Simulation of light scattering and electron energy loss (EELS) by small spatially dispersive plasmonic nanodimers

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Abstract. Despite the tremendous progress in the field of nanoplasmonics, complex plasmonic nanostructures such as dimers still present a significant challenge for proper numerical characterization. In particular, for the particles which size is smaller than electron mean free path in metals it is necessary to account for effects of spatial nonlocality in simulations. To address these problems a new mathematical model based on the Discrete Sources Method was developed and corresponding computer model was implemented. It enables one to successfully resolve the problem of accounting for spatial dispersion effects, which is especially important in the systems with very small gap and particle size, and it retains all key features of the Discrete Sources numerical approach including flexibility and a posteriori error estimation. We compute such scattering characteristics as electron energy loss probability and total scattered field intensity of nanodimers as one typically has to rely on methods of both optical and electron spectroscopy to experimentally investigate these structures. The developed model also allows to simultaneously consider several external excitations of the plasmonic system, including both electron and plane wave, in order to obtain more information about the system and to significantly speed up computational performance.

1. Introduction

It is well known that increasing demand in accurate characterization of plasmonic microstructures, such as dimers, nanoparticles (NPs) or thin films, requires precise experimental and theoretical techniques. For this reason both optical and electron spectroscopy methods, including such approaches as electron energy-loss spectroscopy (EELS), have recently gained much attention in nanophotonics research [1-5].

Due to these facts we would like to especially consider EELS in the current paper in addition to the optical plane wave excitation. Within EELS fast electrons (with kinetic energies ranging from 50keV to 300keV) are passing nearby the structure exciting plasmonic modes of the system and therefore losing a corresponding amount of kinetic energy. By performing spectroscopy on the transmitted electrons one can therefore locally measure the required excitation spectrum of the plasmonic structure with high spatial resolution. EELS also allows to excite resonances that are optically dark due to their vanishing electric dipole moments, and therefore to thoroughly study properties of small metal nanoparticles that are of interest. These features make EELS an attractive tool for studying surface plasmons related to various applications including nanoantennas, sensing, optical trapping, development of new devices such as nanolasers, characterization of lithium ion battery materials, and many others. It is especially important to note that particle scattering properties highly depend on...
particle shape, size, and refractive index, and also on the refractive index of the surrounding medium, which increases the problem complexity. Special attention is currently devoted to the fact that small NPs, as well as systems with small distance between particles (less than 5nm) exhibit excitation spectrum not predicted by methods based on classic electromagnetics. Although these spectral deviations have quantum origin, it has been shown that they could be accounted for within traditional numerical techniques via inclusion of nonlocal spatial dispersion effects through implementing Generalized Nonlocal Optical Response (GNOR) approach [6-9].

In order to better understand experimental measurements and to properly interpret the results, accurate simulations are required, creating demand for flexible and reliable numerical approaches capable of efficiently modeling single NPs and NP systems [3-5]. Efficiency of the model is determined by various factors, including performance, reliability and flexibility. In this regard approaches allowing to simultaneously simulate various external excitations using the single pre-generated matrix of the particle system and allowing to conduct error estimation seem to be of interest.

Correspondingly, in the focus of the current paper is implementation of a model for dimer particle system irradiated by an electron beam with the efficient Discrete Sources Method (DSM) approach due to the high demand for analysis of particle systems in applications. Specific highlights of the DSM include the ability to perform fast high-performance computations and the ability to conduct an a posteriori error estimation.

2. Problem statement accounting for spatial nonlocality

In the following we would consider scattering problem of electromagnetic field $\{E_0^{inc}, H_0^{inc}\}$ emitted by an external source such as electron or laser beam for a single axisymmetric plasmonic nanoparticle with size from 2 to 10nm or for a dimer containing a pair $D_1$, $D_2$ of such particles deposited in homogeneous medium $D_0$. We will suggest that axis $z$ of the Cartesian coordinate system coincides with axes of both dimer particles, if not stated otherwise (for the EELS example geometry see figure 1). Considering NP size the laser beam excitation can be treated as a plane wave (PW), which in our case propagates along the introduced $z$ axis without the loss of generality [9]. For the case of electron beam excitation the general setup could be described as follows: an electron with velocity $v$ moves along the $z$ axis and does not pass through any of the particles. We assume that it is represented by point charge in uniform straight motion [4,5,7]. Of special importance here is the impact parameter $b$ which defines the electron position via distance between its trajectory and $z$ axis. $O$ is origin of the Cartesian coordinate system and $d$ is gap distance between particles.

![Figure 1. EELS problem geometry.](image)

Nanoparticles could be placed anywhere in the medium, so that electron trajectory can be either located at the edge of the whole system or directly at the dimer gap (see figure 4). We also suppose
that both scatterers are homogeneous particles with smooth boundaries, and that for each medium we know dielectric permittivity \( \varepsilon \) assuming permeability \( \mu \) to be unit. In this work each particle is modeled by a sphere of radius \( a \), however it should be explicitly noted, that generally the proposed approach is capable of handling non-spherical particles.

Mathematical problem statement accounting for the spatial dispersion effects can then be written in a way similar to the previously studied case of single particle [6-9]:

\[
\begin{align*}
\text{rot} \mathbf{H}_o(M) &= jk \left( \varepsilon_r \mathbf{E}_o(M) + \xi_v^2 \text{grad} \text{div} \mathbf{E}_{z,O}(M) \right), \\
\text{rot} \mathbf{E}_o(M) &= -j k \mu_0 \mathbf{H}_o(M), \\
\mathbf{E}_o(M) &= \mathbf{E}_{r,O}(M) + \mathbf{E}_{L,O}(M), \quad M \in D_0, \quad Q = 1,2 \quad \Rightarrow \quad \mathbf{E}_o(M) = \mathbf{E}_{o}^i(M) + \mathbf{E}_{o}^{exc}(M), \quad M \in D_0,
\end{align*}
\]

\[
\begin{align*}
\mathbf{n}_p \times [\mathbf{E}_o(P) - \mathbf{E}_o^i(P)] &= \mathbf{n}_p \times \mathbf{E}_{o}^{exc}(P), \\
\mathbf{n}_p \times [\mathbf{H}_o(P) - \mathbf{H}_o^i(P)] &= \mathbf{n}_p \times \mathbf{H}_{o}^{exc}(P), \\
\mathbf{n}_p \cdot \xi_v \mathbf{E}_o(P) &= \mathbf{n}_p \cdot \xi_v \mathbf{E}_o^i(P), \quad P \in \partial D_0, \quad Q = 1,2,
\end{align*}
\]

\[
\lim_{r \to \infty} \left( \xi_v \mathbf{E}_o^i(M) \times \frac{r}{r} - \sqrt{\mu_0} \mathbf{H}_o^i(M) \right) = 0, \quad r = |M| \to \infty.
\]

Here index \( Q = 1,2 \) refers to the first or second particle of the dimer, \( k \) is vacuum wavenumber of the external excitation, \( \{ \mathbf{E}_o^i, \mathbf{H}_o^i \} \) represents the scattered field, \( \{ \mathbf{E}_o, \mathbf{H}_o \} \) is the internal field of the corresponding particle which in turn is a linear combination of transversal \( \mathbf{E}_{r,O} \) and longitudinal \( \mathbf{E}_{L,O} \) components, \( \mathbf{n}_p \) is a unit outward normal to the particle surface in point \( P \), \( \xi_v \) corresponds to the response of bound ions in metal. Both latter values are determined via GNOR [6-9].

Incident electron energy loss probability \( P \) is the main parameter we would compute and analyze in this work:

\[
P(\omega) = \frac{e}{\pi \hbar \omega} \int_{-\infty}^{\infty} \left[ \text{Re} \left\{ \mathbf{E}_{scw}(\mathbf{r}, \omega) e^{-i\omega t} \right\} \right] d\mathbf{r},
\]

Here \( \hbar \) is a reduced Planck constant used throughout this work, \( e \) is electron charge, \( \nu \) is an absolute value of electron speed, \( \text{Re} \) means the real part of the value inside brackets, and \( \mathbf{r} \) reflects electron position related to the origin of the Cartesian coordinate system. As electron moves along the \( z \) axis, this integral eventually reduces to the integral along \( z \) [5]. It should also be explicitly noted that given expression for \( P \) is valid under the assumption that the electron energy loss (\(-0.5\text{eV} - 50\text{eV}\) in the valence-loss region) is small compared to the initial kinetic energy of the incident electron (\(\sim 50\text{keV} - 300\text{keV}\), also known as EELS in low-loss region), and the electron velocity \( \nu \) remains constant. This simplification is known as no-recoil approximation.

Also in order to demonstrate its ability to consider different external excitations simultaneously, we would compute total scattered field intensity (scattering cross section, SCS) as a function of wavelength for a scattering problem with plane P-polarized wave propagating along \( z \) axis. For a scattering characteristic we would consider scattering cross-sections of the same dimers. It should be noted that proposed method generally allows to consider any angle of plane wave incidence. The mathematical definition of the considered scattering cross-section (SCS, or \( \sigma \)) that allows to compute it for an incident plane wave with a specific wavelength is given in the following [6-9]:

\[
\mathbf{E}_o(\mathbf{r})/|\mathbf{E}_o^i(\mathbf{r})| = \text{exp}\left(-j k R/R \right) F_\theta(\theta, \theta, \varphi) + O(1/R^2), \quad R \to \infty, \quad z > 0,
\]

\[
DSC(\theta, \varphi) = |F_\theta(\theta, \varphi)|^2 + |F_\varphi(\theta, \varphi)|^2, \quad \sigma(\theta) = \int_{\Omega} \text{DSC}(\theta, \varphi) d\Omega
\]
Here Ω is a unit sphere in external medium and $R$, $\theta$ and $\phi$ are the units of the spherical coordinate system corresponding to the Cartesian coordinates introduced earlier. All considered particles are characterized by material parameters obtained using Johnson and Christy results (http://refractiveindex.info).

3. Hybrid scheme of the Discrete Sources Method

We propose the numerical solution based on the advanced mathematical Discrete Source Method hybrid scheme. It was previously shown that corresponding numerical algorithms possess such key features as high performance, flexibility, a posteriori error estimation and capability of rigorously resolving the nonlocal effect influence on particle properties. These results are presented in the following key publications [6-9]. It appears possible to maintain the enlisted features while developing a new dimer model.

High performance of the method is ensured due to several factors, first one being that within DSM the solution to the scattering problem is constructed as a linear combination of discrete source (DS) fields defined analytically. In order to solve the dimer scattering problem we have introduced DSes located inside each particle and adopted their numerical set carrier according to particle structure and to all external excitations that will be considered in this work including electron beam and plane wave. During this procedure we have maintained account for nonlocal effect in the way similar to previous projects via introducing DSes modeling longitudinal electromagnetic waves propagating in the plasmonic medium which are responsible for the effects of spatial nonlocality. As a consequence, in this paper we implement the same DS types as in previous works devoted to the numerical simulation of spatial nonlocality in plasmonic NPs [6-9].

Another factor that speeds up the numerical algorithm is that it allows to simultaneously consider multiple external excitations at one frequency without recomputing the matrix of the entire system. The matrix is obtained via satisfying boundary conditions at the surface of each particle using Generalized Matching-Point Technique which leads to overdetermined system of linear equations, where matrix elements are represented using only DS fields, unknowns are DS amplitudes, and right-hand part corresponds to values of the incident field at matching points. Thus, employing the known expressions for the incident electromagnetic fields for either electron or plane wave, we could obtain several right-hand parts for one matrix representing our dimer. Solving the given overdetermined system via residual minimization techniques for each case, one obtains corresponding problem solutions in the form of scattered field. In case of the hybrid scheme applied to a dimer matching points are distributed over surfaces of both particles, discrete sources modeling scattered field are matched to the incident field also at both surfaces, and discrete sources modeling internal field of each particle are employed only in the boundary conditions for specific particle.

As far as obtained scattered field is represented in analytical non-integral form, this also simplifies subsequent computation of scattering characteristics that are of interest. So one could, for example, conduct fast analysis of electron beams at different positions and therefore obtain EELS maps showing the spectrum at every point in a plane. This feature makes DSM very attractive for plasmonics and for EELS simulations in particular.

4. Simulation results and discussion

In order to illustrate the capabilities of the developed method let us consider plasmonic nanodimers composed of spheres. We would vary the gap size and electron impact parameter in local and GNOR approximations, and we would also compare the obtained results to the plane wave excitation and to the case of single particle scattering.

Firstly, let us separately consider silver (Ag) nanosphere with radius $a=2nm$ and dimer composed of two identical silver nanospheres with the same radius under plane wave excitation. We would vary dimer gap size $d$, and compare total scattering cross-sections (SCS) obtained for different systems in both local response approximation (LRA) and nonlocal GNOR approximation in order to visually demonstrate the significant impact of nonlocal effects on scattering properties of NPs.
Figure 2: SCS obtained for single Ag sphere (red lines) and dimers of Ag spheres, $a=2$nm. Gap size $d$ (nm) varies. Excitation: P-polarized plane wave propagating along $z$ axis.

We can clearly see that under the given plane wave excitation reduction of gap size leads to the blue shift of surface plasmon resonance wavelength as compared to single sphere (figure 2). Also the intensity of surface plasmon resonance (SPR) scattering peak decreases with the reduction of gap size, however it is significantly larger than intensity of single particle SPR. The same results could be more efficiently demonstrated in the case of nonspherical particles, where the difference between these characteristics could be much more clear. These results are in good agreement with the other published works [10]. We should note that sphere radius $a=2$nm is selected specifically to emphasize the influence of nonlocal spatial dispersion effects as their impact grows with the reduction of particle size.

Another comment on the results presented at figure 2 is connected to the DSM a posteriori error estimate. The residual value of 2% ensures very nice accuracy. However, the residual predictably tends to increase with the reduction of gap size $d$, and its value for i.e. $d=0.4$nm case already equals 5%. This is not a surprise as very small gap sizes not only become more computationally demanding, but generally they also require quantum approaches to accurately account for possible tunneling effect which is beyond the scope of the classical model in either LRA or GNOR approximations. In particular, it has been shown that gap size from 0.5 to 2 nm generally has to be modeled with account for nonlocal effect, closer situated particles have to include quantum description methods, and larger gap sizes could be efficiently considered in the usual LRA approximation, if the size of the NPs is also large enough (more than 15nm).

Secondly, let us consider the same systems under electron beam EELS excitation. Corresponding problem parameters are: impact factor $b_x=2.3$nm $b_y=0$nm, kinetic energy of the incident electron – 50 keV. Nanodimer spheres are located on the $z$ axis.

On Figure 3 corresponding comparison of electron energy loss spectra is presented exhibiting the same physical effects that occurred for plane wave problem. The large increase of the gap size (twice the diameter of the considered sphere) predictably leads to the system of two almost non-interacting particles with the same resonant wavelengths and twice larger electron energy loss probability $P$ than its value for single spherical particle, which is right in both local and GNOR approximations. We can also see that nonlocal influence results in lower energy loss probability values. We should note here
that as EELS problems are solved for the near field, they imply larger values of the residual, especially if electron trajectory is located very close to the particle boundary. This is the reason for selecting $b$ as given above as this value gives acceptable residual and at the same time is close to experimental ones.

Figure 3. EEL spectra obtained for single Ag sphere (red lines) and dimers of Ag spheres, $a=2\text{nm}$. Electron kinetic energy 50 keV, $b_x=2.3\text{nm}$, $b_y=0$. Gap size $d$ (nm) varies.

Finally, more interesting results could be obtained if we direct electron beam to pass through the gap between two particles of the dimer system instead of pointing it to the edge of the system. In our terms that would yield impact parameter $b=0$, and particles would be located on the $x$ or $y$ axis as shown on figure 4.

Let us discuss corresponding results presented at figure 5. Here we can see that maximum of energy loss probability is achieved when dimer particles are very close to each other ($d=1\text{nm}$ in the considered case), on the contrary to the previous case, because particles are located very close not only to each other, but also to the incident electron beam. At the same time the blue shift of SPR resonance frequency is still observed and its value is predictably larger than the one for electron passing by the dimer instead of passing through its gap. We should also note that in this case increase in gap size also leads to the increase of distance between electron beam and scatterers, which in turn results in better a posteriori residual values. Subsequent development and enhancement of the proposed approach seems to be perspective from the point of further method optimization and possible improvement of the residual issues. The similar results could be obtained for other particle materials (i.e. gold) and particle sizes, and also for nonspherical particles.

All spectra computed above for the dimers with fixed gap size were obtained with the same matrix, which enabled to significantly save computational time. This means that we had to compute only one matrix to obtain one corresponding spectral value presented at each of the figures 2 (plane wave excitation), 3 and 5 (EELS excitation) for each dimer.

Let us summarize the presented results. The proposed DSM hybrid scheme appears to accurately and efficiently resolve SPR resonant wavelength shifts and intensity peak changes for different dimer gap sizes, which makes it a good choice for solving these problems. We have also demonstrated that it maintains capability of rigorously accounting for nonlocal effect which highly impacts SPR characteristics of small nanoparticles and of dimers with small gap sizes and therefore cannot be neglected in simulations.
Figure 4. EELS problem geometry for electron beam passing through the gap.

Figure 5. EEL spectra obtained for dimers of Ag spheres with beam passing through the gap, $a=2\text{nm}$. Electron kinetic energy 50 keV. Gap size $d$ varies.

5. Conclusion
For the first time Discrete Sources Method-based mathematical model of EELS was developed for characterization of plasmonic nanodimers. The proposed model was implemented into the efficient and flexible computer program, which computational capability ensures resolving both EEL spectra and plane wave scattering cross-sections for dimers composed of spherical plasmonic particles paving way for many possible enhancements including investigation of nonspherical particles deposited on a substrate. Account for spatial nonlocality of the plasmonic medium was incorporated into the proposed approach via GNOR approach and corresponding influence of the gap size reduction on plane wave scattering spectra and EEL spectra was demonstrated.
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6. References
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