Theory for the nonlinear optical response of a nonspherical metal cluster

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Using classical electrodynamics we determine the higher harmonic radiation by a nonspherical metal cluster in form of a matrix formalism. Extending the theory for the source of the higher harmonic radiation for spherical metal clusters as introduced by Östling et al. [Z. Phys. D 28, 169 (1993)] we calculate the sources for nonspherical particles. Employing these sources we develop the nonlinear Mie theory and determine the radiated higher harmonic fields generated by the cluster. Our theory is valid for arbitrary shape and arbitrary complex refractive index for cluster sizes much smaller and comparable to the wavelength of the incident light.

I. INTRODUCTION

The scattering behavior of clusters can be divided approximately into two regimes. First the scattering by clusters with sizes much smaller than the wavelength of light, the classical Rayleigh limit, which is dominated by microscopic effects and second the Mie range when the particle size becomes equal to or larger than the wavelength of light. The latter is characterized by resonances and interferences of surface electromagnetic modes described by classical physics. Since we are interested in this regime, we neglect microscopic phenomena. For spherical particles, the macroscopic effects known from linear Mie scattering [8] are even more pronounced in second and third harmonic generation, SHG and THG, respectively. Furthermore, they depend much more sensitively on the size and refractive index in the higher harmonic case [9]. For nonspherical particles, another important parameter governs the value and the angular dependence of the radiated intensities, viz. the curvature. Apart from the problem of determining this parameter as well as the size and refractive index from the angular dependence of the scattered intensities, the influence of clusters or well-defined nanostructures at surfaces on the SHG signal in reflection, especially the size dependence and the absolute value of the nonlinear response [10] are of particular interest. An important advantage for the application of higher harmonic techniques is that they are, in contrast to linear optics, not influenced by background noise. Knowledge of the intensities radiated by nanoparticles deposited on surfaces or by surface roughnesses of nanometer size, should be one ingredient to determine the lateral spatial resolution of SHG theoretically, the lower limit of which is as low as 1 nm [11] due to local field enhancements. Even in this range, the classical Rayleigh limit, an essential contribution results from the intensities radiated by nonspherical particles.

In the literature one can find several approximate theories for the linear radiation from nonspherical clusters. The Rayleigh-Gans theory is valid for arbitrary shapes but only for materials where the absolute value of the complex refractive index is close to one (|ε| ≃ 1). Latimer [12] calculates the intensities scattered from ellipsoidal particles by relating every single point on the surface to an equivalent sphere and determines their linear response within Mie theory [3]. Other theories determine the intensities from aspherical particles of arbitrary size within a perturbation approach in terms of the linear deviations from the spherical shapes [13]. In the special case of spheroidal particles Asano and Yamamoto [14] use spheroidal coordinates which decouple the vector wave equations to obtain the exact results.

Here we extend our theory for the nonlinear response of a spherical particle [3] to a particle of arbitrary shape. Therein the sources of the higher harmonic radiation are treated in terms of the surface charge σ, which is, in the case of metals, equal to the normal projection of the polarization on the surface (σ = n·P) and approximates the induced surface charge in the n-th harmonic case by the n-th power of the linear induced surface charge σ(1) ≡ (σ(1))n. This approach is motivated by the classical anharmonic oscillator model (see [3]) which is valid in the Mie regime and gives a good approximation for particles with can be considered as locally smooth. The n-th power of the surface charge, which is induced by the incident field acts as the source for the higher harmonic fields. It yields a discontinuity of the electrical displacement at the surface which can be expressed in terms of the boundary conditions for the radial component of the electrical fields. Using also the continuity of the tangential component of the electric field, the radiated fields can be fully determined. This is a simple task for spherical particles if spherical coordinates are used. In the case of nonspherical particles, however, matrix equations come into play where the size of the matrices depends on the ratio of the particle dimension to the wavelength of the light and also the geometry of the shape.

To obtain the results for the linear scattering, which are necessary to determine the induced surface charge σ(1)
a formalism by Barber and Yeh [12] is used. This is based on an integral equation method by Waterman [13,14] and Schelkunoff’s equivalence principle [15] yielding matrix equations. This is a good choice because Barber and Yeh use nearly the same representation of the fields with spherical coordinates and their theory is valid for arbitrary cluster-shapes and arbitrary complex indices of refraction.

II. THEORY

We determine the $n$-th harmonic electric field $E_{\text{out}}^{(n)}$ radiated from arbitrarily shaped particles as a function of the $n$-th power of the linear surface charge $\sigma^{(1)}$ induced by the incident field which acts as the source of the $n$-th harmonic. The linear surface charge is given by $\sigma^{(1)} = n \cdot P^{(1)}$ where $n$ is the vector normal at the surface of the cluster since in the case of metals only the normal component of the polarization is nonzero. The source $\sigma^{(n)} = (\sigma^{(1)})^n$ induces a discontinuity of the normal component of the dielectrical displacement at the boundary of the particle. As a consequence we use the conventional boundary conditions for the components of the electric fields to derive $E_{\text{out}}^{(n)}$ which then determines the scattering profile and all the characteristics of the nonlinear Mie scattering by nonspherical particles. Obviously

$$n \cdot (D_{\text{out}}^{(n)} - D_{\text{in}}^{(n)}) = 4\pi \sigma^{(n)}$$

and

$$n \times (E_{\text{out}}^{(n)} - E_{\text{in}}^{(n)}) = 0 ,$$

together with $D = \epsilon E$, yield $E_{\text{out}}^{(n)}$ when $\sigma^{(n)}$ is given.

For the calculation all quantities, the fields and the source, are expanded in terms of spherical harmonics. This results in a matrix equation for the coefficient vectors of the fields and the source which completely determines $E_{\text{out}}^{(n)}$. We show in the following how this analysis can be performed in particular for the nonlinear Mie scattering of nonspherical particles, such an analysis had not been done before.

A. Determination of the source $\sigma^{(n)}$

To determine the source $\sigma^{(n)}$ we use the approximation $\sigma^{(n)} = (\sigma^{(1)})^n$. To obtain the $n$-th power of the linear charge we proceed as follows. The linear surface charge is defined as

$$\sigma^{(1)}(\theta, \varphi) = n \cdot P^{(1)}(\theta, \varphi) .$$

and can be expressed as

$$\sigma^{(1)}(\theta, \varphi) = \frac{1}{4\pi} \text{Re} \left[ (1 - \epsilon^{-1}) (E_{\text{sc}} + E_{\text{inc}}) \cdot n \right] e^{-i\omega t} .$$

Here, we denote the scattered field by the index “sc” and the incident field by “inc”. Therein we refer to the boundary conditions of the normal component of the dielectrical displacement in the linear case $n \cdot (D_{\text{sc}} + D_{\text{inc}}) = n \cdot D_{\text{in}}$ (the index “in” states the field inside the cluster) and to the relation $D = \epsilon E = E + 4\pi P$. Furthermore, $\sigma^{(1)}$ is expanded in terms of spherical harmonics

$$\sigma^{(1)}(\theta, \varphi) = \frac{1}{2} \sum_{l,m=\pm 1} a^{(1)}_{l,m} Y_{l,m}(\theta, \varphi) e^{-i\omega t} + c.c. .$$

From this it is easy to expand the $n$-th power of the linear surface charge in the form

$$(\sigma^{(1)})^n(\theta, \varphi) = \frac{1}{2} \sum_{l,m} a^{(n)}_{l,m} Y_{l,m}(\theta, \varphi) e^{-in\omega t} + c.c. .$$

by raising the linear surface charge $\sigma^{(1)}$ to the $n$-th power and neglecting terms with time-dependence different from $e^{in\omega t}$. Thus, we get the nonlinear sources $\sigma^{(n)}$. As an example the coefficients of $\sigma^{(2)}$ yield (3)[11]
\begin{align}
d_{i,2}^{(2)} &= \frac{1}{2} \sum_{i_1=1}^{\infty} \sum_{i_2=1}^{\infty} a_{i_1,1}^{(1)} a_{i_2,1}^{(1)} \int Y_{i_1}^{*} Y_{i_2}^{*} Y_{l_2,1} Y_{l_2,1} d\Omega, \\
d_{i,-2}^{(2)} &= \frac{1}{2} \sum_{i_1=1}^{\infty} \sum_{i_2=1}^{\infty} a_{i_1,-1}^{(1)} a_{i_2,-1}^{(1)} \int Y_{i_1-2}^{*} Y_{i_2-1}^{*} Y_{l_2,-1} Y_{l_2,-1} d\Omega, \\
d_{i,0}^{(2)} &= \frac{1}{2} \sum_{i_1=1}^{\infty} \sum_{i_2=1}^{\infty} a_{i_1,1}^{(1)} a_{i_2,-1}^{(1)} \int Y_{i_1}^{*} Y_{i_2}^{*} Y_{l_2,-1} Y_{l_2,-1} d\Omega. \\
\end{align}

Therein the integrals over the Legendre Polynomials \( Y_{l,m} \) can be expressed in terms of the well known 3j-symbols. To calculate the coefficients the fields \( E_{\text{out}} \) and \( E_{\text{in}} \), which enter via Eq. [4], are expanded in terms of vector spherical harmonics as introduced by Jackson [10] in the form

\[
E_i^{(n)}(x) = \sum_{l,m} C(l) [K_M(l,m) f_l^i(k_1 r) \mathbf{X}_{l,m}(\theta, \varphi) + \frac{m}{|m|} K_E(l,m) \frac{1}{\epsilon(\omega) k} \mathbf{\nabla} \times f_l^i(k_1 r) \mathbf{X}_{l,m}(\theta, \varphi)].
\]

Therein, \( \mathbf{X}_{l,m}(\theta, \varphi) = \mathbf{L} Y_{l,m}(\theta, \varphi)/\sqrt{l(l+1)} \) is a vector spherical harmonic (\( \mathbf{L} = 1/i(\mathbf{r} \times \mathbf{\nabla}) \) is the angular momentum operator), \( C(l) = i^l \sqrt{4\pi(2l+1)}, k = \omega/c \) and \( k_1 = \sqrt{\epsilon(\omega) k} \). The multipole coefficients \( K_M^{(n)}(l,m) \) and \( K_E^{(n)}(l,m) \) refer to the magnetic (transverse electric TE) and electric (transverse magnetic TM) multipoles. The index \( i \) specifies the fields external (\( i \equiv \text{out} \)) or internal (\( i \equiv \text{in} \)) to the cluster. The spherical Hankel functions \( f_{l,m}^{\text{out}}(kr) = h_l^{(1)}(kr) \) and Bessel functions \( f_{l,m}^{\text{in}}(kr) = j_l(k_1 r) \) describe the normal projection of the field inside and outside the particle. In the linear case the external field splits into the incident and the scattered field \( E_{\text{inc}} \) and \( E_{\text{sc}} \), respectively. The coefficients of \( E_{\text{inc}} \) are known from the input field while \( E_{\text{sc}} \) can be calculated by using the results from the theory for the linear problem by Barber and Yeh [12]. They expressed the coefficients of the internal field in terms of the coefficients of the incident field and then obtained the coefficients of the external field in terms of the coefficients of the internal field.

In higher harmonic radiation where we will use the same expansion of the fields, however, only the external field \( E_{\text{out}}^{(n)} \) radiated from the oscillating surface charge and the internal field \( E_{\text{in}}^{(n)} \) occurs, since no incident field is present.

**B. Determination of the radiated field \( E_{\text{out}}^{(n)} \)**

To calculate the radiated field \( E_{\text{out}}^{(n)} \) it is more convenient to introduce the abbreviations

\[
K_M^{(l,m)}(l,m) = C(l) K_M(l,m), \quad K_E^{(l,m)}(l,m) = \frac{m}{|m|} \frac{1}{\epsilon(\omega) k} C(l) K_E(l,m)
\]

in the sum representation of Eq. [4]. This leads to

\[
E_i^{(n)}(x) = \sum_{l,m} \left[ K_M^{(l,m)} f_l^{(1)}(k_1 r) \mathbf{X}_{l,m}(\theta, \varphi) + K_E^{(l,m)} \mathbf{\nabla} \times f_l^{(1)}(k_1 r) \mathbf{X}_{l,m}(\theta, \varphi) \right].
\]

In the \( n \)-th harmonic case the source \( \sigma^{(n)} \) acts as the discontinuity of the normal part of the electrical displacement

\[
\mathbf{n} \cdot \left( \mathbf{D}_{\text{out}}^{(n)} - \mathbf{D}_{\text{in}}^{(n)} \right) = 4\pi \sigma^{(n)}.
\]

(according to our model for the nonlinear sources \( \sigma^{(n)} \) equals \( (\sigma^{(1)})^n \)). Furthermore we will use the continuity condition of the tangential component of the electric fields

\[
\mathbf{n} \times \left( \mathbf{E}_{\text{out}}^{(n)} - \mathbf{E}_{\text{in}}^{(n)} \right) = 0.
\]

For particles of arbitrary shape the radius vector \( \mathbf{r} \) is no longer parallel to \( \mathbf{n} \) and the radius \( r \) rather becomes a function of \( \theta \) and \( \varphi \) at the boundary since every point of the surface is determined by the angles. Furthermore the normal vector \( \mathbf{n} \) now has the form
\[ \mathbf{n}(\theta, \phi) = n_x(\theta, \phi) \cdot \mathbf{e}_x + n_y(\theta, \phi) \cdot \mathbf{e}_y + n_z(\theta, \phi) \cdot \mathbf{e}_z. \]

Here, \( (\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z) \) are the basis vectors corresponding to spherical coordinates. As a result Eq. \( [10] \) splits into three equations, one for every component

\[ \mathbf{n} \cdot (\mathbf{D}_{out}^{(n)} - \mathbf{D}_{in}^{(n)}) = 4\pi \sigma^{(n)} \]
\[ \mathbf{e}_x \cdot [\mathbf{n} \times (\mathbf{E}_{out}^{(n)} - \mathbf{E}_{in}^{(n)})] = 0 \]
\[ \mathbf{e}_y \cdot [\mathbf{n} \times (\mathbf{E}_{out}^{(n)} - \mathbf{E}_{in}^{(n)})] = 0 \]
\[ \mathbf{e}_z \cdot [\mathbf{n} \times (\mathbf{E}_{out}^{(n)} - \mathbf{E}_{in}^{(n)})] = 0. \]  

(11)

By using the series representations

\[ \mathbf{E}_{out}^{(n)} = \sum_{l,m} \left[ A_E^{(n)} h_l^{(1)}(kr) \mathbf{X}_{l,m} + A_M^{(n)} \mathbf{v} \times h_l^{(1)}(kr) \mathbf{X}_{l,m} \right] \]
\[ \mathbf{E}_{in}^{(n)} = \sum_{l,m} \left[ B_E^{(n)} j_l(kr) \mathbf{X}_{l,m} + B_M^{(n)} \mathbf{v} \times j_l(kr) \mathbf{X}_{l,m} \right] \]  

(12)

multiplying every equation by \( Y_{l',m'} \) where \((l', m')\) runs over all \((l, m)\)-combinations used in the series representations of the fields and the source and integrating over the solid angle we get the following matrix equations

\[ S^1 A_M^{(n)} + S^2 A_E^{(n)} - S^3 B_M^{(n)} - S^4 B_E^{(n)} = 2\pi a^{(n)} \]
\[ M^1_A^{(n)} + M^2_A^{(n)} - M^3_A^{(n)} = 0 \]
\[ M^1_B^{(n)} + M^2_B^{(n)} - M^3_B^{(n)} = 0 \]
\[ M^1_C^{(n)} + M^2_C^{(n)} - M^3_C^{(n)} = 0. \]  

(13)

The coefficients are denoted by the vectors

\[ A_M^{(n)} = \begin{pmatrix} A_M^{(n)}(1, -1) \\ A_M^{(n)}(1, 0) \\ \vdots \\ A_M^{(n)}(l, m) \\ A_M^{(n)}(l, m + 1) \\ \vdots \\ A_M^{(n)}(l + 1, m) \\ \vdots \\ A_M^{(n)}(l_{\text{max}}, l_{\text{max}}) \end{pmatrix}, \quad a^{(n)} = \begin{pmatrix} a_{l,-1}^{(n)} \\ a_{l,0}^{(n)} \\ \vdots \\ a_{l,m}^{(n)} \\ a_{l,m+1}^{(n)} \\ \vdots \\ a_{l_{\text{max}},l_{\text{max}}}^{(n)} \end{pmatrix}, \]

where the coefficients in the vectors \( A_E^{(n)}, B_M^{(n)} \) and \( B_E^{(n)} \) are ordered in analogy to \( A_M^{(n)} \). The matrix elements can be determined by using the expression for the curl terms in Eq. \( [2] \) with \( r \) depending on \( \theta \) and \( \varphi \)

\[ \nabla \times f_l(kr) \mathbf{X}_{l,m} = \frac{1}{r} \frac{\partial}{\partial r} [r f_l(kr)] \mathbf{e}_r \times \mathbf{X}_{l,m} + \mathbf{e}_r \left[ \sqrt{l(l+1)f_l(kr)} Y_{l,m} \right. \]
\[ \left. - \frac{1}{\sqrt{l(l+1)}} \frac{\partial f_l(kr)}{\partial r} \left( \frac{\partial r}{\partial \theta} \frac{\partial Y_{l,m}}{\partial \theta} + \frac{1}{\sin \theta} \frac{\partial r}{\partial \varphi} \frac{\partial Y_{l,m}}{\partial \varphi} \right) \right]. \]  

(14)

Then the matrix elements get the form

\[ M_l^1 (l, m; l', m') = \int d\Omega h_l^{(1)}(kr) \cdot \frac{i}{\sqrt{l(l+1)}} \left[ -n_{l,m} \frac{\partial Y_{l,m}}{\partial \theta} - n_{\varphi} \frac{1}{\sin \theta} \frac{\partial Y_{l,m}}{\partial \varphi} \right] Y_{l',m'}^* \]  

(15)
coefficients in the spherical case. One should study experimentally this conclusion of the theory. In the case of spherical particles all the modes vary on the surface of the particle. This leads to the coupling of different electromagnetic modes. This is in contrast to the interesting physics. They are a consequence of the nonsphericity of the particles implying boundary conditions that are a consequence of the nonsphericity of the particles implying boundary conditions that are equal to zero. Furthermore the orthogonality of the spheric al harmonics is preserved.

Replacing the Hankel functions $h_l^{(1)}(kr)$ by the Bessel functions $j_l(kr)$ the matrix elements for the matrices with the suffix 3 and 4 can be derived (see Eq. 23). Using as many $(l', m')$-combinations as $(l, m)$-combinations all matrices will be quadratic. Thus Eq. 23 becomes a matrix equation off the form

$$
\begin{pmatrix}
S^1 & S^2 & S^3 & S^4 \\
M^1 & M^2 & M^3 & M^4 \\
M^1 & M^2 & M^3 & M^4 \\
M^1 & M^2 & M^3 & M^4
\end{pmatrix}
\begin{pmatrix}
A_M^{(n)} \\
A_E^{(n)} \\
B_M^{(n)} \\
B_E^{(n)}
\end{pmatrix}
= \begin{pmatrix}
2\pi a^{(n)} \\
0 \\
0 \\
0
\end{pmatrix}
$$

which can be solved by standard numerical techniques. Moreover it is only necessary to calculate the coefficients $A_E^{(n)}$ and $A_M^{(n)}$ since they fully determine the $n$-th harmonic radiated field. This completes the solution of the nonlinear Mie scattering problem for arbitrary cluster shapes and arbitrary complex index of refraction.

Note that the matrix equations and the many equations presented in this chapter are necessary to describe the interesting physics. They are a consequence of the nonsphericity of the particles implying boundary conditions that vary on the surface of the particle. This leads to the coupling of different electromagnetic modes. This is in contrast to the radiation by a spherical cluster. This feature is of general validity independent of the approximations made for the sources. One should study experimentally this conclusion of the theory. In the case of spherical particles all equations will collapse to those of the spherical case.

### III. DISCUSSION

First we discuss the special case of a spherical cluster where no magnetic multipoles are radiated and thus the coefficients $A_M^{(n)}$ and $B_M^{(n)}$ are equal to zero. Furthermore the orthogonality of the spherical harmonics

$$
\int Y_{l,m}^* (\theta, \phi) Y_{l',m'} (\theta, \phi) d\Omega = \delta_{l,l'}\delta_{m,m'}
$$

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can be applied in the integrals of Eq. 15–22 since the radius \( r \) and the normal vector \( \mathbf{n} \) are independent of \( \theta \) and \( \varphi \). Thus the matrices \( M_l \) and \( S_{1,3} \) become equal to zero and the other matrices become diagonal. The coefficients \( A_e^{(n)}(l, m) \) can then directly obtained from \( a_{l, m}^{(n)} \).

Thus deviations from the spherical shape cause that one mode of the source can excite several modes of the field which is expressed by the fact that the coefficients of the fields are coupled to the coefficients of the source by a system of equation. The shape of the particle directly governs the integrals in Eqs. 15–22 and their nontrivial form for nonspherical particles leads to the system of equations in Eq. 13 which are valid for arbitrary cluster shapes. Also no restrictions to the size of the complex index of refraction are necessary in contrast to theories where a value of \( |\epsilon| \approx 1 \) is needed like the Rayleigh-Gans theory.

Since our theory needs results from theories for the linear scattering it already includes all their numerical problems. In principle all modes must be summed in the series in Eq. 6 to represent nonspherical particles by spherical coordinates. So one limitation of the theory is the finite number of \((l, m)\)-combinations which can be taken into account. As a consequence the matrices \( M \) and \( S \) in Eq. 13 will become very large for strong deviations from the spherical shape. This purely numerical limitation is natural for particle shapes which cannot be described by coordinates which decouple the Helmholtz equation.

On the other hand the theory has the advantage of a very compact form since the source for the nonlinear response is approximated just by \( \sigma^{(n)} = (\sigma^{(1)})^n \) according to Östling et al. [11] and it only needs the boundary conditions for the electric fields from Eqs. 9 and 10 for the derivation of the radiated fields from the source. The theory is especially valid for particles with sizes in the Mie range since it completely takes into account the combinations of the multipoles in the higher harmonic case (see Eq. 6) which are characteristic for the radiation of a particle in the Mie range. The approximation \( \sigma^{(n)} = (\sigma^{(1)})^n \) for the source term should be critically accessed if one is interested in details of the scattering profiles and effects due to the geometry of the cluster.

One of the main purposes of this paper was to stimulate again work on Mie scattering from nonspherical particles. Clearly further work is necessary to demonstrate the validity of the analysis presented here. Our theory might stimulate the mathematical treatment of Mie scattering in the nonlinear case.

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