Simulating Nanoparticles Interaction with Electrons

Alexander A. Kichigin[1,2] and Maxim A. Yurkin[1,2]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Institutskaya 3, 630090 Novosibirsk, Russia*
[2]*Novosibirsk State University, Pirogova 2, 630090 Novosibirsk, Russia*

To simulate nanoparticle interaction with an electron beam, we developed a theory for the general case of an arbitrary host medium. This theory allows fast numerical simulations of the experiments for particles inside a substrate, since there is no need to discretize the host medium. We implemented it in the open-source software ADDA to simulate electron-energy loss spectroscopy and cathodoluminescence by particles of arbitrary shape and internal structure surrounded by arbitrary homogeneous host medium.

INTRODUCTION

Electron microscopy is an advanced experimental technique used for studying the optical properties of plasmonic nanoparticles. While optical methods are limited by the diffraction limit, electron beam allows localization of plasmon resonances on particle's cross-section with spatial resolution of less than 1 nm and energy resolution of less than 0.2 eV [1]. In the experiments, relativistic electrons interacting with the particle lose energy (electron-energy-loss spectroscopy – EELS) and the particle emits light (cathodoluminescence – CL). As a result, EELS and CL spectra are obtained for each electron beam position on the cross-section of the particle.

To accurately interpret the data, a computer simulation of the experiment needs to be done. The existing theory is valid only for vacuum – when only a particle and an electron are present. In reality the particle is placed on (or inside) a substrate to resist gravitation and collisions with fast electrons. We derived theory for the general case of arbitrary host medium, allowing simulations for particles inside a substrate. This theory is implemented in the open-source software ADDA [2], which uses the discrete dipole approximation (DDA) to simulate electromagnetic wave scattering by particles of arbitrary shape and internal structure.

Table 1. Free-space and particle-induced energy losses of a relativistic charge.

Host medium	**Free-space losses**	**Particle-induced losses**
Vacuum, $m_\mathrm{h} \equiv 1$	0	Equal to the particle extinction rate
Non-absorbing, $m_\mathrm{h} \in \mathbb{R}$	Frank-Tamm formula (Cherenkov radiation)	New Integral over the particle volume
Arbitrary, $m_\mathrm{h} \in \mathbb{C}$	Ambiguity due to singularity	New Integral over the particle volume

THEORY

We consider an electron as a classical charge and a particle as a finite object of arbitrary shape and internal structure. Our derivations are based on the volume-integral formulation of Maxwell's equations in the frequency domain [3]. To express the electron's energy losses and the particle's cathodoluminescence, we employed the energy-budget approach [4].

As a result, we derived the electron's *particle-induced* energy loss rate as an integral over the particle volume [5]

$$W_{\text{p.i.}} = -\frac{\omega}{2}\int_{V_{\text{int}}} \mathrm{d}^3\mathbf{r}'\,\mathrm{Im}[\mathbf{E}_1(\mathbf{r}')\cdot\mathbf{P}(\mathbf{r}')], \tag{1}$$

where ω is the angular frequency (corresponding to the photon's wavelength λ, and the electron's energy $\hbar\omega$), $\mathbf{E}_1$ is proportional to the electron's incident field (which is known [6]), and the particle's polarization $\mathbf{P}$ is calculated in the DDA. EELS probability is then proportional to $W_{p.i.}$, and CL probability is proportional to $W_{p.i.}$ minus the particle absorption rate. More details on the theory can be found in [5].

RESULTS

To test the implementation of EELS and CL calculation in ADDA, we compare numerically simulated spectrum against the exact solution (Lorenz-Mie theory for spheres in vacuum [7–9]) in Fig. 1. An electron with the 100 keV energy moves at the 50 nm distance from the center of a 35-nm-radius silver sphere. In this and further numerical simulations, the sphere is discretized with a grid of 64 dipoles per axis. Optical properties for silver are from [10].

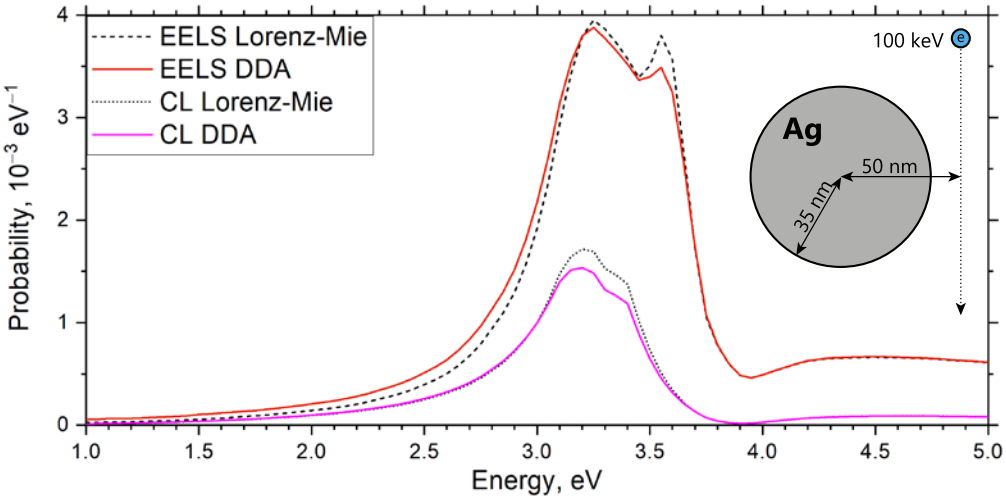

Fig. 1. EELS and CL spectra for a sphere simulated with the Lorenz-Mie theory and the DDA (with 64 dipoles per axis). The inset illustrates problem parameters.

The simulated spectra are close to the exact solution, but can be further improved by refining discretization (at the expense of extra computational resources). A more advanced approach is based on the Richardson extrapolation [11]. In particular, we performed simulations for a set

of discretization levels (16, 19, 23, 27, 32, 38, 45, 54, and 64 dipoles per axis) and extrapolated the dependence of simulated values versus dipole size d to $d = 0$ using the quadratic function. This extrapolation is performed automatically with the wrapper for ADDA written in Python and distributed along with it. See Fig. 2 for an example, where the accuracy is much better than in Fig. 1. Note also that the extrapolation additionally produces reliable confidence ranges, which are especially important when the reference solution is not available.

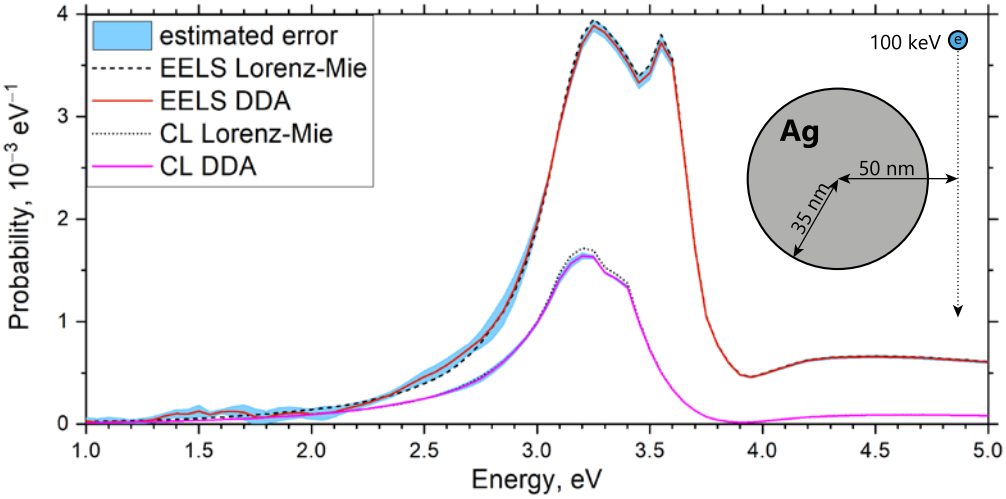

Fig. 2. Same as Fig. 1, but using the Richardson extrapolation for the DDA results (see text for details).

In Fig. 3 we demonstrate the EELS and CL spectra for the same sphere, placed in a host medium with the refractive index of 1.5 (glass), compared to that in vacuum. All simulations are combined with the above-described extrapolation.

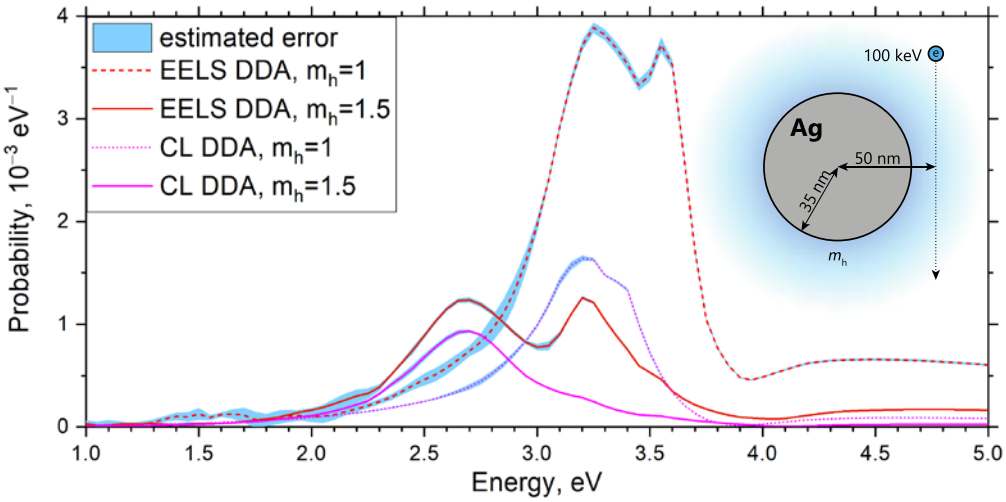

Fig. 3. The DDA simulations of EELS and CL spectra for spheres in the vacuum ($m_\mathrm{h} = 1$) and in a host medium with refractive index $m_\mathrm{h} = 1.5$ (using the same extrapolation as in Fig. 2). The inset illustrates problem parameters.

The peaks in the medium for both EELS and CL were shifted to the lower energies and decreased in magnitude compared to the vacuum.

These new abilities and features for simulating EELS and CL are available at a separate fork https://github.com/alkichigin/adda and will be implemented in the upcoming new official version of ADDA.

REFERENCES

[1] García de Abajo FJ. Optical excitations in electron microscopy. Rev Mod Phys 2010;82:209–75.
[2] Yurkin MA, Hoekstra AG. The discrete-dipole-approximation code ADDA: capabilities and known limitations. J Quant Spectrosc Radiat Transf 2011;112:2234–47.
[3] Mishchenko MI, Yurkin MA. Impressed sources and fields in the volume-integral-equation formulation of electromagnetic scattering by a finite object: A tutorial. J Quant Spectrosc Radiat Transf 2018;214:158–67.
[4] Moskalensky AE, Yurkin MA. Energy budget and optical theorem for scattering of source-induced fields. Phys Rev A 2019;99:053824.
[5] Kichigin AA, Yurkin MA. Electron energy loss spectroscopy in the framework of the discrete dipole approximation. In: AIP Conf. Proc.; 2020 Sep. 14; Online. ITMO University. vol. 2300; p. 020053.
[6] Jackson JD. Classical Electrodynamics. 3rd edition. New York: Wiley; 1998.
[7] García de Abajo - EELS in the sphere [Internet]. Available from: http://widgets.nanophotonics.es/sphere/index.html.
[8] García de Abajo FJ, Howie A. Relativistic Electron Energy Loss and Electron-Induced Photon Emission in Inhomogeneous Dielectrics. Phys Rev Lett 1998;80:5180–3.
[9] García de Abajo FJ. Relativistic energy loss and induced photon emission in the interaction of a dielectric sphere with an external electron beam. Phys Rev B 1999;59:3095–107.
[10] Palik ED. Handbook of Optical Constants of Solids. Academic Press; 1985.
[11] Yurkin MA, Maltsev VP, Hoekstra AG. Convergence of the discrete dipole approximation. II. An extrapolation technique to increase the accuracy. J Opt Soc Am A 2006;23:2592–601.