Numerical simulation of electron energy loss spectroscopy accounting for nonlocal effect in plasmonic nanoparticles

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Abstract. Interaction between an electron in straight uniform motion and a nearby plasmonic nanoparticle deposited in homogeneous medium is examined numerically in no-recoil approximation. To account for the nonlocal effect occurring in the plasmonic medium Generalized Nonlocal Optical Response scattering problem statement is considered. Discrete Source Method is employed to construct the solution. Electron energy loss probability is computed as a function of incident field frequency and obtained surface plasmon resonance energy is compared to local response simulations. It is shown that surface plasmon resonance peak frequency blueshift can be resolved within the proposed approach.

1. Introduction
An increasing demand in accurate characterization of solid microstructures, such as plasmonic nanoparticles (NPs), requires precise experimental and theoretical techniques. For this reason electron-beam spectroscopies, such as electron energy-loss spectroscopy (EELS), have recently gained much attention in nanophotonics research and have proven to be a powerful tool for studying surface plasmons (SPs) related to certain applications in sensing, waveguiding, plasmonic nanoantennas, optical trapping, and others [1,2]. As experimental EELS setup requires very expensive instrumentation, numerical simulations seem to be a promising and cheap way to obtain EEL spectra for detailed analysis of specimens relevant parameters. In order to ensure simulation accuracy an adequate and reliable electromagnetic modeling tool is required.

2. Electron energy loss spectroscopy model
Let us consider the following scattering problem geometry (figure 1): an electron propagating in vacuum $D_0$ with velocity $v$ passes a spherical homogeneous plasmonic particle $D_1$ of radius $r$ in the order of ten nanometers. We hereby assume that electron does not pass through the particle (absolute value of the impact parameter $b$ is larger than $r$) and that it is represented by point charge $e$ in uniform straight motion along $z$ axis. Analytical expressions for the incident electromagnetic field due to given electron beam are available and can be efficiently used in the simulation procedures [3–5]. Moving point charge induces an electromagnetic field scattered back from the sample, which interacts with the electron causing characteristic energy losses.
Consequently, the scattered electromagnetic field has to be calculated in order to compute the energy loss probability $P$ of the incident electron.

Assuming that the electron energy loss is small compared to the initial kinetic energy of the incident electron (0.5eV - 50eV in the valence-loss region against initial 50keV - 300keV), let us consider that the electron velocity $v$ remains constant. This simplification is known as no-recoil approximation. Under the given circumstances a sufficient condition on electron loss probability $P$ can be written in the form of expression that connects $P$ to the scattered electromagnetic field $E_{\text{scat}}$ [3–5]:

$$P(\omega) = \frac{e}{\pi \hbar \omega} \int_{-\infty}^{+\infty} \text{Re} \left\{ E_{\text{scat}}(r_e, \omega)e^{-i\omega z/v} \right\} dr_e. \quad (1)$$

3. Generalized Nonlocal Optical Response

Numerical simulations of the electromagnetic scattering problems are traditionally based on either classic or quantum electromagnetic models, with quantum-based simulations being more precise but at the same time very expensive computationally. In turn, many classic high-performance techniques exist that ensure good accuracy of the solution for relatively large plasmonic particles. However, the studies of SPs in small metal nanoparticles with size less than 10nm demand more accurate yet efficient simulation tools due to nonlocal effects occurring in the plasmonic medium [6]. Despite the quantum nature of these effects it has been shown that they could be efficiently accounted for within the scope of classic approaches via incorporation of the Generalized Nonlocal Optical Response (GNOR) theory into the electromagnetic model [7]. It has also been shown that account for nonlocal effects could drastically influence scattering characteristics and so efficient GNOR-enabled numerical techniques are required to accurately resolve the properties of nanoscaled plasmonic systems [8,9].

Within GNOR model material’s dielectric permittivity is represented as a scalar function with nonlocal supplement. In this case the internal field inside the plasmonic NP ceases to be purely transversal and acquires longitudinal component [7]. Key feature of the longitudinal component is that corresponding wave number significantly differs from the wave number of the transversal field. This leads to fast oscillations of bessel functions employed to construct the solution which makes it more difficult to implement an accurate and efficient computational scheme.

Moreover, as longitudinal component is an additional unknown parameter, scattering problem statement has to be modified. In particular, new boundary condition is required to ensure the
uniqueness of the solution to the Maxwell system. We would generally follow the approach featured in works [7–9] and introduce the electric field normal component discontinuity condition in order to write down the appropriate problem statement.

4. Discrete Sources Method
In this work GNOR-enabled scheme of the Discrete Sources Method (DSM) is applied to solve the problem of plasmonic nanoparticle excitation with electron beam. The proposed method is known to be one of the most flexible techniques for boundary value scattering problems analysis, in particular due to its many remarkable features including a posteriori error estimation, efficient usage of computational resources and capability of rigorously resolving the nonlocal effect influence on particle properties [10, 11].

Within DSM both scattered field everywhere in $D_0$ and total internal field inside the nanoparticle $D_i$ are constructed as finite linear combinations of the fields resulting from discrete sources (DS) located inside the particle. The internal DS fields are chosen to analytically satisfy Maxwells equations in $D_i$. In order to account for the longitudinal component of the internal electromagnetic field (and, consequently, for nonlocal effects) corresponding DS analytically satisfying GNOR governing equations are also introduced [8, 9]. External DS fields in turn satisfy both Maxwells equations in $D_0$ and the required infinity conditions, and so does the constructed solution for the scattered field. Then unknown amplitudes of all discrete sources are determined from the only conditions not satisfied analytically: from boundary conditions enforced at the nanoparticle surface.

In this work we would use the hybrid DSM scheme which employs electric and magnetic dipoles to construct the scattered field solution and internal discrete sources of the same order to approximate the internal field. The sources are distributed along the $z$ axis inside $D_i$. Unknown DS amplitudes are computed via the Generalized Point-Matching Technique and surface residual minimization approaches in least square sense [8], thus ensuring boundary conditions and allowing to numerically obtain scattered field necessary for determining electron energy loss probability via (1).

5. Numerical simulations
We would consider a silver nanosphere in homogeneous medium with diameter $d$ and electron beam with impact factor $b = (b_x, b_y)$, where $b_x = d + 0.5\text{nm}$, $b_y = 0$. Corresponding material data is obtained from [7]. In particular, we would employ metal plasma frequency in $\hbar\omega_p = 8.99$ eV, Drude damping rate $\hbar\gamma = 0.025$ eV, Fermi velocity $v_F = 1.39\cdot10^6\text{ms}^{-1}$ and electron diffusion constant $D = 3.61\cdot10^{-4}\text{m}^2\text{s}^{-1}$. Besides, we would consider $\varepsilon_0 = \mu_0 = \mu_i = 1$.

In order to validate the proposed approach let us analyze how NP diameter $d$ influences the position of plasmon resonance peak in local and GNOR approximations. For this purpose we would conduct series of numerical experiments varying $d$ from 4nm to 15nm and comparing resonance energy $\hbar\omega_0$ obtained from plane wave (PW) scattering and from EELS computations. For the plane wave scattering simulations we would employ both DSM and analytical solution, and for the electron energy loss spectroscopy we would employ the proposed DSM approach. Corresponding results are presented on fig. 2.

As seen on the figure, significant blueshift of the plasmon resonance peak is predicted by GNOR-enabled computations with decrease of diameter $d$, which does not occur at all in the local response approximation. Moreover, DSM is shown to be capable of resolving this blueshift in both PW scattering and electron energy loss probability computations. It should be also noted that these results are in good agreement with available experimental data, where blueshift of plasmon resonance peak is also observed [7].

Generally, DSM allows examining particles and structures of various shapes [11]. For this reason the obtained results provide a promising outlook on further development of the proposed
approach to nonspherical particles and dimers, which is relevant to applications.

![Graph](image)

Figure 2. Dependence of the resonance energy $\hbar \omega_0$ on the NP diameter $d$.

Solid lines: analytically obtained results; line of dots: results obtained from plane wave (PW) scattering analysis via DSM; dash lines: results obtained from EEL spectra analysis via DSM.

6. Conclusion

The problem of electron beam excitation of small plasmonic nanoparticles with diameter less than 15nm was considered. GNOR-enabled Hybrid Discrete Sources Method scheme was successfully applied to construct the solution to the corresponding boundary value problem and to computation of electron energy loss probability spectra. Numerical simulations confirm that proposed approach is capable of resolving surface plasmon resonance blueshift observed for small silver nanoparticles from EEL spectra.

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