

Numerical Analysis of Plasmon Resonances in Nanoparticles Based on Fast Multipole Method

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Abstract— A novel technique for the numerical analysis of plasmon resonances by using fast multipole method (FMM) is presented. This approach is based on the solution of eigenvalue problem for boundary integral equations, which can be naturally implemented by using the fast multipole method. Numerical examples that highlight the efficiency of the fast multipole implementation are reported.

Index Terms—plasmon resonance, nanoparticle, integral equation, fast multipole method.

I. INTRODUCTION

RECENTLY, plasmon resonances in metallic nanoparticles and their assemblies have been a subject of considerable interests. These resonances occur when the free-space wavelength is much larger than the particle dimensions and the dielectric permittivity of metallic nanoparticles is negative. These resonances result in a large enhancement of the local electric fields near the metal surface, which has applications in many areas such as nanophotonics, nanolithography, near-field microscopy and biosensors. The desired resonance frequencies as well as the local fields enhancement can be achieved by controlling the geometry of the metallic nanostructure. The boundary integral equation technique for the direct calculations of the plasmon resonance frequencies in metallic nanoparticles has been developed in the recent publications [1-4]. This integral equation method leads to fully populated discretized matrix equations that are computationally expensive to solve, especially when large number of particles are involved in the metallic nanostructures. Since the fully populated matrices are generated by integrals with $1/r$ -type kernel, this computational problem can be appreciably alleviated by using

the fast multipole method [5-6]. This method greatly speeds up the matrix-vector multiplications.

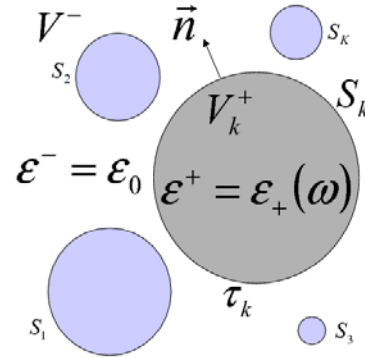


Fig. 1. A group of metallic nanoparticles.

II. TECHNICAL DISCUSSION

To start the discussion, consider clustered metallic nanoparticles with the same dielectric permittivity $\epsilon_+(\omega)$ (see Figure 1). We are interested in such negative values of ϵ_+ for which a source-free field of electric displacement may exist. This existence is the manifestation of plasmon resonances. The above field of electric displacement \vec{D} satisfies the following equations:

$$\nabla \times \vec{D}^\pm = 0, \quad (1)$$

$$\nabla \cdot \vec{D}^\pm = 0, \quad (2)$$

$$\vec{n} \cdot (\vec{D}^+ - \vec{D}^-) = 0, \quad (3)$$

$$\vec{n} \times \left(\begin{array}{c} \epsilon_0 \vec{D}^+ - \vec{D}^- \\ \epsilon_+ \end{array} \right) = 0, \quad (4)$$

where superscripts "+" and "-" are used for the notations of physical quantities inside ($V^+ = V_1^+ \cup V_2^+ \dots \cup V_k^+$) and outside (V^-) the nanoparticles, respectively, while \vec{n} is a unit vector of outward normal to $S = S_1 \cup S_2 \dots \cup S_k$. It is apparent that a scalar potential ϕ can be introduced:

$$\vec{D} = -\nabla \phi, \quad (5)$$

which satisfies the Laplace's equation

$$\nabla^2 \phi^\pm = 0 \quad (6)$$

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inside and outside the nanoparticles as well as the following boundary conditions on S :

$$\varepsilon_0 \phi^+ = \varepsilon_+ \phi^-, \quad (7)$$

$$\frac{\partial \phi^+}{\partial n} = \frac{\partial \phi^-}{\partial n}, \quad (8)$$

and the condition at infinity

$$\phi^-(\infty) = 0. \quad (9)$$

The potential ϕ can be represented as a potential of double-layer electric charges $\tau(M)$ distributed over S :

$$\phi(Q) = \frac{1}{4\pi} \oint_S \tau(M) \frac{\vec{r}_{QM} \cdot \vec{n}_M}{r_{QM}^3} dS_M, \quad (10)$$

where r_{MQ} is the distance between the observation point (Q) and integration point (M). In other words, a double-layer of electric charges $\tau(M)$ distributed over S may create the same field of electric displacement in the free space as the resonant source-free field of electric displacement that would exist in the presence of the nanoparticles. This will be the case if potential (10) satisfies all the conditions of boundary value problem (6)-(9). It is apparent that the double-layer potential (10) satisfies the Laplace's equation in V^+ and V^- , the boundary condition (8) and decays to zero at infinity. To satisfy the boundary condition (7), we recall that the boundary values of a double-layer potential are given by the formulas [7]:

$$\phi_k^\pm(Q) = \pm \frac{\tau_k(Q)}{2} + \frac{1}{4\pi} \sum_k \oint_{S_k} \tau_k(M) \frac{\vec{r}_{QM} \cdot \vec{n}_M}{r_{QM}^3} dS_M, \quad (11)$$

where \vec{n}_M is the outward normal at point M , \vec{r}_{QM} is a position vector directed from the integration point M to the observation point Q . By using (11), it can be concluded that the boundary condition (7) are satisfied if the following homogeneous boundary integral equation is valid:

$$\tau_k(Q) - \frac{\lambda}{2\pi} \sum_k \oint_{S_k} \tau_k(M) \frac{\vec{r}_{QM} \cdot \vec{n}_M}{r_{QM}^3} dS_M = 0, \quad (12)$$

$$\lambda = \frac{\varepsilon_+(\omega) - \varepsilon_0}{\varepsilon_+(\omega) + \varepsilon_0}. \quad (13)$$

The integral equation (12) can be easily extended to the case when nanoparticles are placed on a dielectric substrate. The main modification consists in the replacement of the free-space Green function $\frac{1}{r_{MQ}}$ by the Green function

$$\frac{1}{r_{MQ}} - \frac{\varepsilon_{sub} - \varepsilon_0}{\varepsilon_{sub} + \varepsilon_0} \frac{1}{r_{M'Q}},$$

where ε_{sub} is the permittivity of substrate and M' is the mirror image of M with respect to the substrate plane.

Next, we describe the discretization technique for the solution of integral equation (12). Let us partition S into N small pieces ΔS_j and rewrite integral equation (12) as follows:

$$\tau_k(Q) - \frac{\lambda}{2\pi} \sum_{j=1}^N \int_{\Delta S_j} \tau_j(M) \frac{\vec{r}_{QM} \cdot \vec{n}_M}{r_{QM}^3} dS_M = 0, \quad (14)$$

By introducing notations:

$$\omega_i(M) = \int_{\Delta S_i} \frac{\vec{r}_{QM} \cdot \vec{n}_M}{r_{QM}^3} dS_Q, \quad (15)$$

integrals in (12) can be approximated as follows

$$\int_{\Delta S_j} \tau_j(M) \frac{\vec{r}_{QM} \cdot \vec{n}_M}{r_{QM}^3} dS_M \approx \omega_i(M_j) \tau_j = \omega_{ij} \tau_j. \quad (16)$$

Then the eigenvalue problem (12) can be written in the matrix form as

$$\tau_i = \frac{\lambda}{2\pi} \sum_{j=1}^N \omega_{ij} \tau_j. \quad (17)$$

The solutions of the eigenvalue problem (17) is usually obtained by using iterative techniques, which require matrix-vector product $w \leftarrow Av^{(k)}$ computations. It is apparent that when matrix A is fully populated, the multiplication $Av^{(k)}$ is accomplished in $O(N^2)$ operations. For large N , the computation cost can be prohibitive. However, when matrix elements of A are derived from $1/r$ -type kernel, the fast multipole method allows one to compute the matrix-vector product with the cost of $O(N \log N)$ operations. The fast multipole method, introduced by Greengard and Rokhlin [8-9], seeks to speed up the matrix-vector product. The main idea of the FMM is to split the computations for near field and far field regions, and then utilize factorized representations of the kernel in these regions. These factorized representations in terms of spherical harmonics come from the "addition theorem" expansions.

Indeed, for $1/r$ -type kernel the following spherical harmonic expansion is valid:

$$\frac{1}{r_{QM}} = \frac{1}{|\vec{r}_M - \vec{r}_Q|} = \sum_{l,m} \sum_{m=-l}^l R_{lm}(\vec{r}_Q) S_{lm}(\vec{r}_M), \quad (18)$$

where

$$R_{lm}(\vec{r}) = \frac{r^l P_{lm}(\cos \theta) e^{-im\phi}}{(l+m)!},$$

$$S_{lm}(\vec{r}) = \frac{(l-m)! P_{lm}(\cos \theta) e^{-im\phi}}{r^{l+1}},$$

and (r, θ, ϕ) are the spherical coordinates. This expansion is valid for $\vec{r}_M > \vec{r}_Q$. In the calculations of derivatives of $1/r_{MQ}$, the following recursive relations are instrumental [5]:

$$\begin{aligned}\frac{\partial R_{lm}}{\partial x} &= \frac{1}{2}(R_{l-1,m-1} - R_{l-1,m+1}), \\ \frac{\partial R_{lm}}{\partial y} &= \frac{i}{2}(R_{l-1,m-1} + R_{l-1,m+1}),\end{aligned}\quad (19)$$

$$\begin{aligned}\frac{\partial R_{lm}}{\partial z} &= R_{l-1,m}, \\ \frac{\partial S_{lm}}{\partial x} &= \frac{1}{2}(S_{l+1,m-1} - S_{l+1,m+1}), \\ \frac{\partial S_{lm}}{\partial y} &= \frac{i}{2}(R_{l+1,m+1} + R_{l+1,m-1}), \\ \frac{\partial S_{lm}}{\partial z} &= -S_{l+1,m}.\end{aligned}\quad (20)$$

By using formulas (18)-(20) it can be shown that the matrix-vector product $A\mathbf{v}^{(k)}$ can be evaluated as follows:

$$[A\mathbf{v}^{(k)}]_j = \sum_{l=0}^P \sum_{m,m'=-l}^l R_{lm'}(\vec{r}_Q) \sum_{j=1}^N \alpha_i S'_{lm}(\vec{r}_M) \mathbf{v}_i, \quad (21)$$

where α_i are coefficients obtained through the evaluation of the surface integral in (15), $S'_{lm}(\vec{r}_M)$ is the derivative of $S_{lm}(\vec{r}_M)$. It is clear that the last summation in equation (21) can be computed only once and then used in the rest of the computation. This is not true, however, under the condition $r_M < r_Q$. Nevertheless, the appreciable portion of the last sum in (21) can be precomputed for a certain set of points Q_j that are enclosed in some relatively small box. This portion consists of summation over all these points M_i that are outside the smallest sphere that contains the above box.

When the calculation of $[A\mathbf{v}]_j$ are performed for mesh points Q_j in adjacent boxes, some appreciable part of the precomputed portion of the last sum in (17), that was evaluated for the previous box, can be reused at some small computational cost. This cost is due to the translations of the origins of spherical coordinate systems used for different boxes. This extensive reusing of precomputed portions of the last sum in (17) is the key advantage of the fast multipole method. This extensive reusing of the precomputed data can be best realized by employing ‘‘hierarchical box’’ subdivisions of some large box that contains the nanoparticle surfaces. The detailed description of the fast multipole method is quite involved and can be found in [8-9]. Nevertheless, it can be stressed that the central strategy of FMM is the hierarchical decomposition of the data-space in the form of a quad-tree (or oct-tree for the 3-dimensional case). This hierarchical decomposition is used to cluster mesh points at various spatial scale lengths and compute interactions with other clusters that are sufficiently far away by means of spherical harmonic expansions.

III. NUMERICAL IMPLEMENTATION AND EXAMPLES

The algorithm outlined above has been implemented and extensively tested. We have used the LAPACK for solving the eigenvalue problem, where the reverse communication function is ideally suitable for the inclusion of FMM codes for matrix-vector products.

As a first example, consider a system of two spherical nanoparticles. The computations of resonant free-space frequencies as a function of separation distance between two gold spherical nanoparticles located on a glass substrate ($n = 1.5$) have been performed and shown in Figure 2. In addition, the charge distribution of the resonance modes for gold nanospheres is shown in Figure 3. The dispersion relation for gold published in [10] has been used in calculations. It is clear from Figure 2 that the separation between two spheres can be effectively used for tuning of plasmon resonances to desirable frequencies.

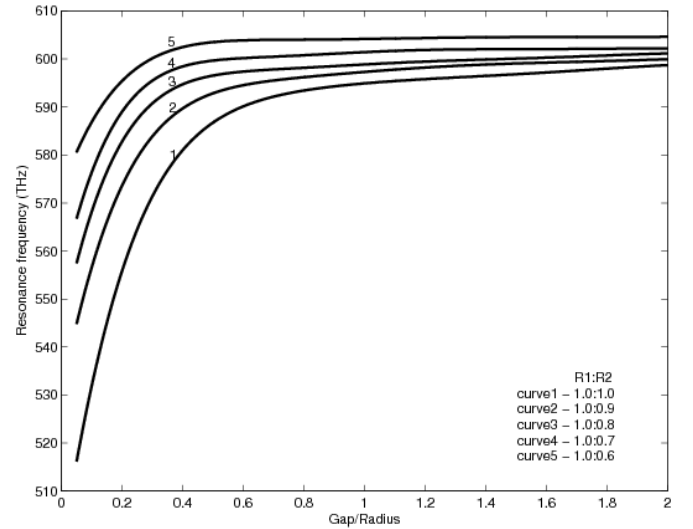


Fig. 2. Resonance wavelength for two gold nanospheres on the substrate

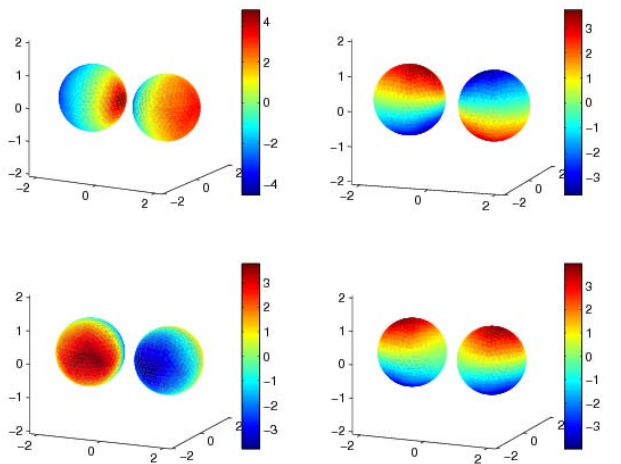


Fig. 3. Charge distribution of resonant modes for two-sphere system.

Table I presents the comparison between the results computed by using outlined technique and reported in [11] for the three silver spherical nanoparticle system. The dispersion relation for silver published in [10] has been used in calculations. This table reveals a very good agreement between our results and results reported in [11].

	CASE 1	CASE 2
	$r_{i+1}/r_i = 1/3$	$r_{i+1}/r_i = 1/3$
Configuration	$d_{i,j+1} = 0.6r_{i+1}$	$d_{i,j+1} = 0.6r_{i+1}$
Resonance wavelength [11]	369 nm	382 nm
Resonance wavelength (Computational)	372 nm	387 nm

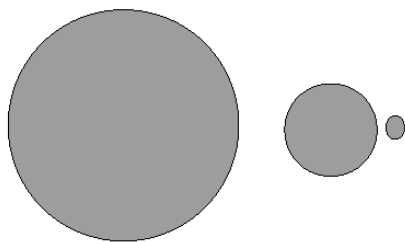


Fig. 4. Three-sphere nanolen system [11]

The testing of the method has been performed for more complicated systems of 20nm gold nanospheres shown in Fig. 5. The separation between the central sphere and surrounding spheres is 7nm. This structure is used to model the aggregation of gold nanospheres due to DNA hybridization [12]. The low density DNA solution is treated in computations as water. The calculations show that the resonance wavelength for single nanosphere is 516nm, while the resonance wavelength for the group of 7 nanospheres shifts to 554nm. These results agree with the experimental results reported in [12] where it is reported that for single gold nanospheres the resonances occur at 525nm, while the resonances for the aggregation of gold nanospheres due to DNA hybridization occur at 560 nm. The above computations have been performed on a 3.0GHz Dell-workstation.

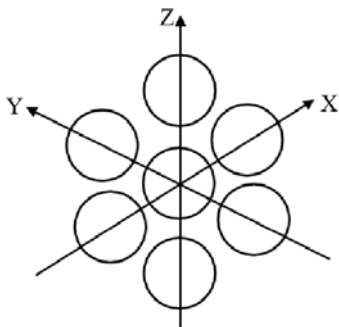


Fig. 5. 7-sphere cluster.

Table II presents the comparison between FMM and conventional direct calculations for the particle configuration shown in Figure 4. Table II clearly reveals the efficiency of the fast multipole method, which is the method of choice for the large size problems.

Method / mesh	8690	33600	134400
FMM	26	118	680
Direct summation	315	14819	237920*

* This computation time is estimated by extrapolation.

IV. CONCLUSION

The novel technique for the numerical analysis of plasmon resonances by using fast multipole method (FMM) has been presented. This approach is based on the solution of eigenvalue problem for boundary integral equations, which can be naturally implemented by using the fast multipole method. Numerical examples that highlight the efficiency of the fast multipole implementation are reported.

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