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Application of the anisotropic bond model to second-harmonic generation from amorphous media

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As a step toward analyzing second-harmonic generation (SHG) from crystalline Si nanospheres in glass, we develop an anisotropic bond model (ABM) that expresses SHG in terms of physically meaningful parameters and provide a detailed understanding of the basic physics of SHG on the atomic scale. Nonlinear-optical (NLO) responses are calculated classically via the four fundamental steps of optics: evaluate the local field at a given bond site, solve the force equation for the acceleration of the charge, calculate the resulting radiation, then superpose the radiation from all charges. Because the emerging NLO signals are orders of magnitude weaker and occur at wavelengths different from that of the pump beam, these steps are independent. Paradoxically, the treatment of NLO is therefore simpler than that of linear optics (LO), where these calculations must be done self-consistently. The ABM goes beyond previous bond models by including the complete set of underlying contributions: retardation (RD), spatial-dispersion (SD), and magnetic (MG) effects, in addition to the anharmonic restoring force acting on the bond charge. Transverse as well as longitudinal motion is also considered. We apply the ABM to obtain analytic expressions for SHG from amorphous materials under Gaussian-beam excitation. These materials represent an interesting test case not only because they are ubiquitous but also because the anharmonic-force contribution that dominates the SHG response of crystalline materials and ordered interfaces vanishes by symmetry. The remaining contributions, and hence the SHG signals, are entirely functions of the LO response and beam geometry, so the only new information available is the anisotropy of the LO response at the bond level. The RD, SD, and MG contributions are all of the same order of magnitude, so none can be ignored. Diffraction is important in determining not only the pattern of the emerging beam but also the phases and amplitudes of the different terms. The plane-wave expansion that gives rise to electric quadrupole magnetic dipole effects in LO appears here as retardation. Using the paraxial-ray approximation, we reduce the results to the isotropic case in two limits, that where the linear restoring force dominates (glasses) and that where it is absent (metals). Both forward- and backscattering geometries are discussed. Estimated signal strengths and conversion efficiencies for fused silica appear to be in general agreement with data where available. Predictions that allow additional critical tests of these results are made.

I. INTRODUCTION

Second-harmonic generation (SHG) is becoming an increasingly important diagnostic tool for a wide range of applications. It is a particularly important probe for studying planar interfaces between centrosymmetric crystals and overlayers with randomly directed bonds because it is dipole allowed only at interfaces where the bonds are simultaneously asymmetric and well ordered.

Recently, Figliozzi *et al.*[1] found that SHG signals generated in transmission from crystalline Si nanospheres (nSi) dispersed in glass were enhanced significantly when driven by two beams with crossed polarizations. Enhancement of any nonlinear-optical (NLO) signal is automatically of interest because, in principle, NLO signals contain significantly more information about material systems than the linear-optical (LO) response; yet, they are intrinsically much weaker. SHG from the dispersed-nSi configuration was recently analyzed from the macroscopic perspective by Brudny *et al.*[2] and Mochán *et al.*,[3] in the former case for a single isolated nanosphere and the latter for arrays of nanospheres. These authors used the "dipolium" approximation,[4] where the inclusions and host are described macroscopically by linear, isotropic dielectric functions. The far-field SHG response was obtained by calculating the effective dipole of the inclusions as a spherical-harmonic expansion of the internal and external fields of a given nanosphere, and then applying standard radiation equations. Various observations were explained, for example, the $(\vec{E}\cdot\nabla)\vec{E}$ symmetry of the SHG intensity, its dependence on sphere size, the importance of screening in determining the contributions from the interiors of the nanospheres, the emission of SHG radiation in a cone for disordered dispersions of nanospheres, and the relatively small intensity of the SHG signal from glass.

While macroscopic treatments efficiently distinguish between allowed and forbidden contributions, they are unable to relate allowed responses to atomic-scale parameters or to provide the same level of understanding of the different contributing processes. In particular, the following questions still need to be answered: (1) How does the SHG intensity from the nSi inclusions compare to that from planar Si-SiO$_2$ interfaces? (2) What are the relevant parameters? (3) What is the maximum intensity that can be obtained? (4) Is this maximum signal useful or simply given by a combination of already known parameters? While much larger SHG signals might be expected from dispersions of nSi inclusions in a transmission configuration simply because the interface area greatly exceeds that of a planar interface, the larger area is offset by the fact that the first-order anharmonic SHG signals from the opposite sides of the nanospheres cancel. Therefore,

the signal is proportional to the gradient of the driving field instead of the field itself.[2] In addition, contributions are limited in depth to the coherence length in the material. Finally, there is the question of whether the enhanced SHG signals observed with dual-beam excitation provide useful information. The atomic-scale modeling done below shows that the contributions of the three underlying mechanisms, retardation (RD), spatial dispersion (SD), and magnetic (MG) can all be predicted from the LO response and beam characteristics, and hence do not necessarily provide new information even though improved geometries may generate large signals.

In addressing these issues, we found it necessary to extend our previous simplified bond-hyperpolarizability model (SBHM), which expands on the even simpler isotropic force model discussed, for example, by Shen.[5] In the SBHM, SHG is expressed as radiation arising from the anharmonic motion of charge localized in bonds assuming that the only motion relevant to SHG is that along the bond direction itself. The SBHM successfully describes, with many fewer parameters than previously required, a wide range of NLO phenomena including SHG (Ref. [6]) and fourth-harmonic generation[7] (FHG) from Si-insulator interfaces, dipole-forbidden SHG (Ref. [8]) and third-harmonic generation[9] (THG) from centrosymmetric materials, and the generation of terahertz radiation from III-V semiconductor surfaces.[10] In addition, the parameters are physically meaningful, and by incorporating crystal symmetry at the atomic level, macroscopic tensor properties are obtained automatically. However, as recently, and correctly, noted by McGilp,[11] the SBHM has limitations regarding quantitative interpretation. Given the simplicity of the approach, this is not surprising, but it needs to be explored further. This is a second objective of this work.

Accordingly, in this paper, we generalize the SBHM to a more complete description, the anisotropic bond model (ABM), which includes charge motion transverse to the bond, RD, SD, and MG effects, including SD effects arising from beam geometry, and SHG signals for off-axis observation angles, i.e., the role of diffraction. In developing our expressions, we follow the approach of Peng *et al.*,[8] framing the calculations in terms of the fundamental four-step process of optics: (1) evaluate the local field at any given charge site that results from the driving (source) field, (2) solve the mechanical equation $\vec{F}=m\vec{a}$ to obtain the acceleration of the charge, (3) calculate the radiation that results from the acceleration, and (4) superpose the radiation from all contributing charges. For random media, we show that step (4) factors into two parts: (4a) average over all possible bond orientations at a single site, and then (4b) calculate the properties of the emerging beam by Fourier transforming the envelope function of the incident radiation. Although not required here, if appreciable energy were transferred from the driving to the generated beams, then it would be necessary to (5) evaluate the energy extracted from the pump beam as a function of position, with the subsequent correction of the local fields evaluated in step (1). We find that for random materials, the RD, SD, and MG contributions are all of the same order of magnitude and must all be considered. Finally, all aspects, including off-axis observation and diffraction, combine to yield a much richer SHG response than previously assumed.

Aside from including bond anisotropy and additional mechanisms, the approach is essentially the NLO equivalent of that which Ewald[12] and Oseen[13] used nearly a century ago to derive the Ewald-Oseen theorem of LO. Paradoxically, from this perspective, NLO is simpler than LO. In LO, the radiated fields have the same wavelength as the driving field and similar intensities, so steps (1), (3), and (4) must be evaluated self-consistently. In contrast, for NLO, the radiated fields are typically orders of magnitude weaker than the driving field and occur at different wavelengths, so all steps are effectively independent. This allows NLO calculations to be done sequentially to levels of approximation that are also independent and may be adjusted to meet particular requirements. This is one of the few cases where a nonlinear problem is simpler than its linear equivalent.

Advantages of an atomic-scale formulation include a better understanding of the physics involved. In this classical model, NLO is a result of distortions of the nominally sinusoidal wave form of the emitted radiation reaching the observer. The obvious contributing factor is anharmonic motion of a charge. This can be due to an anharmonic restoring force (intrinsic anharmonicity), spatial nonuniformity of the driving field (spatial dispersion), or the magnetic field associated with the driving wave. With respect to acceleration, there can clearly be no distinction between anharmonic motion resulting from an anharmonic restoring force, a field that is slightly larger at one limit of the excursion than the other, or a force that is velocity dependent. All these effects enter in step (2). However, another source of distortion is the finite speed of light. This causes the signal reaching the observer from the far limit of the excursion to be delayed slightly relative to that from the near limit, resulting in a waveform distortion equivalent to phase or frequency modulation. The retardation contribution enters in step (3). Retardation involves the same first-order expansion of a plane-wave factor that leads to the electric quadrupole (EQ) magnetic dipole (MD) contribution of LO, but the physics is quite different. This mathematical similarity has led to confusion in the past, and we clarify the distinction below.

Taking into account the complete set of mechanisms contributing to SHG became a larger project than expected, so in this paper, we restrict applications to single-beam excitation of disordered materials and reduction of the resulting expressions to the case where the bond charges are isotropically polarizable in LO. We discuss two limits: first, where the restoring force dominates the acceleration term (glasses) and, second, where the restoring force is absent (metals). This reduction, done in the paraxial-ray approximation, highlights the roles of the different underlying mechanisms, the difference between forward- and backscattering configurations, and allows a simple expression for signal strength and conversion efficiency to be obtained. This work represents a necessary first step toward our goal of understanding, at the atomic level, SHG from Si nanoinclusions in glass under crossed-beam excitation and is further justified by the fact that disordered materials are ubiquitous in many fields.

II. AMORPHOUS MATERIALS

A. Fields at bond sites

In this section, we consider step (1), define basic quantities, and discuss the connection between first- and second-harmonic fields. We suppose that the relevant quantities are electrons of charge $q = -e$ located in bonds j at positions $\vec{r}_q = \vec{r}_j + \Delta\vec{r}_j$, where the $\vec{r}_j$ are the equilibrium positions of the charges relative to the origin of a coordinate system defined in the laboratory and the $\Delta\vec{r}_j$ are the displacements that result from the time-dependent forces acting on them. We represent the directions of the bonds by $\hat{b}_j$, where for Si-O bonds, the $\hat{b}_j$ point from Si to O.

For amorphous materials that are homogeneous on meso- and macroscopic length scales, the driving field can be assumed to be approximately a plane wave with frequency ω, envelope function $\vec{E}_o(\vec{r}_q)$, and wave vector $\vec{k}_o = (\omega n_1/c)\hat{k}_o$, where n_1 is the refractive index of the material at ω. We assume that the Fresnel reflectance coefficients have been appropriately taken into account at the surface of the material to yield the correct amplitude E_o of $\vec{E}_o(\vec{r}_q)$ within the medium. Then, the field at the jth charge can be written to first order in $\Delta\vec{r}_j$ as

$$
\begin{aligned}
\vec{E}(\vec{r}_q, t) &= \vec{E}_o(\vec{r}_q)e^{i\vec{k}_o \cdot \vec{r}_q - i\omega t} = \vec{E}_o(\vec{r}_j + \Delta\vec{r}_j)e^{i\vec{k}_o \cdot (\vec{r}_j + \Delta\vec{r}_j) - i\omega t} \\
&\approx [1 + \Delta\vec{r}_j \cdot \nabla_{\vec{r}_j}]\vec{E}_o(\vec{r}_j)e^{i\vec{k}_o \cdot \vec{r}_j - i\omega t} \\
&= [1 + \Delta\vec{r}_j \cdot \nabla_{\vec{r}_j}]\vec{E}_j e^{-i\omega t}.
\end{aligned}
\tag{1}
$$

For clarity in the following equations, we let $\vec{E}_j = \vec{E}_o(\vec{r}_j)e^{i\vec{k}_o \cdot \vec{r}_j}$ contain the spatial dependences of the envelope and phase. The SHG nature of the correction term follows because $\Delta\vec{r}_j$ is also proportional to $\vec{E}_j$, as shown below, so the gradient term nominally has a time dependence $e^{-i2\omega t}$.

However, the coefficient of an $e^{-i2\omega t}$ term is not simply the product of the coefficients of the parent $e^{-i\omega t}$ terms but must be reduced by a factor of 2 for the following reason. Observables are real quantities, so $e^{-i\omega t} = [\cos(\omega t) - i\sin(\omega t)]$ is actually shorthand for $\mathrm{Re}(e^{-i\omega t}) = \cos(\omega t)$. Thus, the product of two $e^{-i\omega t}$ terms is really a product $\cos^2(\omega t)$, $\sin(\omega t)\cos(\omega t)$, or $\sin^2(\omega t)$, or some combination depending on the phases of the parent coefficients. All trigonometric identities taking ωt products into $2\omega t$ forms involve a factor of $1/2$. We introduce this factor in the far-field radiation expression Eq. (26). We retain the $e^{-i2\omega t}$ notation so average intensities can be calculated in the usual way.

B. Force equation

The general form of the force equation for SHG is

$$
\begin{aligned}
\vec{F} &= m\vec{a} = m\frac{d^2\Delta\vec{r}(t)}{dt^2} \\
&= q\vec{E}(\vec{r}, t) + q\frac{\vec{v}}{c} \times \vec{B}(\vec{r}, t) - \tilde{\kappa}_1 \cdot \Delta\vec{r}(t) - \tilde{\kappa}_2 \cdot \cdot \Delta\vec{r}(t)\Delta\vec{r}(t),
\end{aligned}
\tag{2}
$$

where m is the mass of q and $\tilde{\kappa}_1$ and $\tilde{\kappa}_2$ are second- and

third-rank tensors describing the linear (Hooke's law) and first-order anharmonic restoring forces, respectively, $\vec{v} = d\Delta\vec{r}/dt$, and the magnetic-flux density $\vec{B}(\vec{r}_q, t)$ associated with the driving field is $\vec{B}(\vec{r}_q, t) = -(ic/\omega)\nabla_{\vec{r}_q} \times \vec{E}(\vec{r}_q, t)$. In contrast to the SBHM, we do not assume the force equation to be one dimensional. To find the displacements $\Delta\vec{r}_j$, we substitute Eq. (1) into the force equation to obtain

$$
\begin{aligned}
m\frac{d^2\Delta\vec{r}_j(t)}{dt^2} &= q[1 + \Delta\vec{r}_j(t) \cdot \nabla_{\vec{r}_j}]\vec{E}_j e^{-i\omega t} + \frac{q}{c}\frac{d\Delta\vec{r}_j(t)}{dt} \times \vec{B}_j e^{-i\omega t} \\
&\quad - \tilde{\kappa}_1 \cdot \Delta\vec{r}_j(t) - \tilde{\kappa}_2 \cdot \cdot \Delta\vec{r}_j(t)\Delta\vec{r}_j(t),
\end{aligned}
\tag{3}
$$

where $\vec{B}_j = (-ic/\omega)\nabla_{\vec{r}_j} \times \vec{E}_{\vec{r}_j}$. From the form of $\vec{E}(\vec{r}_q, t)$, we can assume that

$$
\Delta\vec{r}_j(t) = \Delta\vec{r}_{1j}e^{-i\omega t} + \Delta\vec{r}_{2j}e^{-i2\omega t},
\tag{4}
$$

where $\Delta\vec{r}_{1j}$ and $\Delta\vec{r}_{2j}$ are time independent. Substituting this expression in Eq. (3) yields

$$
\begin{aligned}
&-m\omega^2\Delta\vec{r}_{1j}e^{-i\omega t} - 4m\omega^2\Delta\vec{r}_{2j}e^{-i2\omega t} \\
&= q[1 + (\Delta\vec{r}_{1j}e^{-i\omega t}) \cdot \nabla_{\vec{r}_j}]\vec{E}_j e^{-i\omega t} - q(\Delta\vec{r}_{1j}e^{-i\omega t}) \\
&\quad \times (\nabla_{\vec{r}_j} \times \vec{E}_j e^{-i\omega t}) - \tilde{\kappa}_1 \cdot (\Delta\vec{r}_{1j}e^{-i\omega t} + \Delta\vec{r}_{2j}e^{-i2\omega t}) \\
&\quad - \tilde{\kappa}_2 \cdot \cdot \Delta\vec{r}_{1j}\Delta\vec{r}_{1j}e^{-i2\omega t}.
\end{aligned}
\tag{5}
$$

Since $\Delta\vec{r}_j$ is at least first order in $\vec{E}$, the magnetic term is at least second order in $\vec{E}$. Since we are only concerned with SHG, we neglect terms of orders 3ω and 4ω, which would contribute to THG[9] and FHG,[7] respectively.

By isolating the first-harmonic terms, we have

$$
-m\omega^2\Delta\vec{r}_{1j} = q\vec{E}_j - \tilde{\kappa}_1 \cdot \Delta\vec{r}_{1j}.
\tag{6}
$$

While this can be solved, in general, by matrix methods, we now introduce the approximation that $\tilde{\kappa}_1$ and $\tilde{\kappa}_2$ are diagonal in the local coordinate system of the bond, where the z axis is defined by the unit vector $\hat{b}$ parallel to the bond. Diagonalization is equivalent to assuming that the bonds are rotationally symmetric. While bonds in some systems are not rotationally symmetric, we make this simplifying assumption to elucidate the underlying physics. Obviously, if desired, all tensor components of the restoring forces could be kept.

We also define the unit vector $\hat{t}$, which is perpendicular to $\hat{b}$ and lies in the $\hat{b}$-$\vec{E}$ plane. Thus, $\hat{t}$ is given by

$$
\hat{t} = [\vec{E} - \hat{b}(\hat{b} \cdot \vec{E})]/\sqrt{\vec{E}^2 - (\hat{b} \cdot \vec{E})^2}.
\tag{7}
$$

Then, $\tilde{\kappa}_1$ and $\tilde{\kappa}_2$ can be written as

$$
\tilde{\kappa}_1 = \hat{b}\hat{b}\kappa_{1l} + \hat{t}\hat{t}\kappa_{1t},
\tag{8}
$$

$$
\tilde{\kappa}_2 = \hat{b}\hat{b}\hat{b}\kappa_{2l},
\tag{9}
$$

where κ_{1l} and κ_{2l} are the longitudinal linear and anharmonic restoring-force coefficients, respectively, and κ_{1t} is that for transverse displacements. With the assumption of rotational symmetry, κ_{2t} does not exist. However, transverse contributions are still possible through the RD, SD, and MG terms.

Substituting these expressions into Eq. (5) and taking dot products with $\hat{b}$ and $\hat{t}$ leads to the two first-order equations

$$\Delta \vec{r}_{1jl} = \Delta r_{1jl} \hat{b}_j = \frac{q(\hat{b}_j \cdot \vec{E}_j)}{\kappa_{1l} - m\omega^2} \hat{b}_j, \qquad (10)$$

$$\Delta \vec{r}_{1jt} = \Delta r_{1jt} \hat{t}_j = \frac{q(\hat{t}_j \cdot \vec{E}_j)}{\kappa_{1t} - m\omega^2} \hat{t}_j. \qquad (11)$$

Repeating the process for the second-order terms leads to

$$\Delta \vec{r}_{2jl} = \Delta r_{2jl} \hat{b}_j$$
$$= \{q(\Delta \vec{r}_{1j} \cdot \nabla_{\vec{r}_j})(\hat{b}_j \cdot \vec{E}_j) - q[\Delta \vec{r}_{1j} \times (\nabla_{\vec{r}_j} \times \vec{E}_j)]$$
$$\cdot \hat{b}_j - \kappa_{2l} \Delta r_{1jl} \Delta r_{1jl}\} \hat{b}_j / (\kappa_{1l} - 4m\omega^2), \qquad (12)$$

$$\Delta \vec{r}_{2jt} = \Delta r_{2jt} \hat{t}_j = \{q(\Delta \vec{r}_{1j} \cdot \nabla_{\vec{r}_j})(\hat{t}_j \cdot \vec{E}_j)$$
$$- q[\Delta \vec{r}_{1j} \times (\nabla_{\vec{r}_j} \times \vec{E}_j)] \cdot \hat{t}_j\} \hat{t}_j / (\kappa_{1t} - 4m\omega^2), \quad (13)$$

$$\Delta \vec{r}_{2j(b \times t)} = \Delta r_{2j(b \times t)}(\hat{b}_j \times \hat{t}_j) - q\{[\Delta \vec{r}_{1j} \times (\nabla_{\vec{r}_j} \times \vec{E}_j)]$$
$$\cdot (\hat{b}_j \times \hat{t}_j)\}(\hat{b}_j \times \hat{t}_j) / (\kappa_{1t} - 4m\omega^2). \qquad (14)$$

Equation (14) is necessary because the magnetic force generates a component that is perpendicular to both $\hat{b}$ and $\hat{t}$. Equation (12) shows that there is no qualitative distinction between the intrinsic anharmonicity of a bond and an anharmonicity generated by a field, as expected. These are the expressions from which the acceleration, and therefore the far-field signal, will be calculated.

C. Far-field radiation from accelerated charges

We now consider step (3). We follow the development of Peng *et al.*[8] but take into account explicitly the reduction in propagation speed caused by refractive indices n_ν that are different from 1. The two that need to be considered are $n(\omega) = \sqrt{\epsilon(\omega)} = n_1$ for the incoming wave and $n(2\omega) = \sqrt{\epsilon(2\omega)} = n_2$ for the emitted SHG radiation. Accordingly, we write $\vec{k}_o = k_o \hat{k}_o = (\omega n_1/c)\hat{k}_o$ and $\vec{k} = k\hat{k} = (2\omega n_2/c)\hat{k}$ for the incident and emerging radiations, respectively, where $\hat{k}$ points in the direction of the observer.

The general expression for the 4-potential of an accelerated point charge in the medium in Fourier-component form is

$$[\phi(\vec{r},t), \vec{A}(\vec{r},t)]_\nu = \frac{1}{c} \int d^3r' dt'$$
$$\times [c\rho(\vec{r}',t'), \vec{J}(\vec{r}',t')]_\nu G_\nu(\vec{r},\vec{r}',t,t'), \qquad (15)$$

where

$$G_\nu(\vec{r},\vec{r}',t,t') = \frac{\delta\left(t - t' - \frac{n_\nu}{c}|\vec{r} - \vec{r}'|\right)}{|\vec{r} - \vec{r}'|} \qquad (16)$$

is the Green function, ρ and $\vec{J} = \rho\vec{v}$ are the charge and current densities, respectively, and n_ν is n_1 or n_2 according to whether the frequency of interest is ω or 2ω. Here, ρ and $\vec{J}$ are associated with the jth point charge q located at $\vec{r}_q = \vec{r}_j + \Delta\vec{r}_j(t)$. Then,

$$\rho_j(\vec{r}',t') = q\delta[\vec{r}' - \vec{r}_j - \Delta\vec{r}_j(t')], \qquad (17)$$

$$\vec{J}_j(\vec{r}',t') = \rho_j(\vec{r}',t')\frac{d\Delta\vec{r}_j(t')}{dt'}$$
$$= \left(q\frac{d\Delta\vec{r}_j(t')}{dt'}\right)\delta[\vec{r}' - \vec{r}_j - \Delta\vec{r}_j(t')]. \qquad (18)$$

The far-field $\vec{E}_j^{ff}(\vec{r},t)$ that results from q is given by

$$\vec{E}_j^{ff}(\vec{r},t) = -\frac{1}{c}\frac{\partial \vec{A}_j(\vec{r},t)}{\partial t} - \nabla\phi_j(\vec{r},t) = -\frac{1}{c}\frac{\partial \vec{A}_{j\perp}(\vec{r},t)}{\partial t}, \quad (19)$$

where $\vec{A}_{j\perp}(\vec{r},t)$ is the component of $\vec{A}_j(\vec{r},t)$ that is perpendicular to the line between the origin $\vec{r}_j + \Delta\vec{r}_j$ of the radiation and the observer at $\vec{r}$. The second form of Eq. (19) follows because $\nabla\phi_j$ removes the longitudinal component of $\vec{A}_j$, leaving a purely transverse potential. Thus, we need evaluate only $\vec{A}_j(\vec{r},t)$. This can be obtained relatively simply because $\vec{A}_j$ is already of first order in $\vec{v}/c$, where $\vec{v}$ is the velocity of q.

Substituting Eq. (18) into Eq. (15) and performing the integration over $\vec{r}'$ yields

$$\vec{A}_j(\vec{r},t) = \frac{q}{c} \int dt' \frac{d\Delta\vec{r}_j(t')}{dt'} \frac{\delta\left[t - t' - \frac{n_\nu}{c}|\vec{r} - \vec{r}_j - \Delta\vec{r}_j(t')|\right]}{|\vec{r} - \vec{r}_j - \Delta\vec{r}_j(t')|}. \qquad (20)$$

The integration over t' is nontrivial because $\Delta\vec{r}_j(t')$ is also a function of t'. However, to first order in $1/c$, we can expand

$$\frac{n_\nu}{c}|\vec{r} - \vec{r}_j - \Delta\vec{r}_j(t')| \approx \frac{n_\nu r}{c} - \frac{n_\nu}{c}\hat{k} \cdot \vec{r}_j - \frac{n_\nu}{c}\hat{k} \cdot \Delta\vec{r}_j(t'), \qquad (21)$$

so

$$\delta\left(t - t' - \frac{n_\nu}{c}|\vec{r} - \vec{r}_j - \Delta\vec{r}_j(t')|\right) \approx \delta\left(t_o - t' + \frac{n_\nu}{c}\hat{k} \cdot \Delta\vec{r}_j(t')\right), \qquad (22)$$

where $t_o = t - n_\nu r/c + n_\nu \hat{k} \cdot \vec{r}_j/c$. This is still a self-consistent expression, but to first order in $1/c$, we can substitute t_o for t' in the argument of $\Delta\vec{r}_j(t')$. We finally obtain

$$t' = t_{ret} \approx t_o + \frac{n_\nu}{c}\hat{k}\cdot\Delta\vec{r}_j(t_o), \qquad (23)$$

where t_{ret} is the retarded time. The integral over t' can now be performed, and we obtain

$$\vec{A}_j(\vec{r},t) = \frac{q}{rc}\left(\frac{d\Delta\vec{r}_j(t')}{dt'}\right)_{t'=t_{ret}}. \qquad (24)$$

Substituting Eq. (4) into Eq. (24) yields the contribution from the jth charge:

$$\vec{A}_j(\vec{r},t) = -\frac{i\omega q}{rc}(\Delta\vec{r}_{1j}e^{-i\omega t'} + 2\Delta\vec{r}_{2j}e^{-i2\omega t'})_{t'=t_{ret}}$$

$$= -\frac{i\omega q}{rc}(\Delta\vec{r}_{1j}e^{-ik_o\hat{k}\cdot\Delta\vec{r}_{1j}}e^{-ik_o\hat{k}\cdot\vec{r}_j}e^{ik_o r - i\omega t}$$

$$+ 2\Delta\vec{r}_{2j}e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t})$$

$$= -\frac{i\omega q}{rc}\Delta\vec{r}_{1j}e^{-ik_o\hat{k}\cdot\vec{r}_j}e^{ik_o r - i\omega t}$$

$$- \frac{\omega^2 q n_2}{rc^2}\Delta\vec{r}_{1j}(\hat{k}\cdot\Delta\vec{r}_{1j})e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t}$$

$$- \frac{i2\omega q}{rc}\Delta\vec{r}_{2j}e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t}. \qquad (25)$$

The far-field signal $\vec{E}_j^{ff}$ then follows from Eq. (19):

$$\vec{E}_j^{ff}(\vec{r},t) = [\tilde{I} - \hat{k}\hat{k}]\cdot\left[\frac{\omega^2 q}{rc^2}\Delta\vec{r}_{1j}e^{-ik_o\hat{k}\cdot\vec{r}_j}e^{ik_o r - i\omega t}\right.$$

$$- i\frac{\omega^3 q n_2}{rc^3}\Delta\vec{r}_{1j}(\hat{k}\cdot\Delta\vec{r}_{1j})e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t}$$

$$\left. + \frac{2\omega^2 q}{rc^2}\Delta\vec{r}_{2j}e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t}\right]. \qquad (26)$$

Here, $\tilde{I} - \hat{k}\hat{k}$ is the projection operator that eliminates the longitudinal component, and hence performs the function of $-\nabla\phi_j$. As with $-\nabla\phi_j$, $\tilde{I}-\hat{k}\hat{k}$ does not affect the orthogonal component, which will be found to be significant when we discuss off-axis contributions in Secs. III B and III C. In the two nonlinear terms of Eq. (26), we have now incorporated the factor of $1/2$ associated with the change of time dependence from $(e^{-i\omega t})^2$ to $e^{-i2\omega t}$, as discussed in Sec. II A.

Equation (26) is a general expression for linear and second-order far-field radiation from a moving charge in terms of displacements from its equilibrium position. The first term is the linear response. The second term is the RD contribution, and the third is a combination arising from the spatial dependence of the field (SD, MG) and the intrinsic anharmonicity of the bond [the third term in Eq. (12)]. Because the RD contribution originates in propagation, not acceleration, the use of the common expression

$$\vec{E}^{ff} = -\frac{1}{c^2}\frac{\partial^2\vec{a}_\perp}{\partial t^2} \qquad (27)$$

leads for this term to an error of a factor of 2.

To address a point that has caused difficulty in the past, we note that the RD term above and the EQ MD terms of LO both result from an expansion of a phase term $e^{i\vec{k}\cdot\vec{r}}$ to first order in $\vec{k}\cdot\vec{r}$. However, the physics, and consequently the nature of $\vec{E}^{ff}$, is different in the two situations. In LO, $\rho(\vec{r},t)$ is assumed to be a moderately extended but stationary charge density with a multiplicative time dependence $e^{-i\omega t}$, thus having the form $\rho(\vec{r},t) = \rho_o(\vec{r})e^{-i\omega t}$. Here, the t' integration is trivial but the $\vec{r}'$ integration is not. Performing the t' integration yields a multiplicative time factor $e^{-i\omega t}$ and a phase term $e^{i\vec{k}\cdot\vec{r}'}$ that is part of the electrostatic Green function. Because the current $\vec{J}$ needed to calculate $\vec{A}$ has no obvious representation in this case, appropriate vector-calculus identities are used to convert the integration of $\vec{J}$ into a first-moment integration of ρ as $\vec{r}'\rho(\vec{r}')$.[14] The dipole approximation follows by taking $e^{i\vec{k}\cdot\vec{r}'} = 1$, with higher-multipole moments generated from higher-order expansion terms.[5,14] Thus, the LO expansion gives rise to multipole moments but no higher harmonics.

In contrast, in this work, $\rho(\vec{r},t)$ describes a moving point charge $q\delta[\vec{r}'-\vec{r}_o(t)]$, where $\vec{r}_o(t) = \vec{r} + \Delta\vec{r}e^{-i\omega t}$. As seen above, the $\vec{r}'$ integration is now trivial but the t' integration is not. We obtain here higher harmonics but no multipole moments. Thus, what Peng *et al.* labeled EQ/MD in Ref. 8 is due to retardation. That in Ref. 2 is due to spatial dispersion.

D. Superposition of radiation: Averaging and diffraction

In the following, we assume that the charges are driven coherently, so fields must be added rather than intensities. This is expected, and the validity of the assumption is demonstrated experimentally by the vanishing of SHG for amorphous materials in the forward direction.

Returning to Eqs. (1), (10)–(14), and (26), the $\vec{r}_j$ dependence of the SHG signal is either $E_o^2(\vec{r}_j)e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j}$ or a derivative of the form $E_o(\vec{r}_j)[\partial E_o(\vec{r}_j)/\partial x]e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j}$. Both are slowly varying on the atomic scale, whereas the bond directions $\hat{b}$ vary essentially randomly from site to site. Given this large difference of scale, we can factor step (4) into two parts: averaging over bond orientations, effectively at a single site, and then evaluating the sum over all $\vec{r}_j$.

1. Bond averages

We first consider averaging over bond directions. This is accomplished by writing

$$\hat{b} = b_x\hat{x} + b_y\hat{y} + b_z\hat{z} = \hat{x}\sin\theta\cos\phi + \hat{y}\sin\theta\sin\phi + \hat{z}\cos\theta \qquad (28)$$

and then performing the operation

$$\langle f(\hat{b},\hat{t})\rangle = \frac{1}{4\pi}\int d\Omega f(\hat{b},\hat{t}). \qquad (29)$$

The calculation is simplified by grouping the products involving bond directions into dyadics, triadics, etc., and then considering symmetry. For example, for LO, the bond averages that need to be evaluated occur as dyadics $\hat{b}\hat{b}$ and $\hat{t}\hat{t}$. In

the Cartesian-coordinate representation, $\hat{b}\hat{b}$ has nine terms, $b_x b_x \hat{x}\hat{x}$, $b_x b_y \hat{x}\hat{y}$, etc., but only three survive the averaging process because any component involving an odd number of projections averages to zero.

By this reasoning, the triadic $\hat{b}\hat{b}\hat{b}$ clearly vanishes identically, so by Eq. (12), there can be no κ_{2l} contribution to SHG in amorphous materials. Not surprisingly, both microscopic and macroscopic considerations therefore lead to the same conclusion. However, the implications here go further. The terms that remain are only functions of the LO response and the configuration geometry, so the amount of new information obtainable by SHG in amorphous materials in this model is limited to the separation of longitudinal and transverse components of the LO response no matter what geometries are used to enhance the SHG signal.

We now consider the RD contribution to SHG. The terms that need to be considered are $\hat{b}\hat{b}\hat{b}\hat{b}$, $\hat{b}\hat{b}\hat{t}\hat{t}$ and permutations, and $\hat{t}\hat{t}\hat{t}\hat{t}$. If desired, the results can be decomposed into irreducible tensor representations, although we do not do this here. In the calculations that follow, we take advantage of the absence of a preferred direction in amorphous materials. Hence, without loss of generality, we assume that $\vec{k}_o = k_o \hat{z}$ and $\vec{E}_o = E_o \hat{x}$. The expression to be evaluated is then

$$\vec{E}_{RD,j}^{ff} = -i\frac{\omega^3 q n_2}{15rc^3}[\tilde{I} - \hat{k}\hat{k}] \cdot \frac{1}{4\pi}\int d\Omega(\Delta\vec{r}_{1j}\cdot\hat{k})$$
$$\times \Delta\vec{r}_{1j}e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t}. \tag{30}$$

The result is

$$\vec{E}_{RD}^{ff} = -i\frac{\omega^3 q n_2}{15rc^3}[\tilde{I} - \hat{k}\hat{k}] \cdot \{\hat{x}(\hat{k}\cdot\hat{x})(3C_l^2 + 4C_lC_t + 8C_t^2)$$
$$+ [\hat{y}(\hat{k}\cdot\hat{y}) + \hat{z}(\hat{k}\cdot\hat{z})](C_l - C_t)^2\}$$
$$\times\left[\sum_{\vec{r}_j}E_o^2(\vec{r}_j)e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j}\right]e^{ikr-i2\omega t}, \tag{31}$$

where, to simplify the expression, we define

$$C_l = \frac{q}{\kappa_{1l} - m\omega^2}, \quad C_t = \frac{q}{\kappa_{1t} - m\omega^2}. \tag{32}$$

We write the x component, etc., of $\vec{k}$ as $k(\hat{k}\cdot\hat{x})\hat{x}$ so we can move the magnitude of $\vec{k}$ to the prefactor, and therefore eliminate an easily overlooked source of error. The separate longitudinal and transverse contributions can be obtained by setting $C_t = 0$ or $C_l = 0$, respectively. The sum over $\vec{r}_j$ is clearly a Fourier transform of the square of the envelope function of the driving beam and will be evaluated in Sec. II D 2.

We next consider the contributions from SD. These are given by

$$\vec{E}_{SD,j}^{ff} = \frac{2\omega^2 q}{rc^2}[\tilde{I} - \hat{k}\hat{k}] \cdot \frac{1}{4\pi}\int d\Omega\left[\frac{q(\Delta\vec{r}_{1j}\cdot\nabla_{\vec{r}_j})(\hat{b}\cdot\vec{E}_j)}{\kappa_{1l} - 4m\omega^2}\hat{b}\right.$$
$$\left. + \frac{q(\Delta\vec{r}_{1j}\cdot\nabla_{\vec{r}_j})(\hat{t}\cdot\vec{E}_j)}{\kappa_{1t} - 4m\omega^2}\hat{t}\right]e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t}. \tag{33}$$

We evaluate Eq. (33) by dividing the field gradient into longitudinal and transverse parts with respect to $\vec{k}_o$, i.e., letting $\nabla_{\vec{r}_j}E(\vec{r}_j,t) = \hat{x}\frac{\partial E}{\partial x} + \hat{y}\frac{\partial E}{\partial y} + i\hat{z}k_o$. After performing the averages, we obtain

$$\vec{E}_{SD}^{ff}(\vec{r},t) = \frac{2\omega^2 q}{15rc^2}[\tilde{I} - \hat{k}\hat{k}] \cdot \sum_{\vec{r}_j}E_o(\vec{r}_j)$$
$$\times\left\{\hat{x}\frac{\partial E_o(\vec{r}_j)}{\partial x}(3C_lD_l + 2C_lD_t + 2C_tD_l + 8C_tD_t)\right.$$
$$\left. + \left[\hat{y}\frac{\partial E_o(\vec{r}_j)}{\partial y} + i\hat{z}k_oE_o(\vec{r}_j)\right](C_l - C_t)(D_l - D_t)\right\}$$
$$\times e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j}e^{ikr-i2\omega t}, \tag{34}$$

where

$$D_l = \frac{q}{\kappa_{1l} - 4m\omega^2}, \quad D_t = \frac{q}{\kappa_{1t} - 4m\omega^2}. \tag{35}$$

The envelope function for the z component is the same as that for the RD contribution, but those for $\hat{x}$ and $\hat{y}$ involve gradients of the driving field.

The MG contribution is given by

$$\vec{E}_{MG,j}^{ff} = -\frac{2\omega^2 q}{rc^2}[\tilde{I} - \hat{k}\hat{k}] \cdot \frac{1}{4\pi}\int d\Omega(D_l\{[\Delta\vec{r}_{1j}\times(\nabla_{\vec{r}_j}$$
$$\times\vec{E}_j)]\cdot\hat{b}\}\hat{b} + D_t\{[\Delta\vec{r}_{1j}\times(\nabla_{\vec{r}_j}\times\vec{E}_j)]\cdot\hat{t}\}\hat{t} + D_t\{[\Delta\vec{r}_{1j}$$
$$\times(\nabla_{\vec{r}_j}\times\vec{E}_j)]\cdot(\hat{b}\times\hat{t})\}(\hat{b}\times\hat{t}))e^{-i\vec{k}\cdot\vec{r}_j}e^{ikr-i2\omega t}. \tag{36}$$

Here, all three dimensions are involved. By suitable vector-calculus identities, the double-cross-product operation can be cast into apparent spatial-dispersion form, $(\vec{E}\cdot\nabla)\vec{E}$,[5] but an exact cancellation of the resulting dominant terms makes this approach unproductive. After performing the cross-product operations with the assumed propagation and field directions and then averaging over bond orientations, we obtain

$$\vec{E}_{MG}^{ff} = -\frac{2\omega^2 q}{3rc^2}[\tilde{I} - \hat{k}\hat{k}] \cdot \sum_{\vec{r}_j}E_o(\vec{r}_j)(2C_tD_l + C_lD_t)$$
$$\times\left[\hat{y}\frac{\partial E_o(\vec{r}_j)}{\partial y} + i\hat{z}k_oE_o(\vec{r}_j)\right]e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j}e^{ikr-i2\omega t}. \tag{37}$$

2. Diffraction

We consider now the sums over $\vec{r}_j$. These not only yield the geometric properties of the emerging SHG beam but also affect the phases and amplitudes of the prefactors of the individual constituents. In the derivation below, we assume

forward scattering, but will discuss backscattering in Sec. III D. We consider throughout only single-beam excitation. Crossed-beam configurations follow the same principles but are complicated by the need to consider large observation angles, so they will be treated in a subsequent paper.

We assume that the incident beam is Gaussian. For the RD, $\hat{z}$ SD, and $\hat{z}$ MG contributions, the relevant sum is

$$\sum_{\vec{r}_j} E_o^2 e^{-2(x^2+y^2)/W^2} e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j}, \tag{38}$$

where W is the width of the incident beam and for our configuration, $\vec{k}_o = k_o\hat{z}$. Converting the sum to an integral, we have

$$\sum_{\vec{r}_j} \rightarrow N \int_{-\infty}^{\infty} dxdy \int_0^L dz, \tag{39}$$

where N is the volume density and L the thickness of the sample. The integrals are all standard and we find

$$\sum_{\vec{r}_j} E_o(\vec{r}_j)^2 e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j} = i\frac{\pi NW^2 E_o^2}{2(2k_o-k_z)} e^{-(k_x^2+k_y^2)W^2/8}, \tag{40}$$

where we have assumed that L is much larger than the coherence length $1/(2k_o-k_z)$. As expected, the emerging beam also has a Gaussian cross section, with a contributing volume determined by the size of the original beam and the coherence length of the configuration.

For the x and y SD components and the y MG component, the integrals are also standard. Taking the x term as an example, the result is

$$\sum_{\vec{r}_j} E_o(\vec{r}_j)\frac{\partial E_o(\vec{r}_j)}{\partial x} e^{i(2\vec{k}_o-\vec{k})\cdot\vec{r}_j} = -\frac{\pi N k_x W^2 E_o^2}{4(2k_o-k_z)} e^{-(k_x^2+k_y^2)W^2/8}. \tag{41}$$

This is also a Gaussian beam but with a nodal line passing through the center. This is the analytical representation of the two-lobed pattern reported by Figliozzi et al.[1] for various configurations of SHG from an amorphous material and spherical Si nanoinclusions.

E. Net results

We now combine the results of the above sections. The overall RD contribution is

$$\vec{E}_{RD}^{ff} = \frac{\pi\omega^3 qNW^2 E_o^2}{30rc^3(2k_o-k_z)}[\tilde{I}-\hat{k}\hat{k}]\cdot\{\hat{x}(\hat{k}\cdot\hat{x})n_2(3C_l^2+4C_lC_t$$
$$+8C_t^2)+[\hat{y}(\hat{k}\cdot\hat{y})n_2+\hat{z}(\hat{k}\cdot\hat{z})n_2](C_l$$
$$-C_t)^2\}e^{-(k_x^2+k_y^2)W^2/8}e^{ikr-i2\omega t}. \tag{42}$$

The corresponding expressions for SD and MG are, respectively,

$$\vec{E}_{SD}^{ff}(\vec{r},t) = -\frac{\pi\omega^3 qNW^2 E_o^2}{15rc^3(2k_o-k_z)}[\tilde{I}-\hat{k}\hat{k}]\cdot\{\hat{x}(\hat{k}\cdot\hat{x})n_2(3C_lD_l$$
$$+2C_lD_t+2C_tD_l+8C_tD_t)+[\hat{y}(\hat{k}\cdot\hat{y})n_2+\hat{z}n_1](C_l$$
$$-C_t)(D_l-D_t)\}e^{-(k_x^2+k_y^2)W^2/8}e^{ikr-i2\omega t}, \tag{43}$$

$$\vec{E}_{MG}^{ff} = \frac{\pi\omega^3 qNW^2 E_o^2}{3rc^3(2k_o-k_z)}[\tilde{I}-\hat{k}\hat{k}]\cdot[\hat{y}(\hat{k}\cdot\hat{y})n_2+\hat{z}n_1](C_lD_l$$
$$+2C_lD_t)e^{-(k_x^2+k_y^2)W^2/8}e^{ikr-i2\omega t}. \tag{44}$$

Equations (42)–(44) give the far fields from the retardation, spatial-dispersion, and magnetic contributions, respectively. Despite the appearance of assorted phase factors at different stages of the derivation, to the extent that the refractive indices are real, all net contributions have the same phase to within a plus or minus sign. The RD contributions in the two directions perpendicular to that of the polarization of the incident beam are equal, as expected by symmetry. This is not the case for SD and MG, since SD involves gradients and $\vec{B}$ is an axial vector.

As noted in the Introduction, the linear response cannot be calculated by factoring as done above. A full self-consistent Ewald-Oseen treatment is necessary.

III. DISCUSSION

Although Eqs. (42)–(44) are complete, their general properties are not immediately evident. Hence, we consider special cases. We also estimate conversion efficiency for fused silica, basing our calculations on several assumptions and the known LO properties of this material.

A. Paraxial-ray approximation

In the usual case of a highly collimated source beam of relatively small cross section, the emerging beam will also be initially relatively well localized but will diverge over a solid angle where the components essentially add in phase. Taking the diameter of the cross section W to be equal to at least a few wavelengths of the emerging beam, we make the paraxial-ray approximation, writing the observation direction for forward scattering as $\hat{k} = \hat{x}\theta_x + \hat{y}\theta_y + \hat{z}$, where the beam-divergence (observation) angles θ_x and θ_y are first-order quantities. With this representation, the various projection operations are easily evaluated and we find

$$[(\tilde{I}-\hat{k}\hat{k})\cdot\hat{x}](\hat{x}\cdot\hat{k}) = \hat{x}\theta_x,$$

$$[(\tilde{I}-\hat{k}\hat{k})\cdot\hat{y}](\hat{y}\cdot\hat{k}) = \hat{y}\theta_y,$$

$$(\tilde{I}-\hat{k}\hat{k})\cdot\hat{z} = -\hat{x}\theta_x - \hat{y}\theta_y. \tag{45}$$

Considering also Eqs. (42)–(44), it is apparent that all contributions vanish in the forward direction and exhibit two-lobed patterns characteristic of gradient effects. Note that the z component also contributes on the same first-order scale

when the viewer is off axis. We shall use these equations in the following.

B. Reduction to the isotropic case for large κ_1

If the polarizable points are isotropic, then $C_l = C_t = C$ and $D_l = D_t = D$. If we assume further that $\kappa_1 \gg 4m\omega^2$, then $C \approx D$. For clarity, we write

$$g(\vec{k},r,t) = \frac{\pi\omega^2 N W^2 E_o^2 C^2}{8rc^2} e^{-(k_x^2 + k_y^2)W^2/8} e^{ikr - i2\omega t} \quad (46)$$

since this is a common factor for all cases discussed in the rest of Sec. III. Then, Eqs. (42)–(44) reduce to

$$\vec{E}_{RD}^{ff} = -2\hat{x}n_2\theta_x \frac{g(\vec{k},r,t)}{(n_2 - n_1)}, \quad (47)$$

$$\vec{E}_{SD}^{ff} = 4\hat{x}n_2\theta_x \frac{g(\vec{k},r,t)}{(n_2 - n_1)}, \quad (48)$$

$$\vec{E}_{MG}^{ff} = 4[\hat{x}n_1\theta_x - \hat{y}(n_2 - n_1)\theta_y]\frac{g(\vec{k},r,t)}{(n_2 - n_1)}, \quad (49)$$

where we have used the fact that k_z differs from k only by terms of second order in θ. The net result is

$$\vec{E}_{net}^{ff} = 2[\hat{x}(2n_1 + n_2)\theta_x - \hat{y}2(n_2 - n_1)\theta_y]\frac{g(\vec{k},r,t)}{(n_2 - n_1)}. \quad (50)$$

This limit applies to the SHG response of systems where the bond charge is strongly bound, for example, organic materials and glasses. All three mechanisms generate polarization in the direction $\hat{x}$ of the applied field, and all have similar magnitudes, so none can be neglected. The fact that the RD term is important may not be at variance with the conclusion of Brudny et al.[2] which pertains to a configuration where the anharmonic contribution does not vanish completely. In particular, the RD contribution here is exactly half that of SD and with opposite sign, so the net effect of the RD and SD combination is to reduce the SD contribution by half. For $n_1 \approx n_2$, the magnitude of the forward-scattered field intensity clearly significantly benefits from a long coherence length.

Equation (49) shows that two $\hat{y}$ contributions are present, but to the extent that $n_1 \approx n_2$, the overall term is small and can be easily overlooked since detection depends on intensity, not fields. This near cancellation is a result of the sign of the z contribution in off-axis viewing. The cancellation of the y component is exact in Eq. (42) even in the general case where $C_l \neq C_t$. A near cancellation of the y component also occurs in the general case for Eq. (43), although a second near cancellation contributes if $C_l \approx C_t$ or $D_l \approx D_t$. Thus, if the y component is analyzed quantitatively, the more general equations must be used. We conclude that the z component is important in determining the properties of the emerging beam.

C. Metals

A second limit of the above is that corresponding to those metals for which the effective mass of the carriers is itself essentially isotropic. As a result of strong attenuation of optical signals, metals are usually measured in backscattering, where the results can be further complicated by surface reconstructions.[15–17] Although much attention has been focused on these surface contributions,[17–20] we consider here only signals originating from the bulk. In absorbing media, the Green function retains its form, so the above development is still valid although the propagation vectors are now generally complex. With no restoring force, $\kappa_1 = 0$, so $C = 4D$. In the paraxial-ray approximation, the RD contribution is unchanged, but the SD and MG terms are reduced by a factor of 4. For forward scattering, the equations are

$$\vec{E}_{RD,m}^{ff} = -2\hat{x}n_2\theta_x \frac{g(\vec{k},r,t)}{(n_2 - n_1)}, \quad (51)$$

$$\vec{E}_{SD,m}^{ff} = \hat{x}n_2\theta_x \frac{g(\vec{k},r,t)}{(n_2 - n_1)}, \quad (52)$$

$$\vec{E}_{MG,m}^{ff} = [\hat{x}n_1\theta_x - \hat{y}(n_2 - n_1)\theta_y]\frac{g(\vec{k},r,t)}{(n_2 - n_1)}, \quad (53)$$

$$\vec{E}_{net,m}^{ff} = -(n_2 - n_1)[\hat{x}\theta_x - \hat{y}\theta_y]\frac{g(\vec{k},r,t)}{(n_2 - n_1)}. \quad (54)$$

The x and y components now have equal amplitudes, but to the extent that $n_1 \approx n_2$, the net result shows that the enhancement of the signal strength that results from the nearly singular denominator is canceled. Again, all three contributing mechanisms are important. Thus, the assumption that the SHG contribution from metals arises entirely from spatial-dispersion and magnetic effects is not quite correct.[16,17]

SHG signals from surface reconstructions could be described in the above formalism by assigning suitable anisotropies to electrons in the surface region, although we do not do this here.

D. Backscattering

For backscattering, the major difference is the reduction of the correlation length and corresponding reduction in the radiated field since for negative k_z, the two terms of $2k_o - k_z$ add instead of subtract. As we shall show in Sec. III E, this effectively eliminates any possibility of observing SHG from the bulk of amorphous materials. The other effect is to reverse the sign of the result of the projection operation on $\hat{z}$. When everything is taken into account, the paraxial-ray expressions for $\kappa_1 \gg 4m\omega^2$ are

$$\vec{E}_{RD,b}^{ff} = 2\hat{x}n_2\theta_x \frac{g(\vec{k},r,t)}{(n_1 + n_2)}, \quad (55)$$

$$\vec{E}_{SD,b}^{ff} = -4\hat{x}n_2\theta_x\hat{x}\frac{g(\vec{k},r,t)}{(n_1 + n_2)}, \quad (56)$$

$$\vec{E}_{MG,b}^{ff} = 4[\hat{x}n_1\theta_x + \hat{y}(n_1 + n_2)\theta_y]\frac{g(\vec{k},r,t)}{(n_1 + n_2)}, \quad (57)$$

$$\vec{E}_{net,b}^{ff} = 2[\hat{x}(2n_1 - n_2)\theta_x + 2\hat{y}(n_1 + n_2)\theta_y]\frac{g(\vec{k},r,t)}{(n_1 + n_2)}. \quad (58)$$

While both polarizations are present, the dominant contribution in backscattering is that perpendicular to that of the driving field. Although an x contribution is still generated, its strength is expected to be small compared to that polarized along y.

The expressions for isotropic metals are

$$\vec{E}_{RD,mb}^{ff} = 2\hat{x}n_2\theta_x\frac{g(\vec{k},r,t)}{(n_1 + n_2)}, \quad (59)$$

$$\vec{E}_{SD,mb}^{ff} = -\hat{x}n_2\theta_x\frac{g(\vec{k},r,t)}{(n_1 + n_2)}, \quad (60)$$

$$\vec{E}_{MG,mb}^{ff} = [\hat{x}n_1\theta_x + \hat{y}(n_1 + n_2)\theta_y]\frac{g(\vec{k},r,t)}{(n_1 + n_2)}, \quad (61)$$

$$\vec{E}_{net,mb}^{ff} = (n_1 + n_2)[\hat{x}\theta_x + \hat{y}\theta_y]\frac{g(\vec{k},r,t)}{(n_1 + n_2)}. \quad (62)$$

E. Power and conversion efficiency

In many experiments, what is determined is not the SHG intensity but the integrated SHG power. To obtain an order-of-magnitude estimate, we consider the net x-polarized component for forward scattering with $\kappa_1 \gg 4m\omega^2$ and with $C_l = C_t = C$ and $D_l = D_t = D$. The SHG intensity is given by

$$I_{SH} = \frac{cn_2}{8\pi}|\vec{E}_{net}^{ff}|^2. \quad (63)$$

The SHG power is obtained by integrating this expression over a hemisphere of radius r. We are also interested in the conversion efficiency η, which we define as

$$\eta = \frac{P_{SH}}{(P_{inc})^2}, \quad (64)$$

where P_{inc} is the power of the incident beam. By assuming that the incident beam is collimated, the evaluation of its power in terms of the beam properties is straightforward, and we obtain

$$P_{inc} = \int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\frac{cn_1}{8\pi}|E_o|^2e^{-2(x^2+y^2)/W^2} = \frac{cn_1}{16}W^2|E_o|^2. \quad (65)$$

That for the emerging beam is more complicated. The first issue concerns angular dependences. If the incident beam is reasonably well collimated and its diameter is equal to at least several SHG wavelengths, the SHG beam is also fairly well collimated. Then, a small-term expansion in θ is a good approximation. To show this, we consider

$$e^{-(k_x^2+k_y^2)W^2/8} = e^{-(k^2\sin^2\theta)W^2/8}. \quad (66)$$

Taking $k = 2\pi n_2/\lambda_{SH}$, $n_2 = 1.3$, $\lambda_{SH} = 400$ nm, and an incident beam width of 5 μm, we have $k^2W^2/8 \approx 50$. Hence the

small-term approximation $\sin\theta \approx \theta$ is acceptable. This also provides justification for our use of the paraxial-ray approximation in the previous sections. With these simplifications, the area integral is straightforward and we find for $\hat{x}$ polarization

$$P_{SH,x} = \frac{cn_2}{8\pi}\frac{\pi^2\omega^4q^2W^4N^2E_o^4C^4}{16c^4(n_2-n_1)^2}(2n_1+n_2)^2$$

$$\times\int_0^{2\pi}d\phi\int_0^{\infty}\theta d\theta(\theta^2\cos^2\phi)e^{-k^2\theta^2W^2/4}$$

$$= \frac{\pi^2cq^2N^2E_o^4C^2}{64n_2^3(n_2-n_1)^2}(2n_1+n_2)^2. \quad (67)$$

By combining the above expressions, we find the corresponding conversion efficiency to be

$$\eta_x = \frac{4\pi^2q^2N^2C^4(2n_1+n_2)^2}{cW^4n_1^2n_2^3(n_2-n_1)^2}. \quad (68)$$

The efficiency decreases as the fourth power of the diameter of the incident beam. This is in contrast to the intensity, which decreases as $1/W^6$.

From the definition of C_l, we have

$$\vec{p} = \alpha\vec{E}_{loc} = q\Delta\vec{r} = qC_l\vec{E}_{loc}, \quad (69)$$

where E_{loc} is the field at the charge site and α is the linear polarizability. Then, we can write $C = \alpha/q$. We can connect α to the dielectric function $\epsilon_1 = n_1^2$ and bond density N of the material by the Clausius–Mossotti relation

$$\frac{4\pi}{3}N\alpha = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}. \quad (70)$$

Then,

$$\eta_x = \frac{81(2n_1+n_2)^2}{64\pi^2cq^2N^2W^4n_1^2n_2^3(n_2-n_1)^2}\left(\frac{\epsilon_1-1}{\epsilon_1+2}\right)^4. \quad (71)$$

Using a driving wavelength $\lambda = 800$ nm, dielectric functions of quartz of 2.112 and 2.161 at 800 and 400 nm, respectively, a bond density of 1.06×10^{23} cm^{-3},[21] and a Gaussian beam of characteristic dimension $W = 10$ μm, we find $\eta_x = 1.4\times10^{-18}$ W^{-1}. Thus, 1 W input power at 800 nm is expected to generate about 3 SHG photons/s. If W is reduced to 1 μm, the output would increase to about 10^4 SHG photons/s. These results appear to be consistent with experiment,[1] where few if any photons were seen emerging from the glass substrate.

IV. CONCLUSIONS

We have developed an ABM that describes SHG on the atomic scale, uses physically meaningful parameters, and includes all contributing mechanisms, thereby providing a more complete understanding of the physics of SHG than previously available. In disordered materials, the anharmonic restoring force acting on the bond charge does not contribute to the overall SHG signal, which instead arises from a combination of LO and beam-geometry effects, and therefore

provides limited new information about the material. For a Gaussian driving beam, we obtain analytic expressions that give the phase, amplitude, and spatial distribution of the SHG radiation field for each of the remaining contributing mechanisms: RD, SD, and MG effects. All have the same order of magnitude, so any complete description must consider each. The expressions are reduced to simpler forms for both forward- and backscattering configurations in two isotropic limits, the first where the linear restoring force dominates, such as in glasses, and the second where it is absent, such as in metals. We estimate the conversion efficiency for forward scattering in fused quartz. Predictions appear to be in agreement with observations where available.[1] Specific additional predictions allow critical tests of these results.

With the basic physics established, we can now consider more complicated configurations, including nanospherical inclusions in glass and the reported SHG enhancement with crossed-beam, crossed-polarization driving fields.[1] The results presented here are also expected to be useful for analyzing SHG data of liquids and biological materials.

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