, Scan type ='LIN'
- Refractive index of ambient medium: $n_{env} = 1.33$ (water)
- Effective radius of the sphere = 10 nm
- Polarizations : compute the two orthogonal polarizations

Sphere of radius 10 nm with better discretization

- Target generation program: 'ELLIPSOID'
- Shape parameters: Shape1 = 20, SHAPE 2 = 20 SHAPE3 = 20
- Wavelength: initial = 400 nm, Final = 900 nm, Number = 20, Scan type ='LIN'
- Refractive index of ambient medium: $n_{env} = 1.33$ (water)
- Effective radius of the sphere = 10 nm
- Polarizations : compute the two orthogonal polarizations

Using gnuplot, compare the two results.

5.2 Sphere - Influence of environment

Sphere of radius 10 nm in vacuum

- Target generation program: 'ELLIPSOID'
- Shape parameters: Shape1 = 10, SHAPE 2 = 10 SHAPE3 = 10
- Wavelength: initial = 400 nm, Final = 900 nm, Number = 20, Scan type ='LIN'
- Refractive index of ambient medium: $n_{env} = 1$.
- Effective radius of the sphere = 10 nm
- Polarizations : compute the two orthogonal polarizations

5.3 Ellipsoid

5.4 Influence of aspect-ratio

Try to compute the extinction cross-section of gold ellipsoids of different aspect-ratio. These elongated nano-objects now support two surface plasmon modes: one longitudinal plasmon mode and one transverse. You can vary the aspect-ratio of the ellipsoid by changing one of its parameter shape and check the influence on the position of surface plasmon resonances appearing in the extinction cross-section.

5.5 Equilateral Triangle

We now want to simulate the optical response of the gold nanoprisms that will be used in the practical on optical spectroscopy. Here, we want to demonstrate the influence of the refractive index of the environment on the optical response. Try to compute the extinction cross-section of equilateral gold nanoprisms with edge length $a=40$ nm and thickness $t=10$ nm. The built-in function to generate a triangle is 'TRNGLPRSM'.

6 Conclusion

This document is of course only a summary of the basic knowledge required to run basic DDSCAT simulations. The interested reader is strongly advised to read the DDSCAT user guide for further information about the many possibilities of this tool which could not be presented in this practical.