Exactly solvable model of surface second harmonic generation

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We develop a model for surface second harmonic generation (SHG) consisting of a semi-infinite system made up of a continuous distribution of harmonic polarizable entities each of which responds non-linearly to the gradient of the field. The near discontinuity of some field components at the surface yields a finite surface susceptibility tensor characterized by the parameters $a(\omega)$ and $b(\omega)$, as well as a bulk non-linear response characterized by $d(\omega)$. We obtain analytical expressions for $a$, $b$ and $d$ in terms of the linear dielectric functions $\epsilon(\omega)$ and $\epsilon(2\omega)$. These expressions are exact within our model, but can be employed to obtain approximate SHG spectra for arbitrary systems.

I. INTRODUCTION

It has generally been stated [1] that the generation of optical fields at twice the frequency of the incoming light when a centrosymmetric system is illuminated takes place at the surface, since an inversion operation changes the sign of the induced electric dipole density, but leaves invariant both the square of the electric field and the non-linear susceptibility. However, it has also been noted [1] that there are non-vanishing electric quadrupolar and a magnetic dipolar bulk contributions to the non-linear polarization, which are related to the small but finite field gradient within a homogeneous system. An order of magnitude analysis leads to comparable bulk and surface contributions to second harmonic generation (SHG). Although some work is required to disentangle both contributions, SHG is a sensitive optical probe of surfaces [2]. There are different approaches in the literature to study surface SHG. Sipe et. al. [3] have developed a phenomenological analysis of the surface and bulk susceptibility tensors, identifying their independent components, and the possible functional dependence of the second order reflectance on the incidence and azimuthal angles for different crystal surfaces. However, they did not attempt actual calculations of the susceptibility tensor. This has been calculated for metallic surfaces employing hydrodynamic models [4–7]. For simple metals there are self-consistent calculations employing the time dependent local density approximation (TDLDA) applied to the jellium model [6,8]. In the other extreme, crystallinity effects have been incorporated by Schaich and Mendoza [9] who developed a dipolium model that also accounts for local field effects. This model has been applied to semiconductors [10] and it has been combined with jellium and extended to noble metals [11]. However, there are still very few calculations [12] of the nonlinear spectra of realistic models. This scarcity of theoretical work, which contrasts strongly with the situation for bulk SHG of non-centrosymmetric systems [13], may be related to the experimental difficulty of obtaining the frequency dependence of the relatively weak surface SHG signals and the consequent small number of experimental spectra for metallic [14] and for semiconductors surfaces [15,16]. However, we expect this situation to change in the near future [17,18].

The purpose of the present paper is the development of a simple model that permits the calculation of the second order response and the non-linear reflectance of an arbitrary centrosymmetric semi-infinite system, in terms of its linear response. Our model consists of a homogeneous semi-infinite distribution of dipoles that respond harmonically to the perturbing field. This distribution is characterized by the dipoles' number density which interpolates continuously across the surface from zero in vacuum to its constant value at the bulk, and we assume the microscopic response functions of all dipoles are the same, regardless of their distance from the surface. The origin of the nonlinearity in our model is the spatial variation of the field across each dipole. This variation gives a small contribution of order $a/\lambda$ in the bulk, where $a$ is the size of each polarizable entity and $\lambda$ is the optical wavelength. However, the normal
component of the electric field has a very rapid variation at the surface, reminiscent of its discontinuity at an abrupt interface [19]. This steep variation in the microscopic field in a distance much smaller than \( \lambda \) yields a sizable surface non-linear polarization with a dipolar character when written in terms of the macroscopic field.

The paper is organized as follows. In section II we present our model and we obtain closed analytical expressions for the non-linear susceptibility in terms of the bulk linear response. Remarkably enough, our results turn out to be independent of the number density profile, so that they apply unambiguously to the usual limiting case of an abrupt surface. In section III we apply our results to the calculation of the susceptibility for several centrosymmetric systems and we compare their SHG efficiency spectra. Finally, in section IV we present our conclusions.

II. THEORY

We start by considering a single charge \(-e\) with mass \( m \) at a distance \( \vec{x} \) from its equilibrium position, to which it is bound by a harmonic force with resonant frequency \( \omega_0 \). In the presence a spatially varying electromagnetic field \( \vec{E}(\vec{r}, t) \) and \( \vec{B}(\vec{r}, t) \) its classical equation of motion is

\[
m \frac{d^2 \vec{x}}{dt^2} = -e\vec{E} - m\omega_0^2 \vec{x} - \frac{m}{\tau} \frac{d}{dt} \vec{x} - \frac{e}{c} \left( \frac{d}{dt} \vec{x} \right) \times \vec{B},
\]

where we also added a dissipative term with corresponding lifetime \( \tau \). We notice that in this equation, the field has to be evaluated at the actual electron’s position \( \vec{r}_0 + \vec{x} \) and not simply at its equilibrium position \( \vec{r}_0 \). Therefore we write

\[
\vec{E}(\vec{r}_0 + \vec{x}, t) \approx \vec{E}(\vec{r}_0, t) + \vec{x} \cdot \nabla \vec{E}(\vec{r}_0, t) + \ldots
\]

and a similar Taylor expansion for the magnetic interaction. Notice that the scale of variation of the field \( E(\vec{r}) \) is not expected to be smaller than the size of an atom, whereas the displacement \( x \) from the electron’s equilibrium position (or more generally, its expectation value) can be made arbitrarily small for a small enough field. Therefore, the Taylor expansion (2) makes sense even at the surface of a solid where the field displays its most violent spatial variations. Higher order terms in the Taylor expansion would have no effect in the quadratic nonlinear response studied below. Now we assume that the driving field is monochromatic with frequency \( \omega \), \( E(\vec{r}, t) = \text{Re}(\vec{E}(\vec{r})e^{-i\omega t}) \).

Therefore \( \vec{B}(\vec{r}, t) = -c \int^t dt' \nabla \times \vec{E}(\vec{r}, t') = \text{Im} \left( (c/\omega) \nabla \times \vec{E}(\vec{r}) e^{-i\omega t} \right) \) and we may write the equation of motion (1) as

\[
m \frac{d^2 \vec{x}}{dt^2} = -e\vec{E}(\vec{r}_0, t) - m\omega_0^2 \vec{x} - \frac{m}{\tau} \frac{d}{dt} \vec{x} - e\vec{x} \cdot \nabla \vec{E}(\vec{r}_0, t) + e \left( \frac{d}{dt} \vec{x} \right) \times \int^t dt' \nabla \times \vec{E}(\vec{r}_0, t') + \ldots
\]

This is similar to the equation of a forced harmonic oscillator: it has a driving term \(-eE\) and all the other terms are proportional to the displacement \( \vec{x} \). However, the coefficients of \( \vec{x} \) and \( d\vec{x}/dt \) are not constant: they depend on the field gradient and therefore, they are time dependent. Thus, Eq. (3) corresponds to that of a parametric, forced oscillator, a well known non-linear system. Even though we started with the prototypical linear system, the harmonic oscillator, the spatial variations of the driving field lead to a nonlinear system.

Since optical fields are usually much smaller than atomic fields, we proceed to a perturbative solution of Eq. (3) by expanding its solution in powers of \( \vec{E} \),

\[
\vec{x}(t) = \vec{x}^{(1)}(t) + \vec{x}^{(2)}(t) + \ldots
\]

The lowest order stationary solution is \( \vec{x}^{(1)}(t) = \text{Re}(\vec{x}_{\omega} e^{-i\omega t}) \) and obeys the well known algebraic equation of a forced linear oscillator

\[
-m\omega^2 \vec{x}_{\omega} = -m\omega_0^2 \vec{x}_{\omega} + im\omega/\tau \vec{x}_{\omega} - e\vec{E}_{\omega},
\]

which we solve immediately to get

\[
\vec{x}_{\omega} = -e/m \frac{e/\omega_{\omega}^2 - \omega^2 - i\omega/\tau}{\omega_{\omega}^2 - \omega^2 - i\omega/\tau} \vec{E}_{\omega},
\]

and the induced electric dipole moment \( \vec{p}_{\omega} = -e\vec{x}_{\omega} = \alpha(\omega) \vec{E}_{\omega} \), where we identify the linear polarizability
\[ \alpha(\omega) = \frac{e^2}{m} \frac{D(\omega)}{D(\omega)}, \] (7)

with the denominator
\[ D(\omega) \equiv \omega_0^2 - \omega^2 - i\omega/\tau. \] (8)

The second order equation is
\[ m \frac{d^2 x^{(2)}(t)}{dt^2} = -m \omega_0^2 x^{(2)}(t) - \frac{m}{\tau} \frac{d}{dt} x^{(2)}(t) - e x^{(1)}(t) \cdot \nabla \vec{E}(\vec{r}_0, t) + e x^{(1)}(t) \times (\nabla \times \vec{E}(\vec{r}_0, t)). \] (9)

This equation is linear in \( x^{(2)} \) and has a driving term which is quadratic in \( E \) with two frequency components: a DC contribution and an oscillatory term at the second harmonic frequency \( 2\omega \). We look now for \( x_{2\omega} \), the \( 2\omega \) component of \( x^{(2)} \), which obeys
\[ -m(2\omega)^2 x_{2\omega} = -m \omega_0^2 x_{2\omega} + i \frac{m}{\tau} (2\omega) x_{2\omega} + \frac{e^2/m}{D(\omega)} \left( \vec{E}_\omega \cdot \nabla \vec{E}_\omega - \vec{E}_\omega \times (\nabla \times \vec{E}_\omega) \right), \] (10)

whose solution is
\[ x_{2\omega} = \frac{1}{2} \frac{e^2/m^2}{D(\omega)/D(2\omega)} \left( \nabla E_\omega^2 - 4 \vec{E}_\omega \times (\nabla \times \vec{E}_\omega) \right), \] (11)

where we employed the identity \( \vec{V} \cdot \nabla \vec{V} = (1/2)\nabla V^2 - \vec{V} \times (\nabla \times \vec{V}) \). The second order dipole moment at \( 2\omega \) is therefore
\[ p_{2\omega} = -\frac{1}{2e} \alpha(\omega) \alpha(2\omega) (\nabla E_\omega^2 - 4 \vec{E}_\omega \times (\nabla \times \vec{E}_\omega)). \] (12)

There is another moment of second order in the driving field and which oscillates at \( 2\omega \); that is the electric quadrupole moment \( Q_{2\omega} = -e x_{2\omega} x_{2\omega} \). Substituting the first order result Eq. (6) we get
\[ Q_{2\omega}^{(2)} = -\frac{1}{e} \alpha^2(\omega) \vec{E}_\omega \cdot \vec{E}_\omega. \] (13)

It is interesting to note that, as in the case of linear response, the nonlinear response functions of a harmonic oscillator which we have derived above classically, coincide with the corresponding expressions derived from a full quantum mechanical calculation [9]. In analogy to Miller's rule [20,21] for the bulk non-linear response of non-centro-symmetric systems, we conjecture that the corrections to Eqs. (12, 13) in centrosymmetric molecules which are not harmonic oscillators might turn out to be small and with only a slow frequency dependence.

We remark that truncating the Taylor expansion (Eq. (2) at the first order term is appropriate whenever \( x \) is small enough, that is, if the centroid of the electronic charge of the molecule is close to its equilibrium position. Higher order field derivatives in Eq. (2) would lead to higher order non-linearities, and for fields with either extremely large amplitudes or spatial variations, the Taylor expansion may be meaningless, as well as a power expansion of the response functions.

Now we consider a macroscopic semi-infinite system made up of \( n \) polarizable entities per unit volume, and we will allow \( n = n(z) \) to depend on position, changing rapidly, but continuously near the surface \( z = 0 \) from its bulk value \( n(z \to \infty) = n^0 \) to its vacuum value \( n(z \to -\infty) = 0 \). Each entity occupies a different position, which we will denote by \( \vec{r} \) and we will assume that \( \vec{r} \) is a continuous variable. Thus, in the following, we will ignore effects derived from the microscopic crystalline structure of the system. We will also assume the response of each entity to be independent of \( \vec{r} \), so that we will also neglect effects such as those derived from a surface induced modification to the electronic structure. Therefore, we will concentrate our attention only on the contribution to the second harmonic polarization arising from the spatial variation of the electromagnetic field.

We begin by writing the macroscopic second order polarization \( \vec{P}_{2\omega} \) as [22]
\[ \vec{P}_{2\omega} = n \vec{p}_{2\omega} - \frac{1}{2} \nabla \cdot n Q_{2\omega}, \] (14)

where \( P_{2\omega}, p_{2\omega} \) and \( Q_{2\omega} \) are continuously varying functions of \( \vec{r} \). Since we have assumed that all entities are identical, we substitute Eqs. (12) and (13) to obtain
\[
\tilde{P}_{2\omega} = n\alpha(2\omega)\tilde{E}_{2\omega} - \frac{n}{2\varepsilon}\alpha(2\omega)\alpha(2\omega)\nabla E_{2\omega}^2 + \frac{1}{2\varepsilon}\alpha^2(\omega)\nabla \cdot (n\tilde{E}_{2\omega}\tilde{E}_{2\omega}).
\] (15)

At this point we are interested only in the nonlinear response of the selvedge, whose width we can safely assume to be much smaller than the wavelength. Whence, in Eq. (15) we ignored retardation, i.e., we dropped \(\nabla \times \tilde{E}_{2\omega}\). The non-linear bulk response will be considered later. The first term on the RHS of Eq. (15) is the linear response to the SH field \(\tilde{E}_{2\omega}\) which we have added for consistency.

The normal component of the electric field \(E_z\) varies very rapidly across the surface, so we neglect the field variations parallel to the surface and write Eq. (15) as

\[
P_{2\omega, z}(z) = n(z)\alpha(2\omega)E_{2\omega, z}(z)
- \frac{n(z)}{2\varepsilon}\alpha(2\omega)\frac{\partial}{\partial z}E_{2\omega, z}^2(z) + \frac{1}{2\varepsilon}\alpha^2(\omega)\frac{\partial}{\partial z}(n(z)E_{2\omega, z}^2(z)).
\] (16)

The parallel component of \(\tilde{P}_{2\omega}\) will be discussed afterwards. Since we are ignoring retardation we can identify the displacement field \(D_z = E_z + 4\pi P_z\) with the external field. Due to the absence of an external field at \(2\omega\), we may substitute \(E_{2\omega, z}\) by the depolarization field \(-4\pi P_{2\omega, z}\). Now we write \(E_{\omega, z} = D_{\omega, z}/\epsilon(\omega, z)\) where \(\epsilon(\omega, z)\) is the dielectric function which we write as

\[
\epsilon(\omega, z) = 1 + 4\pi n(z)\alpha(\omega).
\] (17)

Even if we interpret \(\alpha(\omega)\) as an effective polarizability that accounts for the local field effect in the bulk, here we have ignored the surface induced corrections to the local field [23]. We also ignore spatial dispersion effects which are expected to be important close to the surface where the field has its most abrupt variations. Making use of the long wavelength approximation (LWA) we assume that the displacement field \(D_{\omega, z}\) is almost constant within the surface region, and we solve Eq. (16) for \(P_{2\omega, z}\) to obtain

\[
P_{2\omega, z}(z) = \frac{1}{2\varepsilon(2\omega, z)} \left[ -\alpha(\omega)\alpha(2\omega)\frac{\partial}{\partial z}n(z) \frac{1}{\epsilon^2(\omega, z)} + \alpha^2(\omega)\frac{\partial}{\partial z}n(z) \right] D_{\omega, z}^2.
\] (18)

The second harmonic polarization given above depends on \(z\) through \(n(z)\) and its spatial derivative (see Eq. (17)) which vanishes in both vacuum and bulk. Therefore \(P_{2\omega, z}\) is different from zero only in the selvedge region. Following the LWA, we characterize the polarization at the surface by its zero-th moment

\[
\tilde{P}^s_{2\omega} \equiv \int_{-\infty}^{\infty} dz \tilde{P}_{2\omega}(z).
\] (19)

Substituting Eq. (18) we obtain terms of the form \(\int dz f(n(z)) dg(n(z))/dz\) where \(f\) and \(g\) are simply rational functions of the density profile \(n(z)\). We divide the integration range into intervals in each of which \(n\) is monotonic, so that we can change the integration variable \(z \rightarrow n\) employing \(dz = dn/(dn/dz)\) and \(dg(n(z))/dz = (dn/dz)(dg/dn)\). It is easily seen that \(dn/dz\) cancels out from the integral so that we are left with integrals over \(dn\) of rational functions of \(n\) with coefficients that depend on \(\alpha(\omega)\) and \(\alpha(2\omega)\). These integrals may be performed analytically for any profile \(n(z)\) yielding

\[
\tilde{P}^s_{2\omega} = \chi^s_{zzz}(\omega)D_{\omega, z}^2,
\] (20)

where we identify the non-linear surface susceptibility component

\[
\chi^s_{zzz}(\omega) = \frac{\alpha^2(\omega)\alpha(2\omega)\log(e^B(\omega)/e^B(2\omega))}{8\pi e} \left(\frac{\alpha(\omega) - \alpha(2\omega)}{(\alpha(\omega) - \alpha(2\omega))^2} + \frac{\alpha^2(\omega) - 1}{\epsilon^B(\omega)} + \frac{\alpha(2\omega)}{\epsilon^B(\omega)}\right),
\] (21)

and \(\epsilon^B(\omega) = 1 + 4\pi n^B(\omega)\) denotes the bulk dielectric function. We remark that the non-linear surface susceptibility (21) is independent of the density profile \(n(z)\) and depends only on its bulk value \(n^B\). Therefore Eq. (21) can be immediately applied in the extreme case of an abrupt surface where it still yields an unambiguous well defined result [24]. The discontinuity of \(E_z\) in the latter case makes our expansion (2) seem questionable since atoms have a finite extent. However, this discontinuity is an artifact of the unphysical assumption of an abrupt transition from vacuum into bulk and is absent from more realistic models. It should be clear that the spatial scale of variation of \(E_z\) cannot
The latter components of the surface susceptibility are similarly parametrized by a phenomenological parameter [6]

\[ a(\omega) \equiv -64\pi^2 n_B e \left( \frac{\epsilon_B(\omega)}{\epsilon_B(\omega) - 1} \right)^2 \chi_{zzz}^s(\omega). \]  

(22)

which in our case is given by

\[
a(\omega) = 2 \left[ (\epsilon^B(2\omega) - \epsilon^B(\omega)) [2\epsilon^B(\omega) - \epsilon^B(2\omega) - \epsilon^B(\omega)\epsilon^B(2\omega)] + [\epsilon^B(\omega)]^2 [1 - \epsilon^B(2\omega)] \log[\epsilon^B(\omega)/\epsilon^B(2\omega)] \right] / [\epsilon^B(2\omega) - \epsilon^B(\omega)]^2.
\]

(23)

This equation may be considered the main result of the present paper; it is an analytical expression which, together with the much simpler Eqs. (28) and (31), permits the calculation of the nonlinear response of the system in terms of its linear dielectric response \( \epsilon(\omega) \).

It is easily verified that our expression (23) agrees in the high frequency limit with the quantum mechanical result [25] \( a(\omega \to \infty) = -2 \). We remark that this limit is a kind of sum rule which should be obeyed by arbitrary systems, thus, constituting a test to which calculations ought to be subjected.

We follow a similar procedure for the parallel components of the polarization \( \vec{P}_{2\omega} \). Starting from Eq. (15) we obtain, in analogy to Eq. (16),

\[
\vec{P}_{2\omega,||}(z) = \frac{1}{2\epsilon^2} \alpha^2(\omega) \frac{\partial}{\partial z} n(z) \vec{E}_{\omega,||} \cdot \vec{E}_{\omega,||} (z),
\]

(24)

which is integrated immediately to yield

\[
\vec{P}_{2\omega,||}^s = \chi_{||||,z}^s(\omega) \vec{E}_{\omega,||} D_{\omega,||},
\]

(25)

where

\[
\chi_{||||,z}^s(\omega) = \chi_{||z}^s(\omega) = \frac{1}{2\epsilon^2} \frac{n B \alpha^2(\omega)}{\epsilon^B(\omega)}.
\]

(26)

The latter components of the surface susceptibility are similarly parametrized by [6]

\[
b(\omega) \equiv -32\pi^2 n_B e \frac{\epsilon^B(\omega)}{(\epsilon^B(\omega) - 1)^2} \chi_{||z}^s(\omega).
\]

(27)

In our case we obtain the simple result

\[ b(\omega) = -1. \]  

(28)

The other components of the surface susceptibility are null due to the symmetry along the flat interface.

We remark that we defined the different components of the surface susceptibility in terms of field components \( D_{\omega,z} \) and \( E_{\omega,||} \) which are continuous at abrupt surfaces and which are slowly varying across smooth interfaces [24,26,27]. This allowed us to employ the LWA and made it unnecessary to specify the position near the surface where the fields are to be evaluated, therefore eliminating a source of confusion in the literature. However, our definitions of \( a(\omega) \) and \( b(\omega) \) do coincide with the usual ones [6,24].

Now we turn our attention to the bulk non-linear response. We start with Eqs. (12) and (13), and we write Eq. (14) as

\[
\vec{P}_{2\omega}^B = -\frac{n B}{e} \alpha(\omega) \alpha(2\omega) \left( 2E_{\omega} \cdot \nabla E_{\omega} - \frac{1}{2} \nabla E_{\omega}^2 \right) - \frac{n B}{2e} \alpha^2(\omega) \nabla \cdot (\vec{E}_{\omega} \vec{E}_{\omega}).
\]

(29)

Since in the bulk of a local system \( \vec{E}_{\omega} \) is perpendicular to its direction of propagation, then Eq. (29) simplifies to

\[
P_{2\omega}^B \equiv \frac{1}{32\pi^2 ne} (\epsilon^B(\omega) - 1)(\epsilon^B(2\omega) - 1) d(\omega) \nabla E^2
\]

(30)
where we introduced the bulk phenomenological parameter \( [24] d(\omega) \) which in our case has the value
\[
d(\omega) = 1. \tag{31}
\]

We have performed an alternate derivation of \( a(\omega) \), \( b(\omega) \) and \( d(\omega) \) starting from the hydrodynamic equations of motion of a non-spatially dispersive semi-infinite electron gas with a continuous equilibrium density profile, and we have verified that the results agree with those above when written in terms of the Drude dielectric function.

The SHG efficiency is defined as \( R = I_{2\omega}/I_{\omega}^2 \) where \( I_{2\omega} \) and \( I_{\omega} \) denote intensities of the reflected second harmonic and the incident waves, respectively. \( R \) can easily be written in terms of \( a(\omega) \), \( b(\omega) \), \( d(\omega) \) and the linear response \( \epsilon^R(\omega) \) and \( \epsilon^R(2\omega) \) by following the usual procedure \([27]\). The result has usually been written in such a way that their applicability is unnecessarily restricted to the electron gas \([4]\). For this reason we rewrite them here in a more general way. For \( p \)-polarized incident light and \( p \)-polarized SH fields the efficiency is
\[
R_{pp} = \frac{8\pi^3\omega^2}{(n^R e)^2 c^3} |r_{pp}|^2, \tag{32}
\]

where
\[
r_{pp} = Q(\omega) \left( \frac{\epsilon^R(\omega) - 1}{4\pi} \right)^2 \frac{t(2\omega)t^2(\omega)}{\epsilon^R(2\omega)\epsilon^R(\omega)}
\times \left( \frac{\epsilon^R(2\omega)}{\epsilon^R(\omega)} \right) \left( \frac{Q(\omega)\epsilon}{\omega} \right)^2 \left( a(\omega) - \frac{k(\omega)k(2\omega)c^2}{\omega^2\epsilon^R(\omega)}b(\omega) - \frac{\epsilon^R(2\omega) - 1}{\epsilon^R(\omega) - 1}d(\omega) \right). \tag{33}
\]

Here we introduced the normal component of the wavevector in vacuum,
\[
q^2(\omega) = \frac{\omega^2}{c^2} - Q^2(\omega), \tag{34}
\]
and in the medium
\[
k^2(\omega) = \frac{\omega^2}{c^2} \epsilon^R(\omega) - Q^2(\omega), \tag{35}
\]
its common parallel component \( Q(\omega) \) which can be written in terms of the incident angle \( \theta \) as \( Q(\omega) = (\omega/c) \sin \theta \), and the Fresnel transmission coefficient for \( p \) polarized light
\[
t(\omega) = \frac{2\epsilon^R(\omega)q(\omega)}{\epsilon^R(\omega)q(\omega) + k(\omega)}, \tag{36}
\]
defined as the quotient between the transmitted and incident magnetic fields.

### III. RESULTS

In this section we employ formulae (23), (28), (31), (32) and (33) to calculate the SHG efficiency of several systems. In Fig. 1 we show \( a(\omega) \) for a semi-infinite system made up of identical harmonic polarizable entities with a single resonance. As could be expected, there are two features in the surface response at the resonant frequency \( \omega_0 \) and at its subharmonic. Furthermore, the logarithmic contribution in last term of Eq. (23) yields a sizable contribution to the imaginary part \( a'' \) of \( a \), in those frequency regions where \( \epsilon^R(\omega) \) is negative, that is, between \( \omega_0 \) and \( \omega_L = (\omega_0^2 + 4\pi n^B e^2/m)^{1/2} \) and also between the corresponding sub-harmonics. For the parameters employed in Fig. 1 the particular frequencies where structure is displayed are \( \omega/\omega_0 = .5, 1/\sqrt{2}, 1, \) and \( \sqrt{2} \). The real part \( a' \) of \( a \) follows these structures according to the causality relations. Except for the sharpness of the peaks in \( a' \) the results are quite insensitive to the dissipation. In Fig. 2 we present the \( p - P \) SHG efficiency calculated for the same harmonic system for an angle of incidence \( \theta = 45^\circ \). \( R_{pp} \) displays peaks close to \( \omega = \omega_0/2, \omega_L/2 \) and \( \omega_0 \). The height of the first two is insensitive to the dissipation while that at \( \omega_0 \) is much larger and very sensitive to \( \tau \). The efficiency remains large in the region between \( \omega_0 \) and \( \omega_L \), where the material is opaque, and also between \( \omega_L \) and \( \omega_c = \sqrt{\omega_L^2 \cos^2 \theta - \omega_0^2 \tan^2 \theta} \approx 1.73\omega_0 \), where there is total internal reflection. Above this region \( R_{pp} \) becomes negligible.
In the following we apply our theoretical results to the calculation of the SHG of arbitrary semi-infinite centrosymmetric crystals by simply substituting the appropriate values of their dielectric functions in our analytical formulae. We remark that in this way we automatically incorporate in our polarizability the bulk local field corrections, so that \( \alpha \) is no longer the bare polarizability of each polarizable entity. However, we still ignore the surface local field corrections [23].

In Fig. 3 we show \( a(\omega) \) for Ge and its corresponding efficiency spectrum \( R_{pp}(\omega) \). These figure was obtained by substituting the experimentally found values [28] of \( e^B(\omega) \) in Eqs. (23), (28), (31), (32) and (33). We remark that to our knowledge, this is the first calculation of the expected SHG spectrum from the surface of a centrosymmetric semiconductor. We note that \( R_{pp} \) is of order \( 10^{-20} \text{cm}^2/\text{eV} \) and it displays structures which can be related to the critical points of the semiconductor’s joint densities of states.

The order of magnitude obtained is to be expected from a simple dimensional analysis. The volume second order susceptibility has units of inverse electric field; a typical field felt by an electron is of the order \( a_B^2/e \), where \( a_B \) is the Bohr radius. As the system is polarized in a region whose width has atomic dimensions the surface non-linear susceptibility has units of inverse electric field; a typical field felt by an electron is of the order \( a_B^2/e \). The field radiated by a polarized sheet goes as \( P_s/\lambda \) so that the second harmonic field \( E(2\omega) \approx (a_B^2/\lambda e)E^2(\omega) \). Finally, the second order intensity is \( I(2\omega) \approx (1/c)(a_B^2/\lambda e)^2P^2(\omega) \), from which we identify the second order reflectance \( R_{pp} \approx (1/c)(a_B^2/\lambda e)^2 \approx 10^{-21} \text{cm}^2/\text{W} \). Due to the generality of this argument, this estimate can be used not only for semiconductors but also for metals, for which we expect a similar order of magnitude. However, the non-linear reflectance may still be increased in regions of resonance and suppressed in regions of transparency.

In Fig. 4 we show similar results for Si. We note that the nonlinear efficiencies of both semiconductors are of comparable size. There are very few spectroscopic measurements of surface SHG, although recently, Daum et al [16], measured the SHG spectra of a clean and oxide covered Si surfaces. They obtained a pronounced peak at \( 2\omega = 3.3 \text{ eV} \), which they ascribed to the well known \( E_1 \) direct band gap transition, which became dipolarly active due to the strain of the first few layers of Si. Our Fig. 4 displays only a slope change at \( \omega = 1.65 \text{ eV} \), though it does have a clear peak at \( \omega = 3.3 \text{ eV} \). Of course, our simple approximate model for clean Si does not consider surface strains.

In Fig. 5 we show the corresponding results for diamond [29]. We remark that in the available frequency range the SHG efficiency is three orders of magnitude smaller than for the previous semiconductors. This fact may explain the difficulty in observing SHG in diamond [30] while measurements in Si and Ge have been comparatively habitual [2,15,16,31]. We expect that the recent advances in laser systems will soon facilitate further measurements in diamond.

### IV. CONCLUSIONS

In this paper we have developed a very simple model which yields analytical formulae for the calculation of the optical second harmonic generation of a semi-infinite centrosymmetric system. Although the model assumes that the system is composed of molecules that respond as harmonic oscillators to the polarizing field, the results are written in terms of the linear dielectric response evaluated at the fundamental and the second harmonic frequencies. Our results may be employed to calculate approximately the SHG spectra of arbitrary centro-symmetric systems, provided their linear response is known from experiment or from linear response theory. Although the accuracy of our expressions may be questioned for non-harmonic-oscillator systems, they might provide a good estimate and an appropriate starting point for more detailed calculations of SHG spectra, provided there is a surface analogue of Miller’s rule [20,21].

We made several assumptions beyond that of harmonicity. We took the molecular (dipolar and quadrupolar) polarizabilities to be position independent. Thus, the effects of transitions to and from surface states [14,17] and those of adsorbed overlayers [32] are beyond the scope of the present theory. We also ignored the crystalline structure and the local field effect [9,11] since we smeared the polarizable molecules and distributed them continuously. Our results turned out to be independent of the shape of the number density surface profile, so that we can calculate the SHG without the need for further microscopic surface structure information. The only source of the surface non-linearity in our calculation is the rapid variation of the normal component of the electric field across the surface region. Therefore, we also ignored any possible contribution arising from the modifications of the electronic structure at the surface.

There is no reason to suppose that the effects we have ignored are inconsequential. For example, it is known [7,33] that in conductors, SHG does indeed depend on the electronic density profile. This dependence originates from the spatial dispersion of the electron gas, so it would be interesting to find out if non-local corrections will also introduce a strong profile dependence in the SHG of insulators. Therefore, it is quite feasible that our results fail to describe the actual SHG spectra of many systems. However, our model permits a simple parameter-free calculation of SHG spectra which may be meaningfully confronted with experimental results, allowing us to learn about the relative importance
of those effects we have incorporated and those we have left out.

We illustrated our scheme by actual calculation of the surface susceptibility and efficiency spectra of a harmonic system, and we identified the origin of their spectral features. We also made a first calculation of the surface SHG spectra of a few semiconductor and insulating systems. Here, our formalism allowed us to understand the shortage of measured SHG in crystals such as diamond.

Most experimental work on surface SHG has concentrated on the dependence of the signal on the incidence and the azimuthal angle as well as on the dependence on the crystalline face. Clearly, these are beyond the scope of our non-crystalline model. However, there are a few experiments that explore the frequency dependence of the SHG, and their number are expected to increase in the near future due to the availability of a new generation of tunable high power pulsed lasers. It is for this reason that we believe that approximate schemes, such as the present one, which allows a simple calculation of SHG spectra based on well understood approximations will prove to be very valuable.

In summary, we obtained analytical formulas for the calculation of the SHG of harmonic systems and we propose their use for simple approximate calculations of the SHG spectra of arbitrary semi-infinite centrosymmetric systems in terms of their linear dielectric function.

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FIG. 1. Real and imaginary part of $a(\omega) = a'(\omega) + a''(\omega)$ vs. $\omega/\omega_0$ for a harmonic solid with resonance frequency $\omega_0$, longitudinal frequency $\omega_L = \sqrt{2\omega_0}$ and lifetime parameter $\tau = 1000/\omega_0$ (solid line) and $20/\omega_0$ (dashed line).

FIG. 2. $p$ in-$p$ out SHG efficiency $(nR e/\omega_0)^2c^3\mathcal{R}_{pp}$ vs. $\omega/\omega_0$ for the same system as in Fig. 1, with a lifetime parameter $\tau = 1000/\omega_0$ and for an angle of incidence of $45^\circ$.

FIG. 3. Real and imaginary part of $a(\omega)$ (upper panel) and SHG efficiency $\mathcal{R}_{pp}$ vs. $h\omega$ for Ge, for $p$ in $p$ out polarizations and $45^\circ$ incidence angle.

FIG. 4. Real and imaginary part of $a(\omega)$ (upper panel) and SHG efficiency $\mathcal{R}_{pp}$ vs. $h\omega$ for Si, for $p$ in $p$ out polarizations and $45^\circ$ incidence angle.

FIG. 5. Real and imaginary part of $a(\omega)$ (upper panel) and SHG efficiency $\mathcal{R}_{pp}$ vs. $h\omega$ for diamond, for $p$ in $p$ out polarizations and $45^\circ$ incidence angle.