Nonlinear Mie scattering from spherical particles

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A theoretical analysis of the second harmonic generation of light from spherical particles is presented that unifies existing theories which are valid in the special cases of small particle size (Rayleigh limit), small refraction index, radiation by nonlocal dipole and quadrupole moments. We study the angular distribution of second harmonic using a nonlinear generalization of the linear Mie theory.

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I. INTRODUCTION

We describe second harmonic generation (SHG) from spherical particles using a classical electrodynamics approach. Although it is well known that SHG response from centrosymmetric systems is forbidden within the electric dipole approximation there are at least three phenomena that allow for its experimental observation.

The first is inversion symmetry breaking on the surface of a sphere. This approach was initiated in the work by Östling, Stampfli, and Bennemann[1] and further developed in the paper by Dewitz, Hübner, and Bennemann.[2] The theory takes advantage of the nonlinear surface charge as a source of the radiation. This stems from the analogy with the anharmonic oscillator model where the oscillator strength of second (third) harmonics oscillation is proportional to the square (cube) of the linear response oscillator strength. In other words, the theory takes into account only the $\chi_{zzz}^{(2\omega)}$ tensor element of the nonlinear response.[3] Although it does not fully account for the specific electronic properties of the material on the *ab initio* level, in particular its electronic resonance structure, it has its power in predicting the *angular distribution* of the scattered field. The microscopic properties of the medium are accounted via the frequency dependent dielectric constant. The theory is a nonlinear extension of Mie scattering[4] and works in a range of particle size parameters up to $ka \sim 100$ ($ka = 2\pi a/\lambda$, a being the radius of the particle, λ denoting the wavelength) where it becomes computationally costly. Thus, a good agreement with experiments was found for third harmonic generation from water microdroplets with sizes from 8 to 32 μm.[5,6] A similar theory was built to explain the experiments with a refraction index of the scattering center close to unity.[7,8] In this case it is possible to use a nonlinear analog of Rayleigh-Gans-Debye (RGD) theory[9] that treats the electric fields inside and outside the sphere as identical and yields the polarization as $\boldsymbol{P}_{2\omega}^{i}(\boldsymbol{r}) = \chi_{ijk}^{(2\omega)} \boldsymbol{E}^{j}(\boldsymbol{r}) \boldsymbol{E}^{k}(\boldsymbol{r})$. The second harmonic electric field at the point $\boldsymbol{r}$ is then obtained as a summation over the volume of the sphere using a Green's function method

$$\boldsymbol{E}_{2\omega}(\boldsymbol{r}) = \frac{(2\omega)^2}{c^2} \int d^3\boldsymbol{r}' \frac{e^{ik_{2\omega}|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|} \boldsymbol{P}_{2\omega}(\boldsymbol{r}'), \quad (1)$$

where $k_{2\omega}^2 = (2\omega)^2/c^2 \varepsilon(2\omega)$, ε is the particle dielectric constant. The integration can be analytically performed in the case when the SHG source is confined to the thin homogeneous layer of nonlinear material covering the sphere.[10] Although the size parameter in all three experimental works (0.8 Ref. 10, 3.7–1.9 Ref. 7, and 1.3 Ref. 8, respectively) lies within the limits of validity of the Rayleigh approximation, it was suggested[10] to use the Mie theory for a more quantitative analysis—in the way already demonstrated by Ref. 5.

Another approach suggested in the work of Dadap *et al.*[11] takes into account all tensor elements of the surface nonlinear response of the sphere. The method was applied in the case of small particle size parameters $ka < 1$ corresponding to the limit of Rayleigh scattering. The radiated SH field in the direction of $\boldsymbol{n}$ results from the nonlocal excitation of the electric dipole and local excitation of the electric quadrupole moments

$$\boldsymbol{p} = 8\pi i k a^3 E_0^2 \chi_1 \boldsymbol{k}(\boldsymbol{\varepsilon}_0 \cdot \boldsymbol{\varepsilon}_0)/15, \quad (2)$$

$$\boldsymbol{Q}(\boldsymbol{n}) = 16\pi a^3 E_0^2 \chi_2 (\boldsymbol{n} \cdot \boldsymbol{\varepsilon}_0) \boldsymbol{\varepsilon}_0/5, \quad (3)$$

which in this case have a comparable strength (the magnetic dipole emission is forbidden because of the axial symmetry of the system). Here the incident electric field is taken as a plane wave propagating in the direction of $\boldsymbol{k}$ with polarization $\boldsymbol{\varepsilon}_0$ and amplitude E_0.[12] The properties of the medium are described by the quantities χ_1 and χ_2, which can be expressed via the dielectric functions of the sphere, the interface, and the exterior region.[13]

The theory predicts the absence of the SHG signal in the forward direction and gives the $(ka)^6$ scaling of the integrated scattering intensity. The latter is obvious in view of the fact that the retardation of the electromagnetic field across the sphere yields the nonlocal dipole moment proportional to the $(a/\lambda)^3$ where λ is the wavelength. This fact, reflecting a very high sensitivity of the SHG signal to the particle size, was emphasized in the work of Brudny, Mendoza, and Mochan.[14]

The theory of SHG by the nonlocal dipole and quadrupole excitations and their interference was extended by several authors to include effects of disorder. Within the single scattering and diffusion approximations, the angular distribution of SHG intensity was studied in the three-dimensional (3D) case of a suspension of small spherical particles confined within a slab.[15] It was found that the intensity varies with the angle θ between the z axis and the direction of the observation and the polar angle ϕ as

$$I_{2\omega} = \chi_1^2 F_1(\theta,\phi) + 4\chi_2^2 F_2(\theta,\phi) + 4\chi_1\chi_2 F_3(\theta,\phi), \qquad (4)$$

where $F_1(\theta,\phi)=\sin^2\theta$, $F_2(\theta,\phi)=\sin^2\theta\sin^2\phi(1-\sin^2\theta\sin^2\phi)$, $F_3(\theta,\phi)=\cos\theta\sin^2\theta\sin^2\phi$. The angular scattering diagram shows two lobes in the forward direction at $\cos\theta=\pm 0.22$ for the realistic parameters of χ_1 and χ_2 and forbids SHG at $\theta=0$ in agreement with previous results.[2,11]

It is also interesting to compare the angular distribution of the SHG intensity from the RGD theory[10] with that of the excitation of nonlocal dipole and local quadrupole moments.[15] Although they both agree about the absence of SHG signal in the forward direction, the RGD theory yields a considerably more complicated pattern with additional but less pronounced lobes.

The nonlocal dipole and quadrupole are excited by a spatial variation of the incident field within the sphere. In the previous example the excitation was due to the variation of the electric field on the wavelength scale. However, as has been shown in Ref. 14, field variations with other length scales can also give rise to the nonlinear response. In Ref. 14 SHG from a single sphere in the inhomogeneous longitudinal field and a sphere placed above a semi-infinite inert dielectric substrate with a flat surface was presented together with a detailed discussion of the frequency dependence of the nonlinear response. In Ref. 16 the analysis was extended to account for the inhomogeneous transverse field which can be applied to a composite medium made up of an array of particles illuminated by beams of finite cross section.[17] The equivalence of the two theories[11,16] in the case of small nonmagnetic spheres excited by the field of a plane wave was explicitly shown.

This paper is an effort to compare possible scenarios for second harmonic generation from a centrosymmetric system for different particle sizes (regimes of Rayleigh, Mie, and geometric optics) and different materials (we develop the theory which is valid in both regimes of small as well as large refraction index). We assume that the microscopical properties of the medium are known *a priori* and are contained in the frequency dependent dielectric function $\varepsilon(\omega)$ and in the tensor of the second-order nonlinear susceptibility $\chi^{(2\omega)}$. The dielectric function can in general be complex allowing for the applicability of the theory to dielectrics as well as to metals. Our goal is to describe the angular dependence of the SHG intensity. The paper is organized as follows. In Sec. II we present the surface sheet model[18] for the dielectric sphere in vacuum. The calculation of the second harmonic response comprises four steps: (i) solution of the classical Mie problem of the light scattering by the sphere resulting in (ii) the second-order polarization $\boldsymbol{P}^i_{2\omega}=\chi^{(2\omega)}_{ijk}\boldsymbol{E}^j\boldsymbol{E}^k$, and, consecutively, in the surface charge and the surface current playing the roles of sources of the second harmonic fields, (iii) solution of the boundary problem in order to find the fields from the known sources, (iv) resolving the angular distribution in the far-field approximation. The theory is a generalization of the results of Ref. 2 for the case when the local symmetry of the surface layer is C_{4v}.[19] Thus, not only surface charges, but also currents contribute to SHG. On the other hand, we extend the work of Dadap *et al.*[11] beyond the Rayleigh limit to the case of arbitrary sized spheres. In Sec. III we apply our theory to study water droplets with a size parameter from $ka=0.001$ to $ka=200.0$. We assume that the local tensor of the second-order nonlinear susceptibility $\chi^{(2\omega)}_{ijk}$ is equal to zero except for the $\chi^{(2\omega)}_{zzz}$ element. The angular distribution and intensity dependence of SHG response on the particle size is analyzed.

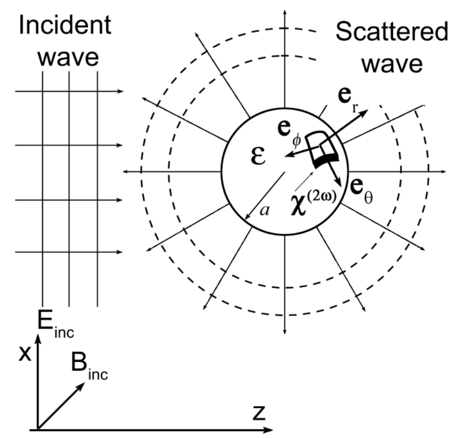

FIG. 1. Scattering of light by a sphere. The sphere of radius a is characterized by the dielectric constants at fundamental and double frequency $\epsilon(\omega)$, $\epsilon(2\omega)$ respectively, and by the tensor of surface second-order nonlinear susceptibility $\chi^{(2\omega)}$.

II. THEORY

The theory consists of a few steps as follows. First, we solve a problem of the electromagnetic field scattering by a sphere (Mie theory) in order to find electric fields close to its surface. The geometry of the problem is shown in Fig. 1. We represent the electric and the magnetic fields as

$$\boldsymbol{E}_i = \frac{1}{2}\sum_{\ell,m} C(\ell)[a^i_{(\ell,m)} f^{(i)}_\ell(kr)\boldsymbol{X}_{\ell,m}(\theta,\phi) + \alpha^i b^i_{(\ell,m)} \boldsymbol{\nabla}\times f^{(i)}_\ell(kr)\boldsymbol{X}_{\ell,m}(\theta,\phi)], \qquad (5)$$

$$c\boldsymbol{B}_i = \frac{1}{2}\sum_{\ell,m} C(\ell)[b^i_{(\ell,m)} f^{(i)}_\ell(kr)\boldsymbol{X}_{\ell,m}(\theta,\phi) + \beta^i a^i_{(\ell,m)} \boldsymbol{\nabla}\times f^{(i)}_\ell(kr)\boldsymbol{X}_{\ell,m}(\theta,\phi)] \qquad (6)$$

in accordance with Eq. (10.57) of Jackson.[20] We denote $C(\ell)=\sqrt{4\pi(2\ell+1)}i^\ell$; $\alpha^i=\alpha^i(k)$, $\beta^i=\beta^i(k)$, and k^i are constants that depend on the medium being considered. Outside the sphere we have $k^{out}=\omega/c=k$, while inside $k^{in}=\sqrt{\varepsilon(\omega)}\times(\omega/c)=nk=k_1$, where we also introduce the complex refraction index n. Here $\boldsymbol{X}_{\ell,m}(\theta,\phi)$ are *vector spherical harmonics*[21] as defined in Ref. 20 (Eq. 9.119). The index i refers to the incident ($i\equiv inc$), the scattered ($i\equiv sc$), or the internal ($i\equiv in$) fields. The functions $f^{(i)}$ are different depending on the region we consider: $f^{(inc,in)}_\ell=j_\ell$ (*spherical Bessel function of the first kind*) and $f^{(sc)}_\ell=h^{(1)}_\ell$ (*spherical Hankel function of the first kind*). Their definitions and properties can be found in Sec. 8.46 of Ref. 22. The expansion coefficients are determined by four boundary conditions

$$\boldsymbol{n} \times (\boldsymbol{E}_{sc} + \boldsymbol{E}_{inc}) = \boldsymbol{n} \times \boldsymbol{E}_{in}, \tag{7}$$

$$\boldsymbol{n} \cdot (\boldsymbol{D}_{sc} + \boldsymbol{D}_{inc}) = \boldsymbol{n} \cdot \boldsymbol{D}_{in}, \tag{8}$$

$$\boldsymbol{n} \times (\boldsymbol{B}_{sc} + \boldsymbol{B}_{inc}) = \boldsymbol{n} \times \boldsymbol{B}_{in}, \tag{9}$$

$$\boldsymbol{n} \cdot (\boldsymbol{B}_{sc} + \boldsymbol{B}_{inc}) = \boldsymbol{n} \cdot \boldsymbol{B}_{in}, \tag{10}$$

where $\boldsymbol{n}=\boldsymbol{e}_r$ is a vector normal to the surface. Solution of the boundary value problem allows one to express coefficients of scattered and inner fields via the incident field

$$\frac{b^{sc}_{(\ell,m)}}{b^{inc}_{(\ell,m)}} = \left. \frac{j_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1r)] - \varepsilon j_\ell(k_1r)\frac{\partial}{\partial r}[rj_\ell(kr)]}{\varepsilon j_\ell(k_1r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1r)]}\right|_{r=a},$$

$$\frac{a^{sc}_{(\ell,m)}}{a^{inc}_{(\ell,m)}} = \left. \frac{j_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1r)] - j_\ell(k_1r)\frac{\partial}{\partial r}[rj_\ell(kr)]}{j_\ell(k_1r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1r)]}\right|_{r=a},$$

$$\frac{b^{in}_{(\ell,m)}}{b^{inc}_{(\ell,m)}} = \left. \frac{j_\ell(kr)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - \varepsilon h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(kr)]}{\varepsilon j_\ell(k_1r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1r)]}\right|_{r=a},$$

$$\frac{a^{in}_{(\ell,m)}}{a^{inc}_{(\ell,m)}} = \left. \frac{j_\ell(kr)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(kr)]}{j_\ell(k_1r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1r)]}\right|_{r=a},$$

where $b^{inc}_{(\ell,1)}=-b^{\mathrm{inc}}_{(\ell,-1)}=-i$, $a^{\mathrm{inc}}_{(\ell,1)}=a^{\mathrm{inc}}_{(\ell,-1)}=1$ and $\alpha^{\mathrm{inc}}=-\beta^{\mathrm{inc}}=i/k$ are coefficients obtained from the multipole expansion of the plane wave [Eq. (10.55) of Jackson[20]].

In the second step of the calculation we determine the sources of the second harmonic fields, namely the surface charge σ and the surface current $\boldsymbol{j}_s$, which are expanded in terms of spherical harmonics $Y_{\ell,m}(\theta,\phi)$ [defined in Ref. 20, Eq. (3.53)] and vector spherical harmonics

$$\sigma(\theta,\phi) = \frac{1}{2}\sum_{\ell,m} \sigma_{\ell,m} Y_{\ell,m}(\theta,\phi),$$

$$\boldsymbol{j}_s(\theta,\phi) = \frac{1}{2}\sum_{\ell,m} [j^{\parallel}_{\ell,m}\boldsymbol{X}_{\ell,m}(\theta,\phi) + j^{\perp}_{\ell,m}\boldsymbol{X}_{\ell,m}(\theta,\phi)\times \boldsymbol{n}].$$

In each point of the surface of the/ sphere the $\boldsymbol{e}_x$, $\boldsymbol{e}_y$, $\boldsymbol{e}_z$ unit vectors of the local coordinate system point along $\boldsymbol{e}_\theta$, $\boldsymbol{e}_\phi$, $\boldsymbol{e}_r$ respectively. Assuming the C_{4v} symmetry of the surface layer[19] the only nonzero nonlinear tensor elements are $\chi_{zxx}=\chi_{zyy}$, χ_{zzz}, and $\chi_{xzx}=\chi_{yzy}$. According to the surface sheet model, SHG takes place in a thin layer above the surface. The second-order polarization $\boldsymbol{P}_{2\omega}$ is expressed via the electric field on the outer surface of the sphere $\boldsymbol{E}_s$

$$P^r_{2\omega} = \chi_{zxx}E^{\theta^2}_s + \chi_{zyy}E^{\phi^2}_s + \chi_{zzz}E^{r^2}_s,$$

$$P^\theta_{2\omega} = \chi_{xzx}E^r_sE^\theta_s,$$

$$P^\phi_{2\omega} = \chi_{yzy}E^r_sE^\phi_s.$$

The surface density is then $\sigma=\boldsymbol{n}\cdot\boldsymbol{P}_{2\omega}$ and the surface current $\boldsymbol{j}_s=-2i\delta\omega\boldsymbol{n}\times(\boldsymbol{P}_{2\omega}\times\boldsymbol{n})$, where δ is the thickness of the surface layer where SHG takes place. In order to find the coefficients of the expansion $\sigma_{\ell,m}$ and $j^{\parallel}_{\ell,m}$ we reexpand the electric field on the surface $\boldsymbol{E}_s=(\varepsilon E^r_{in}\boldsymbol{e}_r+E^\theta_{in}\boldsymbol{e}_\theta+E^\phi_{in}\boldsymbol{e}_\phi)|_{r=a}$ in terms of vector spherical harmonics as

$$\boldsymbol{E}_s = \sum_{\ell,m} A^{(1)}_{\ell,m}\boldsymbol{Y}^{(1)}_{\ell,m} + A^{(0)}_{\ell,m}\boldsymbol{Y}^{(0)}_{\ell,m} + A^{(-1)}_{\ell,m}\boldsymbol{Y}^{(-1)}_{\ell,m},$$

where the vector spherical harmonics $\boldsymbol{Y}^{(1)}_{JM}, \boldsymbol{Y}^{(0)}_{JM}\equiv\boldsymbol{X}_{JM}, \boldsymbol{Y}^{(-1)}_{JM}$ are defined [Ref. 23, Eq. (7.3.9)] as

$$\boldsymbol{Y}^{(1)}_{JM} = \sqrt{\frac{J+1}{2J+1}}\boldsymbol{Y}^{J-1}_{JM} + \sqrt{\frac{J}{2J+1}}\boldsymbol{Y}^{J+1}_{JM},$$

$$\boldsymbol{Y}^{(0)}_{JM} = \boldsymbol{Y}^{J}_{JM},$$

$$\boldsymbol{Y}^{(-1)}_{JM} = \sqrt{\frac{J}{2J+1}}\boldsymbol{Y}^{J-1}_{JM} + \sqrt{\frac{J+1}{2J+1}}\boldsymbol{Y}^{J+1}_{JM}.$$

The coefficients $A^{(1)}_{\ell,m}$, $A^{(0)}_{\ell,m}$, $A^{(-1)}_{\ell,m}$ can be found from the general expression [Eq. (5)] for the electric field

$$A^{(1)}_{\ell,m} = \frac{1}{2}C(\ell)\frac{i}{ka}\left.\frac{d[rj_\ell(nkr)]}{dr}\right|_{r=a}\frac{b^{in}_{(\ell,m)}}{b^{inc}_{(\ell,1)}}, \tag{11}$$

$$A^{(0)}_{\ell,m} = \frac{1}{2}C(\ell)j_\ell(nka)\frac{a^{in}_{(\ell,m)}}{a^{inc}_{(\ell,1)}}, \tag{12}$$

$$A^{(-1)}_{\ell,m} = \frac{1}{2}C(\ell)\frac{i\epsilon(\omega)\sqrt{\ell(\ell+1)}}{ka}j_\ell(nka)\frac{b^{in}_{(\ell,m)}}{b^{inc}_{(\ell,1)}}. \tag{13}$$

Using the orthogonality of the vector spherical harmonics $\boldsymbol{Y}^{(\lambda')}_{\ell,m}\cdot\boldsymbol{Y}^{(\lambda)}_{\ell,m}=0$, if $\lambda'\neq\lambda$ and the properties $\boldsymbol{n}\times\boldsymbol{Y}^{(1)}_{\ell,m}=i\boldsymbol{Y}^{(0)}_{\ell,m}$, $\boldsymbol{n}\times\boldsymbol{Y}^{(0)}_{\ell,m}=i\boldsymbol{Y}^{(1)}_{\ell,m}$, and $\boldsymbol{n}\times\boldsymbol{Y}^{(-1)}_{\ell,m}=0$ we obtain

$$E^{\theta^2}_s + E^{\phi^2}_s = \sum_{\ell_1,m_1}\sum_{\ell_2,m_2} A^{(1)}_{\ell_1,m_1}A^{(1)}_{\ell_2,m_2}\boldsymbol{Y}^{(1)}_{\ell_1,m_1}\cdot\boldsymbol{Y}^{(1)}_{\ell_2,m_2} + A^{(0)}_{\ell_1,m_1}A^{(0)}_{\ell_2,m_2}\boldsymbol{Y}^{(0)}_{\ell_1,m_1}\cdot\boldsymbol{Y}^{(0)}_{\ell_2,m_2},$$

$$E^{r^2}_s = \sum_{\ell_1,m_1}\sum_{\ell_2,m_2} A^{(-1)}_{\ell_1,m_1}A^{(-1)}_{\ell_2,m_2}\boldsymbol{Y}^{(-1)}_{\ell_1,m_1}\cdot\boldsymbol{Y}^{(-1)}_{\ell_2,m_2},$$

$$E^r_s(\boldsymbol{E}^\theta_s + \boldsymbol{E}^\phi_s) = i\sum_{\ell_1,m_1}\sum_{\ell_2,m_2} A^{(-1)}_{\ell_2,m_2}A^{(0)}_{\ell_1,m_1}\boldsymbol{Y}^{(1)}_{\ell_1,m_1}\times\boldsymbol{Y}^{(-1)}_{\ell_2,m_2} + A^{(-1)}_{\ell_2,m_2}A^{(1)}_{\ell_1,m_1}\boldsymbol{Y}^{(0)}_{\ell_1,m_1}\times\boldsymbol{Y}^{(-1)}_{\ell_2,m_2}.$$

Expressions for the coefficients of surface charge and current are then given as

$$\sigma_{\ell,m} = \chi_{zxx}\sum_{\ell_1,m_1}\sum_{\ell_2,m_2}\left(A^{(1)}_{\ell_1,m_1}A^{(1)}_{\ell_2,m_2}C^{(1,1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m} + A^{(0)}_{\ell_1,m_1}A^{(0)}_{\ell_2,m_2}C^{(0,0)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}\right) + \chi_{zzz}\sum_{\ell_1,m_1}\sum_{\ell_2,m_2}A^{(-1)}_{\ell_1,m_1}A^{(-1)}_{\ell_2,m_2}C^{(-1,-1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}, \quad (14)$$

$$j^{\parallel}_{\ell,m} = -2i\omega\delta\chi_{xzx}\sum_{\ell_1,m_1}\sum_{\ell_2,m_2}\left(A^{(1)}_{\ell_1,m_1}A^{(-1)}_{\ell_2,m_2}C^{(1,-1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m} + A^{(0)}_{\ell_1,m_1}A^{(-1)}_{\ell_2,m_2}C^{(0,-1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}\right). \quad (15)$$

The coefficients $C^{(\alpha,\beta)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}$ result from the expansion of scalar (vector) products of the vector spherical harmonics and comprise products of $6j$ ($9j$) coefficients and two Clebsch-Gordan coefficients as is shown in the Appendix. From their explicit expressions follow symmetry properties $C^{(\alpha,\beta)}_{\ell_1,1,\ell_2,1,\ell,2}=C^{(\alpha,\beta)}_{\ell_1,-1,\ell_2,-1,\ell,-2}$, unless $\alpha=0,\beta=-1$. In this case the coefficients are antisymmetric with respect to the change of sign of the angular momentum projections $C^{(0,-1)}_{\ell_1,1,\ell_2,1,\ell,2}=-C^{(0,-1)}_{\ell_1,-1,\ell_2,-1,\ell,-2}$. Thus, the coefficients of the surface charge expansion also are symmetric $\sigma_{\ell,2}=\sigma_{\ell,-2}$, while the current $j^{\parallel}_{\ell,\pm 2}$ has both symmetric and antisymmetric parts.

The third step of the calculation is very similar to the first one. We find the second harmonic fields from the known surface charge and the current by solving a boundary condition problem

$$\boldsymbol{n}\times(\boldsymbol{E}_{out}-\boldsymbol{E}_{in}) = 0, \quad (16)$$

$$\boldsymbol{n}\cdot(\boldsymbol{D}_{out}-\boldsymbol{D}_{in}) = \sigma, \quad (17)$$

$$\boldsymbol{n}\times(\boldsymbol{H}_{out}-\boldsymbol{H}_{in}) = \boldsymbol{j}_s, \quad (18)$$

$$\boldsymbol{n}\cdot(\boldsymbol{B}_{out}-\boldsymbol{B}_{in}) = 0. \quad (19)$$

Calculations show that only the $j^{\parallel}$ component of the surface current contributes to the results. The solution is given by

$$A^{out}_{\ell,m} = \frac{ik\mu_0 c}{C(\ell)}\frac{j_\ell(k_1 r)}{j_\ell(k_1 r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1 r)]}j^{\parallel}_{\ell,m}, \quad (20)$$

$$B^{out}_{\ell,m} = \frac{k}{\varepsilon_0 C(\ell)\sqrt{\ell(\ell+1)}} \times \frac{\frac{\partial}{\partial r}[rj_\ell(k_1 r)]}{\varepsilon j_\ell(k_1 r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1 r)]}\sigma_{\ell,m}, \quad (21)$$

$$A^{in}_{\ell,m} = \frac{ik_1\mu_0 c}{C(\ell)} \times \frac{h^{(1)}_\ell(kr)}{\left(j_\ell(k_1 r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1 r)]\right)}j^{\parallel}_{\ell,m}, \quad (22)$$

$$B^{in}_{\ell,m} = \frac{k_1}{\varepsilon_0 C(\ell)\sqrt{\ell(\ell+1)}} \times \frac{\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)]}{\left(\varepsilon j_\ell(k_1 r)\frac{\partial}{\partial r}[rh^{(1)}_\ell(kr)] - h^{(1)}_\ell(kr)\frac{\partial}{\partial r}[rj_\ell(k_1 r)]\right)}\sigma_{\ell,m}. \quad (23)$$

From the symmetry of the surface charge it follows that $B^{out}_{\ell,2}=B^{out}_{\ell,-2}$, for the $A^{out}_{\ell,m}=A^{+out}_{\ell,m}+A^{-out}_{\ell,m}$ we introduce symmetric and antisymmetric parts.

Last, we determine the angular distribution of the intensities in the far-field approximation. We use the asymptotic expansion of the Hankel functions [Eq. (8.451.3) of Ref. 22]: $h^{(1)}_\ell(kr)\sim(-i)^{\ell+1}e^{ikr}/kr$ and its derivative: $(1/r)\partial/\partial r[rh^{(1)}_\ell(kr)]\sim -(-i)^\ell e^{ikr}/r$. Because $\boldsymbol{E}^r_{out}$ is proportional to $h^{(1)}(kr)/kr$ it decays faster than $1/r$ and therefore is not relevant, thus, we consider only E^θ_{out} and E^ϕ_{out} projections

$$E^\theta_{out} = -\frac{1}{2}\sum_{\ell,m=\pm 2,0}\frac{C(\ell)}{\sqrt{\ell(\ell+1)}}\left(B^{out}_{\ell,m}\frac{i}{kr}\frac{d[rh^{(1)}_\ell(kr)]}{dr}\frac{\partial Y_{\ell,m}}{\partial\theta} + A^{out}_{\ell,m}h^{(1)}_\ell(kr)\frac{mY_{\ell,m}}{\sin\theta}\right),$$

$$E^\phi_{out} = \frac{1}{2i}\sum_{\ell,m=\pm 2,0}\frac{C(\ell)}{\sqrt{\ell(\ell+1)}}\left(B^{out}_{\ell,m}\frac{i}{kr}\frac{[rh^{(1)}_\ell(kr)]}{dr}\frac{mY_{\ell,m}}{\sin\theta} + A^{out}_{\ell,m}h^{(1)}_\ell(kr)\frac{\partial Y_{\ell,m}}{\partial\theta}\right).$$

We substitute asymptotic expansions, skip the overall factor e^{ikr}/ikr, use the symmetry of the expansion coefficients and representation of the spherical harmonics in terms of Legendre polynomials $Y_{\ell,0}(\theta,\phi)=\sqrt{(2\ell+1)/4\pi}P_\ell(\cos\theta)$ and $Y_{\ell,\pm 2}(\theta,\phi)=\sqrt{(2\ell+1)/4\pi}K(\ell)P^2_\ell(\cos\theta)e^{\pm 2i\phi}$, where $K(\ell)=1/\sqrt{(\ell-1)\ell(\ell+1)(\ell+2)}$ in order to obtain

$$E^\theta_{out} = -\frac{1}{2}\sum_{\ell=1}\frac{C(\ell)(-i)^\ell}{\sqrt{\ell(\ell+1)}}\sqrt{\frac{2\ell+1}{4\pi}}\left(\frac{\partial P^0_\ell(\cos\theta)}{\partial\theta}B^{out}_{\ell,0} + 2K(\ell)\frac{\partial P^2_\ell(\cos\theta)}{\partial\theta}B^{out}_{\ell,2}\cos(2\phi) + \frac{4K(\ell)P^2_\ell(\cos\theta)}{\sin\theta}[A^{-out}_{\ell,2}\cos(2\phi)+iA^{+out}_{\ell,2}\sin(2\phi)]\right), \quad (24)$$

$$E_{out}^{\phi} = \frac{1}{2i}\sum_{\ell=1} \frac{C(\ell)(-i)^{\ell}}{\sqrt{\ell(\ell+1)}} \sqrt{\frac{2\ell+1}{4\pi}}\Bigg(\frac{4iK(\ell)P_{\ell}^{2}(\cos\theta)}{\sin\theta} \times B_{\ell,2}^{out}\sin(2\phi) + \frac{\partial P_{\ell}^{0}(\cos\theta)}{\partial\theta}A_{\ell,0}^{+out} + 2K(\ell)\frac{\partial P_{\ell}^{2}(\cos\theta)}{\partial\theta} \times [A_{\ell,2}^{+out}\cos(2\phi) + iA_{\ell,2}^{-out}\sin(2\phi)]\Bigg). \tag{25}$$

Finally, we outline the numerical algorithm based on the theory

- Find coefficients of the surface electric field $\boldsymbol{E}_s$ expansion [Eqs. (11)–(13)].
- Compute the surface charge σ and the current $\boldsymbol{j}_s$ using Clebsch-Gordan algebra [Eqs. (14), (15)].
- Find coefficients of the SH electric field $\boldsymbol{E}_{out}$ expansion [Eqs. (20), (21)].
- Compute the angular dependence of SHG according to Eqs. (24) and (25).

III. NUMERICAL RESULTS

We study the angular distribution and the intensity of SHG radiated in a unit solid angle for different sizes of particles. Water droplets of the size parameter ranging from $ka=10^{-3}$ to $ka=200.0$ with $n(\omega)=1.326-1.250\cdot 10^{-7}i$ and $n(2\omega)=1.350-1.580\cdot 10^{-9}i$ [complex refraction index approximately corresponds to the wavelength of incident light $\lambda=800$ nm (Ref. 24)] are considered. The number of significant terms in the multipole expansion [Eqs. (11)–(13)] varies depending on the value of ka. For $\ell > ka$ the terms decrease rapidly, whereas for $\ell \ll ka$ they have comparable amplitudes. Only the $\chi_{zzz}^{(2\omega)}$ tensor element is assumed to be nonzero. The theory is valid in the regime of small particle sizes ($ka<1$, Rayleigh limit) as well as for large particles. In the former case the angular distribution of SH intensity remains independent on the size parameter (Fig. 2), the integrated intensity grows as $P_{2\omega}(ka)\sim(ka)^6$ (Fig. 3), in agreement with Ref. 11. For reference, we report the small-ka expansion of the first few coefficients of the SH electric field E_{out} [Eqs. (20), (21)]

$$B_{1,0}^{out} = \sqrt{\frac{24}{\pi}}\frac{n^2(\omega)\chi_{zzz}}{[n^2(\omega)+2][2n^2(\omega)+3][n^2(2\omega)+2]}(ka)^4,$$

$$B_{2,0}^{out} = \sqrt{\frac{3}{10\pi}}\frac{n^2(\omega)\chi_{zzz}}{[n^2(\omega)+2]^2[2n^2(2\omega)+3]}i(ka)^4,$$

$$B_{2,2}^{out} = -\sqrt{\frac{9}{20\pi}}\frac{n^2(\omega)\chi_{zzz}}{[n^2(\omega)+2]^2[2n^2(2\omega)+3]}i(ka)^4.$$

This shows that in the lowest order of ka the SH radiation results from the excitation of dipole and quadrupole moments, which have a comparable strength, as has been shown in Ref. 11. The scaling of the SH power should be contrasted with the linear Rayleigh scattering, which is known to scale as $P_{\omega}(ka)\sim(ka)^4$. Increasing the particle size parameter ($ka>10$) leads to two well pronounced maxima in the forward and backward directions (Fig. 4). Their position varies slightly with the particle size within the limits $5° < \theta_1 < 20°$, $160° < \theta_2 < 175°$. Radiation in the strict forward $\theta=0°$ and backward $\theta=180°$ directions is prohibited at any value of ka as can be seen from Eqs. (24) and (25) [$\partial P_{\ell}^{0}(\cos\theta)/\partial\theta = \partial P_{\ell}^{2}(\cos\theta)/\partial\theta = P_{\ell}^{2}(\cos\theta)/\sin\theta = 0$ at $\theta=0, \pi$]. At large values of ka the SH intensity exhibits oscillations, which may be interpreted as a kind of shape resonance phenomena (Fig. 5). A similar behavior has also been found in the linear case, where the position of the intensity maxima is approximately given by $ka[n(\omega)-1]=\pi/2(2p+1)$ (p integer).[25] There is, however, an important difference compared to the linear case. In the linear case shape resonance phenomena are greatly suppressed for the experimental observation due to the presence of dominating forward scattering. In the SHG case the oscillations in the angular distribu-

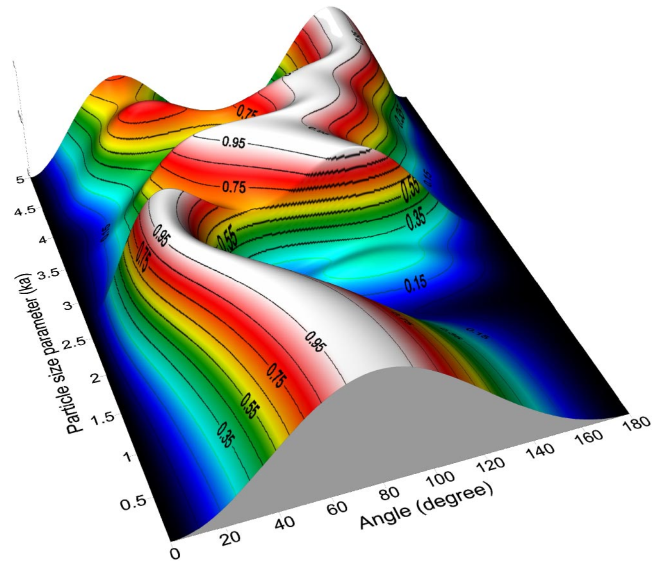

FIG. 2. (Color online) Angular distribution of the SHG intensity for water droplets as a function of particle size parameter laying within the range $0.001 < ka < 5.0$. At each value of ka the angular distribution is normalized, so that the maximum value is unity. At $ka\sim1.0$ the distribution starts to vary with the particle size indicating that the Rayleigh theory ceases to be valid.

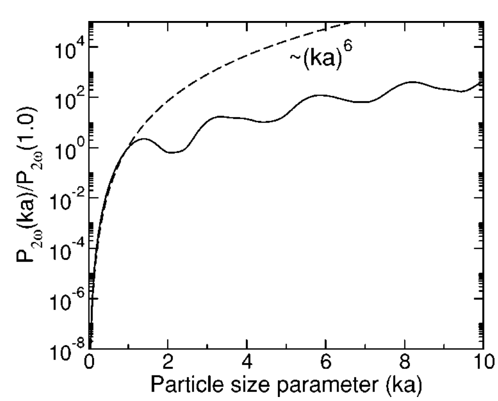

FIG. 3. Integrated SH intensity $P_{2\omega}(ka)$. At small particle size parameter the Rayleigh theory is valid, yielding $(ka)^6$ scaling. Intensity is normalized so that $P_{2\omega}(1.0)=1.0$.

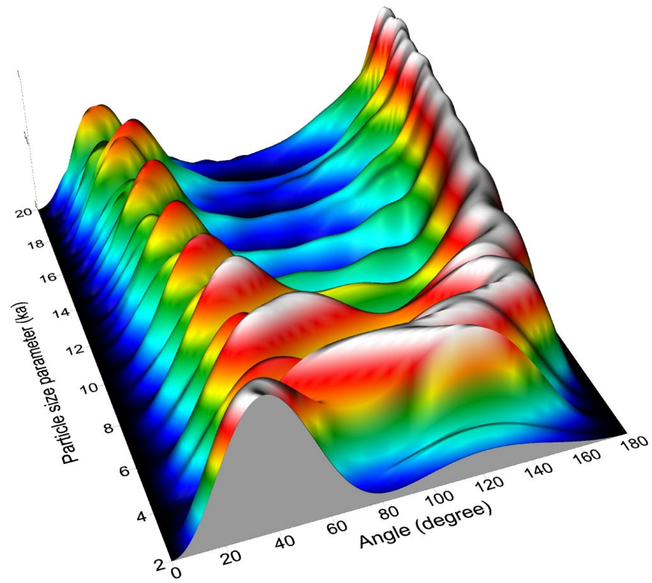

FIG. 4. (Color online) Angular distribution of the SHG intensity for water droplets as a function of particle size parameter $(2<ka<20.0)$ corresponding to the transition regime between Rayleigh and Mie theories.

tion can in fact be revealed with a higher precision provided the laser radiation is monochromatic enough. If, on the other hand, one uses short laser pulses an averaging over a frequency interval is required which would lead to the smoothening of the angular distribution shown in Fig. 5.

IV. CONCLUSIONS AND OUTLOOK

In conclusion, we have developed a theory of second harmonic generation by dielectric spheres of arbitrary size and refraction index. The surface sheet model which assumes inversion symmetry breaking on the surface of the sphere has been employed. A numerical algorithm has been applied to compute the SHG response of water droplets with size parameters up to $ka=200.0$. The analysis shows two pronounced SHG intensity peaks in the forward and backward direction. Their position slightly depends on the particle size. At low values of the size parameter the theory reduces to the well known Rayleigh limit[11] where the peaks merge together forming one lobe. The integrated intensity depends strongly on the particle size, fulfilling $(ka)^6$ scaling at small ka.

The theory in this paper treats the case of Mie scattering from a single particle. Thus for a disordered medium, such as a colloidal suspension of particles, it is restricted to a description of the dilute regime. In this case the mean distance between particles is greater than the absorption length for photons and the scattering events can be considered as independent. However, it is also of interest to study nonlinear optical processes in disordered systems in the high-density regime where coherent interferences among the particles become important. The generalization of our theory to this case will be a subject of a future work.

APPENDIX: EXPANSIONS OF THE PRODUCTS OF VECTOR SPHERICAL HARMONICS

We use the Clebsch-Gordan series for the scalar product of vector spherical harmonics Ref. 23 [Eqs. (7.3.100), (7.3.101)]

$$\boldsymbol{Y}_{J_1M_1}^{L_1}\cdot\boldsymbol{Y}_{J_2M_2}^{L_2}=\sum_L(-1)^{J_2+L_1+L}\times\sqrt{\frac{(2J_1+1)(2J_2+1)(2L_1+1)(2L_2+1)}{4\pi(2L+1)}}\times\begin{Bmatrix}L_1 & L_2 & L\\ J_2 & J_1 & 1\end{Bmatrix}C_{L_10L_20}^{L0}C_{J_1M_1J_2M_2}^{LM}Y_{LM},$$

where $C_{J_1M_1J_2M_2}^{LM}$ is the Clebsch-Gordan coefficient, and {} is the $6j$ symbol. Similarly, one can expand the vector product of vector spherical harmonics using the $9j$ symbol

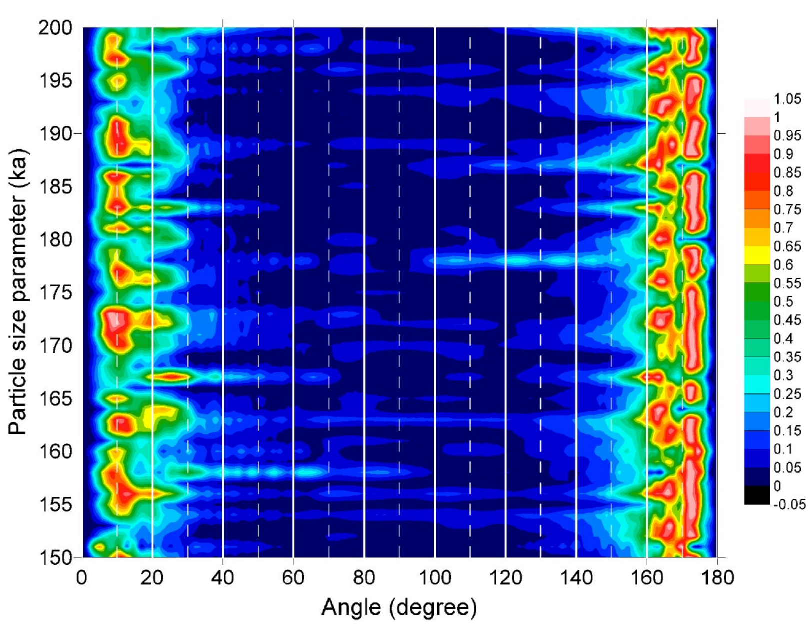

FIG. 5. (Color online) Angular distribution of the SHG intensity for water droplets at large values of particle size parameter $(150.0<ka<200.0)$.

$$\boldsymbol{Y}^{L_1}_{J_1M_1}\times\boldsymbol{Y}^{L_2}_{J_2M_2}=i\sqrt{\frac{3}{2\pi}(2J_1+1)(2J_2+1)(2L_1+1)(2L_2+1)}\times\sum_{JL}\begin{Bmatrix}J_1 & L_1 & 1\\ J_2 & L_2 & 1\\ J & L & 1\end{Bmatrix}C^{L0}_{L_10L_20}C^{LM}_{J_1M_1J_2M_2}\boldsymbol{Y}^{L}_{JM}.$$

The coefficient $C^{(\alpha,\beta)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}$ is expressed as a product of $6j$ $(9j)$ symbols and two Clebsch-Gordan coefficients

$$C^{(1,1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}=\frac{(-1)^{\ell_1+\ell_2+\ell}}{\sqrt{4\pi(2\ell+1)}}\times\Bigg[\sqrt{(\ell_1+1)(2\ell_1-1)(\ell_2+1)(2\ell_2-1)}\times\begin{Bmatrix}\ell_1-1 & \ell_2-1 & \ell\\ \ell_2 & \ell_1 & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1-10\ \ell_2-10}+\sqrt{(\ell_1+1)(2\ell_1-1)(\ell_2)(2\ell_2+1)}\times\begin{Bmatrix}\ell_1-1 & \ell_2+1 & \ell\\ \ell_2 & \ell_1 & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1-10\ \ell_2+10}+\sqrt{(\ell_1)(2\ell_1+1)(\ell_2+1)(2\ell_2-1)}\times\begin{Bmatrix}\ell_1+1 & \ell_2-1 & \ell\\ \ell_2 & \ell_1 & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1+10\ \ell_2-10}+\sqrt{(\ell_1)(2\ell_1+1)(\ell_2)(2\ell_2+1)}\times\begin{Bmatrix}\ell_1+1 & \ell_2+1 & \ell\\ \ell_2 & \ell_1 & 1\end{Bmatrix}\times C^{\ell\,0}_{\ell_1+10\ \ell_2+10}\Bigg]C^{\ell m}_{\ell_1m_1\ell_2m_2},$$

$$C^{(0,0)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}=\frac{(-1)^{\ell_1+\ell_2+\ell}}{\sqrt{4\pi(2\ell+1)}}(2\ell_1+1)(2\ell_2+1)\times\begin{Bmatrix}\ell_1 & \ell_2 & \ell\\ \ell_2 & \ell_1 & 1\end{Bmatrix}C^{\ell0}_{\ell_10\ell_20}C^{\ell m}_{\ell_1m_1\ell_2m_2},$$

$$C^{(-1,-1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}=\sqrt{\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell+1)}}C^{\ell0}_{\ell_10\ell_20}C^{\ell m}_{\ell_1m_1\ell_2m_2},$$

$$C^{(1,-1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}=\sqrt{\frac{3}{2\pi}}\Bigg[\sqrt{(\ell_1+1)(2\ell_1-1)(\ell_2)(2\ell_2-1)}\times\begin{Bmatrix}\ell_1 & \ell_1-1 & 1\\ \ell_2 & \ell_2-1 & 1\\ \ell & \ell & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1-10\ \ell_2-10}+\sqrt{(\ell_1+1)(2\ell_1-1)(\ell_2+1)(2\ell_2+1)}\times\begin{Bmatrix}\ell_1 & \ell_1-1 & 1\\ \ell_2 & \ell_2+1 & 1\\ \ell & \ell & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1-10\ \ell_2+10}+\sqrt{(\ell_1)(2\ell_1+1)(\ell_2)(2\ell_2-1)}\times\begin{Bmatrix}\ell_1 & \ell_1+1 & 1\\ \ell_2 & \ell_2-1 & 1\\ \ell & \ell & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1+10\ \ell_2-10}+\sqrt{(\ell_1)(2\ell_1+1)(\ell_2+1)(2\ell_2+1)}\times\begin{Bmatrix}\ell_1 & \ell_1+1 & 1\\ \ell_2 & \ell_2+1 & 1\\ \ell & \ell & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1+10\ \ell_2+10}\Bigg]C^{\ell m}_{\ell_1m_1\ell_2m_2},$$

$$C^{(0,-1)}_{\ell_1,m_1,\ell_2,m_2,\ell,m}=\sqrt{\frac{3}{2\pi}}(2\ell_1+1)\Bigg[\sqrt{(\ell_2)(2\ell_2-1)}\times\begin{Bmatrix}\ell_1 & \ell_1-1 & 1\\ \ell_2 & \ell_2-1 & 1\\ \ell & \ell & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1 0\ \ell_2-10}+\sqrt{(\ell_2+1)(2\ell_2+1)}\times\begin{Bmatrix}\ell_1 & \ell_1+1 & 1\\ \ell_2 & \ell_2+1 & 1\\ \ell & \ell & 1\end{Bmatrix}C^{\ell\,0}_{\ell_1 0\ \ell_2+10}\Bigg]C^{\ell m}_{\ell_1m_1\ell_2m_2}.$$

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surface charge equals $\sigma=[(\epsilon-1)/(4\pi\epsilon)]E_s^{\perp}$ where E_s is the field on the outer surface of the sphere. Collecting everything together we obtain $P_{2\omega}^{\perp}=[(\epsilon-1)/4\pi\epsilon]^2 E_s^{\perp}E_s^{\perp}$. Making the identification $\perp\equiv z$ in the local coordinate system on the surface of the sphere as further explained in the text we obtain $\chi_{zzz}^{(2\omega)}=[(\epsilon-1)/4\pi\epsilon]^2$ for the approximation of Dewitz and co-workers.

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