Novel approach for modeling optical properties of systems containing large number of metal nanoparticles

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We propose a novel method for optical properties calculation of very large and complex-shaped systems of metal nanoparticles having size of the order of 10 nm. The method is based on the volume integral equation that describes the electromagnetic scattering. In the numerical algorithm, the generalized minimal residual method is used to enlarge the domain of the applicability of the method.

INTRODUCTION

With the development of fabrication of complex nanostructured composite media [1] there have been intensively elaborated several approaches for modeling their optical properties. Approaches that appear to be the most useful in applications and analysis of experiments can be divided into two types. The first type includes effective medium approximations [2]. The second type includes different techniques of exact electromagnetic analysis of scattering structures [3]. Both of them exhibit evident disadvantages. Notably, the effective medium theory cannot take into account additional structuring of a medium. By applying an exact approach one shortly reaches the limit of calculation resources while attempting to analyze structures with growing complexity.

In this work we propose a method that represents a combination of the two mentioned approaches. It gives the possibility to calculate the light scattering on systems containing thousands of metal nanoparticles with radii of dozens of nanometers and sufficiently low volume density with the restrictions being imposed by the use of quasistatic (dipole) approximation and the assumption that the field from one particle to another comes in the form of a spherical wave.

DESCRIPTION OF THE METHOD

The numerical derivation of the method is close to the procedure used in volume integral equation methods [3] and is based on the generalized source method (GSM) written in the

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form developed earlier [4]. The volume integral equation that gives the solution of the Helmholtz equation writes:

$$\mathbf{A} = \mu_0 \mathbf{J} * G_s = \int_{V'} \mu_0 \mathbf{J}(\mathbf{r}')G_s(\mathbf{r} - \mathbf{r}')dV',$$

(1)

where G_s is the scalar free-space Green's function of the Helmholtz equation. The GSM implies the use of "generalized" sources which reflect the difference in spatial permittivity distribution of a given problem and some basis value ε_s :

$$\mathbf{J}_{gen} = -i\omega(\varepsilon - \varepsilon_s)\mathbf{E}$$

(2)

The standard discretization procedure of Eq. (1) consists in partition of a scattering volume into a number of spatial cells each characterized by some constant value of permittivity ε_i with index i giving the cell number. Then one obtains an algebraic equation which is usually solved by the conjugate gradient method or its variations.

We also use the spatial partitioning of the scattering volume into cells, the size of which is small with respect to the wavelength of incident radiation. However, we suppose that these cells contain both the host material and metal inclusions which implies for some effective permittivity $\varepsilon_{i\,eff}$. Since the quasi-static approximation is quite acceptable in this case, we use the well-known relation [2]

$$\varepsilon_{i\,eff} = \varepsilon_s\left(1 + f_i \frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + 2\varepsilon_s}\right)$$

(3)

where ε_m is the dielectric permittivity of metal nanoparticles and f_i is the volume density of metal inclusions. Note that both these values can vary from one cell to another.

So, after the mentioned discretization subject to formula (3) we arrive to the system of algebraic equations that can be written in form:

$$\vec{E} = \vec{E}_0 + \mathbf{D}\mathbf{A}\vec{E}.$$

(4)

Here the vectors $\vec{E}_0$ and $\vec{E}$ stand for the components of incident and scattered field in all spatial cells, diagonal matrix $\mathbf{D}$ contains factors with effective permittivities and matrix $\mathbf{A}$ contains geometric factors depending on relative spatial positions of all cells. Note that the diagonal of matrix A is chosen to be zero to avoid the appearance of nonphysical field singularities.

Frequently, linear systems like (4) are solved by the conjugate gradient method. However, it often reveals poor convergence rate and, to overcome this drawback, we use the generalized minimal residual method (GMRES). With the use of GMRES, the capabilities of the

method allow considering very large systems partitioned into about 100×100×100 cells by the use of PC.

EXAMPLE AND DISCUSSION

As an example, we calculated the effective refractive index of the transparent medium (refractive index 1) consisting of silica particles of radii 100 nm covered by a layer of silver nanoparticles of radii 10 nm with volume density about 0.2 (Fig. 1).
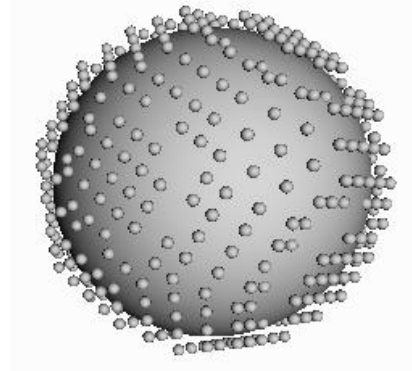

Figure 1. Scatterer that represents a silica particle of radius 100 nm covered by a layer of silver nanoparticles of radii 10 nm.

It is supposed that such "particles" (silica with a core of silver impurities) are located far enough one from another so that re-scattering can be neglected. Such systems appear, for example, in the process of growth of metal covers on dielectric nanoparticles [1]. The spectrum of the refractive index modification in comparison with transparent host medium is depicted in Fig. 2. For the calculation we used the formula

$$n_{eff} - n_2 = 2\pi N R^3 n_2 \frac{(\varepsilon_1 - \varepsilon_2)}{(2\varepsilon_2 + \varepsilon_1)} \tag{5}$$

where n_{eff} is the effective index of the inhomogeneous medium; n_2 is the refractive index of the host material (and ε_2 is the corresponding permittivity); N is the volume density of metal spheres with permittivity ε_1 and R is the effective radius of a single sphere corresponding to its extinction cross-section.

The present method is especially useful beyond effective medium approximations when it is necessary to introduce some additional structure in the system under consideration. Together with the powerful numerical technique, it provides facilities for modeling optical behavior of a wide class of nanostructured media.
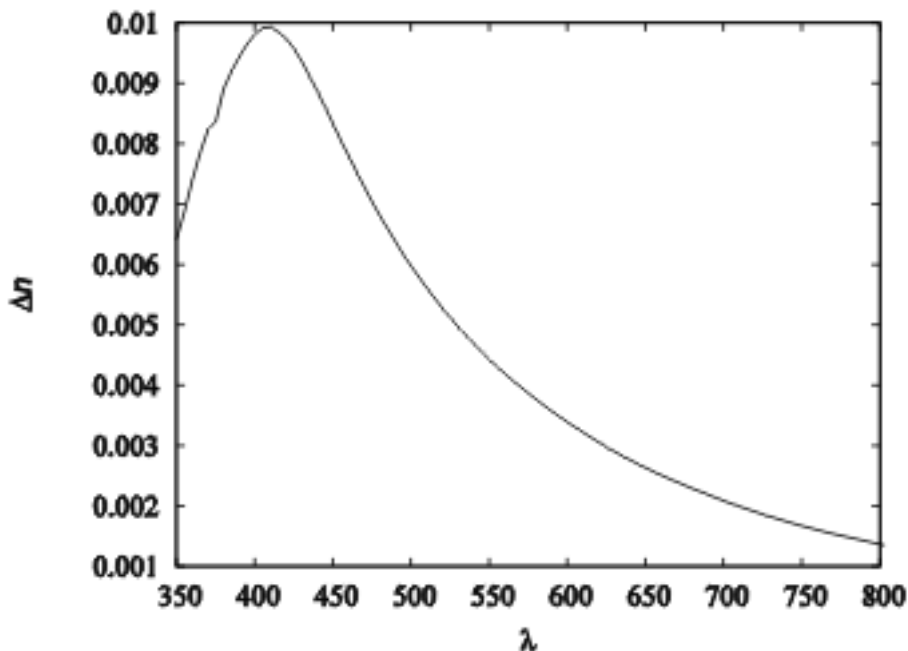
Figure 2. Spectral dependence of the change in the effective refractive index.

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