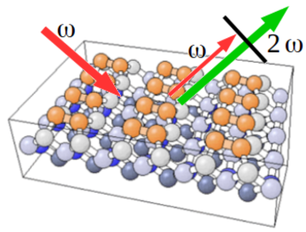
2 Second harmonic generation at surface of nonlinear media



Understanding what is measured is an intricate task and it has occupied physicists for hundred of years. In the case of Second-Harmonic Generation (SHG), the properties of the nonlinear medium, i.e., the intensity and the polarisation dependence of SHG, are often measured in reflection for bulk materials[**?**]Ref, surfaces and interfaces[**?**]Ref and layered materials [**?**, **?**]Ref. In that setup, a fundamental laser at a frequency ω reflects on the surface of the material, yielding two waves. One is a fraction of the fundamental light, reflected following Fresnel laws. The other one is the second-harmonic emmited by the nonlinear medium and oscilating at the frequency 2ω. A filter is used to discard between the reflected fundamental light and the second harmonic signal, which contains the informations concerning the material investigated. Thus, by controlling the polarisation or the angle of incidence, one can easily probe the nonlinear or symmetry properties of a wide class of materials. The first theoretical description of second harmonic generation at surfaces of nonlinear media is due to Bloembergen and Pershan [**?**], followed by papers from Tom *et al.* [**?**] and Mizhahi and Sipe [**?**]. Along the years, the generation of second harmonic at surface of nonlinear media as been widely studied, resulting in a nice theoretical description which is a generalization of Fresnel reflection coefficients to the case of SHG.

The second harmonic reflection coefficients or generalized reflection coefficients, denoted R, are defined as the ratio of the reflected second-harmonic intensity to the square of the fundamental intensity.

$$R = \frac{I_{out}(2\omega)}{I_{in}(\omega)^2}, \tag{2.1}$$

where the intensity $I(\omega)$ is related to the electric field by the relation $I(\omega) = 2c\epsilon_0|E(\omega)|^2$.

In the most general case, this reflection coefficients depends on the input polarisation, the measured polarisation, the incidence angle and the rotation angle in the plane of the surface.

In general, the fundamental and reflected waves are p-polarized or s-polarized. To distinguish between the four different possible combinations of polarisation, one annotates R with two letters (s or p), the first one standing for the polarisation of the fundamental wave and the second one for the reflected wave. [1]

[1]Any other possible polarisation will be labelled by α, as explained in Fig. **??**.

For instance, R_{sp} denotes the second-harmonic reflection coefficient obtained for a s-polarized incident wave and p-polarized reflected wave. [2]

Despite the growing interest in SHG, the literature remains unclear concerning the derivation of the reflection coefficients and lot of papers contains mistakes or do not define clearly what is the phenomenological treatment used or which approximations are involved in the derivation of that coefficients, an exception been Ref.[**?**].
Here I present a clear derivation of the expressions of the different reflection coefficients, for both surface and bulk contributions, based on the work of Ref. [**?**]. By opposition to most previous theoretical works, all formulae reported in that chapter are expressed in the S.I. unit system, allowing one to use this expressions to compare with experimental result.

Modelling the experiment

The experiment is modelled by a semi-infinite medium as represented in Fig. **??**. The z-axis is choosen to be perpendicular to the surface plane. The upper half-space ($z > 0$) corresponds to the vacuum region whereas the lower half-space is filled with the nonlinear medium. The angle between the incident beam and the normal to the surface (z-axis) is called θ_i (see Fig. **??**a). In the surface plane ($x - y$ plane), the azimuthal angle, i.e., the angle between the projection of the incident beam and the x-axis, is called ϕ. To avoid unnecessary complications, the birefringence of the medium is neglected and only one refracted ray is assumed to propagate, which is correct for cubic system as GaAs or Silicon. The formalism presented here is a *macroscopic* formalism, therefore the medium is considered to be homogeneous and isotropic for the linear properties and thus the dielectric tensor $\overset{\leftrightarrow}{\epsilon}(\mathbf{r}, \mathbf{r}'; \omega)$ is replaced by a macroscopic dielectric function $\epsilon(\omega)$. [3]

As shown by Bloembergen and Pershan in Ref. [**?**], the harmonic waves reflected and transmitted at the boundary of a nonlinear medium follow generalized Fresnel laws. In the case of SHG, this leads to a reflected wave propagating along a direction that exhibits the same angle to the normal θ_r than the fundamental light. In the following, we do not label incident and reflected angles by letters i and r because of the equality $\theta_i = \theta_r = \theta$ and we keep only θ in our notations.

Fig. 2.1: (a) SHG geometry in reflection from a surface. θ is the incidence angle and ϕ is the azimuthal angle. α is the polarisation angle in the plane of incidence : p-polarization has $\alpha = 0°$and the s-polarisation has $\alpha = 90°$. Adapted from Ref. [**?**] (b) a slab of nonlinear polarisation is considered at $z = 0^-$, surrounded by an isotropic and homogeneous linear medium, characterised by a dielectric response ϵ. (c) Representation of the $\hat{\mathbf{s}}$, $\hat{\mathbf{p}}$ and $\hat{\mathbf{q}}$, as explained in the text.

Following Ref. [**?**], we express any electric field $\mathbf{E}(\mathbf{r})$ for $z \neq 0$, as the sum of two waves, the upward-propagating wave and the downward-propagating wave, denoted respectively $\mathbf{E}_+$ and $\mathbf{E}_-$.

[2] Sometimes, one can also find in the literature a q-polarized light, corresponding to the polarisation at 45°between s and p. Also, the reader must be careful when comparing with the litterature because some authors use the opposite convention.

[3] Taking into account the anisotropy of the dielectric tensor is straightforward but makes the notations heavier, it is why it is assumed here the isotropy of the dielectric tensor.

So one can write that

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_+(\mathbf{r})\theta(z) + \mathbf{E}_-(\mathbf{r})\theta(-z) \qquad z \neq 0 \tag{2.2}$$

where $\theta(z)$ is the Heaviside function, $\theta(z) = 1$ as $z > 0$ and 0 elsewhere.
The wave vectors for upward/downward propagating waves are written as

$$\begin{aligned} \mathbf{q}^i_+(\omega) &= q_{||}(\omega)\hat{\boldsymbol{\kappa}} + q^i_\perp(\omega)\hat{\mathbf{z}} \\ \mathbf{q}^i_-(\omega) &= q_{||}(\omega)\hat{\boldsymbol{\kappa}} - q^i_\perp(\omega)\hat{\mathbf{z}} \end{aligned} \tag{2.3}$$

where $\hat{\boldsymbol{\kappa}}$ is the in-plane unit vector defined by $\hat{\boldsymbol{\kappa}} = cos(\phi)\hat{\mathbf{x}} + sin(\phi)\hat{\mathbf{y}}$ and i can be the medium (m) or the vacuum (v). We define $q_{||}$ to be the in-plane wave-vector component and $q_\perp$ the out-of-plane wave-vector component. Here $q^i(\omega)^2 = \sqrt{\epsilon_i(\omega)}\left(\frac{\omega}{c}\right)^2$and $q^i_\perp(\omega) = \left(\epsilon_i(\omega)\frac{\omega^2}{c^2} - q^2_{||}(\omega)\right)^{1/2} = \frac{\omega}{c}\left(\epsilon_i(\omega) - sin\theta\right)^{1/2}$, $q^i_\perp$ being chosen to have $\mathrm{Im}[q^i_\perp] \geq 0$ and $\mathrm{Re}[q^i_\perp] \geq 0$ if $\mathrm{Im}[q^i_\perp] = 0$. This convention allows us to be sure that the wave associated with $\mathbf{q}^i_+$ is upward propagating and that the one associated with $\mathbf{q}^i_-$ is downward-propagating.
The s and p polarisations are defined by the following vectors

$$\begin{aligned} \hat{\mathbf{s}} &= \hat{\boldsymbol{\kappa}} \times \hat{\mathbf{z}} \\ \hat{\mathbf{p}}^i_\pm &= \frac{(q_{||}\hat{\mathbf{z}} \mp q^i_\perp\hat{\boldsymbol{\kappa}})}{q^i} \end{aligned} \tag{2.4}$$

This is illustrated in Fig. **??**(c). For conciseness, we omit the frequency dependence here.
One can easily check that we have the following relations

$$\begin{aligned} &\hat{\mathbf{s}} \times \hat{\mathbf{q}}^i_\pm = \hat{\mathbf{p}}^i_\pm \\ &\hat{\mathbf{q}}^i_\pm \times \hat{\mathbf{p}}^i_\pm = \hat{\mathbf{s}} \\ &\hat{\mathbf{p}}^i_\pm \times \hat{\mathbf{s}} = \hat{\mathbf{q}}^i_\pm \end{aligned} \tag{2.5}$$

and thus $(\hat{\mathbf{s}}; \hat{\mathbf{q}}^i_+; \hat{\mathbf{p}}^i_+)$ and $(\hat{\mathbf{s}}; \hat{\mathbf{q}}^i_-; \hat{\mathbf{p}}^i_-)$ are direct basis.
The consequence is that for the wave associated with $\hat{\mathbf{q}}^i_+$ ($\hat{\mathbf{q}}^i_-$), one could only have components propagating along $\hat{\mathbf{s}}$ et $\hat{\mathbf{p}}^i_+$ ($\hat{\mathbf{p}}^i_-$).
From Maxwell equations, the upward and the downward propagating waves reads as

$$\begin{aligned} \mathbf{E}^i_+(\mathbf{r};\omega) &= (E^i_{s+}(\omega)\hat{\mathbf{s}} + E^i_{p+}(\omega)\hat{\mathbf{p}}^i_+)e^{i\mathbf{q}^i_+\mathbf{r}} \\ \mathbf{B}^i_+(\mathbf{r};\omega) &= c^{-1}\sqrt{\epsilon_i(\omega)}(E^i_{p+}(\omega)\hat{\mathbf{s}} - E^i_{s+}(\omega)\hat{\mathbf{p}}^i_+)e^{i\mathbf{q}^i_+\mathbf{r}} \\ \mathbf{E}^i_-(\mathbf{r};\omega) &= (E^i_{s-}(\omega)\hat{\mathbf{s}} + E^i_{p-}(\omega)\hat{\mathbf{p}}^i_-)e^{i\mathbf{q}^i_-\mathbf{r}} \\ \mathbf{B}^i_-(\mathbf{r};\omega) &= c^{-1}\sqrt{\epsilon_i(\omega)}(E^i_{p-}(\omega)\hat{\mathbf{s}} - E^i_{s-}(\omega)\hat{\mathbf{p}}^i_-)e^{i\mathbf{q}^i_-\mathbf{r}} \end{aligned} \qquad z \neq 0 \tag{2.6}$$

2.1 Second order polarisation induced by incident light

Let call the incident field in the vacuum $\mathbf{E}_{in}(\omega)$. The polarisation of that field is denoted $\hat{\mathbf{e}}^{\mathbf{in}}$ which can be $\hat{\mathbf{s}}$ or $\hat{\mathbf{p}}_-$ depending if the field is s- or p-polarised. At the boundary with the medium, this field

Polarisation	Reflection	Transmition
s	$r^s_{ij}(\omega) = \frac{q^i_\perp(\omega) - q^j_\perp(\omega)}{q^i_\perp(\omega) + q^j_\perp(\omega)}$	$t^s_{ij}(\omega) = \frac{2q^i_\perp(\omega)}{q^i_\perp(\omega) + q^j_\perp(\omega)}$
p	$r^p_{ij}(\omega) = \frac{q^i_\perp(\omega)\epsilon_j(\omega) - q^j_\perp(\omega)\epsilon_i(\omega)}{q^i_\perp(\omega)\epsilon_j(\omega) + q^j_\perp(\omega)\epsilon_i(\omega)}$	$t^p_{ij}(\omega) = \frac{2q^i_\perp(\omega)\sqrt{\epsilon_j(\omega)\epsilon_i(\omega)}}{q^i_\perp(\omega)\epsilon_j(\omega) + q^j_\perp(\omega)\epsilon_i(\omega)}$

Tab. 2.1: Fresnel coefficients in reflection and in transmission for s and p-polarized light.

is transmitted.
One has

$$\mathbf{E}_{in}(\mathbf{r};\omega) = \left(E^s_{in}\hat{\mathbf{s}} + E^p_{in}\hat{\mathbf{p}}^v_-\right) e^{i(\mathbf{q}_{||}(\omega)\mathbf{r}_{||} - q^v_\perp(\omega)z)} = \hat{\mathbf{e}}^{\mathbf{in}}|E_{in}|e^{i(\mathbf{q}_{||}(\omega)\mathbf{r}_{||} - q^v_\perp(\omega)z)}. \tag{2.7}$$

The change in phase and amplitude of the wave at the boundary of the medium is described by the Fresnel transmission and reflection coefficients (see Tab. **??**). t^{pol}_{ij} denotes a transmission coefficient where pol is s or p and i and j can be the medium (m) or the vacuum (v). In this thesis, I do not consider the reflection of the fundamental light because for my geometry of interest (see Fig. **??**(b)), I only consider transmitted incomming fields.
The linear field inside the medium, $\mathbf{E}^\omega(\mathbf{r})$, is given by

$$\mathbf{E}^\omega(\mathbf{r}) = \left(E^s_{in}t^s_{vm}(\omega)\hat{\mathbf{s}} + E^p_{in}t^p_{vm}(\omega)\hat{\mathbf{p}}^m_-\right) e^{i(\mathbf{q}_{||}(\omega)\mathbf{r}_{||} - q^m_\perp(\omega)z)} = \hat{\mathbf{e}}^\omega|E_{in}|e^{i(\mathbf{q}_{||}(\omega)\mathbf{r}_{||} - q^m_\perp(\omega)z)}, \tag{2.8}$$

where the change of direction of the field is taken into account by replacing $q^v_\perp$ by $q^m_\perp$, $\hat{\mathbf{p}}^v_-$ by $\hat{\mathbf{p}}^m_-$ and $\hat{\mathbf{e}}^{\mathbf{in}}$ by $\hat{\mathbf{e}}^\omega$. Here $\hat{\mathbf{e}}^\omega = \left[\hat{\mathbf{s}}t^s_{vm}(\omega)\hat{\mathbf{s}} + \hat{\mathbf{p}}_- t^p_{vm}(\omega)\hat{\mathbf{p}}^v_-\right]\hat{\mathbf{e}}^{\mathbf{in}}$.

This incident field $\mathbf{E}^\omega$ leads to the apparition of a second-order polarisation in the medium denoted $\mathbf{P}^{(2)}$, given by

$$\mathbf{P}^{(2)}(\mathbf{r};2\omega) = \epsilon_0 \int_{-\infty}^{0} d^3\mathbf{r}' \int_{-\infty}^{0} d^3\mathbf{r}'' \overset{\leftrightarrow}{\chi}^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega) : \mathbf{E}^\omega(\mathbf{r}')\mathbf{E}^\omega(\mathbf{r}'') \tag{2.9}$$

where $\overset{\leftrightarrow}{\chi}^{(2)}$ is the second-order susceptibility of the medium.
Introducing the definition of the linear field inside the medium $\mathbf{E}^\omega$ in the previous expression gives directly

$$\mathbf{P}^{(2)}(\mathbf{r};2\omega) = \epsilon_0 \int_{-\infty}^{0} d^3\mathbf{r}' \int_{-\infty}^{0} d^3\mathbf{r}'' \overset{\leftrightarrow}{\chi}^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega) : \hat{\mathbf{e}}^\omega\hat{\mathbf{e}}^\omega|E_{in}|^2 e^{i(\mathbf{q}_{||}(\omega)(\mathbf{r}'_{||}+\mathbf{r}''_{||}) - q^m_\perp(\omega)(z'+z''))} \tag{2.10}$$

2.2 Harmonic field inside the material

The expression of the polarization is general and no approximation has been introduced at that stage. Following Ref. [**?**], instead of Eq. **??**, we consider a second-order polarisation having the the following form

$$\mathbf{P}^{(2)}(\mathbf{r};2\omega) = \epsilon_0 \overset{\leftrightarrow}{\chi}^{(2)s}(\omega) : \hat{\mathbf{e}}^\omega\hat{\mathbf{e}}^\omega, |E_{in}|^2 e^{2i(\mathbf{q}_{||}(\omega)\mathbf{r}_{||} - q^m_\perp(\omega)z)}\delta(z - z_0) \tag{2.11}$$

where the second-order susceptibility is replaced by a second order surface susceptibility $\overset{\leftrightarrow}{\chi}^{(2)s}$, assumed to be local and homogeneous in the plane of the surface. Moreover, the surface polarisation is assumed to be a polarisation sheet located at $z = z_0$.
In order to simplify notations, one define the quantity $\boldsymbol{\mathcal{P}}(2\omega)$

$$\mathbf{P}^{(2)}(\mathbf{r}; 2\omega) = \boldsymbol{\mathcal{P}}(2\omega) e^{i\mathbf{qr}} \delta(z - z_0), \tag{2.12}$$

where $\boldsymbol{\mathcal{P}}(2\omega) = \epsilon_0 \overset{\leftrightarrow}{\chi}^{(2)s}(\omega) : \hat{\mathbf{e}}^\omega \hat{\mathbf{e}}^\omega |E_{in}|^2$.
This is where the phenomenological treatment stems. This second-order polarisation becomes a source term in Maxwell equations that leads to the second harmonic field created at the surface of the non-linear medium. The reflected harmonic light will be thus given by the solution of the upward-propagating second harmonic wave in presence of the second order polarisation as a source term.
As pointed out by Mizrahi *et al.*[?], the position of the polarisation sheet ($z_0 = 0^-$ or $z_0 = 0^+$) only results in global normalisation of the reflection coefficients and does not modify the weight of the contributions of the different components of the $\overset{\leftrightarrow}{\chi}^{(2)s}$ tensor to the reflection coefficients. Unless stated differently, I use formulae with the polarisation sheet at $z_0 = 0^-$ throughout this thesis.

From the macroscopic Maxwell equations **??**, without magnetisation and in presence of a polarisation of the form **??**, one get the following set of equations

$$\begin{aligned} \nabla \times \mathbf{B}(\mathbf{r}, 2\omega) - i\frac{\tilde{\Omega}}{c}\epsilon \mathbf{E}(\mathbf{r}, 2\omega) &= i\frac{\tilde{\Omega}}{\epsilon_0 c}\mathbf{P}^{(2)}(\mathbf{r}, 2\omega) \\ \nabla \times \mathbf{E}(\mathbf{r}, 2\omega) - i\omega \mathbf{B}(\mathbf{r}, 2\omega) &= 0, \end{aligned} \tag{2.13}$$

where $\tilde{\Omega} = \frac{2\omega}{c}$.

The physical solution of Maxwell equations inside the medium (which exclude exponentially diverging waves) has the following form

$$\begin{aligned} \mathbf{E}^{2\omega}(\mathbf{r}) &= \left[\mathbf{E}^m_+(2\omega)\theta(z - z_0)e^{-iq^m_\perp(2\omega)z_0} + \mathbf{E}^m_-(2\omega)\theta(z_0 - z)e^{iq^m_\perp(2\omega)z_0} + \mathcal{E}(2\omega)\delta(z - z_0)\right] e^{i\mathbf{q}_{||}(2\omega)\mathbf{r}_{||}} \\ \mathbf{B}^{2\omega}(\mathbf{r}) &= \left[\mathbf{B}^m_+(2\omega)\theta(z - z_0)e^{-iq^m_\perp(2\omega)z_0} + \mathbf{B}^m_-(2\omega)\theta(z_0 - z)e^{iq^m_\perp(2\omega)z_0} + \mathcal{B}(2\omega)\delta(z - z_0)\right] e^{i\mathbf{q}_{||}(2\omega)\mathbf{r}_{||}}. \end{aligned} \tag{2.14}$$

We now search for the coefficients $E^m_{s\pm}(2\omega)$ et $E^m_{p\pm}(2\omega)$ of Eq. **??**, considering the following relations

$$\begin{aligned} &\mathcal{E} = \mathcal{E}_s\hat{\mathbf{s}} + \mathcal{E}_\kappa\hat{\kappa} + \mathcal{E}_\perp\hat{\mathbf{z}} \\ &\nabla\theta(z - z_0) = \hat{z}\delta(z - z_0) \\ &\nabla\delta(z - z_0) = \hat{z}\delta'(z - z_0) \end{aligned} \tag{2.15}$$

with δ' being the derivative of the Dirac δ distribution. Considering that different order of singularities (δ et δ') must cancel separately, we get, from the equation $\nabla \times \mathbf{E}(\mathbf{r}, 2\omega) - i\omega\mathbf{B}(\mathbf{r}, 2\omega) = 0$,

$$\begin{aligned}
&E^m_{p+} + E^m_{p-} + i\frac{q_{||}q^m}{q^m_\perp}\mathcal{E}_z - i\frac{2\omega q^m}{q^m_\perp}\mathcal{B}_s = 0 \\
&E^m_{s+} - E^m_{s-} - 2i\omega\mathcal{B}_\kappa = 0 \\
&\mathcal{E}_\kappa = \mathcal{E}_s = 0 \\
&\mathcal{B}_\perp = 0.
\end{aligned} \tag{2.16}$$

Doing the same for Eq. $\nabla \times \mathbf{B}(\mathbf{r}, 2\omega) - i\frac{\tilde{\Omega}}{c}\epsilon\mathbf{E}(\mathbf{r}, 2\omega) = i\frac{\tilde{\Omega}}{\epsilon_0 c}\mathbf{P}(\mathbf{r}, 2\omega)$ leads to the relations

$$\begin{aligned}
&E^m_{p+} - E^m_{p-} = i\frac{\tilde{\Omega}}{\epsilon^{1/2}\epsilon_0}\mathcal{P}_\kappa \\
&E^m_{s+} + E^m_{s-} = i\frac{\tilde{\Omega}q^m}{\epsilon^{1/2}\epsilon_0 q^m_\perp}\mathcal{P}_s \\
&\mathcal{E}_\perp = -\frac{1}{\epsilon_0\epsilon}\mathcal{P}_\perp \\
&\mathcal{B}_s = \mathcal{B}_\kappa = 0
\end{aligned} \tag{2.17}$$

Putting all together, and after some algebra, one finally get,

$$\begin{aligned}
&E^m_{s\pm}(2\omega) = E^m_s(2\omega) = \frac{i\tilde{\Omega}^2}{2\epsilon_0 q^m_\perp(2\omega)}\hat{\mathbf{s}}.\boldsymbol{\mathcal{P}}(2\omega) \\
&E^m_{p\pm}(2\omega) = \frac{i\tilde{\Omega}^2}{2\epsilon_0 q^m_\perp(2\omega)}\hat{\mathbf{p}}_\pm.\boldsymbol{\mathcal{P}}(2\omega).
\end{aligned} \tag{2.18}$$

2.3 Reflected harmonic light from a surface

We consider that we know the expression of the upward-propagating second harmonic field, called $\mathbf{E}^{2\omega}(\mathbf{r})$, induced by the second order polarisation inside the medium.

Assuming the expression of Eq. **??** for the second harmonic field, one get that

$$\mathbf{E}^{2\omega}(\mathbf{r}) = \frac{i\tilde{\Omega}^2}{2\epsilon_0 q^m_\perp(2\omega)}\boldsymbol{\mathcal{P}}(2\omega)e^{i(\mathbf{q}_{||}(2\omega)\mathbf{r}_{||} - q^m_\perp(2\omega)z)}. \tag{2.19}$$

At the boundary with the vacuum, this upward-propagating field is transmitted into the vacuum, yielding $\mathbf{E}_{out}(\mathbf{r}; 2\omega)$ which is the second harmonic field measured during the experiment.
Using that

$$\begin{aligned}
\mathbf{E}_{out}(\mathbf{r}; 2\omega) &= \frac{i\tilde{\Omega}^2}{2\epsilon_0 q^m_\perp(2\omega)}\hat{\mathbf{e}}^{\mathbf{out}}\left[\hat{\mathbf{s}}t^s_{mv}(2\omega)\hat{\mathbf{s}} + \hat{\mathbf{p}}_{\mathbf{0}^+}t^s_{mv}(2\omega)\hat{\mathbf{p}}^m_+\right]\boldsymbol{\mathcal{P}}e^{i(\mathbf{q}_{||}(2\omega)\mathbf{r}_{||} - q^m_\perp(2\omega)z)} \\
&= \frac{i\tilde{\Omega}^2}{2\epsilon_0 q^m_\perp(2\omega)}\hat{\mathbf{e}}^{\mathbf{2\omega}}\boldsymbol{\mathcal{P}}(2\omega)e^{i(\mathbf{q}_{||}(\mathbf{2\omega})\mathbf{r}_{||} - q^m_\perp(2\omega)z)},
\end{aligned} \tag{2.20}$$

one can finally express the intensity of the second harmonic field in the vacuum

$$I_{out}(2\omega) \quad = \quad 2c\epsilon_0|\mathbf{E}_{out}(2\omega)|^2 = \frac{1}{8c\epsilon_0}\left|\frac{\tilde{\Omega}^2}{q^v_\perp(2\omega)}\right|^2 \left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)}\right|^2 \left|\hat{\mathbf{e}}^{\mathbf{2}\omega}\overset{\leftrightarrow}{\chi}^{(2)s}:\hat{\mathbf{e}}^\omega\hat{\mathbf{e}}^\omega\right|^2 I^2_{in}(\omega). \qquad (2.21)$$

Inserting the definition of the $\tilde{\Omega}$ and $q^v_\perp(2\omega)$, one finally obtain the general form of the reflection coefficients

$$R(\theta,\phi) = \frac{\omega^2}{2c^3\epsilon_0}\frac{1}{cos^2(\theta)}\left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)}\right|^2\left|\hat{\mathbf{e}}^{\mathbf{2}\omega}\overset{\leftrightarrow}{\chi}^{(2)s}:\hat{\mathbf{e}}^\omega\hat{\mathbf{e}}^\omega\right|^2 \qquad (2.22)$$

This reflection coefficient has a unit in the S.I. system of cm^2/W. One has to be careful here that the second order susceptibility is label with the s superscript because it is a *surface* second order susceptibility, expressed in the S.I. unit system in pm^2/V whereas the second order susceptibility is expressed in pm/V in the S.I unit system. [4]

For obtaining the expression of the different reflection coefficients used in the litterature, one has to replace $\hat{\mathbf{e}}^{\mathbf{in}}$ and $\hat{\mathbf{e}}^{\mathbf{out}}$ by the wanted polarizations. For instance, the R_{ps} coefficient (sometime referred in the literature as p-in s-out), is obtained by choosing $\hat{\mathbf{e}}^{\mathbf{in}} = \hat{\mathbf{p}}^v_-$ and $\hat{\mathbf{e}}^{\mathbf{out}} = \hat{\mathbf{s}}$.
In that case, Eq. (**??**) becomes

$$R_{ps}(\theta,\phi) = \frac{\omega^2}{2c^3\epsilon_0}\frac{1}{cos^2(\theta)}\left|t^s_{mv}(2\omega)t^p_{vm}(\omega)^2\right|^2\left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)}\right|^2\left|\hat{\mathbf{s}}\overset{\leftrightarrow}{\chi}^{(2)s}:\hat{\mathbf{p}}^m_-(\omega)\hat{\mathbf{p}}^m_-(\omega)\right|^2. \qquad (2.24)$$

Then from Eq.(**??**) and the definition of $\hat{\kappa}$, one gets that

$$\begin{aligned}\hat{\mathbf{s}} &= sin(\phi)\hat{\mathbf{x}} - cos(\phi)\hat{\mathbf{y}} \\ \hat{\mathbf{p}}^m_\pm(\omega) &= \frac{c}{\sqrt{\epsilon(\omega)}\omega}\left[\mp q^m_\perp(\omega)cos(\phi)\hat{\mathbf{x}} \mp q^m_\perp(\omega)sin(\phi)\hat{\mathbf{y}} + q_{||}(\omega)\hat{\mathbf{z}}\right].\end{aligned} \qquad (2.25)$$

In the case of an arbitrary input polarisation along α angle (see Fig. **??**(a)), one has $\hat{\mathbf{e}}^{\mathbf{in}} = cos\alpha\hat{\mathbf{p}}^v_- + sin\alpha\hat{\mathbf{s}}$.
I consider now the special case of a $4mm$ or higher symmetry surface, where the only non-zero components of the $\chi^{(2)}$ tensor are $\chi^{(2)}_{\|\|\perp} = \chi^{(2)}_{xxz} = \chi^{(2)}_{yyz}$, $\chi^{(2)}_{\perp\|\|} = \chi^{(2)}_{zxx} = \chi^{(2)}_{zyy}$ and $\chi^{(2)}_{\perp\perp\perp} = \chi^{(2)}_{zzz}$.
This symmetry corresponds for instance to the Si(001)1x1:2H (dihydride) silicon surface. The same components also appears for the reflection coefficients of the clean Si(001)2×1 or the Si(001)2×1:H surfaces (see Chapter. **??** for more details concerning that surface), even if they have less symmetries than the dihydride surface. [5]

[4] In atomic units, Eq. **??** reads

$$R(\theta,\phi) = \frac{32\pi^3\omega^2}{c^3}\frac{1}{cos^2(\theta)}\left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)}\right|^2\left|\hat{\mathbf{e}}^{2\omega}\overset{\leftrightarrow}{\chi}^{(2)s}:\hat{\mathbf{e}}^\omega\hat{\mathbf{e}}^\omega\right|^2. \qquad (2.23)$$

[5] As explained by Sipe *et al.* in Ref. [**?**], this two surfaces exhibit a macroscopic symmetry, which is different from the single domain symmetry. For instance, the Si(001)2×1 surface has equal population of m-symmetry (1×2) and (2×1) domains of Si dimers. It results in a macroscopic $p2mm$ symmetry for the surface, from the point of view of the laser spot. Even if one was able to produce large enough domain, bigger than the laser spot size, this does not correspond to industrial Si surfaces, which are of major interest. This macroscopic symmetry is confirmed experimentally by Rotational Anisotropy

From previous equations, one obtain the expression for the four reflection coefficients

$$R_{pp}(\theta) = \frac{2\omega^2}{c^3\epsilon_0} tan^2\theta \left| \frac{t^p_{mv}(2\omega)t^p_{vm}(\omega)^2}{\sqrt{\epsilon(2\omega)}\epsilon(\omega)} \right|^2 \left| \frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)} \right|^2 \times \left| sin^2\theta\chi^{(2)}_{\perp\perp\perp} + \frac{c^2}{\omega^2} q^m_\perp(\omega)^2 \chi^{(2)}_{\perp\|\|} - \frac{c^2}{\omega^2} q^m_\perp(2\omega) q^m_\perp(\omega) \chi^{(2)}_{\|\|\perp} \right|^2 \tag{2.26}$$

$$R_{sp}(\theta) = \frac{2\omega^2}{c^3\epsilon_0} tan^2\theta \left| \frac{t^p_{mv}(2\omega)t^s_{vm}(\omega)^2}{\sqrt{\epsilon(2\omega)}} \right|^2 \left| \frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)} \right|^2 \left| \chi^{(2)}_{\perp\|\|} \right|^2 \tag{2.27}$$

$$R_{ps}(\theta,\phi) = R_{ss}(\theta,\phi) = 0 \tag{2.28}$$

Due to symmetries, the two coefficients corresponding to an output s-polarisation are zero. Moreover R_{pp} and R_{sp} do not depend on the azimuthal angle ϕ, due to the in-plane isotropy of a surface with a symmetry $4mm$. This result has been used, e.g. in Ref. [**?**, **?**], to separate the contributions to the signal from the surface and from the bulk for the dihydride surface. Also the R_{pp} coefficient contains contributions from all the non-zero components.
The general expression of this coefficients and the expression in the case of a m symmetry are given in appendix **??**.

2.4 Bulk contribution

So far, I do not have discussed the contribution from the bulk to the reflected signal. There is two different cases in which the bulk can contribute to the reflected harmonic waves : i) the case of the non-centrosymmetric bulk, which is the case for instance of GaAs. In that case, the signal is dominated by the bulk contribution. ii) the case of centrosymmetric materials, where the dipolar contribution vanishes, but not the quadrupolar contribution. The quadrupolar contribution has been found non-negligible compared to the surface signal [**?**]Ref Ref Ref. Both cases can be treated using the same approach that I present here. Following Ref. [**?**], I first approximate the nonlinear polarisation in the medium by

$$\mathbf{P}^{(2)}(\mathbf{r};2\omega) = \epsilon_0 \overset{\leftrightarrow}{\chi}^{(2)b} : \mathbf{E}^\omega(\mathbf{r})\mathbf{E}^\omega(\mathbf{r}) + \epsilon_0\gamma_B \nabla[\mathbf{E}^\omega(\mathbf{r}).\mathbf{E}^\omega(\mathbf{r})], \tag{2.29}$$

where $\mathbf{E}^\omega(\mathbf{r})$ is the fundamental electric field inside the material, $\overset{\leftrightarrow}{\chi}^{(2)b}$ is the bulk second-order susceptibility tensor and γ_B serves for describing the quadrupolar response of the bulk. Here I have choosen the simplest case for the quadrupolar contribution. More complicated expressions can be obtain addind extra terms as in Ref. Ref PRL 51 1983.

SHG (RASHG), where one can analyse the symmetries of the surface.

Introducing the expression of $\mathbf{E}^\omega(\mathbf{r})$ in the expression of the polarization gives

$$\mathbf{P}^{(2)}(\mathbf{r};2\omega)=\epsilon_0\left(\overset{\leftrightarrow(2)b}{\chi}+\gamma_B\left[2iq_{\|}(\omega)\hat{\kappa}-2iq^m_\perp(\omega)\hat{\mathbf{z}}\right]\right):\hat{\mathbf{e}}^\omega\hat{\mathbf{e}}^\omega|E_{in}|^2e^{2i(\mathbf{q}_{\|}(\omega)\mathbf{r}_{\|}-q^m_\perp(\omega)z)}. \tag{2.30}$$

As explained in Ref. [?], this polarisation can be seen has a sum of individual sheets of polarisation, as introduced previously, located at a distance z from the surface. This allows us to use the same formalism to describe the harmonic field generated inside the medium. At the interface with the vacuum, the field is modified according to Fresnel coefficients. The electric field that reach the detector is thus $\mathbf{E}_{out}(z;2\omega)=\mathbf{E}_{out}(z=0^+;2\omega)e^{iq^v_\perp(2\omega)z}=\mathbf{E}_{out}(2\omega)e^{iq^v_\perp(2\omega)z}$ with

$$\mathbf{E}_{out}(2\omega)=\frac{i\tilde{\Omega}^2}{2\epsilon_0q^m_\perp(2\omega)}\hat{\mathbf{e}}^{\mathbf{out}}\left[\hat{\mathbf{s}}t^s_{mv}(2\omega)\hat{\mathbf{s}}+\hat{\mathbf{p}}^v_+t^s_{mv}(2\omega)\hat{\mathbf{p}}^v_+\right]\int_{-\infty}^0dz'e^{-iq^m_\perp(2\omega)z'}\mathbf{P}^{(2)}(z';2\omega), \tag{2.31}$$

where $e^{-iq^m_\perp(2\omega)z'}$ describes the propagation in the medium from $-z'$ to the interface at 0^-. Coefficients are identicals to the case of a surface polarisation. In the following, I focus on the example of a cubic symmetry for a medium that lack inversion symmetry. As mentioned previously, this case apply to GaAs and has been used in Ref. [?] for extracting the $\chi^{(2)}_{xyz}$ component from the experimental reflection spectrum. The contribution of the quadrupolar term in a centro-symmetric material can be obtained similarly.

In the case of a cubic material, the second-order susceptibility has only one non-zero component, $\chi^{(2)}_{xyz}$.

The reflection coefficients in that reads have the general form

$$R(\theta,\phi)=\frac{2\omega^2}{c^3\epsilon_0}\frac{1}{cos^2\theta}\left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)[q^m_\perp(2\omega)+2q^m_\perp(\omega)]}\right|^2\left|\hat{\mathbf{e}}^{\mathbf{2}\omega}\overset{\leftrightarrow(2)}{\chi}:\hat{\mathbf{e}}^\omega\hat{\mathbf{e}}^\omega\right|^2 \tag{2.32}$$

From that we get directly the four usual reflection coefficients

$$\begin{aligned}R_{pp}(\theta,\phi)&=\frac{2\omega^2}{c^3\epsilon_0}tan^2\theta sin^2(2\phi)\left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)}\right|^2\left|\frac{t^p_{mv}(2\omega)t^p_{vm}(\omega)^2}{\sqrt{\epsilon(2\omega)}\epsilon(\omega)}\right|^2\\&\times\left|\frac{\frac{c^2}{\omega^2}q^m_\perp(\omega)(q^m_\perp(\omega)-q^m_\perp(2\omega))}{[q^m_\perp(2\omega)+2q^m_\perp(\omega)]}\right|^2\left|\chi^{(2)}_{xyz}\right|^2\end{aligned} \tag{2.33}$$

$$\begin{aligned}R_{ps}(\theta,\phi)&=\frac{8}{c\epsilon_0}tan^2\theta cos^2(2\phi)\left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)}\right|^2\left|\frac{t^s_{mv}(2\omega)t^p_{vm}(\omega)^2}{\epsilon(\omega)}\right|^2\\&\times\left|\frac{q^m_\perp(\omega)}{[q^m_\perp(2\omega)+2q^m_\perp(\omega)]}\right|^2\left|\chi^{(2)}_{xyz}\right|^2\end{aligned} \tag{2.34}$$

$$R_{sp}(\theta,\phi)=\frac{2\omega^2}{c^3\epsilon_0}tan^2\theta sin^2(2\phi)\left|\frac{t^p_{mv}(2\omega)t^s_{vm}(\omega)^2}{\sqrt{\epsilon(2\omega)}}\right|^2\left|\frac{q^v_\perp(2\omega)}{q^m_\perp(2\omega)[q^m_\perp(2\omega)+2q^m_\perp(\omega)]}\right|^2\left|\chi^{(2)}_{xyz}\right|^2 \tag{2.35}$$

$$R_{ss}(\theta,\phi)=0 \tag{2.36}$$

As one can see here, this reflection coefficients depend on both the incident and the rotational angles.

Summary

In this chapter, I have reported the derivation of the expression of the generalized reflection coefficients. They describe how second-harmonic light is generated by reflection of light from a surface of non-linear media. We have seen that a second-order polarisation is induced by incident light and how that polarisation, acting as a source term for the Maxwell equations, yields a second harmonic field, reflected from the surface. This formalism allows one to treat both bulk and surface dipolar contributions and also the bulk quadrupolar contribution, for any combination of input and output polarisation of the light. To finish, if one wants to obtain the contributions of the bulk and the surface at the same time, the reflection coefficients can be obtained by the mean of the Eq. **??** using an effective polarisation given by

$$\mathbf{P}^{(2)}(\mathbf{r};2\omega) = \epsilon_0 \left(\overset{\leftrightarrow}{\chi}^{(2)s}(\omega)\delta(z-z_0) + \frac{\overset{\leftrightarrow}{\chi}^{(2)}(\omega) + \gamma_B(\omega)\left[2iq_{\|}(\omega)\hat{\boldsymbol{\kappa}} - 2iq_{\perp}^{m}(\omega)\hat{\mathbf{z}}\right]}{\left[q_{\perp}^{m}(2\omega) + 2q_{\perp}^{m}(\omega)\right]} \right) : \hat{\mathbf{e}}^{\omega}\hat{\mathbf{e}}^{\omega}|E_{in}|^2 e^{2i(\mathbf{q}_{||}\mathbf{r}_{||} - q_z^m z)}, \tag{2.37}$$

where one can easily use a more sophisticated expression for the quadrupolar contribution.
The most difficult part still remains : the *ab initio* description of the macroscopic second-order response function of the bulk and the surface part of the material. In the next chapter, I briefly present the (time-dependent) density functional theory and how this framework allows us to compute the density response function $\chi^{(2)}$ from the linear response theory.