

2015 BioNanotechnology Summer Institute

Cancer Nanotechnology and Cell Mechanics
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University of Illinois at Urbana–Champaign



NANO-OPTICS MODULE

Discrete Dipole Approximation Simulation of Scattering and Absorption of Metal Nanoparticles

Location: 1000 MNTL

Instructors: Prashant Jain, Chemistry and Jeremy Smith, Chemical Physics

Purpose

The purpose of this lab module is to provide experience using the discrete dipole approximation (DDA) to simulate the interaction of metal nanoparticles with the electric field of incident light and use this computational method to produce the scattering and absorption spectra of metal nanoparticles as a function of size, geometry, and medium. The goal is to equip students with a method for predictive design of optical properties of metal nanoparticles for their use in biological and medical applications.

Background

The strongly enhanced surface plasmon resonance of noble metal nanoparticles at optical frequencies makes them excellent scatterers and absorbers of physical light. Superior optical properties, coupled with recent advances in nanoparticle synthesis, conjugation, and assembly, have stimulated interest in the use of plasmon-resonant nanoparticles and nanostructures for optical and photonic applications and, more recently, for biomedical applications. Nanoparticles composed of gold offer, in addition to their enhanced absorption and scattering, good biocompatibility, facile synthesis, and conjugation to a variety of biomolecular ligands, antibodies, and other targeting moieties, making them suitable for use in biochemical sensing and detection, medical diagnostics, and therapeutic applications. There have been several demonstrations of bioaffinity sensors based on the plasmon absorption and scattering of nanoparticles and their assemblies.

Another notable use of gold nanoparticles has been as contrast agents in cellular and biological imaging. Contrast agents in medical and biological imaging improve the sensitivity and diagnostic ability of the imaging modality by site-specifically labeling tissues or cells of interest. The effectiveness of nanoparticles as biomedical imaging contrast and therapeutic agents depends on their optical properties. For instance, a high-scattering cross-section is essential for cell imaging applications based on light-scattering microscopy. On the other hand, effective photothermal therapy with minimal laser dosage requires a high nanoparticle absorption cross-section with low scattering losses. Biosensing applications based on surface plasmon resonance shifts necessitate strong resonance in the wavelength sensitivity range of the instrument as well as narrow optical resonance line widths. For actual *in vivo* imaging and therapeutic applications, the optical resonance of the nanoparticles is strongly desired to be in the near-infrared (NIR) region of the biological water window, where the tissue transmissivity is the highest. In addition, the nanoparticle size is also an important consideration for nanoparticle uptake and retention by cells and tissue.

It is well-known that the plasmon resonance of metal nanoparticles is strongly sensitive to the nanoparticle size, shape, and the dielectric properties of the surrounding medium. Optical properties of gold nanoparticles can thus be readily tuned by varying their size and shape. In order to harness the full power of these phenomena, scientists need to understand the interactions of light with nanoparticles at very small length scales. There have been several experimental reports on the optical properties of metal nanoparticles, including gold nanospheres, nanorods, and nanoprisms, silver nanospheres, nanowires, and nanoprisms, copper nanospheres, aluminum

nanospheres, bimetallic nanoparticles, composite nanoparticles with a core-shell structure, and nanoparticle chains and assemblies. At the same time, well-established theoretical tools based on the Mie theory and the discrete dipole approximation (DDA) method have been readily exploited for a quantitative study of the nanoparticle optical properties of different size, shape, composition, and aggregation state, etc.

A very powerful method for determining the interaction of electromagnetic radiation with particles is known as the Discrete Dipole Approximation (DDA). Using DDA, the particle is discretized into an array of dipoles, or polarizable points. This method then solves Maxwell's equations for an incident field interacting with each of the dipoles individually. The resulting data can be used to compute scattering and absorption properties of the array of dipoles and, hence, the particle. This method relies on the assumption that the dielectric properties of the particle, and its interaction with the incident field, are directly related to the polarizability of the constituent dipoles.

A popular code for the implementation of DDA calculations is called DDSCAT. DDSCAT allows for the computation of absorption and scattering properties of particles with arbitrary shapes and geometries, and provide outputs of light extinction, absorption, and scattering properties at various wavelengths of incident light.

The nanobioNODE at University of Illinois has developed a tool on nanoHUB.org that creates a simple and intuitive interface for using the DDSCAT code developed by Draine and Flatau. This allows experimental chemists and biologist not familiar with computational methods a visual interface in which they can simulate the interaction of light with nanoparticles of any geometry and compute light scattering, absorption, and plasmonic near field enhancement.

References

- Draine, Bruce T., and Piotr J. Flatau. "Discrete-dipole Approximation for Scattering Calculations." *Journal of the Optical Society of America A* 11.4 (1994): 1491. Web. (pdf)
- Draine, Bruce T., and Piotr J. Flatau. *User Guide for the Discrete Dipole Approximation Code DDSCAT 7.2*. N.p., 2012. Web. (pdf)
- Jain, Prashant K., Kyeong Seok Lee, Ivan H. El-Sayed, and Mostafa A. El-Sayed. "Calculated Absorption and Scattering Properties of Gold Nanoparticles of Different Size, Shape, and Composition: Applications in Biological Imaging and Biomedicine." *The Journal of Physical Chemistry B* 10.14 (2006): 7238-248. Web. (pdf)
- Jain, Prashant K. "Plasmons in assembled metal nanostructures: radiative and nonradiative properties, near-field coupling and its universal scaling behavior." (2008). (pdf)

Running a Simulation

Generating and running a simple target shape file

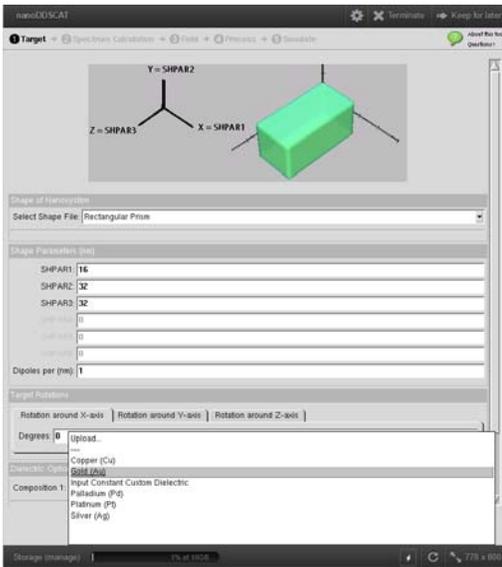
- 1) Log onto nanohub.org. You can either create a login to save your jobs for future reference, or login as a guest. Go to the resources tab and click on Tools.

The screenshot shows the nanoHUB homepage. At the top, there is a navigation bar with links for Home, Resources, Members, Explore, nanoHUB-U, Partners, About, and Support. A search bar is located on the right. Below the navigation bar, there is a large banner with text: "SIMULATE with over 330 tools for nanoelectronics, nanophotonics and more...", "RESEARCH & COLLABORATE via groups, question board and more...", "TEACH & LEARN with nanoHUB-U, topic specific materials, tool-powered tutorials, simulations, and more...", and "SHARE & PUBLISH tools and research through our easy upload process". On the left, there is a sidebar with a "NANO HUB USER CODE" and a "Registration" button. Below the banner, there is a "POPULAR TOOLS" section with a list of tools including "Newer's Law Basics", "CMOS Process Steps", "Thin Film Solar Cells", "Changing Effects", "Nanoscale Semiconductor Interfaces", "Industry Diodes", "Atomic Force Microscopy", "Density States", "Scanning Probe Microscopy", "Introduction To The MEMS Nanotechnology", and "Cyclic Peptide Nanobiosensors". To the right of the tools list, there is a "FEATURED" section with items like "nanoHUB-U: Your source for cutting-edge topics...", "NEEDS: The NSF-Funded Electronics Content Needs", "nanoBIO: The NSF-Funded nanoBIO Content Needs", "BESTA: Use BESTA to perform electronic structure calculations...", "NCN NEMS Research Seminars - in Series", "BME 665A Lecture 13: Assessing Data Potentials - in Online Presentations", and "Lecture 5: NEGF Simulation of Graphene Nanodevices - featured on iTunes U". Further right, there is a "NEW IN RESOURCES" section with items like "Breakdown Voltage and Current Density in Microgaps Calculator in Tools, 03 Jul 2015", "System of Systems Analytic Workbench Toolset in Tools, 03 Jul 2015", "Nanomanufacturing of Smart Thin Films: Applications to Pharmacy, Ag, Food, Packaging, Health Care in Online Presentations, 25 Jun 2015", "Along for the Ride: Reflections on the Past, Present, and Future of Nanoelectronics in Online Presentations, 25 Jun 2015", and "Framework for Evaluating Simulations: Analysis of Student Developed Interactive Computer Tool in Presentation Materials, 25 Jun 2015".

- 2) From the list on the left scroll down to DDA. From the central list select DDSCAT discrete dipole approximation. On the right hand list click launch tool.

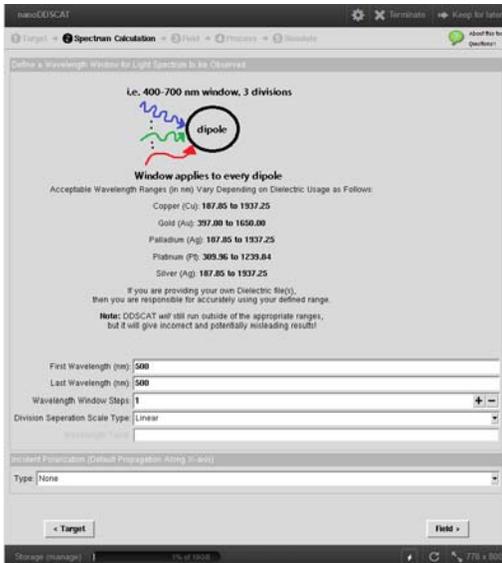
The screenshot shows the nanoHUB "Resources: Tools" page. The page has a navigation bar at the top with links for Home, Resources, Members, Explore, nanoHUB-U, Partners, About, and Support. Below the navigation bar, there is a search bar and a "Start a new Tool" button. The main content area is titled "Resources: Tools" and has a "Browse by Tags" section with a "Browse Visually" button. Below this, there is a "Type" dropdown menu set to "Tools" and a "Go" button. The main list of tools is titled "Resources" and is sorted by "Title". The list includes: "current (2)", "current voltage simulation (1)", "CV curves (1)", "cyberinfrastructure (1)", "cylindrical lens (1)", "damping (1)", "DDA (3)", "DDSCAT (3)", "decay (1)", "degenerate semiconductor (1)", "Delta to Wye (1)", "density functional theory (7)", "density of states (4)", "depletion (5)", and "depletion approximation (5)". The "DDSCAT (3)" tool is selected, and its details are shown on the right. The details include the title "nanoDDSCAT", a description "Calculate scattering and absorption of light by targets with arbitrary geometries and complex refractive index. Learn more...", a "Launch Tool" button, a "5.0 RANKING" badge, and statistics: "304 users, detailed usage", "3 citations", "16 questions (ask a question)", "1 review(s) (Review this)", and "2 watches (New Watch)". There is also a "Share" button with social media icons.

- 3) Now you have opened the DDA tool on Nanohub which will perform the calculation for you. We must go through a number steps to correctly setup the calculation. The first window is to specify the object, calculation resolution, medium and light polarization relative to the object.

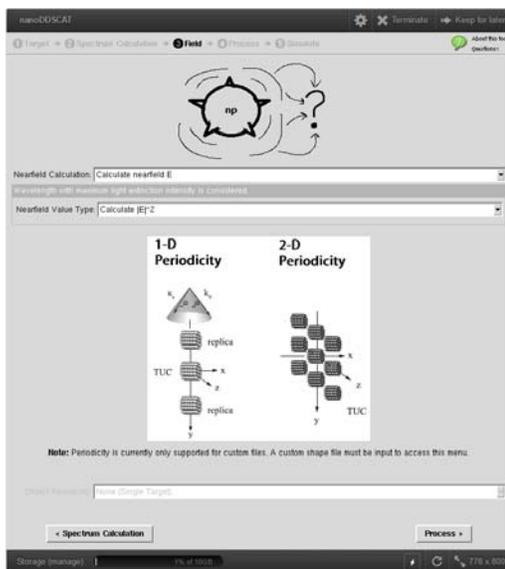


To start we will use built in shapes to motivate and understanding of the way the calculation is performed and the effect of important parameters on the spectra and electric field distribution. Under the shape file tab, select ellipsoid. In the three rows of the SHPAR dialogue box select 10,10 and 10 (nm). This will build a 10 nm sphere. In the dipole per nm bow enter 1. This defines the resolution of the calculation. Decreasing this number will describe a more accurate calculation, however it will take much longer, since the calculation scales as the (number of dipoles)². The target rotations tab allows one to rotate the object relative to the incident light. By default, the light propagates along the x direction. Since the light is fixed, rotating the object will change the angle between the electric field vector of the light and the object, and thus change the types of “modes” which are excited by the light. In the dielectric tab select 1 dielectric and select the material as Au. A materials dielectric function is a frequency (wavelength) dependent function that defines the response of a material to electromagnetic radiation. It essentially defines everything about the inherent response of a material in the absence of any particular geometry and what makes one material different from another (in terms of its response to light). Set the medium refractive index to 1.33 (water). Move to the next tab.

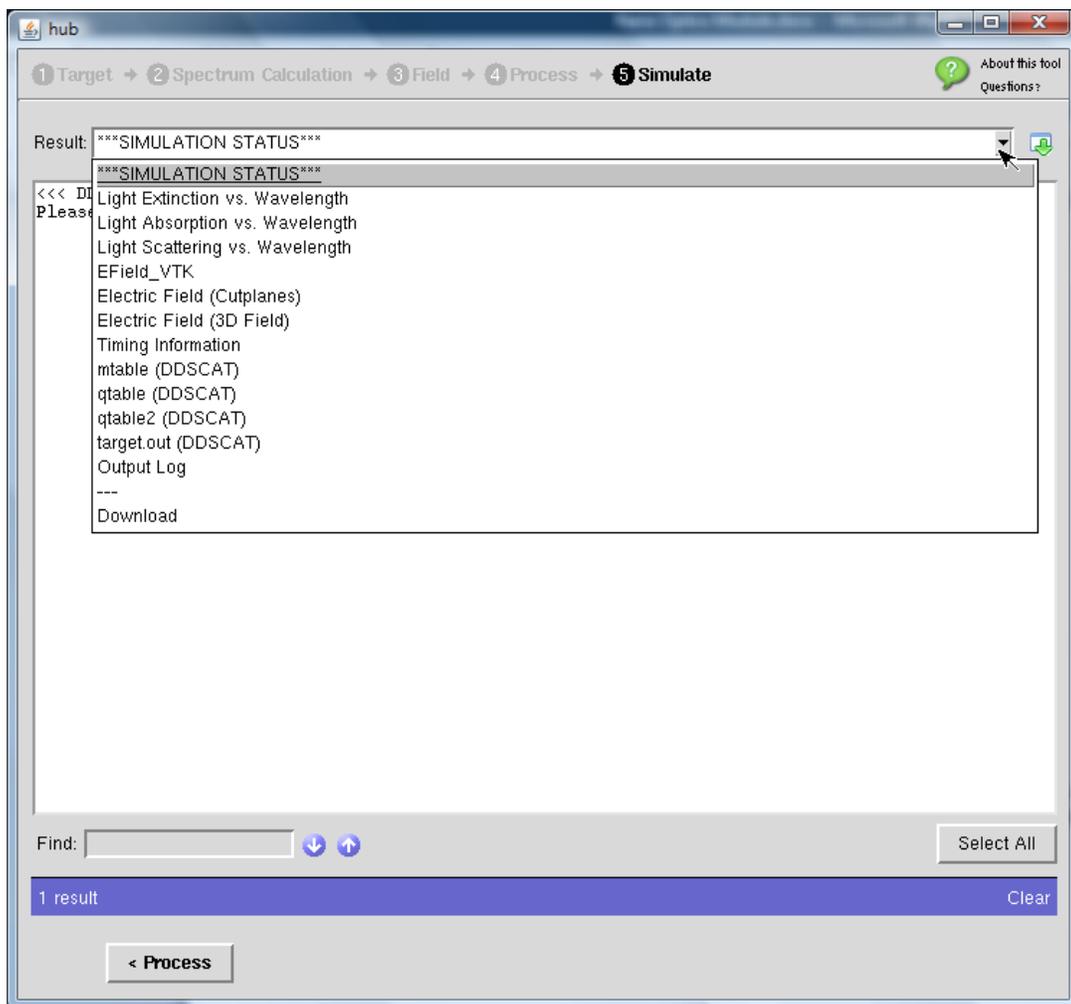
- 4) The second tab is where we specify how many division we want to use to calculate the spectrum of the object. Choose 500 to 600 nm, in 10 divisions. It is known from experiments that the plasmon resonance of an Au sphere should lie somewhere in this range. Changing the shape may require one to change the wavelength range to perform the calculation. Select define polarization in order to change the light polarization. Set this value to linear polarized in y (propagation along x, magnetic field in z).



- 5) In the field tab, select calculate nearfield E, then select E^2 . This will calculate the field in the vicinity of the particle (or rather its magnitude, since we chose E^2).



- 6) In the process tab select virtual local ddscat. This will use one process to perform the calculation. The tool is supported for performing calculations on a large cluster, which is desirable when we want to calculate large shapes, high resolution or many wavelengths. For the homework assignment you should select remote parallel DDSCAT, since the arbitrary geometry you will generate will likely take longer to run (and be performed over a large set of wavelengths).
- 7) The calculation should run in a matter of seconds. In the result tab there will be several files which you can look at and download. Absorption and scattering represent the absorption and scattering spectra respectively. Extinction is the sum of both of these. Download and save all three of these files. For fun you can click on the electric field cutplanes tab. This will plot the electric field in the vicinity of the object. This is by default at the maximum of the extinction spectrum. This will clearly illustrate the predominantly dipole nature of the observed resonance at $\lambda \sim 530$ nm.



Exercises – Day 1

Size Dependence

Repeat the above procedure with Au spheres of sizes 20, 30, 40, 50 and 60 nm. Plot the resonance maximum, peak absorption, and peak scattering cross-section (m^2) as a function of size. How does the absolute and relative magnitude of absorption and scattering change as a function of size? What is the physical reason for this dependence? What are the implications for biomedical applications? (Hint: Imaging vs photothermal therapy). (see *J. Phys. Chem. B*, **2006**, *110* (14), pp 7238–7248).

Plasmon Modes of Anisotropic Nanoparticles

In the first tab of the DDA tool, (see above part 3) change the shape of the ellipsoid such that it is anisotropic. Namely, set SHPAR 1 and 2 = 5 nm and SHPAR 3 = 20 nm. This will elongate the shape along one axis (x in this case). Repeat the same calculation with all of the same parameters, except change the spectral window to 500-1000 nm in 10 steps. Save the scattering, absorbance and extinction spectra. Look at the E-field cut plane visualization to see what the field distribution looks like. Which axis is the field localized to? Next repeat the calculation with the same shape, but (on the first tab) change the target rotation to 90° in x. Rerun the calculation. Save the scattering, absorbance and extinction spectra. Now which axis have we excited? How do the spectra of the long and short axis differ in terms of their resonance peak? Which one has higher extinction? Now change SHPAR 3 to make the aspect ratio larger. How do the long-axis and short-axis peaks differ depending on aspect ratio of the rod? Discuss these observations. (see *J. Phys. Chem. B*, **2001**, *105* (19), pp 4065–4067).

Dielectric Sensing

In the first tab of the DDA tool, reset the shape to “concentric ellipsoids”. This will generate an ellipsoid of one dielectric material with a shell of another dielectric material. Set the SHPAR 4, 5, and 6 = 70 nm and set the dielectric of this material to SiO₂ to make a silica nanoparticle core 70 nm in diameter. Next, set the SHPAR 1, 2, and 3 to either 74, 80, or 90 nm to make a symmetric shell around the silica nanoparticle of 4, 10, or 20 nm. Set the dielectric of this material to Au. For the spectrum, choose 500 to 700 nm, in 10 divisions. Set the refractive index of the medium to $n=1$. Run the simulation, save, and plot the extinction spectra. Now change the refractive index of the medium to $n=1.2$ and run the simulation again. Increase the refractive index of the medium another time to $n=1.4$ and the run the simulation again. Plot the peak maximum of the extinction as a function of medium refractive index. Now compare with another person or group who used a different shell thickness. How does the sensitivity of the peak maximum with respect to medium refractive index change based on the thickness of the gold shell? (See *J. Phys. Chem. C*, **2007**, *111*, (47), 17451-17454.)

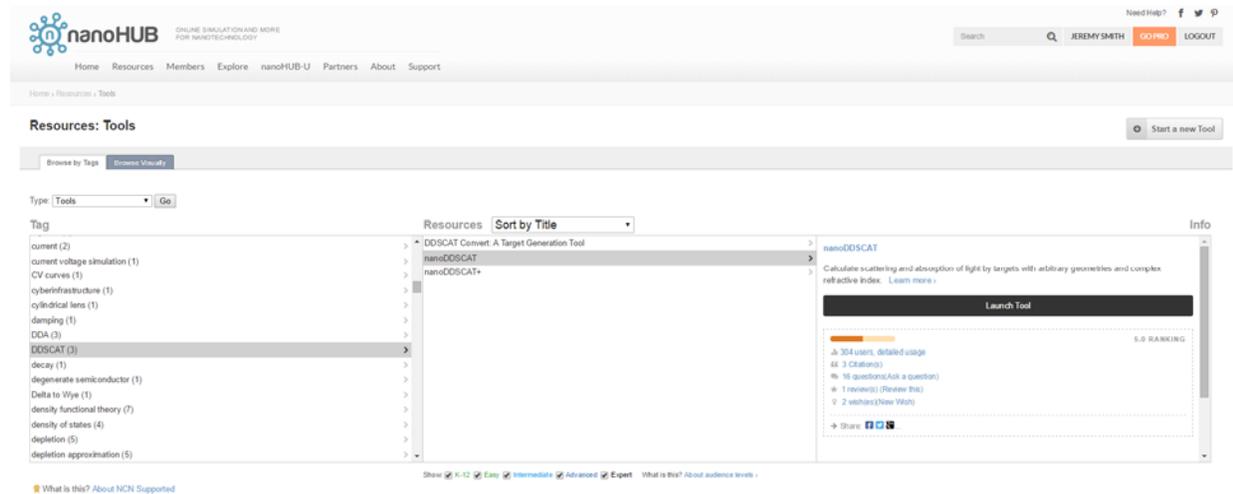
Exercises – Day 2

Simulations of New Geometries of Metal Nanoparticles

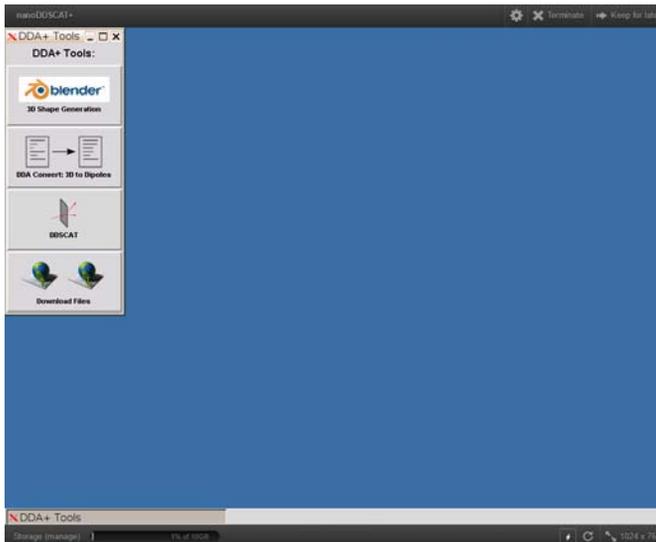
The DDSCAT tool has a collection of fixed geometries such as ellipsoids and cylinders that can be used to generate shape files. While this can be instructive for learning purposes, most experimentalists prefer to use DDA calculations to simulate materials that they can synthesize in their labs. For this purpose nanohub has created the nanoddscat+ tool.

This tool allows a user to generate their own arbitrary objects and simulate the electric fields and scattering and absorption spectra of these materials.

- 1) Launch the nanoddscat+ tool. This will be located directly below nanoddscat in the tools tab.

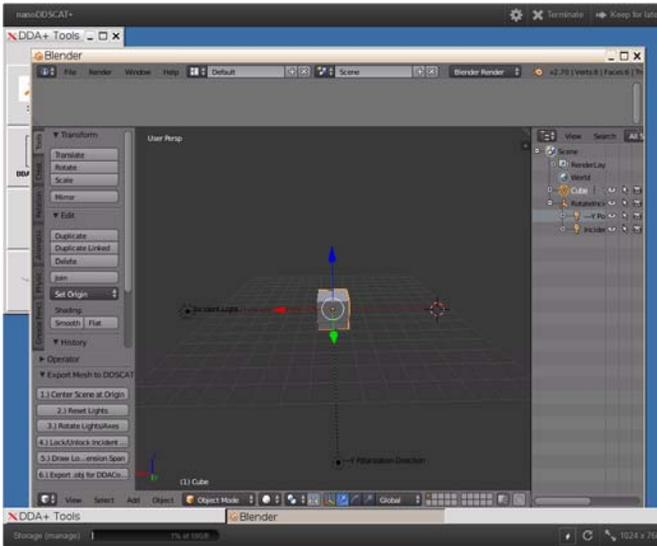


- 2) The program will launch a window that looks like this:

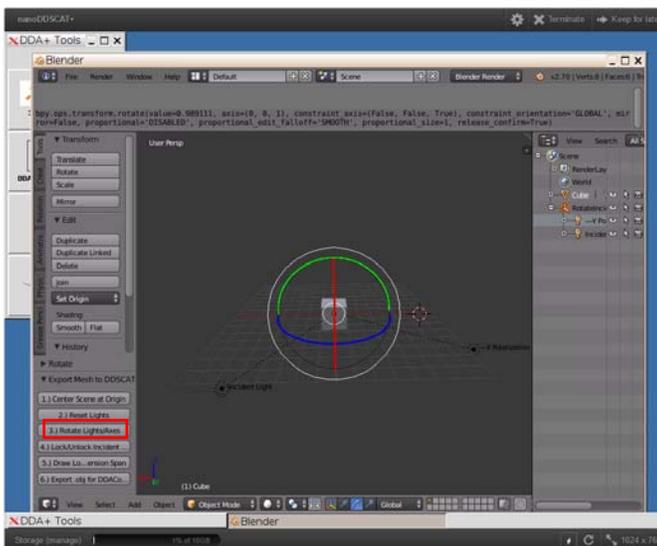


This is the nanoddscat+ interface. It is logging you in to a remote desktop on a nanohub server that allows you access to three programs. You will need to navigate through them, *in order*, to generate and simulate the plasmonic properties of light interacting with an arbitrary structure. The first of these is the top tab, the one for blender.

- 3) Clicking this will launch the blender application. Blender is primarily a 3D rendering and animation software, with a lot of powerful functionality, most of which will not be used by the typical user looking to run ddsicat simulations. Some important basic will be needed however.
- 4)



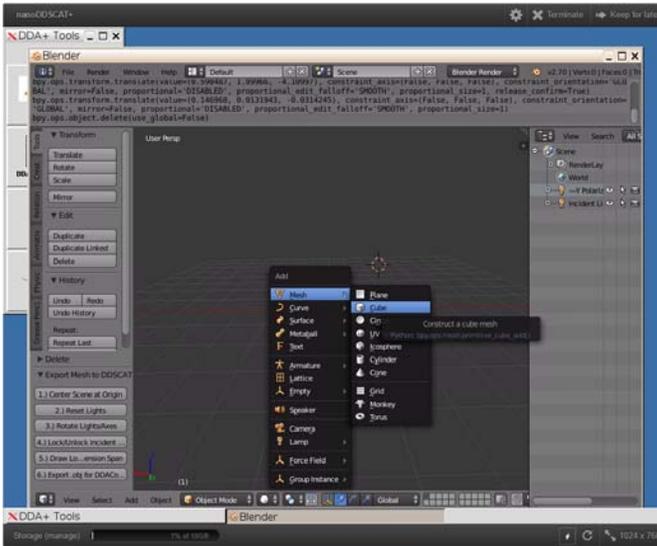
First note the two parallel black lines marked in the figure. The first of these is the light propagation direction, and the second is the light electric field polarization. This will define what direction the light is being shone on the object. Typically plasmon resonance will be excited based on the oscillating electric field (the magnetic field typically interacts with the electrons more weakly), and thus the electric field will define a plane along which excitations of the electrons occur strongly. Based upon the contours of the object in this plane, the scattering, absorption and electric field will change. When you create objects, keep that rotating the electric field polarization may dramatically affect how the light interacts with the object. This can be changed by clicking the rotate lights axis tab on the left as shown below.



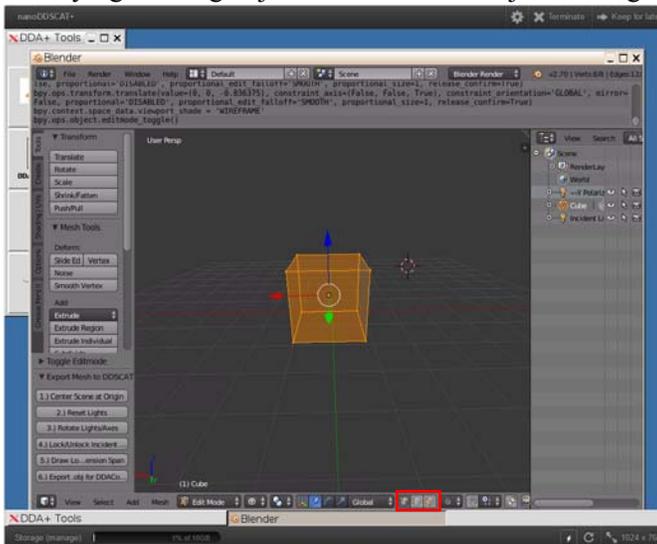
Some basics will help you navigate in blender. First holding down the center button (or the wheel) of typical mouse will allow you to rotate the scene to get a good look at your object.

Objects can be selected by right clicking on them. Once selected objects can be deleted using the delete key. A new object can be added by pressing Shift+a. This will bring up a dialogue prompting you to add

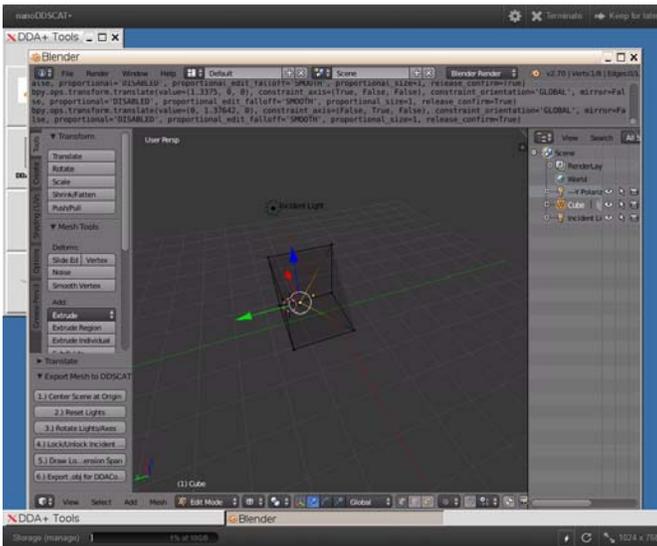
a new mesh, there are several useful built in shapes. Typically, it is easiest to start with a shape somewhat similar to the one you desire, and then modify that existing shape to suit your purpose. I am going to start with a cube for an example.



First for object editing, it is usually easier to switch the view to wireframe. The mode everything starts in is called object mode, which is usually reserved for organizing multiple objects in a frame, not for modifying existing objects. To switch to object editing mode, press tab.

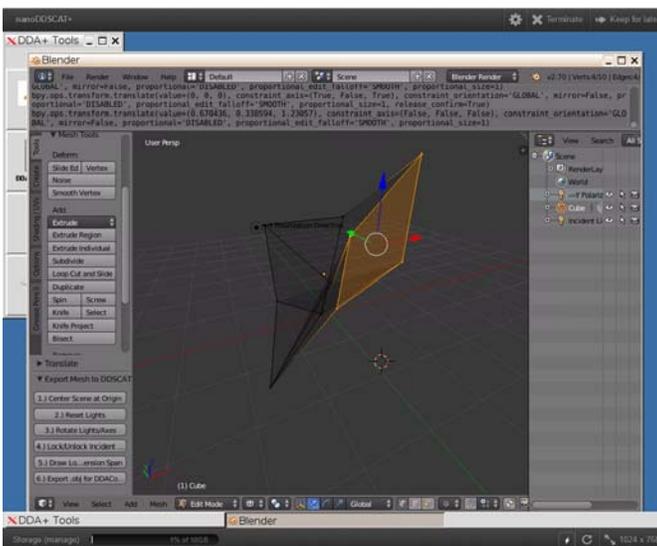


The types of editing can be done, editing of faces, edges and vertices. These are changed in the bottom menu as shown above. Clicking on a particular vertex, edge or face and pressing “g” will allow you to move it freely. Left clicking on one of the red, blue or green arrows will allow you move these along a specific cardinal direction.

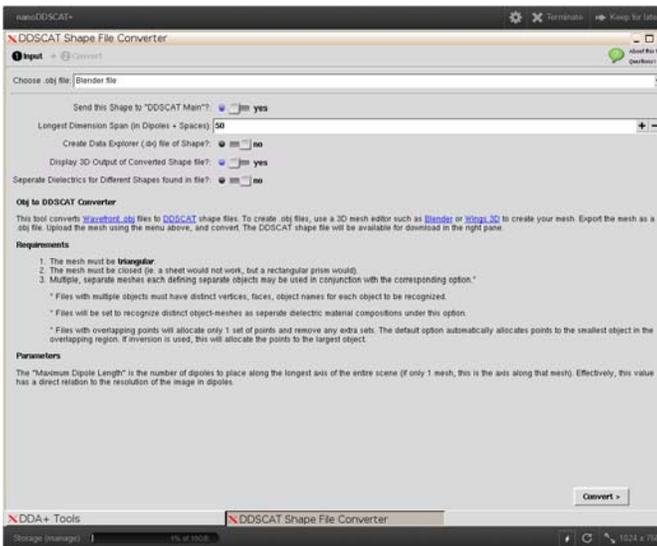


A very useful option is the subdivide option located in the mesh tools options on the left. This will allow you to create more vertices, or edges to make new faces and make your object more complicated. You can then drag these new vertices to define a shape. It is important to note that after subdividing objects you need to redefine the faces of your object. Do this by selecting all of the vertices which define a specific face and pressing “f”. Failure to do so will result in your object not being simulated correctly.

Once you have created a shape you are happy with, press the export .obj file button. This will save your object in the correct format to run the dda calculation. It is important to note at this point that the calculation will be default center your object at the origin. This is why the center object at origin button is provided, so you can get an accurate idea of where the electric field plane of the light will bisect your objects.



- 5) The next step will be to open the second program in the work flow, which is the DDA file convert tool.



In the top dropdown menu, you need to select Blender File. This will load the most recent blender file that was saved in this nanoddscat+ session. There is also an option to upload your own .obj file. You can choose this option if you prefer to run blender locally on your own computer, and then export a file to use with the file converter and ddscat. This is not advisable, as there are several specific details about formatting and saving the file (details can be found in the online manual for nanoddscat+) which the specialized version of blender on the website takes care of for you.

Once you have selected your file, be sure to check yes in the second box to send the generated shape ddscat main. This will set up to run the DDA calculation in the following step.

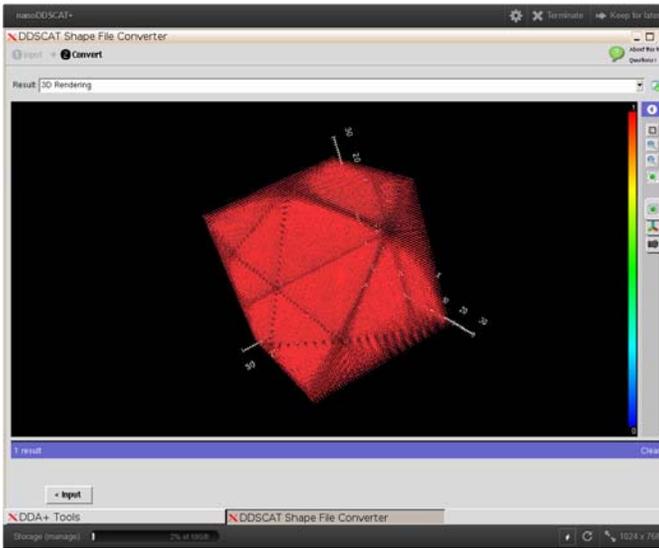
The third box is admittedly the most confusing, and is actually in the process of being corrected. As of writing this, this box asks you to specify the maximum length (in dipoles) of the object. The reason this is confusing is because as it stands the number of dipoles alone does not define the size of the object, this is later specified when you tell the calculation the resolution (which will be asked for subsequently as the number of dipoles per nm).

Thus at this point you need to figure out the size you want your object to be (typically in nm for typical plasmonic materials) along its longest dimension, then divide this number by the desired resolution (typical values are 1 dipole/nm for rough calculations or alternatively very smooth objects and 0.5 dipoles/nm for very accurate calculations or alternatively objects with sharp corners). Typically you want the resolution to be such that the sharpest point along your object is described by at least 2 dipoles. The time it takes to run the calculation will scale superlinearly with the number of dipoles however, so you want to limit this value as much as possible. Typically it is best to start with maybe 2 dipoles/nm, run the calculation, switch to 1 dipole/nm then 0.5 dipole/nm and see if the answer changes substantially. If it is still changing in going from 1 to 0.5 dipole/nm, you probably need to increase the resolution to get an accurate answer.

We will not be concerned with being massively accurate today, so please restrict your calculations to 1 dipole/nm. Thus the value you should put into this box is the longest dimension of your object in nm. If you make your object too large, the calculation will throw an error back at you that your calculation has timed out.

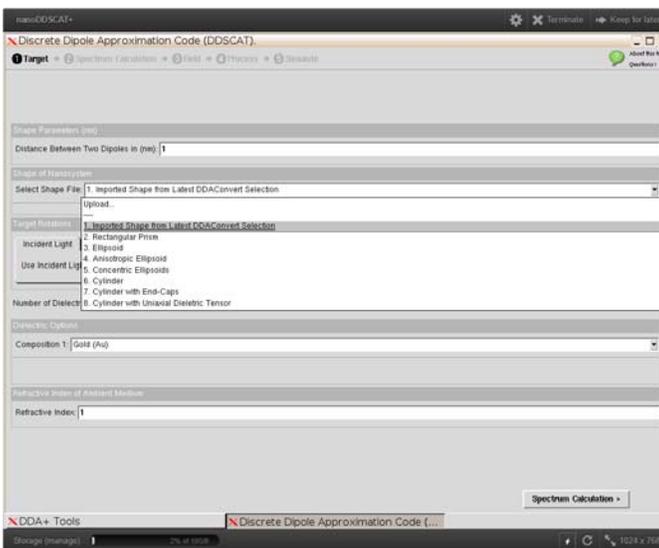
Of the next three boxes, you should select the middle one only. This will generate a 3D preview of the actual object the calculation will run on. You should ensure that this object matches what you intended in blender before proceeding. Possible problems usually stem from a failure to correctly define all faces in blender before exporting the object.

The third option is important if you include multiple objects of different composition in your calculation. The program will automatically assume different objects are composed of the same material unless this box is checked.



Following the target generation you can view your shape by selecting the 3D rendering tab as shown above.

- 6) Now you are ready to run the actual calculation. To do this navigate back to the main menu. And select the third program, DDSCAT. This will open a window similar to what was used in day 1, but with some significant differences.



First, as mentioned previously you should set the number of dipoles per nm to 1 for today's purposes, but recall that the combination of this value and the number of dipoles you selected in the file convert tool will define the length of your object. Secondly, in the shape file dialogue, you should select imported shape from last ddaconvert session. If the previous step was done successfully, then it should upload you shape file to run the calculation on.

Next in the target rotations tab you select import light polarization from blender session. This should set the propagation and polarization of the light as was defined in blender visually. For number of dielectric materials to use, select one, unless you produced multiple objects in blender and selected separate dielectrics for objects in file in the file convert tool. At this point you can select any of the preset dielectrics and compare if you wish. Try out different options to see the result! You can guess what the effect of changing the medium dielectric will be also based on the day 1 exercises.

In the spectrum tab, you may want to select a fairly wide range of frequencies (wavelengths) in order to find any resonances of your object. Do not change the light polarization from linear y, or this will scramble everything relative to what you defined in blender. Again we are still working out some bugs in this tool. Finally, in the fourth tab, you will likely want to select remote parallel ddsat, rather than local. The reason for this is that calculations of arbitrary geometries usually take substantially longer to converge than simple shapes. For this reason nanohub provides us with a cluster to run such calculations on that will run much faster than the local machine. By default nanohub allows jobs to run for 1 week before terminating a session, so a job that takes longer than that would require special permission. Typically jobs on single objects will almost never take more than a day, even at very high resolutions, but jobs involving large arrays of objects can take significantly longer.

Try to generate a few objects of different shapes, put a couple of objects of different types in close proximity, rotate the light around the object, whatever your heart desires. Some questions you may want to keep in mind as you work through this:

What does the spectra look like?

Is my object primarily scattering or absorbing light?

Where are the positions of high field located?

If you have multiple objects how is the light localized?

How sensitive is my objects to changes in the environment dielectric constant?

How do objects of different composition vary in sensitivity and field strength?