Generation, reflection and transmission of nonlinear harmonic waves by direct superposition of anharmonic dipoles

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Abstract
It is well known that the linear and nonlinear light reflection and transmission formula can be obtained from the standard macroscopic Maxwell equation. In the past, a microscopic approach based on the Ewald–Oseen extinction theorem to derive the reflection and transmission formula by direct dipole summation has been performed by Fearn et al where they successfully derived the Fresnel formula in linear optics. In this work, we extend their work for the first time to derive the nonlinear reflection and transmission formula by direct summation of anharmonically oscillating dipoles for the case of a normal incidence wave, yielding similar results with coupled-mode-theory (CMT). We demonstrate for a decaying incoming field that dipolar radiation is no longer forbidden inside the bulk of a centrosymmetric material. Using the simplified bond hyperpolarizability model (SBHM), we find that these additional bulk dipole contribution must be accounted along with the surface dipoles and bulk quadrupolar contribution to explain recent rotational anisotropy SHG intensity experimental data of Si(111) with high precision.

Keywords: nonlinear dipoles, Ewald–Oseen extinction theory, harmonic generation, bulk dipole

1. Introduction
Since the invention of femtosecond lasers, nonlinear optics has become one of the standard tools for material analysis. The numerous nonlinear optical phenomenon have greatly enhanced our knowledge regarding the interaction of light and matter as well as revolutionized our technology in optics [1]. Nonlinear optical laser techniques are attractive because they provide a high temporal, spatial, and spectral resolution, as well as its applicability to all interfaces accessible by light [2].

The standard classical method to obtain expressions of transmission and reflection of the field inside a dielectric material is usually performed by applying the macroscopic Maxwell equation on the boundary between two media where one will then obtain the Fresnel equation [3–5]. From the microscopic classical point of view, the dielectric consists of polarizable atoms or molecules, each of which is radiating in vacuum in response to the incident field and in response to the fields radiated by the other atoms. The induced dipoles in the medium irradiate a field of the same frequency of the impinging field in linear optical regime. The total radiated field in linear optics is then the superposition of the incident field with all radiated fields generating the correct reflected and transmitted field. Mathematically this is expressed as an integral equation for the field either inside or outside the material. The equivalence can be seen e.g. by comparing near field, far field, dispersion relation and Fresnel formulas for stratified layers [4, 6].

Microscopically, nonlinear harmonic generation can be seen as radiation from the charges that experience anharmonic oscillation due to an external driving field. This view is

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actually an extension of the idea in linear optics that an external field impinging on a dielectric material produces dipole oscillations in the material and their superposition constitute a radiating field. Using this approach, Ewald [7] and Oseen [8] were able to demonstrate linear refraction and transmission phenomena inside the dielectric microscopically, yielding an equivalent result if calculated from the solution of the macroscopic Maxwell equation. Although the macroscopic Maxwell equations yield the correct solutions, they do not provide any significant insights in the microscopic behavior of the light–matter interaction.

Fearn et al [6] has shown for the linear case that an incoming plane wave that is entering the material at normal incidence will produce dipole oscillations inside the material that radiate waves at the speed of light, c. The integral equation describing the total field at a depth \( z \) from the surface is obtained by direct integration of dipoles is [6]:

\[
E_T(z) = E_i^{(0)} e^{ik_0 z} + \frac{ik_0}{2} \int_0^\infty \left[ e^{i\omega} - 1 \right] dz' E_i^{(0)} e^{ik_0 |z - z'|}. \tag{1}
\]

In linear optics this is an integral equation, which has to be solved. For the case of nonlinear harmonic generation, however, the mathematical structure of the underlying equation to be derived will be, as seen below, much simpler. This is due to the following facts: (a) There is no incoming nonlinear incident field, all the nonlinear fields are generated by the anharmonic oscillating dipoles driven by the nonlinear polarization inside the material and (b) the amplitude of the nonlinear field is far smaller than the amplitude of the driving one. Strictly speaking, if the nonlinear field amplitude obtains the same size than the driving one, coupled integral equations between the linear and the nonlinear field(s) would result. However, in the low depletion approximation we assume that the amplitude of the fundamental field is space independent, and then, instead of an integral equation, only an integration has to be performed. Surprisingly enough, to the best of our knowledge no one has calculated this nonlinear dipole superposition explicitly using equation (1) even for the normal incidence case. Therefore the aim of this work is to fill this gap and provide a new insight in how to look at the nonlinear reflection and transmission formula from the microscopic viewpoint of Ewald, Oseen, and Fearn et al. Using anharmonic dipole summation, we will demonstrate that the formula for transmission and reflection of SHG can be obtained. We also show how field absorption inside the material can produce additional bulk dipolar SHG radiation in reflection and that it is different than the known quadrupolar effects.

We proceed now in the following way. Taking the approach of Fearn et al [6], we first derive the equation for the nonlinear field. We then derive for a material with coherence length \( L \) and finite thickness \( z \), the superposition of the nonlinear radiation fields in transmission and compare our result for the case of second-harmonic-generation (SHG) with the standard macroscopic approach e.g. coupled-mode-theory (CMT) calculations. The reflection due to integration of all nonlinear dipoles as well as the effect of bulk dipolar contribution due to an incoming field decay inside the material is also calculated and discussed. We apply the simplified bond hyperpolarizability model (SBHM) to show that the experimental rotational anisotropy SHG data of Si(111) for arbitrary output polarization angle in our previous work [9] can be modelled with high precision if the bulk dipole contribution is accounted along with the surface and quadrupolar contribution. Finally we provide a brief summary of our work.

2. Summing over nonlinear dipoles

Here we present a way to obtain an expression for the transmitted and reflected nonlinear field that is produced by superposition of all radiating (anharmonic) dipoles inside the dielectric where only the nonlinear term is treated. Although it will lead to the same classical macroscopic nonlinear transmission and reflection formula, our classical microscopic approach has several advantages: (a) It provides a physical ‘atomistic’ picture from the classical microscopic point of view, in particular how anharmonic dipole radiation sums up to produce these formulas. (b) As has been explained earlier, the linear microscopic calculation of Fearn et al can be extended more easily to nonlinear optics if low depletion is assumed because instead of an integral equation, only an integration has to be performed. (c) We will show later that the calculation can be extended straightforward to account for bulk dipolar contribution due to field absorption rather than using standard macroscopic coupled equation such as in [10].

We follow a similar approach as in [6] but use the nonlinear polarization instead of the linear case. It has to be noted however that one should not expect to obtain the same results as in the linear case because no second harmonic field is incidence on the material and that the nonlinear dipoles are driven by the nonlinear fundamental external field. For simplicity, let us assume the external field is sufficient large to generate SHG inside a dielectric and that it is incoming at normal incidence.

To obtain the nonlinear field we calculate the contribution from all nonlinear dipoles. We start by expressing the electric field produced by a single dipole (Hertz dipole) at \( r' \) inside the dielectric [3]

\[
E_d(r,t) = \left[ 3(\hat{p} \cdot \hat{n}) \hat{n} - \hat{p} \right] \left[ \frac{1}{R^3} p \left( t - \frac{R}{c} \right) + \frac{1}{c R^2} \frac{dp}{dt} \left( t - \frac{R}{c} \right) \right] + \left[ (\hat{p} \cdot \hat{n}) \hat{n} - \hat{p} \right] \frac{1}{c R} \frac{d^2 p}{dt^2} \left( t - \frac{R}{c} \right). \tag{2}
\]

Here \( \hat{p} \) is the unit vector for the dipole polarization, \( R = |r - r'| \), and \( \hat{n} \) is the unit vector directed towards \( r - r' \). Note that as in the linear case, the retarded term \( \left( t - \frac{R}{c} \right) \) describes the time evolution of the dipole field from each atom that is propagating at the speed of light \( c \) in vacuum.

The linear case can be extended to cope with nonlinearity by considering that if the field intensity is sufficiently high, the nonlinear far fields emerges from the anharmonic motion of the charges. As in the linear case a nonlinear polarization results from this process. The nonlinear polarization for
SHG (single frequency input) can be obtained classically by expanding the harmonic oscillator Lorentz model assuming nonlinear restoring forces exerted on the electron [11]

\[ \ddot{r} + 2\gamma \dot{r} + \omega_0^2 r + \beta_2 r^2 + \beta_3 r^3 + \ldots = -\frac{e(E_\omega (r,t) + E_{2\omega} (r,t) + E_{3\omega} (r,t) + \ldots)}{m} \]  

(3)

where \( m, e, r \) are respectively the electron mass, charge, and its displacement from equilibrium, \(-\gamma \dot{r} \) is the damping force and the restoring force \(-\omega_0^2 mr - \beta_2 mr^2 - \beta_3 mr^3 + \ldots \) describes the linear, second, and third order nonlinear effects respectively. Here \( \beta \) is a nonlinear property of a molecule describing the nonlinear response of the material and is called the hyperpolarizability which is in general a tensor. Note that \( \beta \) is aside of the linear part a tensor. Also it has to be stated here that we neglect local field effects which is merely adding a multiplication factor for the field. Because the linear field \( E_\omega \) is far higher than the nonlinear fields we can neglect the higher nonlinear driving fields \( E_{2\omega}, E_{3\omega} \), etc. For simplicity we consider like in the linear case that the driving field comes at normal incidence into the material hence propagating along the \( z \) direction and we consider anharmonic oscillation only along the \( x \)-axis. We assume here that the medium is isotropic so that the nonlinear hyperpolarizability \( \beta \) can be attributed as a scalar quantity. This also requires that the applied fundamental electric fields can only induce a nonlinear polarization components parallel to the field and that the polarization response to the applied electric field in the \( x, y, \) and \( z \) directions are equal.

In this case the electric field is directed along the \( x \) axis only, and therefore triggering dipole oscillation along the same axis and equation (3) becomes:

\[ \ddot{x} + 2\gamma \dot{x} + \omega_0^2 x + \beta_2 x^2 + \beta_3 x^3 + \ldots = -\frac{eE_\omega (x,t)}{m}. \]  

(4)

Because \( E_\omega \) is a physical observable the value must be real. Stated otherwise, \( E_\omega \) can be written in the form of an analytic signal

\[ E_\omega (x,t) = E_0 \cos(kz - \omega t) = \frac{1}{2} [E_\omega (x)] e^{-i\omega t} + c.c. \]  

(5)

where we have used the nomenclature convention in [11].

Equation (4) cannot be solved explicitly for \( x \) but it is standard to seek a solution if the applied field \( E_\omega (x,t) \) is considered small by means of perturbation theory. This can be done by expressing the applied field as \( E_\omega (x,t) = \lambda E_\omega (x,t) \) and writing the displacement in terms of a power series expansion

\[ x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \ldots \]  

(6)

where \( \lambda \) is a perturbative parameter ranging from zero to one. The solution for \( x \) and therefore the linear and nonlinear polarization \( p = ex \) where \( e \) is the electron charge can now be solved approximately and can be found in many standard textbook of nonlinear optics such as [5, 11]. The induced dipole moment that is located at an atom at point \( x', y', \) and \( z' \) inside the dielectric is given by

\[ p = \sum_{n=1} E_\omega (z') e^{-i\omega t} + c.c. \]  

where \( n \) denotes the harmonic order and c.c. is the corresponding complex conjugate which ensures that the polarization has a real value.

We now calculate the total dipole radiation due an incoming field and assume for the sake of simplicity that it is incoming at normal incidence parallel to the optical axis. Omitting the complex conjugate term or negative frequency for the moment in equation (7) and insert it in equation (2) with \( \dot{\bar{r}} = \dot{x} \) and \( \dot{\bar{x}} = (x - x')/R \), then integrating over all volumes and summing over all the terms yields for \( N \) nonlinear dipoles

\[ E_{d(+\omega) (r,t)} = \sum_{n=1} \int \int \int \int \sum_{n=1} N_\beta \left\{ \int \left[ \frac{1}{R} \int (1 - \frac{ik_{2\omega} R}{R}) \left( 3(x - x')^2 - 1 \right) \frac{k_{2\omega}^2}{R^2} \right] \right\} \]  

where the propagation constants \( k_{2\omega} \) are computed for each different harmonic \( 2\omega \). Here we have used the notation \( n \) to describe the higher nonlinear harmonic wave vector. It turns out that in polar coordinates by introducing the coordinate transformation \( x - x' = \rho \cos \varphi \) and \( \rho^2 = R^2 - (z - z')^2 \).

The mathematical methods to perform the integration follows a similar path as in [5] with a generalized wave vector \( k_{2\omega} \) obtained in the solution instead of \( k_0 \)

\[ E_{d(+\omega) (z)} = \sum_{n=1} \int \int \int \sum_{n=1} n\pi ik_{2\omega} N_\beta \int_0^\infty dz' \times [E_\omega (z')]^n e^{-ik_{2\omega} |z - z'|} \]  

(9)

The same method can be repeated for the complex conjugate polarization term in equation (7). One then obtains

\[ E_{d(-\omega) (z)} = \sum_{n=1} \int \int \int \sum_{n=1} N_\beta \int_0^\infty dz' \times [E_\omega (z')]^n e^{-ik_{2\omega} |z - z'|} \]  

(10)

which differs from equation (9) only by its minus sign. The total field is thus the sum of equations (9) and (10)

\[ E_d (z) = E_{d(+\omega) (z)} + E_{d(-\omega) (z)} = \sum_{n=1} n\pi ik_{2\omega} N_\beta \int_0^\infty dz' \times [E_\omega (z')]^n e^{-ik_{2\omega} |z - z'|} + c.c. \]  

(11)

Equation (11) can be used to calculate the transmission and reflection formulas for nonlinear optics. Note that it is real valued and that there is a linear propagation given by \( e^{ik_{2\omega} |z - z'|} \) which is similar to the results obtained from the antenna dipole SHG approach in [10].

3. SHG in transmission

Experimentally, the electric fields in vacuum are measured using the relation \( \bar{P}(2\omega) = \varepsilon_0 \chi^{(3)} \bar{E}(\omega) \bar{E}(\omega) \) where \( \bar{E}(\omega) \) corresponds to the macroscopic electric fields and \( E_{d(2\omega)} (z) \) the
measured second harmonic electric field in vacuum [12]. Therefore, defining the nonlinear susceptibility as the total \((N\) times) dipole moment \(p\) per unit volume we obtain

\[
E_{\omega 2}(z) = \frac{\overline{P}(2\omega)}{\varepsilon_0 (\varepsilon(2\omega) - 1)} = \frac{(N/V)p}{\chi^{(2)}(2\omega)}
\]  

(12)

here \(N\) is the total number of radiating dipoles inside the bulk, \(V\) is volume and \(\chi^{(2)}(2\omega)\) is the linear susceptibility at \(2\omega\). For SHG we simply take equation (12) into consideration and set \(n = 2\) in equation (11) so that

\[
E_{\omega 2}(z) = \frac{2\pi i k_{2\omega} (N/V) \beta_2}{\chi^{(2)}(2\omega)} \int_0^\infty dz' \times \left( \left| E_\omega(z') \right|^2 e^{i k_{2\omega} |z-z'|} + c.c. \right)
\]  

(13)

where \(\beta_2\) is the SH nonlinear hyperpolarizability.

Before we proceed further we stop to state two important assumption which will significantly simplify the calculation. First, because the negative frequency component that resides in the complex conjugate term in equation (12) satisfies

\[
\left| E_\omega(z') \right|^2 e^{-i k_{2\omega} |z-z'|} = \left| E_\omega(z') \right|^2 e^{i k_{2\omega} |z-z'|}
\]  

(14)

we can obtain full equality in all of the following calculation by evaluating either the first or its complex conjugate term. Second, for many cases e.g. studying SHG in centrosymmetric media, the nonlinear field \(E_{2\omega}\) is far smaller than the linear field \(E_\omega\). Therefore, the calculation does not require self consistency and can be performed independently for each nonlinear polarization term. This assumption is similar to the low depletion approximation which allows coupled mode calculations be analyzed independently [10, 11].

Calculation of the nonlinear transmission intensity is usually solved either by coupled mode theory [11] or by means of the dipole antenna method [10] which for second harmonic generation can be written in the form of

\[
I_{2\omega} \sim L^2 \text{sinc}^2(\Delta k L/2)
\]  

(15)

where \(\omega_2\) is the second harmonic frequency, \(L\) is the penetration depth, and \(\Delta k\) is the phase matching condition expressed as \(\Delta k = k_{2\omega} - nk\). As is well understood, if the total penetration depth of the material is smaller than the coherence length \(L_{coh} = \frac{\lambda}{2\pi}\) a nonlinear signal is always enhanced and phase matching is not necessary as is often the case for thin films. However because generally the depth of the sample exceeds \(L_{coh}\) phase matching is important to ensure constructive interference between the radiating nonlinear field and the driving field.

To calculate the nonlinear transmission for SHG we integrate equation (13) over \(z > 0\) by omitting the complex conjugate because of equality and substitute as in the linear case (e.g. see equation (32) in [5]) \(\left| E_\omega(z') \right|^2 = \left| E_\omega e^{ikz'} \right|^2 = E_\omega^2 e^{2ikz'}\) where \(k_{2\omega}\) is the SH propagation vector. The dipole field in transmission is therefore calculated using

\[
E_{\omega 2}(z) = \frac{2\pi i k_{2\omega} (N/V) \beta_2}{\chi^{(2)}(2\omega)} \left[ \int_0^z dz' \left( E_\omega(z')^2 e^{i k_{2\omega} z'} + c.c. \right) + \int_z^\infty dz' \left( E_\omega(z')^2 e^{i k_{2\omega} z'} + c.c. \right) \right].
\]  

(16)

From figure 1 it is clear that for the transmission case only the integral in the first term which describe the dipole contribution from the top has to be considered from the transmission case. Thus \(z\) is chosen to be the total penetration depth of the material because only over this depth a nonlinear signal is driven. Therefore we need only to integrate over \((z-z')\) from \(0\) to \(L\)

\[
E_{\omega 2}(z) = \frac{2\pi i k_{2\omega} (N/V) \beta_2}{\chi^{(2)}(2\omega)} \left[ \int_0^z dz' \left( E_\omega(z')^2 e^{i k_{2\omega} z'} + c.c. \right) \right] + \int_z^\infty dz' \left( E_\omega(z')^2 e^{i k_{2\omega} z'} + c.c. \right).
\]  

(17)

The part in the parenthesis denotes the evolution of the wave envelope whereas the remaining describe the phase propagation of the harmonic wave. Note that \(\beta_2\) is the nonlinear SHG hyperpolarizability. Furthermore it has been shown in [6] that

\[
E(\omega) = F(\omega) E_0
\]  

(18)

here \(F(\omega) = \frac{1}{\pi(\omega)^{1/2}(\omega)}\) is the linear Fresnel transmission coefficient (which we state for the sake of clarity is dimensionless) for a normal incoming wave \(E_0\). With regard to equations (16)–(18) can be written in the form of

\[
E_{\omega 2}(z) = \frac{(F(\omega) E_0)^2}{\chi^{(2)}(2\omega)} 2\pi i k_{2\omega} (N/V) \beta_2 \left[ \frac{e^{i k_{2\omega} z'} - 1}{i k_{2\omega}} \right] e^{i k_{2\omega} z'}. \]  

(19)
be small or in other words the phase matching condition is necessary. To check the validity of equation (19) we perform dimensional analysis. As stated before, the nonlinear hyperpolarizability corresponding to SHG, $\beta_2$ is the nonliner susceptibility times volume and has a unit of (m$^4$ V$^{-1}$), $V$ has a unit of m$^3$, $N$ and $\chi^{(1)}(2\omega)$ are both dimensionless, and the unit of $k$ and $\Delta k$ is (1 m$^{-1}$) so that both the left and right side show dimensional consistency (e.g. V m$^{-1}$). The SHG intensity $I_{2\omega}$ is simply obtained by squaring the field envelope equation (20) and using the identity [11]

$$|e^{i(\Delta k - 1)}|^2 = L^2 \left( \frac{e^{i(\Delta k - 1)}}{i\Delta k} \right) \left( \frac{e^{i(\Delta k - 1)}}{i\Delta k} \right) = L^2 \sin^2(\Delta k L/2) \frac{(\Delta k L/2)}{(\Delta k L/2)}$$

(20)

yielding

$$I_{2\omega} = \frac{(F(\omega)E_0)^4}{(\chi^{(1)}(2\omega))^2} 4\pi^2 k^2_e (N/V)^2 \beta_2^2 L^2 \sin^2(\Delta k L/2)$$

$$\sim L^2 \sin^2(\Delta k L/2)$$.

Equation (21) is the celebrated SHG intensity formula obtained from coupled mode theory (equation (14)) which we have derived from the first time using the Ewald–Oseen anharmonic dipole summation approach.

4. SHG in reflection

We now move on to describe SHG generated inside the bulk of a nonlinear medium where the SHG far field is measured in reflection. Figure 2 gives an illustration to present this effect more clearly for an incoming wave at normal incidence. The expression for reflection can be analyzed in a similar manner with $z < 0$ or taking the second integration in equation (15) and evaluate from 0 to infinity for $n = 2$

$$E_d(z)_{2\omega} = 2\pi i k_{2\omega}(N/V)\beta_2 \frac{F(\omega)^2 F(2\omega)E_0^2}{\chi^{(1)}(2\omega)}$$

$$\int_0^\infty dz' \times (E_2(z')^* e^{ik_{2\omega}z'} e^{ik_{2\omega}(z'-z)}$$

$$= -2\pi (N/V)\beta_2 F(\omega)^2 F(2\omega)E_0^2 \frac{(2k + k_{2\omega})}{2k + k_{2\omega}} e^{-ik_{2\omega}z}$$

(22)

Equation (22) is dimensionally consistent with the minus sign denoting a reflected SHG field. Here we have to be more cautious because now the Fresnel coefficients in reflection not only contain the square of the transmitted coefficient $F(\omega)$ but also the coefficient due to second harmonic upward propagating wave [12–14], $F(2\omega)$. Thus as in the linear case the reflection depends on $k_w$ and $k_{2\omega}$. For a centrosymmetric material e.g. materials with inversion symmetry or $V(x,y,z) = V(-x,-y,-z)$ the value of $\beta_n = 0$ for all $n$ that are even numbers, hence no higher harmonic generation occurs both in transmission and in reflection for SHG, FHG, etc. Therefore the main contribution for even higher harmonic generation in centrosymmetric material must come from symmetry breaking/anisotropy in the surface where $\beta_2 \neq 0$ or from higher order monopole contribution in the bulk.

However, to the best of our knowledge the contribution of bulk dipolar contribution (field gradient) due to field absorption inside the material bulk is seldom discussed and can be explained by direct dipole summation. Indeed it has been shown recently using the nonlinear bond model that both bulk dipole from the surface and quadrupole contribution from the bulk alone cannot explain perfectly the six-fold SHG intensity pattern in reflection [9, 15, 16]. We will show in the following discussion that SHG bulk dipolar contribution contribution can indeed be explained in principle as originating from an uncancelling dipole contribution inside the bulk. To illustrate the example more explicitly we consider the case where the fundamental field penetrates through the bulk of a nonlinear material as given by figure 2. If the material is not fully transparent, the field inside the bulk will decay with a complex wave vector $k = \omega n/c$ therefore the dipoles located at different height within the optical penetration depth along the vertical $z$-axis will experience a different incoming driving field strength producing a net SHG contribution even if the material is inversion symmetric. The SHG field propagates with a dispersion relation given by the linear optic relation of $2\omega$

$$\varepsilon(2\omega) \cdot (2\omega)^2 = c^2 (2\omega)^2$$.

(23)

To model this decay we define an absorption coefficient $\alpha_{2\omega}$, given by $\frac{\partial \varepsilon(2\omega)}{\partial \omega} = i\alpha_{2\omega}$, where $\lambda_0$ is the vacuum wavelength, and $\kappa_i$ is the imaginary part of the refractive index. The $2\omega$ wave that propagates upward also experience absorption by $\alpha_{2\omega}/2$. The second harmonic polarization is proportional to the the square of the fundamental field, therefore the linear absorption factor must be squared whereas the SHG absorption is not squared. Thus if we assume an exponential decaying field along the $z$ direction the response of the dipoles along the $z$ direction does not fully cancel each other out because each dipole in different height experience a different field. Mathematically this phenomena can be stated more explicitly as (taking the real field)

$$E(2\omega) = -2\pi k_{2\omega}(N/V)\beta_2 F(\omega)^2 F(2\omega)E_0^2$$

$$\chi^{(1)}(2\omega)$$

$$\int_0^\infty dz (\cos (k_w z) e^{-i\kappa_{2\omega} z})^2 \cos (k_{2\omega} z) e^{-i\kappa_{2\omega} z}$$

(24)

where we have use the real expression for the field. Performing the integration we obtain

$$E(2\omega) = -2\pi k_{2\omega}(N/V)\beta_2 F(\omega)^2 F(2\omega)E_0^2$$

$$\chi^{(1)}(2\omega)$$

$$\kappa_{SHG} \frac{2}{4\kappa_{SHG}^2 + 4(k_{2\omega} - 2k_w)^2 + \frac{1}{4}(4(k_{2\omega} + 2k_w)^2 + \kappa_{SHG}^2)}$$

(25)

here we have use $\kappa_{SHG} = 2\kappa_{2\omega} + 2\kappa_{2\omega}$. As before, we perform dimensional analysis on equation (25). We recall that $\beta_2$
Figure 2. Bulk dipolar contribution due to absorption of the incoming fundamental field along the optical axis (z-axis). The field gradient along this axis will cause anharmonic dipoles at different atomic layer height as seen in the figure insert (Si(111) as example) experiencing a different field strength producing a nonlinear contribution in addition to the surface dipole and bulk quadrupole contribution in inversion symmetric materials.

has a unit of m⁴ V⁻¹, V has a unit of m³, N and $\chi^{(1)}_r$ are both dimensionless, and both the unit of $\kappa_{\text{SHG}}$ and $k$ is m⁻¹ yielding right hand-left hand side dimensional consistency and corresponding to a second harmonic field magnitude estimate of 1 V m⁻¹ which is a reasonable number. Evaluating the terms and assuming phase matching condition we found that the only term that is significant compared to the other is

$$E(2\omega) = -2\pi k_{2\omega}(N/V)\beta_2 \frac{F(\omega)^2 F(2\omega)E_0^2}{\chi^{(1)}_r(2\omega)} \beta_2 \times \left( \frac{\kappa_{\text{SHG}}}{2} \frac{1}{4(k_{2\omega} - 2k_\omega)^2 + \kappa_{\text{SHG}}^2} \right). \quad (26)$$

Comparing with equation (22), we now get an additional absorption term $\kappa_{\text{SHG}}$ in the denominator.

Figure 3 depicts the SHG reflection intensity as a function of the absorption coefficient. It can be seen that if the nonlinear absorption coefficient is very small the SHG intensity from bulk dipolar contribution is low. This corresponds to a material that is very transparent so the energy conversion into nonlinear intensity is small hence a low signal is obtained in reflection. Contrary, for a very large absorption the intensity is also decreasing. This effect is related to a very small light penetration into the bulk thus only a few dipoles inside of the material can radiate SHG.

We will now show using the simplified bond hyperpolarizability model (SBHM) that bulk dipolar contribution is important to produce a perfect fit of the rotational anisotropy (RA) SHG experimental data of Si(111) in our previous work [9]. SBHM was first introduced by Aspnes et al [17] to explain RASHG data from vicinal silicon and a full description about the fundamentals and implementation of the model can be found in our earlier work [9, 15, 18]. To ensure that the bulk dipolar contribution is not merely a redefinition of the quadrupolar effect we also include the calculation of the quadrupolar contribution and compare it with the former. We also plot the result for four different RASHG ingoing fundamental and outgoing SH polarization to ensure that the intensity fit is indeed unique. Figure 4 shows the comparison of the experimental work in figure 3(d) of [9]. The RASHG experiment was conducted at a fundamental wavelength of 890 nm for four different polarization states: p-fundamental ingoing and p-SH outgoing denoted as pp (blue), p60° (green), p30° (red) and pS (black). The formulas and parameters to fit the experimental data can be found in equations (1) and (2) of [9]. It can be seen in figure 4(a) that all four polarization RASHG intensity experimental data (dashed lines) for Si(111) cannot be perfectly fitted simultaneously using the surface dipoles and
quadrupole SH contribution alone even if we vary the phase difference e.g., introducing an imaginary parameter for the surface and quadrupolar hyperpolarizability fit (e.g., figure 4 of [9]). The discrepancy in the smaller SH peak in figure 4(a) can be seen for the \( pp \) (blue), 60° (green), and 30° (red) where earlier fit without assuming bulk dipolar contribution results in an overestimation of the smaller peak by a factor of roughly two times.

The inclusion of bulk dipolar contribution into the SBHM is straightforward because it mimics the formula used in modelling the surface dipole (interface) contribution but now using equation (26) in this work into the dipolar formula in equation (1) of [9] for the bulk dipolar field. Therefore in the modified SBHM we have to take into account the bulk Fresnel factors for arbitrary polarization similar to [12]. Second, we have to assign a different angle of incidence (AOI) and angle of exit (AOE) for the propagating fundamental (890 nm) and SH (445 nm) wave inside bulk due to Snell’s law and assign different refractive indices for the fundamental and SH wave. To obtain the AOI and AOE as well as the absorption coefficient (\( \alpha \)) we apply the data in table II of Aspnes and Studna [19] whereas the parameters for the nonlinear hyperpolarizabilities are obtained from [9, 16].

The absorption coefficient is important to ensure that the wave is penetrating significantly inside the bulk before being fully absorbed so that many bulk dipoles can experience the field gradient and produce SH radiation that can compete with surface dipole SH sources. For our case the penetration depth is in the order of around hundreds of nanometers which is enough to generate significant bulk SH effects. The AOI and AOE for the surface dipolar sources in our simulation is 45° whereas the AOI for the bulk dipoles at a fundamental wavelength of 890 nm is 11.3° and the AOE for the SH wavelength of 445 nm is 8.5°. Applying surface dipolar, bulk quadrupole, and bulk dipolar sources at once we now obtain a perfect SH intensity fit for all four polarization as depicted in figures 4(b)–(e) without having to adjust any phase difference between surface and bulk sources (e.g., all the sources are radiating coherently). Furthermore, the contribution from bulk dipolar sources is clearly different than the quadrupolar contribution and is considerably larger compared to the two other sources which have roughly equal contribution.

5. Summary

We have derived the nonlinear transmission and reflection formula for the case of SHG by performing a direct superposition of anharmonic dipoles yielding similar results as obtained by the macroscopic approach e.g., coupled mode theory. Dimensional analysis yields consistency for all the obtained expressions. We also provide a description how a field gradient or bulk dipolar contribution due to a decaying incoming field can produce a net SHG contribution from within the material bulk. This effect accounts for the net radiation coming from all the anharmonic bulk dipoles at different height driven by the decaying field along the \( z \)-axis. The SHG intensity in reflection due to bulk dipolar contribution will decay quadratically if the absorption coefficient is increased and vanishes for fully transparent material. Nonlinear bond model simulation show that the bulk dipolar contribution can be distinguished from the quadrupolar contribution and that it is significant in reproducing the RASHG experiment with better precision.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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