A new method by extending Mie theory to calculate local field in outside/inside of aggregates of arbitrary spheres

Hong-Xing Xu

Division of Solid State Physics, Lund University, Box 118, S-22100, Sweden

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Abstract

In this Letter we describe a new method to combine the methods of matrix inversion and order-of-scattering to solve the light scattering of aggregates of arbitrary spheres by extending Mie theory, which is more expedient for calculations of the local field in both outside and inside of the spheres.

E-mail address: hongxing.xu@ftf.lth.se (H.-X. Xu).

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1. Introduction

The scattering and absorption of light by small particles is a fundamental issue in electromagnetic (EM) theory, which has been intensively studied and applied in various disciplines from physics, chemistry, materials and environmental sciences to biology and medicine [1]. Recently, ultra sensitive surface enhanced Raman scattering (SERS) [2] up to single molecule sensitivity [3], surface plasmon photonic forces [4] and high spatial resolution of near-field optical microscopy [5] trigged enormous interests of optical near-field surrounding nanoparticles. In the mean time, technologies of particle sorting [6] and nano-particle based surface plasmon resonance (SPR) sensors [7] require detailed understanding of optical far-field of nanoparticles. A most common theory to solve light propagation surrounding spherical particles is the Mie theory [8], which gives the exact solution of EM scattering by a sphere of arbitrary radius and refractive index, embedded in an arbitrary homogeneous medium. Since a lot of phenomena relate to the aggregates of particles, the Mie theory needs to be extended to be suitable for aggregates.

Typically, there were two methods to extend Mie theory for aggregates, one was the so-called “matrix inversion” (MI) [9], and the other one is the so-called “order-of-scattering” (OS) [10]. MI method is based on the boundary conditions, from that exact results could be obtained in principle. However, it will become extremely difficult in practice when the matrix becomes large. Especially, the elements of the matrix will increase with L^2, where L is
the number of particles in aggregates. Moreover, MI would not work well for the points, near the spherical surfaces through the origin of one sphere and centered at the origin of another sphere, due to the poor convergence there. OS method is based on the different scattering orders. One problem for the OS method is that one has to truncate to a finite scattering order, which will loss the precise, especially for nearly attached spheres. The other problem is that it is not clear to trace the different scattering orders in Ref. [10] when the scatterers are more than two spheres.

In this Letter, we merge these two methods together to deduce a new method, in order to avoid the above weaknesses. This method consists of a summation of simple scattering events where the boundary conditions have already been applied earlier for the single units with use of known coefficients \((a, b, c\) and \(d)\). Therefore, we turn a boundary condition problem into a problem of multiple scattering with some translation rules between scatterers whose simple individual coefficients have already been calculated. The mathematical treatment allow all the scattering events be accounted, while not be truncated. Moreover, the formulae for calculations of the local field in the inside of spheres are also given, which is possible for the first time in this Letter as the best knowledge of ours.

2. Model and formalism

We begin with two-sphere system. Bruning and Lo was the first group to get the exact solution of the light scattering of two spheres, which agreed quite well with the far-field experimental results as well [9]. They used the multipole expansion to obtain a self-consistent set of coupled equations, which were then solved by the direct matrix inversion. A relatively simple three-term recurrence relation was also discovered by them, which facilitated calculations. Inoue and Ohtaka [11] applied a similar method to investigate the light scattering in SERS. Fuller [10] then introduced the order-of-scattering (OS) method to trace the light paths between two particles.

Here, the scattered fields from the different spheres are considered separately as illustrated in Fig. 1. The scattered field by sphere 1 and sphere 2 are represented by \(S_1\) and \(S_2\), respectively. Let us first consider the scattered field from sphere 1 as shown in Fig. 1. The first order of scattering has two parts: one part is the field scattered by sphere 1 from the incident field directly, marked as \(S_1\); the other part is the incident field scattered by sphere 2, and then scattered by sphere 1, marked as \(S_2 M_{21} S_1\) \((M_{21}\) denotes the coordinate transfer from sphere 2 to sphere 1). The first order of scattering is thus written as \(S_1 + S_2 M_{21} S_1\). The first order of scattered field is then scattered again by sphere 2, and then scattered by sphere 1 to form the second order of scattered field, marked as \((S_1 + S_2 M_{21} S_1) M_{12} S_2 M_{21} S_1\). Similarly, the \(n\)th order of scattering is the first order of scattered field reflected \(n - 1\) times by sphere 2 and then by sphere 1, marked as \((S_1 + S_2 M_{21} S_1)(M_{12} S_2 M_{21} S_1)^{n-1}\). The scattered field from sphere 1 is the sum of all orders of scattering:

\[
E_1 = \sum_{n=1}^{\infty} \frac{(S_1 + S_2 M_{21} S_1)(M_{12} S_2 M_{21} S_1)^{n-1}}{1 - M_{12} S_2 M_{21} S_1} = \frac{S_1 + S_2 M_{21} S_1}{1 - M_{12} S_2 M_{21} S_1}.
\]
Similarly, the scattered field from sphere 2 can be represented as

$$E_2^s = \sum_{n=1}^{\infty} \left( S_2 + S_1 M_{12} S_2 \right) \left( M_{21} S_1 M_{12} S_2 \right)^{n-1} = \frac{S_2 + S_1 M_{12} S_2}{1 - M_{21} S_1 M_{12} S_2}. \quad (2)$$

The total scattered field is the sum of the scattered fields from the two spheres:

$$E^s = E_1^s + E_2^s = \frac{S_1 + S_2 M_{21} S_1}{1 - M_{12} S_2 M_{21} S_1} + \frac{S_2 + S_1 M_{12} S_2}{1 - M_{21} S_1 M_{12} S_2}, \quad (3)$$

and the total field is the sum of the incident field and the scattered field $E = E^i + E^s$.

Similarly, the first order of penetrating field is represented as $T_1 + S_2 M_{21} T_1$, where $T_1$ donates the penetrating field in the inside of sphere 1. The second order penetrating field is the first order of scattered field scattered by sphere 2, then penetrating inside to sphere 1, marked as $(S_1 + S_2 M_{21} S_1) M_{12} S_2 M_{21} T_1$. In a similar way, the nth order of penetrating field is represented as $(S_1 + S_2 M_{21} S_1)(M_{12} S_2 M_{21} S_1)^{n-2} M_{12} S_2 M_{21} T_1$. The penetrating field in sphere 1 is the sum of all orders of penetrating fields:

$$E_1^i = (T_1 + S_2 M_{21} T_1) + \sum_{n=2}^{\infty} \left( S_1 + S_2 M_{21} S_1 \right) \left( M_{12} S_2 M_{21} S_1 \right)^{n-2} M_{12} S_2 M_{21} T_1$$

$$= (T_1 + S_2 M_{21} T_1) + \frac{S_1 + S_2 M_{21} S_1}{1 - M_{12} S_2 M_{21} S_1} M_{12} S_2 M_{21} T_1. \quad (4)$$

Similarly, the penetrating field in sphere 2 can be represented as

$$E_2^i = (T_2 + S_1 M_{12} T_2) + \sum_{n=2}^{\infty} \left( S_2 + S_1 M_{12} S_2 \right) \left( M_{21} S_1 M_{12} S_2 \right)^{n-2} M_{21} S_1 M_{12} T_2$$

$$= (T_2 + S_1 M_{12} T_2) + \frac{S_2 + S_1 M_{12} S_2}{1 - M_{21} S_1 M_{12} S_2} M_{21} S_1 M_{12} T_2. \quad (5)$$

In the general case, we consider a cluster of $L$ different spheres. An arbitrary sphere, e.g., the $l$th sphere, is picked first, and the scattered field from this sphere is denoted as $S_l$. The total scattered field from the rest of $L - 1$ spheres as a whole is denoted as $S_{L-1}$. Similar to the two-particle system, the first order of scattered field from the $l$th sphere is represented as $S_l + S_{L-1} M_{L-1,l} S_l$, where $M_{L-1,l}$ represents the coordinate transfer from an arbitrary sphere (e.g., the $q$th sphere) in the $L - 1$ spheres to the $l$th sphere. This order of scattered field is scattered by the $L - 1$ spheres as a whole, and then scattered by the $l$th sphere, to infinite order. Thus, the total scattered field from the $l$th sphere can be denoted as

$$E_l^s = \sum_{n=1}^{\infty} \left( S_l + S_{L-1} M_{L-1,l} S_l \right) \left( M_{l,L-1} S_{L-1} M_{L-1,l} S_l \right)^{n-1} = \frac{S_l + S_{L-1} M_{L-1,l} S_l}{1 - M_{l,L-1} S_{L-1} M_{L-1,l} S_l}. \quad (6)$$

The total scattered field is the sum of the scattered fields from the $l$th sphere and from the rest of $L - 1$ spheres as a whole as

$$E^s = \frac{S_l + S_{L-1} M_{L-1,l} S_l}{1 - M_{l,L-1} S_{L-1} M_{L-1,l} S_l} + \frac{S_{L-1} + S_l M_{L-1} S_{L-1}}{1 - M_{L-1,l} S_l M_{L-1} S_{L-1}}. \quad (7)$$

Here, $S_{L-1}$ can be represented as

$$S_{L-1} = \frac{S_q + S_{L-2} M_{L-2,q} S_q}{1 - M_{q,L-2} S_{L-2} M_{L-2,q} S_q} + \frac{S_{L-2} + S_q M_{L-2,q} S_{L-2}}{1 - M_{L-2,q} S_q M_{L-2,q} S_{L-2}}.$$

which is originated in an arbitrary sphere, the $q$th sphere. Similarly, $S_{L-2}$ is the scattering from the remaining $L - 2$ spheres excluding the $l$th and $q$th spheres, which can be written down similar to $S_{L-1}$. Continuing this process for
The expansion coefficients will have very concise forms as

\[ M^j_{mn} = \langle \hat{r}, \hat{\theta}, \hat{\phi} \left| \begin{array}{c} 0 \\ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \phi} \end{array} \right| \zeta_n^{(j)}(kr)Y_n^{m}(\theta, \phi) \rangle, \quad N^j_{mn} = \langle \hat{r}, \hat{\theta}, \hat{\phi} \left| \begin{array}{c} (l+1)\zeta_n^{(j)}(kr) \\ -\frac{\partial}{\partial \theta} \zeta_n^{(j)}(kr) \\ \frac{\partial}{\partial \phi} \zeta_n^{(j)}(kr) \end{array} \right| \frac{1}{kr} Y_n^{m}(\theta, \phi) \rangle, \]

(8)

where \( \hat{r}, \hat{\theta}, \hat{\phi} \) are unit vectors, \( k \) is the absolute value of the wave vector \( k \), and \( Y_n^{m}(\theta, \phi) \) is defined using associated Legendre functions \( P_n^m \) as

\[ Y_n^{m}(\theta, \phi) = \sqrt{\frac{(2l+1)(n-m)!!}{4\pi(n+m)!!}} P_n^m(\cos \theta) \exp(i m \phi), \]

and \( h_n^{(1)} = j_n + i y_n, h_n^{(2)} = j_n - i y_n \). For simplicity, VSH is donated as \( |nmjp\) \), with \( p = 1 \) for \( M^j_{mn} \), and with \( p = 2 \) for \( N^j_{mn} \), respectively.

An incident field \( |i, E\rangle \) can be expanded in an infinite series of VSHs as

\[ |i, E\rangle = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} CM_{mn} |nm11\rangle + CN_{mn} |nm12\rangle. \]

(9)

The expansion coefficients will have very concise forms as

\[ CM_{mn} = \frac{\langle nm11 | i, E \rangle}{\langle nm11 | nm11 \rangle} \quad \text{and} \quad CN_{mn} = \frac{\langle nm12 | i, E \rangle}{\langle nm12 | nm12 \rangle}. \]

For a plane wave, the expansion coefficients can be deduced as

\[ CM_{mn} = \frac{2\pi i^n}{n(n+1)} \left\{ -(i E_x - E_y) \sqrt{(n+m+1)(n-m)} Y_{n,m+1}^*(\hat{k}) + (n+1)(n+m+2)(2n+1)(2n+3)(i E_x - E_y) Y_{n+1,m+1}^*(\hat{k}) \right\}, \]

\[ CN_{mn} = \frac{2\pi i^n}{n(n+1)} \left\{ n \sqrt{(n+m+1)(n-m)} \frac{(i E_x - E_y) Y_{n+1,m-1}^*(\hat{k})}{(2n+1)(2n+3)} - (n+1) \sqrt{(n-m+1)(n+m)} \frac{(i E_x + E_y) Y_{n-1,m-1}^*(\hat{k})}{(2n-1)(2n+1)} - (n+1) \sqrt{(n-m+1)(n+m)} \frac{(-i E_x + E_y) Y_{n-1,m+1}^*(\hat{k})}{(2n-1)(2n+1)} \right\}. \]
The magnetic field is thus expanded as

\[ b_n Y_{n+1,m}(\hat{k}) \]

scattering coefficients scattered and the penetrating fields for a single sphere are written as strength at the origin of multipoles. But the normal modes in the penetrating field do not need to be changed. The \( E \) of the incident wave. The expansion of the magnetic field is easily obtained by applying the relations between the normal modes in the penetrating field do not need to be changed. The normal modes for the incident wave. The expansion of the magnetic field is easily obtained by applying the relations between the normal modes [12]:

\[ \mathbf{E} = \frac{1}{i\omega \mu} \nabla \times \mathbf{E}, \quad \mathbf{N} = \frac{1}{k} \nabla \times \mathbf{M}, \quad \mathbf{M} = \frac{1}{k} \nabla \times \mathbf{N}. \] (11)

The magnetic field is thus expanded as

\[ |s, H\rangle = \frac{1}{i\omega \mu} \sum_{n=1}^{\infty} \sum_{m=-n}^{n} (CM_{mn}|mn11\rangle + CN_{mn}|mn12\rangle). \] (12)

Each component of the transverse electrical and magnetic modes: \(|mn11\rangle\) and \(|mn12\rangle\), are diffracted with the scattering coefficients \(b_n\) and \(a_n\), and the transmission coefficients \(d_n\) and \(c_n\), respectively. Those coefficients can be obtained by applying the Maxwell boundary conditions [12]. Even for homogeneous coatings, it is not difficult to obtain those coefficients according to Sinzig and Quinten [13]. At the mean time, the normal modes for the scattered wave are changed to the spherical Hankel forms: \(|mn31\rangle\) and \(|mn32\rangle\) by exchanging the spherical Bessel functions \(j_n\) to the spherical Hankel functions \(h_n^{(1)} = j_n + iy_n\) in Eq. (8), which are required by the infinite field strength at the origin of multipoles. But the normal modes in the penetrating field do not need to be changed. The scattered and the penetrating fields for a single sphere are written as

\[ |s, E\rangle = CM_{mn}b_n|m n 31\rangle + CN_{mn}a_n|m n 32\rangle, \quad |s, H\rangle = \frac{k}{i\omega \mu} (CM_{mn}b_n|m n 32\rangle + CN_{mn}a_n|m n 31\rangle), \]

\[ |t, E\rangle = CM_{mn}d_n|m n 11\rangle + CN_{mn}c_n|m n 12\rangle, \quad |t, H\rangle = \frac{k}{i\omega \mu} (CM_{mn}d_n|m n 12\rangle + CN_{mn}c_n|m n 11\rangle). \] (13)

The total electromagnetic field is the sum of the incident field and the scattered field as \(|s + i, E\rangle, |s + i, H\rangle\) out of the sphere, and \(|t, E\rangle, |t, H\rangle\) in sphere, respectively.

In order to expediently calculate the scattering field for two-particle system, we define the following matrix:

\[
C_m = [CM_{m1} \quad CM_{m2} \ldots \quad CM_{mN} \quad CN_{m1} \quad CN_{m2} \ldots \quad CN_{mN}],
\]

\[
W_m^{E,i} = \begin{bmatrix} |1m11\rangle & \ldots & |Nm11\rangle & |1m12\rangle & \ldots & |Nm12\rangle \end{bmatrix}^T,
\]

\[
W_m^{H,i} = \begin{bmatrix} |1m12\rangle & \ldots & |Nm12\rangle & |1m11\rangle & \ldots & |Nm11\rangle \end{bmatrix}^T,
\]

\[
W_m^{E,h} = \begin{bmatrix} |1m31\rangle & \ldots & |Nm31\rangle & |1m32\rangle & \ldots & |Nm32\rangle \end{bmatrix}^T,
\]

\[
W_m^{H,h} = \begin{bmatrix} |1m32\rangle & \ldots & |Nm32\rangle & |1m31\rangle & \ldots & |Nm31\rangle \end{bmatrix}^T,
\]

\[
S_1 = \begin{bmatrix} 1b_1 \quad 1b_2 \quad \ldots \quad 1b_N \quad 0 \quad 0 \quad 0 \quad \ldots \quad 0 \quad 0 \end{bmatrix},
\]

\[
S_2 = \begin{bmatrix} 2b_1 \quad 2b_2 \quad \ldots \quad 2b_N \quad 0 \quad 0 \quad 0 \quad \ldots \quad 0 \quad 0 \end{bmatrix}.
\]
To obtain the reverse coordinate transfer to the large multipole number \( N \), the number of multipole \( n \) and \( l \) are diagonal, the suitable modification is allowed and facilitates the calculation as

\[
E^s = \sum_{m=-N}^{N} C_m S_1 + S_2 M_{12}^{m} S_1 \left( W_{m,i}^{E,h} \right) \otimes e^{i kd} \sum_{m=-N}^{N} C_m S_2 + S_1 M_{12}^{m} S_2 \left( W_{m,i}^{E,h} \right),
\]

where the left superscript of \( W \) means the different coordinate, \( \otimes \) means the plus should occur in the Cartesian coordinate, and \( d \) is the vector from the origin of sphere 1 to the origin of sphere 2.

Since the elements in \( M_{12}^{m} S_1, M_{12}^{m} S_2 \) are uneven, it is difficult to do matrix inversion in Eq. (15), especially for the large multipole number \( \tilde{N} \). Since \( S_j \) operators are diagonal, the suitable modification is allowed and facilitates calculations

\[
E^s = \sum_{m=-N}^{N} C_m \left( 1 + S_2 M_{12}^{m} \sqrt{S_1} \right) \left( 1 - S_1 M_{12}^{m} \sqrt{S_1} \right) \left( W_{m,i}^{E,h} \right) \otimes e^{i kd} \sum_{m=-N}^{N} C_m S_2 + S_1 M_{12}^{m} S_2 \left( W_{m,i}^{E,h} \right).
\]

Similar to Eq. (12), the scattered magnetic field can be written down straightforwardly as

\[
H^s = \frac{k}{i \omega} \sum_{m=-N}^{N} C_m \left( 1 + S_2 M_{12}^{m} \sqrt{S_1} \right) \left( 1 - S_1 M_{12}^{m} \sqrt{S_1} \right) \left( W_{m,i}^{H,h} \right) \otimes e^{i kd} \sum_{m=-N}^{N} C_m S_2 + S_1 M_{12}^{m} S_2 \left( W_{m,i}^{H,h} \right).
\]

Similarly, the penetrating field in the inside of sphere 1 is

\[
E^t = \sum_{m=-N}^{N} C_m \left( T_1 + S_2 M_{21}^{m} T_1 \right) \left( 1 + S_2 M_{21}^{m} \sqrt{S_1} \right) \left( 1 - S_1 M_{21}^{m} \sqrt{S_1} \right) \left( W_{m,i}^{E,j} \right),
\]
Fig. 2 gives an example for calculations of the local field in both outside and inside of two non-identical spheres: Au sphere (upper) and Ag sphere (down) for the different incident wave vector $k$ or different incident wavelength. The local field in the cavity between two particles is enhanced enormously, which is similar to the calculations for two identical particles [16]. It has been demonstrated that such strongly enhanced local field is crucial for single molecule SERS [17]. Hence, single molecule SERS can also be achieved by mixing of Au and Ag particles as substrates as well. It will become very interesting when Au and Ag spheres are designed for different functions, e.g., different bio-recognitions by biological coating [18]. For the large aggregates, we show here a case of 4 different spheres as an example in Fig. 3.

$$H'_1 = \frac{k}{i\omega\mu} \sum_{m=-N}^{N} C_m \left( T_1 + S_2 M_{21}^m T_2 + \frac{\sqrt{S_1 + S_2 M_{21}^m}}{1 - \sqrt{S_1} S_2 M_{21}^m} \sqrt{S_1 S_2 M_{21}^m T_1} \right) W_{m}^{H,j}. \tag{18}$$

The penetrating field in the inside of sphere 2 is

$$E'_2 = \sum_{m=-N}^{N} C_m \left( T_2 + S_1 M_{12}^m T_2 + \frac{\sqrt{S_2 + S_1 M_{12}^m}}{1 - \sqrt{S_2} S_1 M_{12}^m} \sqrt{S_2 S_1 M_{12}^m T_2} \right) W_{m}^{E,j},$$

$$H'_2 = \frac{k}{i\omega\mu} \sum_{m=-N}^{N} C_m \left( T_2 + S_1 M_{12}^m T_2 + \frac{\sqrt{S_2 + S_1 M_{12}^m}}{1 - \sqrt{S_2} S_1 M_{12}^m} \sqrt{S_2 S_1 M_{12}^m T_2} \right) W_{m}^{H,j}. \tag{19}$$

### 3. Numerical results and discussions

Fig. 2 gives an example for calculations of the local field in both outside and inside of two non-identical spheres: Au sphere (upper) and Ag sphere (down) for the different incident wave vector $k$ or different incident wavelength. The local field in the cavity between two particles is enhanced enormously, which is similar to the calculations for two identical particles [16]. It has been demonstrated that such strongly enhanced local field is crucial for single molecule SERS [17]. Hence, single molecule SERS can also be achieved by mixing of Au and Ag particles as substrates as well. It will become very interesting when Au and Ag spheres are designed for different functions, e.g., different bio-recognitions by biological coating [18]. For the large aggregates, we show here a case of 4 different spheres as an example in Fig. 3.
Fig. 3. Local intensity distribution $I/I_0$ in the logarithmic scale in the plane of the wave vector $k$ (white arrow) and the electric field $E$ (black arrow) through the centers of 4 spheres: A (Au, $R = 40$ nm), B (Ag, $R = 35$ nm), C (Au, $R = 30$ nm) and D (Ag, $R = 25$ nm) at the incident wavelength 514.5 nm.

We also notice that the streams of the EM energy $S = \frac{1}{2} E \times H^*$ (solid lines) flow differently near the particles. Notably, a large part of energy flow end by the Au sphere in Fig. 2(a) and (b), which means the Au sphere absorb more than the Ag sphere. Since the incident wavelength 514.5 nm is very close the resonance wavelength of Au surface plasmon at $\sim 520$ nm, it should be the case. Interestingly, the absorbed energy is actually lost on the surface of Au particle. It indicates that the strong surface current should consume much more energy than the body. For the longer wavelength 800 nm in Fig. 2(c), the Au sphere does not absorb much compared to Fig. 2(a) and (b). This is due to that the resonance wavelengths for both Au and Ag ($\sim 380$ nm) surface plasmons are much less than the incident wavelength.

Comparing to the MI method, the current method will be at least four times faster due to the smaller size of the matrix, i.e., $2N \times 2N$, according the definitions of the operators in Eq. (14), while the size of the matrix is $2NL \times 2NL$ in the MI method. Comparing to the OS method, the current method will be much faster when the strong EM coupling, i.e., the short separation distance exists between particles. For example, for 1 nm separation distance in the case of Fig. 2, the scattering orders should be accounted at least up to 600 in order to get convergence. The corresponding calculation time will be ten times more than the current method. But, when the separation distance increases to, e.g., 10 nm, the scattering orders can be accounted only about 50 to get convergence. The corresponding calculation time will be similar to the current method. Nevertheless, the current method is an improvement for the near-field calculation of strongly coupled particles.

4. Summary

In summary, we have deduced a new method blending the methods of matrix inversion and order-of-scattering, which is suitable for calculations of the local field in both inside and outside of aggregates of arbitrary spheres. The example calculations for aggregates of no-identical Au and Ag spheres show the details of the variations of...
the local field and the corresponding energy flow, which can give more detailed optics and physics for aggregated particles.

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References