Electron Energy Loss Spectroscopy in the Framework of the Discrete Dipole Approximation

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Abstract. Electron-energy-loss spectroscopy (EELS) is a widely used experimental technique for characterization of nanoparticles, being an extension of a standard electron microscopy. In EELS a particle under study is exposed to an electron beam and the loss of electron kinetic energy is measured after the interaction, varying the transverse position of the beam. This technique is particularly suitable for plasmonic nanoparticles, which exhibit unique optical properties caused by localized surface plasmon resonances (LSPRs). EELS excites full set of LSPRs and allows mapping them with unprecedented spatial resolution of down to 1 nm. The discrete dipole approximation (DDA) is a numerically exact method for simulating interaction of electromagnetic waves with particles of arbitrary shape and internal structure. It is based on volume-integral equation (VIE) in the frequency domain. In this work we extend the DDA to simulate EELS. We base all theoretical derivations on the VIE, in particular, the electric field of a moving electron is given as a line integral of the Green's tensor. Although the final expressions agree with classical textbooks, our approach allows us to employ the energy-budget considerations in the frequency domain. First, this framework leads to an expression for energy losses of electron moving faster than the speed of light in non-absorbing homogeneous medium (Cherenkov radiation), that is in agreement with the classical result (Frank-Tamm formula). Second, it leads to rigorous and general expressions for additional losses in the presence of a scatterer. These expressions are given as integrals over the volume of the scatterer (very convenient for the DDA) and are valid not only for the case of vacuum, but for arbitrary (even absorbing) host medium. We are working on implementing them in the open-source software package ADDA.

INTRODUCTION

Plasmonic nanoparticles exhibit unique optical properties. Their scattering and absorption spectra have strong peaks in the visible region at wavelengths of hundreds of nanometers, while the particle itself is only the size of tens of nanometers. Such unusual behavior is caused by Localized Surface Plasmon Resonances (LSPRs) – collective resonant oscillations of free electron gas inside the particle that couple with the applied electromagnetic field. Excitation energies of LSPRs are strongly dependent on particle's geometry, size, internal structure, and refractive index of the surrounding medium. Variation of these parameters leads to significant changes in the optical response of a particle.

Electron-energy-loss spectroscopy (EELS) is an experimental technique – an extension of the standard electron microscope [1]. In EELS a particle under study is exposed to a beam of relativistic electrons with energy selected in the range 100–300 keV. The beam is pointed at the particle with the positioning precision of down to 1 nm. Next, after the interaction with the particle kinetic energies of transmitted electrons are measured (measurement precision is down to 0.1 eV) and their losses of energy are calculated. Obtained energy losses present the EELS spectrum, which is typically separated into two main regions. First region contains low-loss peaks ($\Delta E < 50$ eV), including zero-loss one (intact electrons) and plasmon peaks due to LSPRs. Second region contains high-loss peaks ($\Delta E > 50$ eV), corresponding to core losses, that are usually used to study elemental composition of the sample.

In investigation of LSPRs the object of interest is the low-loss region of the EELS spectrum. Spectrum for a particular position of the beam contains information about plasmon peaks for this exact spot in or near the cross section

of the particle. By varying transverse position of the beam, spectra for the whole particle cross section are obtained. The latter allows distinguishing different energy-loss peaks and mapping them to the different parts of the particle. Thus, in EELS experiment not only information about excitation energies of LSPRs is obtained, but also about their location inside the particle. To accurately interpret the results of EELS experiment, it is necessary to have a theoretical description of particle interaction with the electromagnetic field of a fast electron, complemented by a numerical simulation method.

The discrete dipole approximation (DDA) is a numerically exact method for simulating interaction of electromagnetic waves with particles of arbitrary shape and internal structure [2]. It is based on volume-integral equation (VIE) formulation of Maxwell's equations in the frequency domain [3]. In the DDA the volume of the particle is divided into an array of cubical elementary volumes, then each elementary volume is replaced by a point dipole. Polarizabilities of the dipoles are chosen for their interaction with electromagnetic wave to match the refractive index of the particle. This reduces the solution of Maxwell's equations for a particle of arbitrary shape to an algebraic problem for a finite set of dipoles. By design the DDA provides an effective way for numerical calculation of quantities expressed as integrals of the expressions involving the internal field (or induced polarization density) over the volume of the particle. In the light-scattering problems the most relevant of such quantities are extinction and absorption cross sections, as well as angle-resolved scattering intensity. Initially designed for the plane waves, DDA is suitable for simulating interaction of particles with arbitrary electromagnetic fields, including the field of a fast electron. Previous approaches to simulate EELS with the DDA are e-DDA [4] and DDEELS [5], which are only suitable for the common case of vacuum. The goal of this work is to rigorously derive all relevant quantities for arbitrary host medium and implement them in the computationally efficient open-source code ADDA [6].

THEORY

We base all theoretical derivations on the VIE, in particular, the electric field of a moving electron is given as a line integral of the Green's tensor over the electron's trajectory. Our approach is intended to employ the energy-budget considerations in the frequency domain [7]. This framework allows us to express enhanced energy losses (due to interaction with the particle) of a fast electron as integral over the volume of the particle – very convenient for the DDA.

Energy-Budget Framework

The central component of the VIE framework for time-harmonic fields is the free-space Green's tensor [3]

$$\overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \overset{\text{def}}{=} \left(\overline{\mathbf{I}} + \frac{\nabla \otimes \nabla}{k^2}\right) \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|}, \tag{1}$$

where i – imaginary unit, k – wavenumber, $\overline{\mathbf{I}}$ – identity dyadic, $\otimes$ denotes tensor (dyadic) product of two vectors. If $\mathbf{J}_\text{s}(\mathbf{r})$ is the current density of external sources, then the incident (source-generated) electric field is

$$\mathbf{E}_\text{inc}(\mathbf{r}) = i\omega\mu_0 \lim_{V_0 \to 0} \int_{V_\text{s} \setminus V_0} d^3\mathbf{r}' \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}_\text{s}(\mathbf{r}') - i\frac{\mathbf{J}_\text{s}(\mathbf{r})}{3\omega\varepsilon_0}, \tag{2}$$

where V_s is the region, where the sources are located, and V_0 is the spherical exclusion volume. And if $\mathbf{P}(\mathbf{r})$ is the polarization density inside the particle, then the scattered electric field is

$$\mathbf{E}_\text{sca}(\mathbf{r}) = \omega^2\mu_0 \lim_{V_0 \to 0} \int_{V_\text{int} \setminus V_0} d^3\mathbf{r}' \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') - \frac{\mathbf{P}(\mathbf{r})}{3\varepsilon_0}, \tag{3}$$

where V_int is the region, where the particles are located.

These representations for fields are then substituted into expressions for power rates (assuming that $V_\text{s} \cup V_\text{int} = \emptyset$): W_0 – power emitted by sources in the absence of the scatterer, W_enh – additional power emitted due to the scatterer, W_ext – extinction power rate,

$$W_0 = -\frac{1}{2} \int_{V_\text{s}} d^3\mathbf{r} \, \text{Re}[\mathbf{E}_\text{inc}(\mathbf{r}) \cdot \mathbf{J}_\text{s}^*(\mathbf{r})] = \frac{\omega\mu_0}{2} \int_{V_\text{s}} d^3\mathbf{r} \int_{V_\text{s}} d^3\mathbf{r}' \text{Im}[\mathbf{J}_\text{s}^*(\mathbf{r}) \cdot \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}_\text{s}(\mathbf{r}')], \tag{4}$$

$$W_\text{enh} = -\frac{1}{2} \int_{V_\text{s}} d^3\mathbf{r} \, \text{Re}[\mathbf{E}_\text{sca}(\mathbf{r}) \cdot \mathbf{J}_\text{s}^*(\mathbf{r})] = -\frac{\omega^2\mu_0}{2} \int_{V_\text{s}} d^3\mathbf{r} \int_{V_\text{int}} d^3\mathbf{r}' \text{Re}[\mathbf{J}_\text{s}^*(\mathbf{r}) \cdot \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}')], \tag{5}$$

$$W_\text{ext} = -\frac{\omega}{2} \int_{V_\text{int}} d^3\mathbf{r} \, \text{Im}[\mathbf{E}_\text{inc}(\mathbf{r}) \cdot \mathbf{P}^*(\mathbf{r})] = -\frac{\omega^2\mu_0}{2} \int_{V_\text{int}} d^3\mathbf{r} \int_{V_\text{s}} d^3\mathbf{r}' \text{Re}[\mathbf{P}^*(\mathbf{r}) \cdot \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}_\text{s}(\mathbf{r}')]. \tag{6}$$

EELS in Terms of Energy-budget

If we consider a probe electron as a classical charge q moving along z-axis in the positive direction with the speed v, then

$$\mathbf{J}_s(\mathbf{r}) = \left\{ 0, 0, q\delta(x - x_0)\delta(y - y_0) \exp\left[\mathrm{i}\frac{\omega}{v}(z - z_0) \right] \right\}. \tag{7}$$

Substituting Eq. (7) into Eq. (4) immediately gives $W_0 = 0$ for the case of electron moving in vacuum ($\varepsilon(\omega) = 1$). If the electron is moving in arbitrary homogeneous isotropic non-absorbing medium ($\varepsilon(\omega) \in \mathbb{R}$) faster than the speed of light $c/\sqrt{\varepsilon(\omega)}$ in this medium, then, according to Eq. (4), the electron would be losing energy at a rate

$$\frac{\partial}{\partial z} W_0 = \frac{1}{8\varepsilon_0}\frac{q^2}{c^2}\omega\left(1 - \frac{c^2}{v^2\varepsilon(\omega)} \right), \tag{8}$$

which corresponds to a well-known Frank-Tamm formula [8] for the case of Cherenkov radiation [9].

If the electron is moving in homogeneous isotropic medium with arbitrary dielectric permittivity ($\varepsilon(\omega) \in \mathbb{C}$), then the electric field of the electron given by Eq. (2) would match classical result [10]:

$$E_{\mathrm{inc},x} = \frac{q\omega}{2\pi\varepsilon_0\varepsilon(\omega)v^2\gamma_\varepsilon}\frac{x - x_0}{b}\exp\left[\mathrm{i}\frac{\omega}{v}(z - z_0) \right] K_1\left(\frac{\omega b}{\gamma_\varepsilon v} \right),$$

$$E_{\mathrm{inc},y} = \frac{q\omega}{2\pi\varepsilon_0\varepsilon(\omega)v^2\gamma_\varepsilon}\frac{y - y_0}{b}\exp\left[\mathrm{i}\frac{\omega}{v}(z - z_0) \right] K_1\left(\frac{\omega b}{\gamma_\varepsilon v} \right), \tag{9}$$

$$E_{\mathrm{inc},z} = -\mathrm{i}\frac{q\omega}{2\pi\varepsilon_0\varepsilon(\omega)v^2\gamma_\varepsilon^2}\exp\left[\mathrm{i}\frac{\omega}{v}(z - z_0) \right] K_0\left(\frac{\omega b}{\gamma_\varepsilon v} \right),$$

where $b = \sqrt{(x - x_0)^2 + (y - y_0)^2}$, K is the modified Bessel function of the second kind, and we introduced

$$\gamma_\varepsilon = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}\varepsilon(\omega)}}.$$

We need to find the enhanced energy losses of the electron due to interaction with the particle. If we take Eq. (5) and interchange the integration order in it, we obtain

$$W_{\mathrm{enh}} = -\frac{\omega}{2}\int_{V_{\mathrm{int}}} \mathrm{d}^3\mathbf{r}'\mathrm{Im}[\mathbf{E}_1(\mathbf{r}') \cdot \mathbf{P}(\mathbf{r}')], \tag{10}$$

where we introduced an auxiliary field

$$\mathbf{E}_1(\mathbf{r}) \overset{\text{def}}{=} \mathrm{i}\omega\mu_0 \lim_{V_0 \to 0} \int_{V_s \setminus V_0} \mathrm{d}^3\mathbf{r}'\overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}_s^*(\mathbf{r}') - \mathrm{i}\frac{\mathbf{J}_s^*(\mathbf{r})}{3\omega\varepsilon_0} = \begin{pmatrix} -E_{\mathrm{inc},x} \\ -E_{\mathrm{inc},y} \\ E_{\mathrm{inc},z} \end{pmatrix} \exp\left(-2\mathrm{i}\frac{\omega}{v}(z - z_0) \right). \tag{11}$$

For a special case of vacuum as a surrounding medium, $\mathbf{E}_1(\mathbf{r}) = -\mathbf{E}_{\mathrm{inc}}^*(\mathbf{r})$, which, upon insertion into Eq. (10) immediately leads to $W_{\mathrm{enh}} = W_{\mathrm{ext}}$ – a previously known result [4,5]: probability of electron-energy loss $\Gamma_{\mathrm{EELS}}(\hbar\omega)$, in our approach described by W_{enh}, was found to be proportional to extinction power rate W_{ext}, but only for the case of interaction in the vacuum. Our general Eq. (10) describes enhanced energy losses for interaction in arbitrary medium.

IMPLEMENTATION IN THE DDA

The simulations are performed independently for many values of ω. First modification to the standard DDA is the generation of $\mathbf{E}_{\mathrm{inc}}(\mathbf{r})$ inside the scatterer (at all dipole positions) according to Eq. (9). After that the standard DDA workflow calculates polarization $\mathbf{P}(\mathbf{r})$. Second modification is the calculation of W_{enh} according to Eq. (10), but it is very similar to W_{ext} [Eq. (6)] and is effectively calculated in the DDA. For that $\mathbf{E}_1(\mathbf{r})$ is computed on the fly using Eq. (11) at negligible extra cost. Moreover, the standard DDA machinery to compute angle-resolved scattering intensities from $\mathbf{P}(\mathbf{r})$ will describe cathodoluminescence. We are currently working on implementing these ideas in the open-source code ADDA [6], specifically – at a separate branch https://github.com/alkichigin/adda.

Precision of EELS simulation with ADDA is compared to Lorenz-Mie theory [11] at Fig. 1. Simulated spectrum is almost identical to analytically obtained. Inaccuracy at energies > 4 eV is less than 1%. Inaccuracy at energies < 4 eV can be explained by refractive index of silver being close to imaginary axis at this energy range.
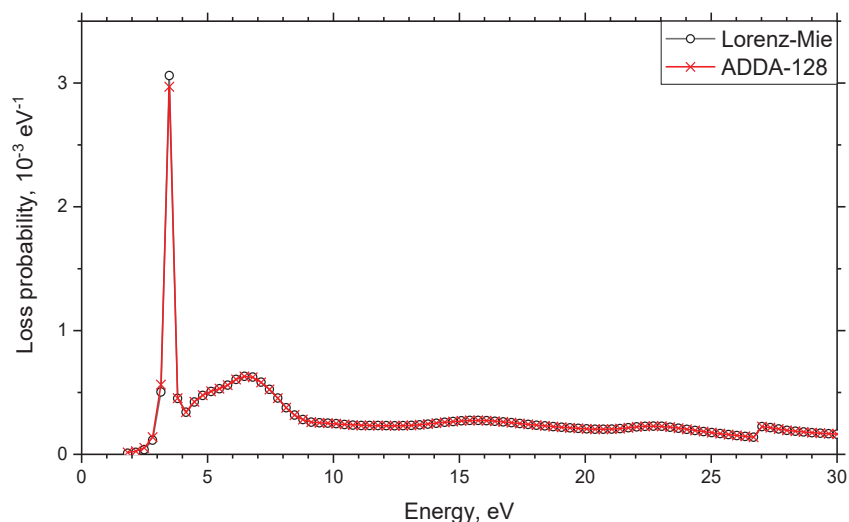
FIGURE 1. EELS spectra obtained with ADDA (with grid 128 dipoles per axis) and Lorenz-Mie theory (data is taken from http://widgets.nanophotonics.es/sphere/index.html). An electron with energy 100 keV moves at distance of 6 nm from the center of a silver nanosphere with 5 nm radius.

CONCLUSION

We built all derivations of EELS quantities on top of the energy-budget framework. All final expressions either match the previously known results discussed in classical literature, or appear to be new. We introduced a general expression for enhanced electron energy losses, which can be effectively calculated in the DDA. The expression remains valid for any arbitrary (even absorbing) host medium; in the case of vacuum it reduces to previously known result. While all previous realizations for EELS simulations were limited to the case of vacuum, our approach is valid for arbitrary medium, which is especially important as LSPRs are strongly dependent on dielectric properties of the surrounding medium. Practically, this may be relevant for particles or voids in a larger homogeneous slab. Moreover, ADDA already allows for rigorous and efficient treatment of particles on substrate [12], so it should be easy to combine this feature with EELS simulation. This is, however, left for the future research.

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REFERENCES

1. C. Cherqui, N. Thakkar, G. Li, J.P. Camden, and D. Masiello, Annu. Rev. Phys. Chem. **67**, 331–357 (2016).
2. M.A. Yurkin and A.G. Hoekstra, J. Quant. Spectrosc. Radiat. Transfer **106**, 558–589 (2007).
3. M.I. Mishchenko and M.A. Yurkin, J. Quant. Spectrosc. Radiat. Transfer **214**, 158–167 (2018).
4. N.W. Bigelow, A. Vaschillo, V. Iberi, J.P. Camden, and D.J. Masiello, ACS Nano **6**, 7497–7504 (2012).
5. N. Geuquet and L. Henrard, Ultramicroscopy **110**, 1075–1080 (2010).
6. M.A. Yurkin and A.G. Hoekstra, J. Quant. Spectrosc. Radiat. Transfer **112**, 2234–2247 (2011).
7. A.E. Moskalensky and M.A. Yurkin, Phys. Rev. A **99**, 053824 (2019).
8. I. Frank and I. Tamm, *Coherent Visible Radiation from Fast Electrons Passing through Matter* (1937).
9. P.A. Cherenkov, Phys. Rev. **52**, 378–379 (1937).
10. J.D. Jackson, *Classical Electrodynamics*, 3rd edition (Wiley, New York, 1998).
11. F.J. García de Abajo and A. Howie, Phys. Rev. Lett. **80**, 5180–5183 (1998).
12. M.A. Yurkin and M. Huntemann, J. Phys. Chem. C **119**, 29088–29094 (2015).