A treatise on phenomenological models of surface second-harmonic generation from crystalline surfaces

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Contents

Chapter 1

SHG Yield

1.1 Three layer model for SHG yield, without Multiple Reflections

In this section we derive the formulas required for the calculation of the SHG yield, defined by

$$R(\omega) = \frac{I(2\omega)}{I^2(\omega)},$$

with the intensity

$$I(\omega) = \frac{c}{2\pi}|E(\omega)|^2,$$

There are several ways to calculate R, one of which is the procedure followed by Cini [1]. This approach calculates the nonlinear susceptibility and at the same time the radiated fields. However, we present an alternative derivation based in the work of Mizrahi and Sipe [2], since the derivation of the three-layer-model is straightforward. Within our level of approximation this is the best model that we can use. In this scheme, we assume that the SH conversion takes place in a thin layer, just below the surface, that is characterized by a surface dielectric function $\epsilon_\ell(\omega)$. This layer is below vacuum and sits on top of the bulk characterized by $\epsilon_b(\omega)$ (see Fig. 1.1). The nonlinear polarization immersed in the thin layer, will radiate an electric field directly into vacuum and also into the bulk. This bulk directed field, will be reflected back into vacuum. Thus, the total field radiated into vacuum will be the sum of these two contributions (see Fig. 1.1). We decompose the field into s and p polarizations, then the electric field radiated by a polarization sheet,

$$\mathcal{P}_i(2\omega) = \chi_{ijk}E_j(\omega)E_k(\omega), \tag{1.1}$$

is given by [2],

$$(E_{p\pm}, E_s) = (\frac{2\pi i\tilde{\omega}^2}{w}\,\hat{\mathbf{p}}_\pm \cdot \boldsymbol{\mathcal{P}}, \frac{2\pi i\tilde{\omega}^2}{w}\,\hat{\mathbf{s}} \cdot \boldsymbol{\mathcal{P}}),$$

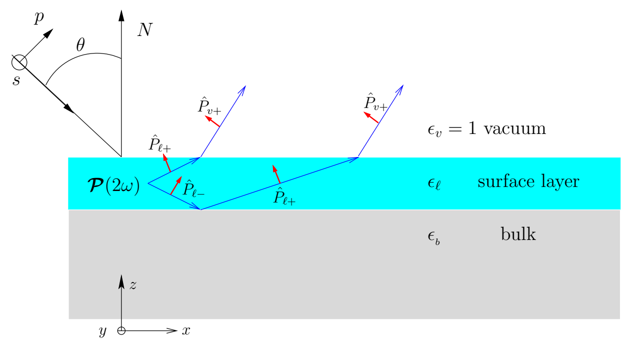

Figure 1.1: Sketch of the three layer model for SHG. Vacuum is on top with $\epsilon = 1$, the layer with nonlinear polarization $\mathbf{P}(2\omega)$ ischaracterized with $\epsilon_\ell(\omega)$ and the bulk with $\epsilon_b(\omega)$. In the dipolar approximation the bulk does not radiate SHG. The thin arrows are along the direction of propagation, and the unit vectors for p-polarization are denoted with thick arrows (capital letters denote SH components). The unit vector for s-polarization points along $-y$ (out of the page).

where $\hat{\mathbf{s}}$ and $\hat{\mathbf{p}}_\pm$ are the unitary vectors for s and p polarization, respectively, and the $\pm$ refers to upward ($+$) or downward ($-$) direction of propagation. Also, $\tilde{\omega} = \omega/c$ and $w_i = \tilde{\omega} k_i$, with

$$k_i(\omega) = \sqrt{\epsilon_i(\omega) - \sin^2\theta_i},$$

where $i = v, \ell, b$, with

$$\hat{\mathbf{p}}_{i\pm} = \frac{\mp k_i(\omega)\hat{\mathbf{x}} + \sin\theta_i \hat{\mathbf{z}}}{\sqrt{\epsilon_i(\omega)}}$$

In the above equations z is the direction perpendicular to the surface that points towards the vacuum, x is parallel to the surface, and θ is the angle of incidence, where the plane of incidence is chosen as the xz plane (see Fig. 1.1), thus $\hat{\mathbf{s}} = -\hat{\mathbf{y}}$. The function $k_i(\omega)$ is the projection of the wave vector perpendicular to the surface. As we see from Fig. 1.1, the SH field is refracted at the layer-vacuum interface (ℓv), and reflected from the layer-bulk (ℓb) interface, thus we can define the transmission, $\mathbf{T}$, and reflection, $\mathbf{R}$, tensors as,

$$\mathbf{T}_{\ell v} = \hat{\mathbf{s}} T_s^{\ell v} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{\ell v} \hat{\mathbf{P}}_{\ell+},$$

and

$$\mathbf{R}_{\ell b} = \hat{\mathbf{s}} R_s^{\ell b} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell+} R_p^{\ell b} \hat{\mathbf{P}}_{\ell-},$$

where variables in capital letters are evaluated at the harmonic frequency 2ω. Notice that since $\hat{\mathbf{s}}$ is independent of ω, then $\hat{\mathbf{S}} = \hat{\mathbf{s}}$. The Fresnel factors, T_i, R_i, for $i = s, p$ polarization, are evaluated at the appropriate interface ℓv or ℓb, and will be given below. The extra subscript in $\hat{\mathbf{P}}$ denotes the corresponding dielectric function to be used in its evaluation, i.e. $\epsilon_v = 1$ for vacuum (v), ϵ_ℓ for the layer (ℓ), and ϵ_b for the bulk (b). Therefore, the total radiated field at 2ω is

$$\begin{aligned}\mathbf{E}(2\omega) = {} & E_s(2\omega)\left(\mathbf{T}^{\ell v} + \mathbf{T}^{\ell v}\cdot\mathbf{R}^{\ell b}\right)\cdot\hat{\mathbf{s}} \\ & + E_{p+}(2\omega)\mathbf{T}^{\ell v}\cdot\hat{\mathbf{P}}_{\ell +} + E_{p-}(2\omega)\mathbf{T}^{\ell v}\cdot\mathbf{R}^{\ell b}\cdot\hat{\mathbf{P}}_{\ell -}.\end{aligned}$$

The first term is the transmitted s-polarized field, the second one is the reflected and then transmitted s-polarized field and the third and fourth terms are the equivalent fields for p-polarization. The transmission is from the layer into vacuum, and the reflection between the layer and the bulk. After some simple algebra, we obtain

$$\mathbf{E}(2\omega) = \frac{2\pi i\tilde{\Omega}}{K_\ell}\mathbf{H}_\ell\cdot\boldsymbol{\mathcal{P}}(2\omega),$$

where,

$$\mathbf{H}_\ell = \hat{\mathbf{s}}\,T_s^{\ell v}\left(1 + R_s^{\ell b}\right)\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}T_p^{\ell v}\left(\hat{\mathbf{P}}_{\ell +} + R_p^{\ell b}\hat{\mathbf{P}}_{\ell -}\right). \tag{1.2}$$

The magnitude of the radiated field is given by $E(2\omega) = \hat{\mathbf{e}}^{\mathrm{out}}\cdot\mathbf{E}(2\omega)$, where $\hat{\mathbf{e}}^{\mathrm{out}}$ is the polarization vector of the radiated field, for instance $\hat{\mathbf{s}}$ or $\hat{\mathbf{P}}_{v+}$. Then, we write

$$\begin{aligned}\hat{\mathbf{P}}_{\ell +} + R_p^{\ell b}\hat{\mathbf{P}}_{\ell -} &= \frac{\sin\theta_{\mathrm{in}}\hat{\mathbf{z}} - K_\ell\hat{\mathbf{x}}}{\sqrt{\epsilon_\ell(2\omega)}} + R_p^{\ell b}\frac{\sin\theta_{\mathrm{in}}\hat{\mathbf{z}} + K_\ell\hat{\mathbf{x}}}{\sqrt{\epsilon_\ell(2\omega)}} \\ &= \frac{1}{\sqrt{\epsilon_\ell(2\omega)}}\left(\sin\theta_{\mathrm{in}}(1 + R_p^{\ell b})\hat{\mathbf{z}} - K_\ell(1 - R_p^{\ell b})\hat{\mathbf{x}}\right) \\ &= \frac{T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}\left(\epsilon_b(2\omega)\sin\theta_{\mathrm{in}}\hat{\mathbf{z}} - \epsilon_\ell(2\omega)K_b\hat{\mathbf{x}}\right),\end{aligned}$$

where using

$$\begin{aligned}1 + R_s^{\ell b} &= T_s^{\ell b} \\ 1 + R_p^{\ell b} &= \sqrt{\frac{\epsilon_b(2\omega)}{\epsilon_\ell(2\omega)}}T_p^{\ell b} \\ 1 - R_p^{\ell b} &= \sqrt{\frac{\epsilon_\ell(2\omega)}{\epsilon_b(2\omega)}}\frac{K_b}{K_\ell}T_p^{\ell b} \\ T_p^{\ell v} &= \frac{K_\ell}{K_v}T_p^{v\ell} \\ T_s^{\ell v} &= \frac{K_\ell}{K_v}T_s^{v\ell},\end{aligned} \tag{1.3}$$

we can write

$$E(2\omega) = \frac{4\pi i\omega}{cK_v}\hat{\mathbf{e}}^{\mathrm{out}}\cdot\mathbf{H}_\ell\cdot\boldsymbol{\mathcal{P}}(2\omega) = \frac{4\pi i\omega}{cK_v}\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\mathcal{P}}(2\omega).$$

where,

$$\mathbf{e}_\ell^{2\omega} = \hat{\mathbf{e}}^{\text{out}} \cdot \left[\hat{\mathbf{s}} T_s^{v\ell} T_s^{\ell b} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} \frac{T_p^{v\ell} T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega) \sin\theta_{\text{in}} \hat{\mathbf{z}} - \epsilon_\ell(2\omega) K_b \hat{\mathbf{x}} \right) \right]. \tag{1.4}$$

We pause here to reduce above result to the case where the nonlinear polarization $\mathbf{P}(2\omega)$ radiates from vacuum instead from the layer ℓ. For such case we simply take $\epsilon_\ell(2\omega) = 1$ and $\ell = v$ ($T_{s,p}^{\ell v} = 1$), to get

$$\mathbf{e}_v^{2\omega} = \hat{\mathbf{e}}^{\text{out}} \cdot \left[\hat{\mathbf{s}} T_s^{vb} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} \frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega) \sin\theta_{\text{in}} \hat{\mathbf{z}} - K_b \hat{\mathbf{x}} \right) \right], \tag{1.5}$$

which agrees with Eq. (3.8) of Ref. [2].

In the three layer model the nonlinear polarization is located in layer ℓ, and then we evaluate the fundamental field required in Eq. (1.1) in this layer as well, then we write

$$\mathbf{E}_\ell(\omega) = E_0 \left(\hat{\mathbf{s}} t_s^{v\ell} (1 + r_s^{\ell b}) \hat{\mathbf{s}} + \hat{\mathbf{p}}_{\ell-} t_p^{v\ell} \hat{\mathbf{p}}_{v-} + \hat{\mathbf{p}}_{\ell+} t_p^{v\ell} r_p^{\ell b} \hat{\mathbf{p}}_{v-} \right) \cdot \hat{\mathbf{e}}^{\text{in}} = E_0 \mathbf{e}_\ell^\omega, \tag{1.6}$$

and following the steps that lead to Eq. (1.4), we find that

$$\mathbf{e}_\ell^\omega = \left[\hat{\mathbf{s}} t_s^{v\ell} t_s^{\ell b} \hat{\mathbf{s}} + \frac{t_p^{v\ell} t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}} \left(\epsilon_b(\omega) \sin\theta_{\text{in}} \hat{\mathbf{z}} + \epsilon_\ell(\omega) k_b \hat{\mathbf{x}} \right) \hat{\mathbf{p}}_{v-} \right] \cdot \hat{\mathbf{e}}^{\text{in}}. \tag{1.7}$$

If we would like to evaluate the fields in the bulk, instead of the layer ℓ, we simply take $\epsilon_\ell(\omega) = \epsilon_b(\omega)$ ($t_{s,p}^{\ell b} = 1$), to obtain

$$\mathbf{e}_b^\omega = \left[\hat{\mathbf{s}} t_s^{vb} \hat{\mathbf{s}} + \frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}} \left(\sin\theta_{\text{in}} \hat{\mathbf{z}} + k_b \hat{\mathbf{x}} \right) \hat{\mathbf{p}}_{v-} \right] \cdot \hat{\mathbf{e}}^{\text{in}}, \tag{1.8}$$

that is in agreement with Eq. (3.5) of Ref. [2].

With $\mathbf{e}^\omega$ we can write Eq. (1.1) as

$$\boldsymbol{\mathcal{P}}(2\omega) = E_0^2 \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega,$$

and then from Eq. (1.1) we obtain that

$$\begin{aligned}
|E(2\omega)|^2 &= |E_0|^4 \frac{16\pi^2\omega^2}{c^2 K_v^2} \left| \mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega \right|^2 \\
\frac{c}{2\pi} |E(2\omega)|^2 &= \frac{32\pi^3\omega^2}{c^3 \cos^2\theta_{\text{in}}} \left| \mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega \right|^2 \left(\frac{c}{2\pi} |E_0|^2 \right)^2, \\
I(2\omega) &= \frac{32\pi^3\omega^2}{c^3 \cos^2\theta_{\text{in}}} \left| \mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega \right|^2 I^2(\omega), \\
R(2\omega) &= \frac{32\pi^3\omega^2}{c^3 \cos^2\theta_{\text{in}}} \left| \mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega \right|^2,
\end{aligned} \tag{1.9}$$

as the SHG yield. At this point we mention that to recover the results of Ref. [2] which are equivalent of those of Ref. [3], we take $\mathbf{e}_\ell^{2\omega} \to \mathbf{e}_v^{2\omega}$, $\mathbf{e}_\ell^{\omega} \to \mathbf{e}_b^{\omega}$ and then

$$R(2\omega) = \frac{32\pi^3\omega^2}{c^3\cos^2\theta_{\rm in}} \left|\mathbf{e}_v^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega}\right|^2, \tag{1.10}$$

will give the SHG yield of a nonlinear polarization sheet radiating from vacuum on top of the surface and where the fundamental field is evaluated below the surface that is characterized by $\epsilon_b(\omega)$.

To complete the required formulas, we write down the Fresnel factors,

$$t_s^{ij}(\omega) = \frac{2k_i(\omega)}{k_i(\omega)+k_j(\omega)}, \qquad t_p^{ij}(\omega) = \frac{2k_i(\omega)\sqrt{\epsilon_i(\omega)\epsilon_j(\omega)}}{k_i(\omega)\epsilon_j(\omega)+k_j(\omega)\epsilon_i(\omega)},$$
$$r_s^{ij}(\omega) = \frac{k_i(\omega)-k_j(\omega)}{k_i(\omega)+k_j(\omega)}, \qquad r_p^{ij}(\omega) = \frac{k_i(\omega)\epsilon_j(\omega)-k_j\epsilon_i(\omega)}{k_i(\omega)\epsilon_j(\omega)+k_j(\omega)\epsilon_i(\omega)}.$$

1.2 $\mathcal{R}$ for different polarization cases

1.2.1 $\mathcal{R}_{pP}$

We develop five different scenarios for $\mathcal{R}_{pP}$ that explore different cases for where the polarization and fundamental fields are located. In all these scenarios, we use $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{p}}_{v-}$ in Eq. (1.7), and $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{P}}_{v+}$ in Eq. (1.4).

This scenario involves $\mathcal{P}(2\omega)$ and the fundamental fields to be taken in a thin layer of material below the surface, which we designate as ℓ. Thus,

$$\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega} \equiv \Gamma_{pP}^{\ell}\, r_{pP}^{\ell},$$

where

$$\begin{aligned} r_{pP}^{\ell} &= \epsilon_b(2\omega)\sin\theta_{\rm in}\Big(\epsilon_b^2(\omega)\sin^2\theta_{\rm in}\chi_{zzz} + \epsilon_\ell^2(\omega)k_b^2\chi_{zxx}\Big) \\ &\quad - \epsilon_\ell(2\omega)\epsilon_\ell(\omega)k_bK_b\Big(2\epsilon_b(\omega)\sin\theta_{\rm in}\chi_{xxz} + \epsilon_\ell(\omega)k_b\chi_{xxx}\cos(3\phi)\Big), \end{aligned} \tag{1.11}$$

and

$$\Gamma_{pP}^{\ell} = \frac{T_p^{\ell v}T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2. \tag{1.12}$$

1.2.2 $\mathcal{R}_{pS}$

To obtain $R_{pS}(2\omega)$ we use $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{p}}_{v-}$ in Eq. (1.7), and $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{S}}$ in Eq. (1.4). We also use the unit vectors defined in Eqs. (A.1) and (A.2). Substituting, we get

$$\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega} \equiv \Gamma_{sP}^{\ell}\, r_{sP}^{\ell},$$

where

$$r_{pS}^{\ell} = -\epsilon_\ell^2(\omega)k_b^2\sin 3\phi\chi_{xxx}, \tag{1.13}$$

and

$$\Gamma^{\ell}_{pS} = T^{v\ell}_{s} T^{\ell b}_{s} \left(\frac{t^{v\ell}_{p} t^{\ell b}_{p}}{\epsilon_{\ell}(\omega)\sqrt{\epsilon_{b}(\omega)}} \right)^{2}. \tag{1.14}$$

In order to reduce above result to that of Ref. [2] and [3], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_{\ell}(2\omega) = 1$, $T^{v\ell}_{s} = 1$, $T^{\ell b}_{s} = T^{vb}_{s}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_{\ell}(\omega) = \epsilon_{b}(\omega)$, $t^{v\ell}_{p} = t^{vb}_{p}$, and $t^{\ell b}_{p} = 1$. With these choices,

$$r^{b}_{pS} = -k^{2}_{b} \sin 3\phi \chi_{xxx},$$

and

$$\Gamma^{b}_{pS} = T^{vb}_{s} \left(\frac{t^{vb}_{p}}{\sqrt{\epsilon_{b}(\omega)}} \right)^{2}.$$

1.2.3 $\mathcal{R}_{sP}$

To obtain $R_{sP}(2\omega)$ we use $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{s}}$ in Eq. (1.7), and $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{P}}_{v+}$ in Eq. (1.4). We also use the unit vectors defined in Eqs. (A.1) and (A.2). Substituting, we get

$$\mathbf{e}^{2\omega}_{\ell} \cdot \boldsymbol{\chi} : \mathbf{e}^{\omega}_{\ell} \mathbf{e}^{\omega}_{\ell} \equiv \Gamma^{\ell}_{sP}\, r^{\ell}_{sP},$$

where

$$r^{\ell}_{sP} = \epsilon_{b}(2\omega) \sin\theta_{\rm in} \chi_{zxx} + \epsilon_{\ell}(2\omega) K_{b} \chi_{xxx} \cos 3\phi, \tag{1.15}$$

and

$$\Gamma^{\ell}_{sP} = \frac{T^{\ell v}_{p} T^{\ell b}_{p} \left(t^{v\ell}_{s} t^{\ell b}_{s}\right)^{2}}{\epsilon_{\ell}(2\omega)\sqrt{\epsilon_{b}(2\omega)}}. \tag{1.16}$$

In order to reduce above result to that of Ref. [2] and [3], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_{\ell}(2\omega) = 1$, $T^{v\ell}_{p} = 1$, $T^{\ell b}_{p} = T^{vb}_{p}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_{\ell}(\omega) = \epsilon_{b}(\omega)$, $t^{v\ell}_{s} = t^{vb}_{s}$, and $t^{\ell b}_{s} = 1$. With these choices,

$$r^{b}_{sP} = \epsilon_{b}(2\omega) \sin\theta_{\rm in} \chi_{zxx} + K_{b} \chi_{xxx} \cos 3\phi,$$

and

$$\Gamma^{b}_{sP} = \frac{T^{vb}_{p} (t^{vb}_{s})^{2}}{\sqrt{\epsilon_{b}(2\omega)}}.$$

1.2.4 $\mathcal{R}_{sS}$

For $\mathcal{R}_{sS}$ we have that $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{s}}$ and $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{S}}$. This leads to

$$\mathbf{e}^{2\omega}_{\ell} \cdot \boldsymbol{\chi} : \mathbf{e}^{\omega}_{\ell} \mathbf{e}^{\omega}_{\ell} \equiv \Gamma^{\ell}_{sS}\, r^{\ell}_{sS},$$

where

$$r^{\ell}_{sS} = \chi_{xxx} \sin 3\phi, \tag{1.17}$$

iF	Γ^{ℓ}_{iF}	r^{ℓ}_{iF}
pP	$\frac{T_p^{v\ell}}{N_\ell}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{n_\ell^2 n_b}\right)^2$	$R_p^{M+}\sin\theta_0(n_b^4\sin^2\theta_0\chi_{zzz}+n_\ell^4 w_b^2\chi_{zxx})$ $-R_p^{M-}n_\ell^2 w_b W_\ell(2n_b^2\sin\theta_0\chi_{xxz}+n_\ell^2 w_b\chi_{xxx}\cos 3\phi)$
pS	$T_s^{v\ell}R_s^{M+}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{n_\ell^2 n_b}\right)^2$	$-n_\ell^4 w_b^2\chi_{xxx}\sin 3\phi$
sP	$\frac{T_p^{v\ell}}{N_\ell}\left(t_s^{v\ell}t_s^{\ell b}\right)^2$	$R_p^{M+}\sin\theta_0\chi_{zxx}+R_p^{M-}W_\ell\chi_{xxx}\cos 3\phi$
sS	$T_s^{v\ell}R_s^{M+}\left(t_s^{v\ell}t_s^{\ell b}\right)^2$	$\chi_{xxx}\sin 3\phi$

Table 1.1: The expressions needed to calculate the SHG yield for the (111) surface, for each polarization case.

and

$$\Gamma^{\ell}_{sS} = T_s^{v\ell}T_s^{\ell b}\left(t_s^{v\ell}t_s^{\ell b}\right)^2. \tag{1.18}$$

In order to reduce above result to that of Ref. [2] and [3], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_s^{v\ell} = 1$, $T_s^{\ell b} = T_s^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_s^{v\ell} = t_s^{vb}$, and $t_s^{\ell b} = 1$. With these choices,

$$r^b_{sS} = \chi_{xxx}\sin 3\phi,$$

and

$$\Gamma^b_{sS} = T_s^{vb}\left(t_s^{vb}\right)^2.$$

1.2.5 Summary

We present the final expressions for each polarization case in Table 1.1.

Appendix A

Derived expressions for the SHG yield

A.1 Some useful expressions

We are interested in finding

$$\Upsilon = \mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega}$$

for each different polarization case. We choose the plane of incidence along the $\boldsymbol{\kappa}z$ plane, and define

$$\hat{\boldsymbol{\kappa}} = \cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}}, \tag{A.1}$$

and

$$\hat{\mathbf{s}} = -\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}, \tag{A.2}$$

where ϕ the angle with respect to the x axis.

A.1.1 2ω terms

Including multiple reflecions, the $\mathbf{e}_\ell^{2\omega}$ term is

$$\mathbf{e}_\ell^{2\omega} = \hat{\mathbf{e}}^{\mathrm{out}} \cdot \left[\hat{\mathbf{s}}T_s^{v\ell}R_s^{M+}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\frac{T_p^{v\ell}}{N_\ell}\left(\sin\theta_0 R_p^{M+}\hat{\mathbf{z}} - W_\ell R_p^{M-}\hat{\boldsymbol{\kappa}}\right)\right], \tag{A.3}$$

and neglecting the multiple reflections reduces this expression to

$$\mathbf{e}_\ell^{2\omega} = \hat{\mathbf{e}}^{\mathrm{out}} \cdot \left[\hat{\mathbf{s}}T_s^{v\ell}T_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\frac{T_p^{v\ell}T_p^{\ell b}}{N_\ell^2 N_b}\left(N_b^2\sin\theta_0\hat{\mathbf{z}} - N_\ell^2 W_b\hat{\mathbf{x}}\right)\right]. \tag{A.4}$$

We first expand these equations for clarity. Substituting Eqs. (A.1) and (A.2) into Eq. (A.3),

$$\mathbf{e}_\ell^{2\omega} = \hat{\mathbf{e}}^{\mathrm{out}} \cdot \Bigg[\hat{\mathbf{s}} T_s^{v\ell} R_s^{M+} \left(-\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}\right) + \hat{\mathbf{P}}_{v+} \frac{T_p^{v\ell}}{N_\ell} \left(\sin\theta_0 R_p^{M+}\hat{\mathbf{z}} - W_\ell R_p^{M-}\cos\phi\hat{\mathbf{x}} - W_\ell R_p^{M-}\sin\phi\hat{\mathbf{y}}\right)\Bigg].$$

We now have $\mathbf{e}_\ell^{2\omega}$ in terms of $\hat{\mathbf{P}}_{v+}$,

$$\mathbf{e}_\ell^{2\omega} = \frac{T_p^{v\ell}}{N_\ell} \left(\sin\theta_0 R_p^{M+}\hat{\mathbf{z}} - W_\ell R_p^{M-}\cos\phi\hat{\mathbf{x}} - W_\ell R_p^{M-}\sin\phi\hat{\mathbf{y}}\right), \tag{A.5}$$

and in terms of $\hat{\mathbf{s}}$,

$$\mathbf{e}_\ell^{2\omega} = T_s^{v\ell} R_s^{M+} \left(-\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}\right). \tag{A.6}$$

Likewise, we do the exact same for Eq. (A.4), and get the following term for $\hat{\mathbf{P}}_{v+}$,

$$\mathbf{e}_\ell^{2\omega} = \frac{T_p^{v\ell} T_p^{\ell b}}{N_\ell^2 N_b} \left(N_b^2 \sin\theta_0\hat{\mathbf{z}} - N_\ell^2 W_b\cos\phi\hat{\mathbf{x}} - N_\ell^2 W_b\sin\phi\hat{\mathbf{y}}\right), \tag{A.7}$$

and $\hat{\mathbf{s}}$,

$$\mathbf{e}_\ell^{2\omega} = T_s^{v\ell} T_s^{\ell b} \left[-\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}\right]. \tag{A.8}$$

A.1.2 1ω terms

We posit that the effects of the multiple reflections can be neglected for the $\mathbf{e}_\ell^{\omega}$ term. This term is

$$\mathbf{e}_\ell^{\omega} = \left[\hat{\mathbf{s}} t_s^{v\ell} t_s^{\ell b}\hat{\mathbf{s}} + \frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b} \left(n_b^2 \sin\theta_0\hat{\mathbf{z}} + n_\ell^2 w_b\hat{\boldsymbol{\kappa}}\right)\hat{\mathbf{p}}_{v-}\right] \cdot \hat{\mathbf{e}}^{\mathrm{in}}.$$

For all cases, we require a $\mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega}$ product. For brevity, we will directly list these terms for both polarizations. For $\hat{\mathbf{e}}^{\mathrm{in}} = \hat{\mathbf{p}}_{v-}$,

$$\begin{aligned}\mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega} = \left(\frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b}\right)^2 \big(&n_\ell^4 w_b^2 \cos^2\phi\hat{\mathbf{x}}\hat{\mathbf{x}} + 2n_\ell^4 w_b^2 \sin\phi\cos\phi\hat{\mathbf{x}}\hat{\mathbf{y}} \\ &+ 2n_\ell^2 n_b^2 w_b \sin\theta_0\cos\phi\hat{\mathbf{x}}\hat{\mathbf{z}} + n_\ell^4 w_b^2 \sin^2\phi\hat{\mathbf{y}}\hat{\mathbf{y}} \\ &+ 2n_\ell^2 n_b^2 w_b \sin\theta_0\sin\phi\hat{\mathbf{y}}\hat{\mathbf{z}} + n_b^4 \sin^2\theta_0\hat{\mathbf{z}}\hat{\mathbf{z}}\big),\end{aligned} \tag{A.9}$$

and for $\hat{\mathbf{e}}^{\mathrm{in}} = \hat{\mathbf{s}}$,

$$\mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega} = \left(t_s^{v\ell} t_s^{\ell b}\right)^2 \left(\sin^2\phi\hat{\mathbf{x}}\hat{\mathbf{x}} + \cos^2\phi\hat{\mathbf{y}}\hat{\mathbf{y}} - 2\sin\phi\cos\phi\hat{\mathbf{x}}\hat{\mathbf{y}}\right). \tag{A.10}$$

We summarize these expressions in Table A.1. In order to derive the equations for a given polarization case, we refer to the equations listed there. Then it is simply a matter of multiplying the terms correctly and obtaining the appropriate components of $\boldsymbol{\chi}(-2\omega;\omega,\omega)$.

A.1.3 Nonzero components of $\boldsymbol{\chi}(-2\omega;\omega,\omega)$

For a (111) surface with C_{3v} symmetry, we have the following nonzero components:

$$\begin{aligned}
&\chi_{xxx} = -\chi_{xyy} = -\chi_{yyx},\\
&\chi_{xxz} = \chi_{yyz},\\
&\chi_{zxx} = \chi_{zyy},\\
&\chi_{zzz}.
\end{aligned} \tag{A.11}$$

For a (110) surface with C_{2v} symmetry, we have the following nonzero components:

$$\chi_{xxz}, \chi_{yyz}, \chi_{zxx}, \chi_{zyy}, \chi_{zzz}. \tag{A.12}$$

Lastly, for a (001) surface with C_{4v} symmetry, we have the following nonzero components:

$$\begin{aligned}
&\chi_{xxz} = \chi_{yyz},\\
&\chi_{zxx} = \chi_{zyy},\\
&\chi_{zzz}.
\end{aligned} \tag{A.13}$$

Case	$\hat{\mathbf{e}}^{\mathrm{out}}$	$\hat{\mathbf{e}}^{\mathrm{in}}$	$\mathbf{e}_\ell^{2\omega}$	$\mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega}$
$\mathcal{R}_{pP}$	$\hat{\mathbf{P}}_{v+}$	$\hat{\mathbf{p}}_{v-}$	Eq. (A.5) or (A.7)	Eq. (A.9)
$\mathcal{R}_{pS}$	$\hat{\mathbf{s}}$	$\hat{\mathbf{p}}_{v-}$	Eq. (A.6) or (A.8)	Eq. (A.9)
$\mathcal{R}_{sP}$	$\hat{\mathbf{P}}_{v+}$	$\hat{\mathbf{s}}$	Eq. (A.5) or (A.7)	Eq. (A.10)
$\mathcal{R}_{sS}$	$\hat{\mathbf{s}}$	$\hat{\mathbf{s}}$	Eq. (A.6) or (A.8)	Eq. (A.10)

Table A.1: Polarization unit vectors for $\hat{\mathbf{e}}^{\mathrm{out}}$ and $\hat{\mathbf{e}}^{\mathrm{in}}$, and equations describing $\mathbf{e}_\ell^{2\omega}$ and $\mathbf{e}_\ell^{\omega}\mathbf{e}_\ell^{\omega}$ for each polarization case. When there are two equations to choose from, the former includes the effects of multiple reflections, and the latter neglects them.

A.2 $\mathcal{R}_{pP}$

Per Table A.1, $\mathcal{R}_{pP}$ requires Eqs. (A.7) and (A.9). After some algebra, we obtain that

$$\begin{aligned}
\Upsilon_{pP}^{\mathrm{MR}} = \Gamma_{pP}^{\mathrm{MR}}\Big[& -R_p^{M-} W_\ell \big(n_\ell^4 w_b^2 \cos^3\phi\chi_{xxx} + 2n_\ell^4 w_b^2 \sin\phi\cos^2\phi\chi_{xxy} \\
&\qquad + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \cos^2\phi\chi_{xxz} + n_\ell^4 w_b^2 \sin^2\phi\cos\phi\chi_{xyy} \\
&\qquad + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{xyz} + n_b^4 \sin^2\theta_0 \cos\phi\chi_{xzz}\big) \\
& -R_p^{M-} W_\ell \big(n_\ell^4 w_b^2 \sin\phi\cos^2\phi\chi_{yxx} + 2n_\ell^4 w_b^2 \sin^2\phi\cos\phi\chi_{yxy} \\
&\qquad + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{yxz} + n_\ell^4 w_b^2 \sin^3\phi\chi_{yyy} \\
&\qquad + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin^2\phi\chi_{yyz} + n_b^4 \sin^2\theta_0 \sin\phi\chi_{yzz}\big) \\
& +R_p^{M+} \sin\theta_0 \big(n_\ell^4 w_b^2 \cos^2\phi\chi_{zxx} + 2n_\ell^4 w_b^2 \sin\phi\cos\phi\chi_{zxy} \\
&\qquad + n_\ell^4 w_b^2 \sin^2\phi\chi_{zyy} + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \cos\phi\chi_{zzx} \\
&\qquad + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\chi_{zzy} + n_b^4 \sin^2\theta_0\chi_{zzz}\big)\Big].
\end{aligned} \tag{A.14}$$

We take this opportunity to introduce a quantity that will be repeated throughout this section,

$$\Gamma_{pP}^{\mathrm{MR}} = \frac{T_p^{v\ell}}{N_\ell}\left(\frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b}\right)^2. \tag{A.15}$$

If we neglect the multiple reflections, as described in the manuscript, we have that

$$
\begin{aligned}
\Upsilon_{pP} = \Gamma_{pP}\Big[& -N_\ell^2 W_b\big(+ n_\ell^4 w_b^2 \cos^3\phi\chi_{xxx} + 2n_\ell^4 w_b^2 \sin\phi\cos^2\phi\chi_{xxy} \\
& \qquad + 2n_b^2 n_\ell^2 w_b \sin\theta_0 \cos^2\phi\chi_{xxz} + n_\ell^4 w_b^2 \sin^2\phi\cos\phi\chi_{xyy} \\
& \qquad + 2n_b^2 n_\ell^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{xyz} + n_b^4 \sin^2\theta_0 \cos\phi\chi_{xzz}\big) \\
& -N_\ell^2 W_b\big(+ n_\ell^4 w_b^2 \sin\phi\cos^2\phi\chi_{yxx} + 2n_\ell^4 w_b^2 \sin^2\phi\cos\phi\chi_{yxy} \\
& \qquad + 2n_b^2 n_\ell^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{yxz} + n_\ell^4 w_b^2 \sin^3\phi\chi_{yyy} \\
& \qquad + 2n_b^2 n_\ell^2 w_b \sin\theta_0 \sin^2\phi\chi_{yyz} + n_b^4 \sin^2\theta_0 \sin\phi\chi_{yzz}\big) \\
& +N_b^2 \sin\theta_0\big(+ n_\ell^4 w_b^2 \cos^2\phi\chi_{zxx} + 2n_\ell^4 w_b^2 \sin\phi\cos\phi\chi_{zxy} \\
& \qquad + n_\ell^4 w_b^2 \sin^2\phi\chi_{zyy} + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \cos\phi\chi_{zzx} \\
& \qquad + 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\chi_{zzy} + n_b^4 \sin^2\theta_0\chi_{zzz}\big)\Big],
\end{aligned}
\tag{A.16}
$$

and again we introduce a quantity that will be repeated throughout this section,

$$
\Gamma_{pP} = \frac{T_p^{v\ell} T_p^{\ell b}}{N_\ell^2 N_b}\left(\frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b}\right)^2. \tag{A.17}
$$

A.2.1 For the (111) surface

We take Eqs. (A.14) and (A.11), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$
\begin{aligned}
\Upsilon_{pP}^{\mathrm{MR},(111)} = \Gamma_{pP}^{\mathrm{MR}}\big[& + R_p^{M+} n_b^4 \sin^3\theta_0\chi_{zzz} \\
& + R_p^{M+} n_\ell^4 w_b^2 \sin\theta_0 \cos^2\phi\chi_{zxx} \\
& + R_p^{M+} n_\ell^4 w_b^2 \sin\theta_0 \sin^2\phi\chi_{zxx} \\
& - 2R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0 \cos^2\phi\chi_{xxz} \\
& - 2R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0 \sin^2\phi\chi_{xxz} \\
& - R_p^{M-} n_\ell^4 w_b^2 W_\ell \cos^3\phi\chi_{xxx} \\
& + R_p^{M-} n_\ell^4 w_b^2 W_\ell \sin^2\phi\cos\phi\chi_{xxx} \\
& + 2R_p^{M-} n_\ell^4 w_b^2 W_\ell \sin^2\phi\cos\phi\chi_{xxx}\big].
\end{aligned}
$$

We reduce terms,

$$
\begin{aligned}
\Upsilon_{pP}^{\mathrm{MR},(111)} = \Gamma_{pP}^{\mathrm{MR}} \big[&+ R_p^{M+} n_b^4 \sin^3\theta_0 \chi_{zzz} \\
&+ R_p^{M+} n_\ell^4 w_b^2 \sin\theta_0 (\sin^2\phi + \cos^2\phi) \chi_{zxx} \\
&- 2R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0 (\sin^2\phi + \cos^2\phi) \chi_{xxz} \\
&+ R_p^{M-} n_\ell^4 w_b^2 W_\ell (3\sin^2\phi\cos\phi - \cos^3\phi) \chi_{xxx} \big] \\
\\
= \Gamma_{pP}^{\mathrm{MR}} \big[& R_p^{M+} \sin\theta_0 (n_b^4 \sin^2\theta_0 \chi_{zzz} + n_\ell^4 w_b^2 \chi_{zxx}) \\
&- R_p^{M-} n_\ell^2 w_b W_\ell (2n_b^2 \sin\theta_0 \chi_{xxz} + n_\ell^2 w_b \chi_{xxx} \cos 3\phi) \big] \\
\\
= \Gamma_{pP}^{\mathrm{MR}} \, & r_{pP}^{\mathrm{MR},(111)},
\end{aligned}
$$

where

$$
\begin{aligned}
r_{pP}^{\mathrm{MR},(111)} = & R_p^{M+} \sin\theta_0 (n_b^4 \sin^2\theta_0 \chi_{zzz} + n_\ell^4 w_b^2 \chi_{zxx}) \\
&- R_p^{M-} n_\ell^2 w_b W_\ell (2n_b^2 \sin\theta_0 \chi_{xxz} + n_\ell^2 w_b \chi_{xxx} \cos 3\phi).
\end{aligned}
\tag{A.18}
$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (A.16),

$$
\begin{aligned}
\Upsilon_{pP}^{(111)} = \Gamma_{pP} \big[&+ n_b^4 N_b^2 \sin^3\theta_0 \chi_{zzz} \\
&+ n_\ell^4 N_b^2 w_b^2 \sin\theta_0 \cos^2\phi \chi_{zxx} \\
&+ n_\ell^4 N_b^2 w_b^2 \sin\theta_0 \sin^2\phi \chi_{zxx} \\
&- 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b \sin\theta_0 \cos^2\phi \chi_{xxz} \\
&- 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b \sin\theta_0 \sin^2\phi \chi_{xxz} \\
&- n_\ell^4 N_\ell^2 w_b^2 W_b \cos^3\phi \chi_{xxx} \\
&+ n_\ell^4 N_\ell^2 w_b^2 W_b \sin^2\phi \cos\phi \chi_{xxx} \\
&+ 2n_\ell^4 N_\ell^2 w_b^2 W_b \sin^2\phi \cos\phi \chi_{xxx} \big],
\end{aligned}
$$

and reduce,

$$
\begin{aligned}
\Upsilon_{pP}^{(111)} = \Gamma_{pP} \big[&+ n_b^4 N_b^2 \sin^3\theta_0 \chi_{zzz} \\
&+ n_\ell^4 N_b^2 w_b^2 \sin\theta_0 (\sin^2\phi + \cos^2\phi) \chi_{zxx} \\
&- 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b \sin\theta_0 (\sin^2\phi + \cos^2\phi) \phi \chi_{xxz} \\
&+ n_\ell^4 N_\ell^2 w_b^2 W_b (3\sin^2\phi\cos\phi - \cos^3\phi) \chi_{xxx} \big] \\
\\
= \Gamma_{pP} \big[& N_b^2 \sin\theta_0 (n_b^4 \sin^2\theta_0 \chi_{zzz} + n_\ell^4 w_b^2 \chi_{zxx}) \\
&- n_\ell^2 N_\ell^2 w_b W_b (2n_b^2 \sin\theta_0 \chi_{xxz} + n_\ell^2 w_b \chi_{xxx} \cos 3\phi) \big] \\
\\
= \Gamma_{pP} \, & r_{pP}^{(111)},
\end{aligned}
$$

where

$$
\begin{aligned}
r_{pP}^{(111)} =& N_b^2 \sin\theta_0 (n_b^4 \sin^2\theta_0 \chi_{zzz} + n_\ell^4 w_b^2 \chi_{zxx}) \\
&- n_\ell^2 N_\ell^2 w_b W_b (2 n_b^2 \sin\theta_0 \chi_{xxz} + n_\ell^2 w_b \chi_{xxx} \cos 3\phi).
\end{aligned}
\tag{A.19}
$$

A.2.2 For the (110) surface

We take Eqs. (A.14) and (A.12), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$
\begin{aligned}
\Upsilon_{pP}^{\mathrm{MR},(110)} &= \Gamma_{pP}^{\mathrm{MR}} \Big[R_p^{M+} \sin\theta_0 \big(n_b^4 \sin^2\theta_0 \chi_{zzz} + n_\ell^4 w_b^2 (\sin^2\phi \chi_{zyy} + \cos^2\phi \chi_{zxx}) \big) \\
&\qquad - 2 R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0 (\sin^2\phi \chi_{yyz} + \cos^2\phi \chi_{xxz}) \Big] \\
&= \Gamma_{pP}^{\mathrm{MR}} \Bigg[R_p^{M+} \sin\theta_0 \Bigg(n_b^4 \sin^2\theta_0 \chi_{zzz} \\
&+ n_\ell^4 w_b^2 \left(\frac{1}{2}(1 - \cos 2\phi)\chi_{zyy} + \frac{1}{2}(\cos 2\phi + 1)\chi_{zxx} \right) \Bigg) \\
&- 2 R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0 \left(\frac{1}{2}(1 - \cos 2\phi)\chi_{yyz} + \frac{1}{2}(\cos 2\phi + 1)\chi_{xxz} \right) \Bigg] \\
&= \Gamma_{pP}^{\mathrm{MR}} \Bigg[R_p^{M+} \sin\theta_0 \Bigg(n_b^4 \sin^2\theta_0 \chi_{zzz} \\
&\qquad + n_\ell^4 w_b^2 \left(\frac{\chi_{zyy} + \chi_{zxx}}{2} + \frac{\chi_{zyy} - \chi_{zxx}}{2} \cos 2\phi \right) \Bigg) \\
&\qquad - 2 R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0 \left(\frac{\chi_{yyz} + \chi_{xxz}}{2} + \frac{\chi_{yyz} - \chi_{xxz}}{2} \cos 2\phi \right) \Bigg] \\
&= \Gamma_{pP}^{\mathrm{MR}} r_{pP}^{\mathrm{MR},(110)},
\end{aligned}
$$

where

$$
\begin{aligned}
r_{pP}^{\mathrm{MR},(110)} &= R_p^{M+} \sin\theta_0 \Bigg[n_b^4 \sin^2\theta_0 \chi_{zzz} \\
&\qquad + n_\ell^4 w_b^2 \left(\frac{\chi_{zyy} + \chi_{zxx}}{2} + \frac{\chi_{zyy} - \chi_{zxx}}{2} \cos 2\phi \right) \Bigg] \\
&\qquad - 2 R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0 \left(\frac{\chi_{yyz} + \chi_{xxz}}{2} + \frac{\chi_{yyz} - \chi_{xxz}}{2} \cos 2\phi \right).
\end{aligned}
\tag{A.20}
$$

If we wish to neglect the effects of the multiple reflections, we follow the

exact same procedure but starting with Eq. (A.16),

$$\begin{aligned}\Upsilon_{pP}^{(110)} &= \Gamma_{pP}\Bigg[N_b^2\sin\theta_0\Big(n_b^4\sin^2\theta_0\chi_{zzz} + n_\ell^4 w_b^2(\sin^2\phi\chi_{zyy} + \cos^2\phi\chi_{zxx})\Big) \\ &\qquad - 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b \sin\theta_0\big(\sin^2\phi\chi_{yyz} + \cos^2\phi\chi_{xxz}\big)\Bigg] \\ &= \Gamma_{pP}\Bigg[N_b^2\sin\theta_0\Bigg(n_b^4\sin^2\theta_0\chi_{zzz} \\ &\qquad + n_\ell^4 w_b^2\left(\frac{\chi_{zyy}+\chi_{zxx}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right)\Bigg) \\ &\qquad - 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b\sin\theta_0\left(\frac{\chi_{yyz}+\chi_{xxz}}{2} + \frac{\chi_{yyz}-\chi_{xxz}}{2}\cos 2\phi\right)\Bigg] \\ &= \Gamma_{pP}\, r_{pP}^{(110)},\end{aligned}$$

where

$$\begin{aligned}r_{pP}^{(110)} = N_b^2\sin\theta_0\Bigg[n_b^4\sin^2\theta_0\chi_{zzz} + n_\ell^4 w_b^2\left(\frac{\chi_{zyy}+\chi_{zxx}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right)\Bigg] \\ - 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b\sin\theta_0\left(\frac{\chi_{yyz}+\chi_{xxz}}{2} + \frac{\chi_{yyz}-\chi_{xxz}}{2}\cos 2\phi\right).\end{aligned} \tag{A.21}$$

A.2.3 For the (001) surface

We take Eqs. (A.14) and (A.12), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{pP}^{\mathrm{MR},(001)} &= \Gamma_{pP}^{\mathrm{MR}}\big[R_p^{M+} n_b^4\sin^3\theta_0\chi_{zzz} \\ &\qquad + R_p^{M+} n_\ell^4 w_b^2\sin\theta_0\cos^2\phi\chi_{zxx} \\ &\qquad + R_p^{M+} n_\ell^4 w_b^2\sin\theta_0\sin^2\phi\chi_{zxx} \\ &\qquad - 2R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell\sin\theta_0\cos^2\phi\chi_{xxz} \\ &\qquad - 2R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell\sin\theta_0\sin^2\phi\chi_{xxz}\big] \\ &= \Gamma_{pP}^{\ell}\big[R_p^{M+}\sin\theta_0(n_b^4\sin^2\theta_0\chi_{zzz} + n_\ell^4 w_b^2\chi_{zxx}) \\ &\qquad - 2R_p^{M-} n_\ell^2 n_b^2 w_b W_\ell\sin\theta_0\chi_{xxz}\big] \\ &= \Gamma_{pP}^{\mathrm{MR}}\, r_{pP}^{\mathrm{MR},(001)},\end{aligned}$$

where

$$r_{pP}^{\mathrm{MR},(001)} = R_p^{M+}\sin\theta_0(n_b^4\sin^2\theta_0\chi_{zzz} + n_\ell^4 w_b^2\chi_{zxx}) \\ - 2R_p^{M-}n_\ell^2 n_b^2 w_b W_\ell \sin\theta_0\chi_{xxz}, \tag{A.22}$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (A.16),

$$\begin{aligned}\Upsilon_{pP}^{(001)} &= \Gamma_{pP}\big[N_b^2\sin\theta_0(n_b^4\sin^2\theta_0\chi_{zzz} + n_\ell^4 w_b^2\chi_{zxx}) \\ &\qquad - 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b\sin\theta_0\chi_{xxz}\big] \\ &= \Gamma_{pP}\, r_{pp}^{(001)},\end{aligned}$$

where

$$r_{pP}^{(001)} = N_b^2\sin\theta_0(n_b^4\sin^2\theta_0\chi_{zzz} + n_\ell^4 w_b^2\chi_{zxx}) \\ - 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b\sin\theta_0\chi_{xxz}. \tag{A.23}$$

A.3 $\mathcal{R}_{pS}$

Per Table 1.1, $\mathcal{R}_{pS}$ requires Eqs. (A.6) and (A.9). After some algebra, we obtain that

$$\begin{aligned}\Upsilon_{pS}^{\mathrm{MR}} = \Gamma_{pS}^{\mathrm{MR}}\big[&- n_\ell^4 w_b^2\sin\phi\cos^2\phi\chi_{xxx} - 2n_\ell^4 w_b^2\sin^2\phi\cos\phi\chi_{xxy} \\ &- 2n_\ell^2 n_b^2 w_b\sin\theta_0\sin\phi\cos\phi\chi_{xxz} - n_\ell^4 w_b^2\sin^3\phi\chi_{xyy} \\ &- 2n_\ell^2 n_b^2 w_b\sin\theta_0\sin^2\phi\chi_{xyz} - n_b^4\sin^2\theta_0\sin\phi\chi_{xzz} \\ &+ n_\ell^4 w_b^2\cos^3\phi\chi_{yxx} + 2n_\ell^4 w_b^2\sin\phi\cos^2\phi\chi_{yxy} \\ &+ 2n_\ell^2 n_b^2 w_b\sin\theta_0\cos^2\phi\chi_{yxz} + n_\ell^4 w_b^2\sin^2\phi\cos\phi\chi_{yyy} \\ &+ 2n_\ell^2 n_b^2 w_b\sin\theta_0\sin\phi\cos\phi\chi_{yyz} + n_b^4\sin^2\theta_0\cos\phi\chi_{yzz}\big].\end{aligned} \tag{A.24}$$

We take this opportunity to introduce a quantity that will be repeated throughout this section,

$$\Gamma_{pS}^{\mathrm{MR}} = T_s^{v\ell}R_s^{M+}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{n_\ell^2 n_b}\right)^2 \tag{A.25}$$

If we neglect the multiple reflections, as described in the manuscript, we have that

$$\begin{aligned}\Upsilon_{pS} = \Gamma_{pS}\big[&- n_\ell^4 w_b^2\sin\phi\cos^2\phi\chi_{xxx} - 2n_\ell^4 w_b^2\sin^2\phi\cos\phi\chi_{xxy} \\ &- 2n_\ell^2 n_b^2 w_b\sin\theta_0\sin\phi\cos\phi\chi_{xxz} - n_\ell^4 w_b^2\sin^3\phi\chi_{xyy} \\ &- 2n_\ell^2 n_b^2 w_b\sin\theta_0\sin^2\phi\chi_{xyz} - n_b^4\sin^2\theta_0\sin\phi\chi_{xzz} \\ &+ n_\ell^4 w_b^2\cos^3\phi\chi_{yxx} + 2n_\ell^4 w_b^2\sin\phi\cos^2\phi\chi_{yxy} \\ &+ 2n_\ell^2 n_b^2 w_b\sin\theta_0\cos^2\phi\chi_{yxz} + n_\ell^4 w_b^2\sin^2\phi\cos\phi\chi_{yyy} \\ &+ 2n_\ell^2 n_b^2 w_b\sin\theta_0\sin\phi\cos\phi\chi_{yyz} + n_b^4\sin^2\theta_0\cos\phi\chi_{yzz}\big],\end{aligned} \tag{A.26}$$

and again we introduce a quantity that will be repeated throughout this section,

$$\Gamma_{pS} = T_s^{v\ell} T_s^{\ell b} \left(\frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b} \right)^2 . \tag{A.27}$$

We note that both Eqs. (A.24) and (A.26) are identical save for the different Γ_{pS} terms. Therefore, we can safely derive the equations only once, and then use $\Gamma_{pS}^{\mathrm{MR}}$ when we wish to include multiple reflections, or Γ_{pS} when we do not.

A.3.1 For the (111) surface

We take Eqs. (A.24) and (A.11), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$\begin{aligned}
\Upsilon_{pS}^{\mathrm{MR},(111)} = \Gamma_{pS}^{\mathrm{MR}} \big[&+ n_\ell^4 w_b^2 \sin^3\phi \chi_{xxx} \\
&- n_\ell^4 w_b^2 \sin\phi \cos^2\phi \chi_{xxx} \\
&- 2n_\ell^4 w_b^2 \sin\phi \cos^2\phi \chi_{xxx} \\
&- 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi \cos\phi \chi_{xxz} \\
&+ 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi \cos\phi \chi_{xxz} \big].
\end{aligned}$$

We reduce terms,

$$\begin{aligned}
\Upsilon_{pS}^{\mathrm{MR},(111)} &= \Gamma_{pS}^{\mathrm{MR}} \big[n_\ell^4 w_b^2 (\sin^3\phi - 3\sin\phi\cos^2\phi) \chi_{xxx} \big] \\
&= \Gamma_{pS}^{\mathrm{MR}} \big[- n_\ell^4 w_b^2 \chi_{xxx} \sin 3\phi \big] \\
&= \Gamma_{pS}^{\mathrm{MR}} \, r_{pS}^{\mathrm{MR},(111)},
\end{aligned}$$

where

$$r_{pS}^{\mathrm{MR},(111)} = -n_\ell^4 w_b^2 \chi_{xxx} \sin 3\phi. \tag{A.28}$$

As mentioned above,

$$r_{pS}^{(111)} = r_{pS}^{\mathrm{MR},(111)}, \tag{A.29}$$

so if we wish to neglect the effects of the multiple reflections, we simply use Γ_{pS} instead of $\Gamma_{pS}^{\mathrm{MR}}$.

A.3.2 For the (110) surface

We take Eqs. (A.24) and (A.12), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{pS}^{\mathrm{MR},(110)} &= \Gamma_{pS}^{\mathrm{MR}}\left[2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\cos\phi(\chi_{yyz}-\chi_{xxz})\right] \\ &= \Gamma_{pS}^{\mathrm{MR}}\left[n_\ell^2 n_b^2 w_b \sin\theta_0 (\chi_{yyz}-\chi_{xxz})\sin 2\phi\right] \\ &= \Gamma_{pS}^{\mathrm{MR}} r_{pS}^{\mathrm{MR},(110)}.\end{aligned}$$

where

$$r_{pS}^{\mathrm{MR},(110)} = n_\ell^2 n_b^2 w_b \sin\theta_0 (\chi_{yyz}-\chi_{xxz})\sin 2\phi. \tag{A.30}$$

As mentioned above,

$$r_{pS}^{(110)} = r_{pS}^{\mathrm{MR},(110)}, \tag{A.31}$$

so if we wish to neglect the effects of the multiple reflections, we simply use Γ_{pS} instead of $\Gamma_{pS}^{\mathrm{MR}}$.

A.3.3 For the (001) surface

We take Eqs. (A.24) and (A.12), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{pS}^{\mathrm{MR},(001)} = \Gamma_{pS}^{\mathrm{MR}}\big[&-2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{xxz} \\ &+ 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{xxz}\big] = 0,\end{aligned}$$

and thus,

$$\Upsilon_{pS}^{\mathrm{MR},(001)} = \Upsilon_{pS}^{(001)} = 0. \tag{A.32}$$

A.4 $\mathcal{R}_{sP}$

Per Table 1.1, $\mathcal{R}_{sP}$ requires Eqs. (A.5) and (A.10). After some algebra, we obtain that

$$\begin{aligned}\Upsilon_{sP}^{\mathrm{MR}} = \Gamma_{sP}^{\mathrm{MR}}\Big[&R_p^{M-} W_\ell\big(-\sin^2\phi\cos\phi\chi_{xxx} + 2\sin\phi\cos^2\phi\chi_{xxy} - \cos^3\phi\chi_{xyy}\big) \\ &+R_p^{M-} W_\ell\big(-\sin^3\phi\chi_{yxx} + 2\sin^2\phi\cos\phi\chi_{yxy} - \sin\phi\cos^2\phi\chi_{yyy}\big) \\ &+R_p^{M+}\sin\theta_0\big(+\sin^2\phi\chi_{zxx} - 2\sin\phi\cos\phi\chi_{zxy} + \cos^2\phi\chi_{zyy}\big)\Big].\end{aligned} \tag{A.33}$$

We take this opportunity to introduce a quantity that will be repeated throughout this section,

$$\Gamma_{sP}^{\mathrm{MR}} = \frac{T_p^{v\ell}}{N_\ell}\left(t_s^{v\ell} t_s^{\ell b}\right)^2 \tag{A.34}$$

If we neglect the multiple reflections, as described in the manuscript, we have that

$$\begin{aligned}\Upsilon_{sP} = \Gamma_{sP}\Big[&N_\ell^2 W_b\big(-\sin^2\phi\cos\phi\chi_{xxx} + 2\sin\phi\cos^2\phi\chi_{xxy} - \cos^3\phi\chi_{xyy}\big)\\ &+N_\ell^2 W_b\big(-\sin^3\phi\chi_{yxx} + 2\sin^2\phi\cos\phi\chi_{yxy} - \sin\phi\cos^2\phi\chi_{yyy}\big)\\ &+N_b^2\sin\theta_0\big(+\sin^2\phi\chi_{zxx} - 2\sin\phi\cos\phi\chi_{zxy} + \cos^2\phi\chi_{zyy}\big)\Big],\end{aligned} \tag{A.35}$$

and again we introduce a quantity that will be repeated throughout this section,

$$\Gamma_{pS} = \frac{T_p^{v\ell}T_p^{\ell b}}{N_\ell^2 N_b}\left(t_s^{v\ell}t_s^{\ell b}\right)^2. \tag{A.36}$$

A.4.1 For the (111) surface

We take Eqs. (A.33) and (A.11), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{sP}^{\mathrm{MR},(111)} = \Gamma_{sP}^{\mathrm{MR}}\big[&+R_p^{M-}W_\ell\cos^3\phi\chi_{xxx}\\ &-R_p^{M-}W_\ell\sin^2\phi\cos\phi\chi_{xxx}\\ &-2R_p^{M-}W_\ell\sin^2\phi\cos\phi\chi_{xxx}\\ &+R_p^{M+}\sin\theta_0\sin^2\phi\chi_{zxx}\\ &+R_p^{M+}\sin\theta_0\cos^2\phi\chi_{zxx}\big].\end{aligned}$$

We reduce terms,

$$\begin{aligned}\Upsilon_{sP}^{\mathrm{MR},(111)} &= \Gamma_{sP}^{\mathrm{MR}}\big[R_p^{M-}W_\ell(\cos^3\phi - 3\sin^2\phi\cos\phi)\chi_{xxx}\\ &\qquad + R_p^{M+}\sin\theta_0(\sin^2\phi+\cos^2\phi)\chi_{zxx}\big]\\ &= \Gamma_{sP}^{\mathrm{MR}}\big[R_p^{M-}W_\ell\chi_{xxx}\cos 3\phi + R_p^{M+}\sin\theta_0\chi_{zxx}\big]\\ &= \Gamma_{sP}^{\mathrm{MR}}\, r_{sP}^{\mathrm{MR},(111)},\end{aligned}$$

where

$$r_{sP}^{\mathrm{MR},(111)} = R_p^{M+}\sin\theta_0\chi_{zxx} + R_p^{M-}W_\ell\chi_{xxx}\cos 3\phi. \tag{A.37}$$

If we wish to neglect the effects of the multiple reflections, we follow the

exact same procedure but starting with Eq. (A.35),

$$\begin{aligned}\Upsilon_{sP}^{(111)} = \Gamma_{sP}\big[&- N_\ell^2 W_b \sin^2\phi\cos\phi\chi_{xxx}\\ &+ N_\ell^2 W_b\cos^3\phi\chi_{xxx}\\ &- 2N_\ell^2 W_b\sin^2\phi\cos\phi\chi_{yyx}\\ &+ N_b^2\sin\theta_0\sin^2\phi\chi_{zxx}\\ &+ N_b^2\sin\theta_0\cos^2\phi\chi_{zxx}\big],\end{aligned}$$

and reduce,

$$\begin{aligned}\Upsilon_{sP}^{(111)} &= \Gamma_{sP}\big[N_\ell^2 W_b(\cos^3\phi - 3\sin^2\phi\cos\phi)\chi_{xxx}\\ &\qquad + N_b^2\sin\theta_0(\sin^2\phi+\cos^2\phi)\chi_{zxx}\big]\\ &= \Gamma_{sP}\big[N_\ell^2 W_b\chi_{xxx}\cos 3\phi + N_b^2\sin\theta_0\chi_{zxx}\big]\\ &= \Gamma_{sP}\, r_{sP}^{(111)},\end{aligned}$$

where

$$r_{sP}^{(111)} = N_b^2\sin\theta_0\chi_{zxx} + N_\ell^2 W_b\chi_{xxx}\cos 3\phi. \tag{A.38}$$

A.4.2 For the (110) surface

We take Eqs. (A.33) and (A.12), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{sP}^{\mathrm{MR},(110)} &= \Gamma_{sP}^{\mathrm{MR}}\big[R_p^{M+}\sin\theta_0(\sin^2\phi\chi_{zxx}+\cos^2\phi\chi_{zyy})\big]\\ &= \Gamma_{sP}^{\mathrm{MR}}\left[R_p^{M+}\sin\theta_0\left(\frac{1}{2}(1-\cos 2\phi)\chi_{zxx} + \frac{1}{2}(\cos 2\phi + 1)\chi_{zyy}\right)\right]\\ &= \Gamma_{sP}^{\mathrm{MR}}\left[R_p^{M+}\sin\theta_0\left(\frac{\chi_{zyy}+\chi_{zxx}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right)\right]\\ &= \Gamma_{sP}^{\mathrm{MR}}\, r_{sP}^{\mathrm{MR},(110)},\end{aligned}$$

where

$$r_{sP}^{\mathrm{MR},(110)} = R_p^{M+}\sin\theta_0\left(\frac{\chi_{zxx}+\chi_{zyy}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right). \tag{A.39}$$

If we wish to neglect the effects of the multiple reflections, we follow the

exact same procedure but starting with Eq. (A.35),

$$
\begin{aligned}
\Upsilon_{sP}^{(110)} &= \Gamma_{sP}\left[N_b^2 \sin\theta_0 (\sin^2\phi\chi_{zxx} + \cos^2\phi\chi_{zyy})\right] \\
&= \Gamma_{sP}\left[N_b^2 \sin\theta_0 \left(\frac{1}{2}(1-\cos 2\phi)\chi_{zxx} + \frac{1}{2}(\cos 2\phi + 1)\chi_{zyy}\right)\right] \\
&= \Gamma_{sP}\left[N_b^2 \sin\theta_0 \left(\frac{\chi_{zxx}+\chi_{zyy}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right)\right] \\
&= \Gamma_{sP}\, r_{sP}^{(110)},
\end{aligned}
$$

where

$$
r_{sP}^{(110)} = N_b^2 \sin\theta_0 \left(\frac{\chi_{zxx}+\chi_{zyy}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right). \tag{A.40}
$$

A.4.3 For the (001) surface

We take Eqs. (A.33) and (A.12), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$
\begin{aligned}
\Upsilon_{sP}^{\mathrm{MR},(001)} &= \Gamma_{sP}^{\mathrm{MR}}\left[R_p^{M+} \sin\theta_0 (\sin^2\phi + \cos^2\phi)\chi_{zxx}\right] \\
&= \Gamma_{sP}^{\mathrm{MR}}\left[R_p^{M+} \sin\theta_0 \chi_{zxx}\right] \\
&= \Gamma_{sP}^{\mathrm{MR}}\, r_{sP}^{\mathrm{MR},(001)}.
\end{aligned}
$$

where

$$
r_{sP}^{\mathrm{MR},(001)} = R_p^{M+} \sin\theta_0 \chi_{zxx}. \tag{A.41}
$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (A.35),

$$
\begin{aligned}
\Upsilon_{sP}^{(001)} &= \Gamma_{sP}\left[N_b^2 \sin\theta_0 (\sin^2\phi + \cos^2\phi)\chi_{zxx}\right] \\
&= \Gamma_{sP}\left[N_b^2 \sin\theta_0 \chi_{zxx}\right] \\
&= \Gamma_{sP}\, r_{sP}^{(001)},
\end{aligned}
$$

where

$$
r_{sP}^{(001)} = N_b^2 \sin\theta_0 \chi_{zxx}. \tag{A.42}
$$

A.5 $\mathcal{R}_{sS}$

Per Table 1.1, $\mathcal{R}_{sS}$ requires Eqs. (A.8) and (A.10). After some algebra, we obtain that

$$\begin{aligned}\Upsilon_{sS}^{\mathrm{MR}} = \Gamma_{sS}^{\mathrm{MR}}\big[&-\sin^3\phi\chi_{xxx} + 2\sin^2\phi\cos\phi\chi_{xxy} - \sin\phi\cos^2\phi\chi_{xyy} \\ &+ \sin^2\phi\cos\phi\chi_{yxx} - 2\sin\phi\cos^2\phi\chi_{yxy} + \cos^3\phi\chi_{yyy}\big].\end{aligned} \tag{A.43}$$

We take this opportunity to introduce a quantity that will be repeated throughout this section,

$$\Gamma_{sS}^{\mathrm{MR}} = T_s^{v\ell}R_s^{M+}\left(t_s^{v\ell}t_s^{\ell b}\right)^2 \tag{A.44}$$

If we neglect the multiple reflections, as described in the manuscript, we have that

$$\begin{aligned}\Upsilon_{sS} = \Gamma_{sS}\big[&-\sin^3\phi\chi_{xxx} + 2\sin^2\phi\cos\phi\chi_{xxy} - \sin\phi\cos^2\phi\chi_{xyy} \\ &+ \sin^2\phi\cos\phi\chi_{yxx} - 2\sin\phi\cos^2\phi\chi_{yxy} + \cos^3\phi\chi_{yyy}\big],\end{aligned} \tag{A.45}$$

and again we introduce a quantity that will be repeated throughout this section,

$$\Gamma_{sS} = T_s^{v\ell}T_s^{\ell b}\left(t_s^{v\ell}t_s^{\ell b}\right)^2. \tag{A.46}$$

We note that both Eqs. (A.43) and (A.45) are identical save for the different Γ_{sS} terms. Therefore, we can safely derive the equations only once, and then use $\Gamma_{sS}^{\mathrm{MR}}$ when we wish to include multiple reflections, or Γ_{sS} when we do not.

A.5.1 For the (111) surface

We take Eqs. (A.43) and (A.11), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{sS}^{\mathrm{MR}} &= \Gamma_{sS}^{\mathrm{MR}}\big[(3\sin\phi\cos^2\phi - \sin^3\phi)\chi_{xxx}\big] \\ &= \Gamma_{sS}^{\mathrm{MR}}\big[\chi_{xxx}\sin 3\phi\big] \\ &= \Gamma_{sS}^{\mathrm{MR}}\, r_{sS}^{\mathrm{MR},(111)},\end{aligned}$$

where

$$r_{sS}^{\mathrm{MR},(111)} = \chi_{xxx}\sin 3\phi. \tag{A.47}$$

As mentioned above,

$$r_{sS}^{(111)} = r_{sS}^{\mathrm{MR},(111)}, \tag{A.48}$$

so if we wish to neglect the effects of the multiple reflections, we simply use Γ_{sS} instead of $\Gamma_{sS}^{\mathrm{MR}}$.

A.5.2 For the (110) surface

When considering Eqs. (A.43) and (A.12), we see that there are no nonzero components that contribute. Therefore,

$$\Upsilon_{pS}^{\mathrm{MR},(110)} = \Upsilon_{pS}^{(110)} = 0. \tag{A.49}$$

A.5.3 For the (001) surface

When considering Eqs. (A.43) and (A.12), we see that there are no nonzero components that contribute. Therefore,

$$\Upsilon_{sS}^{\mathrm{MR},(001)} = \Upsilon_{sS}^{(001)} = 0. \tag{A.50}$$

Appendix B

Some limiting cases of interest

In this section, we derive the expresions for $\mathcal{R}_{pP}$ for different limiting cases. We evaluate $\mathcal{P}(2\omega)$ and the fundamental fields in different regions. It is worth noting that the first case, the three layer model, can be reduced to any of the other cases by simply considering where we want to evaluate the 1ω and 2ω terms.

B.1 The two layer model

In order to reduce above result to that of Ref. [2] and [3], we now consider that $\mathcal{P}(2\omega)$ is evaluated in the vacuum region, while the fundamental fields are evaluated in the bulk region. To do this, we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_p^{\ell v} = 1$, $T_p^{\ell b} = T_p^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_p^{v\ell} = t_p^{vb}$, and $t_p^{\ell b} = 1$. With these choices

$$\mathbf{e}_v^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} \equiv \Gamma_{pP}^{vb}\, r_{pP}^{vb},$$

where,

$$\begin{aligned} r_{pP}^{vb} &= \epsilon_b(2\omega)\sin\theta_0\Big(\sin^2\theta_0\chi_{zzz} + k_b^2\chi_{zxx}\Big) \\ &\quad - k_b K_b\Big(2\sin\theta_0\chi_{xxz} + k_b\chi_{xxx}\cos(3\phi)\Big), \end{aligned}$$

and

$$\Gamma_{pP}^{vb} = \frac{T_p^{vb}(t_p^{vb})^2}{\epsilon_b(\omega)\sqrt{\epsilon_b(2\omega)}}.$$

B.2 Taking $\mathcal{P}(2\omega)$ and the fundamental fields in the bulk

To consider the 2ω fields in the bulk, we start with Eq. (1.2) but substitute $\ell \to b$, thus

$$\mathbf{H}_b = \hat{\mathbf{s}}\, T_s^{bv}\left(1 + R_s^{bb}\right)\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{bv}\left(\hat{\mathbf{P}}_{b+} + R_p^{bb}\hat{\mathbf{P}}_{b-}\right).$$

R_p^{bb} and R_s^{bb} are zero, so we are left with

$$\begin{aligned}
\mathbf{H}_b &= \hat{\mathbf{s}}\, T_s^{bv}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{bv}\hat{\mathbf{P}}_{b+} \\
&= \frac{K_b}{K_v}\left(\hat{\mathbf{s}}\, T_s^{vb}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{vb}\hat{\mathbf{P}}_{b+}\right) \\
&= \frac{K_b}{K_v}\left[\hat{\mathbf{s}}\, T_s^{vb}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}}(\sin\theta_0\hat{\mathbf{z}} - K_b\cos\phi\hat{\mathbf{x}} - K_b\sin\phi\hat{\mathbf{y}})\right],
\end{aligned}$$

and we define

$$\mathbf{e}_b^{2\omega} = \frac{K_b}{K_v}\,\hat{\mathbf{e}}^{\text{out}}\cdot\left[\hat{\mathbf{s}}\, T_s^{vb}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}}(\sin\theta_0\hat{\mathbf{z}} - K_b\cos\phi\hat{\mathbf{x}} - K_b\sin\phi\hat{\mathbf{y}})\right].$$

For $\mathcal{R}_{pP}$, we require $\hat{\mathbf{e}}^{\text{out}} = \hat{\mathbf{P}}_{v+}$, so we have that

$$\mathbf{e}_b^{2\omega} = \frac{K_b}{K_v}\frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}}(\sin\theta_0\hat{\mathbf{z}} - K_b\cos\phi\hat{\mathbf{x}} - K_b\sin\phi\hat{\mathbf{y}}).$$

The 1ω fields will still be evaluated inside the bulk, so we have Eq. (1.8)

$$\mathbf{e}_b^{\omega} = \left[\hat{\mathbf{s}} t_s^{vb}\hat{\mathbf{s}} + \frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}}\left(\sin\theta_0\hat{\mathbf{z}} + k_b\cos\phi\hat{\mathbf{x}} + k_b\sin\phi\hat{\mathbf{y}}\right)\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\text{in}},$$

and for our particular case of $\hat{\mathbf{e}}^{\text{in}} = \hat{\mathbf{p}}_{v-}$,

$$\mathbf{e}_b^{\omega} = \frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}}\left(\sin\theta_0\hat{\mathbf{z}} + k_b\cos\phi\hat{\mathbf{x}} + k_b\sin\phi\hat{\mathbf{y}}\right),$$

and

$$\begin{aligned}
\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} &= \frac{\left(t_p^{vb}\right)^2}{\epsilon_b(\omega)}\left(\sin\theta_0\hat{\mathbf{z}} + k_b\cos\phi\hat{\mathbf{x}} + k_b\sin\phi\hat{\mathbf{y}}\right)^2 \\
&= \frac{\left(t_p^{vb}\right)^2}{\epsilon_b(\omega)}\Big(\sin^2\theta_0\hat{\mathbf{z}}\hat{\mathbf{z}} + k_b^2\cos^2\phi\hat{\mathbf{x}}\hat{\mathbf{x}} + k_b^2\sin^2\phi\hat{\mathbf{y}}\hat{\mathbf{y}} \\
&\qquad + 2k_b\sin\theta_0\cos\phi\hat{\mathbf{z}}\hat{\mathbf{x}} + 2k_b\sin\theta_0\sin\phi\hat{\mathbf{z}}\hat{\mathbf{y}} + 2k_b^2\sin\phi\cos\phi\hat{\mathbf{x}}\hat{\mathbf{y}}\Big)
\end{aligned}$$

So lastly, we have that

$$
\begin{aligned}
\mathbf{e}_b^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \frac{K_b}{K_v}\frac{T_p^{vb}\left(t_p^{vb}\right)^2}{\epsilon_b(\omega)\sqrt{\epsilon_b(2\omega)}}\big(&\sin^3\theta_0\chi_{zzz}\\
&+k_b^2\sin\theta_0\cos^2\phi\chi_{zxx}\\
&+k_b^2\sin\theta_0\sin^2\phi\chi_{zyy}\\
&+2k_b\sin^2\theta_0\cos\phi\chi_{zzx}\\
&+2k_b\sin^2\theta_0\sin\phi\chi_{zzy}\\
&+2k_b^2\sin\theta_0\sin\phi\cos\phi\chi_{zxy}\\
&-K_b\sin^2\theta_0\cos\phi\chi_{xzz}\\
&-k_b^2K_b\cos^3\phi\chi_{xxx}\\
&-k_b^2K_b\sin^2\phi\cos\phi\chi_{xyy}\\
&-2k_bK_b\sin\theta_0\cos^2\phi\chi_{xzx}\\
&-2k_bK_b\sin\theta_0\sin\phi\cos\phi\chi_{xzy}\\
&-2k_b^2K_b\sin\phi\cos^2\phi\chi_{xxy}\\
&-K_b\sin^2\theta_0\sin\phi\chi_{yzz}\\
&-k_b^2K_b\sin\phi\cos^2\phi\chi_{yxx}\\
&-k_b^2K_b\sin^3\phi\chi_{yyy}\\
&-2k_bK_b\sin\theta_0\sin\phi\cos\phi\chi_{yzx}\\
&-2k_bK_b\sin\theta_0\sin^2\phi\chi_{yzy}\\
&-2k_b^2K_b\sin^2\phi\cos\phi\chi_{yxy}\big),
\end{aligned}
$$

and we can eliminate many terms since $\chi_{zzx} = \chi_{zzy} = \chi_{zxy} = \chi_{xzz} = \chi_{xzy} = \chi_{xxy} = \chi_{yzz} = \chi_{yxx} = \chi_{yyy} = \chi_{yzx} = 0$, and substituting the equivalent components of $\boldsymbol{\chi}$,

$$
\begin{aligned}
= \frac{K_b}{K_v}\Gamma_{pP}^{b}\big(&\sin^3\theta_0\chi_{zzz}\\
&+k_b^2\sin\theta_0\cos^2\phi\chi_{zxx}\\
&+k_b^2\sin\theta_0\sin^2\phi\chi_{zxx}\\
&-2k_bK_b\sin\theta_0\cos^2\phi\chi_{xxz}\\
&-2k_bK_b\sin\theta_0\sin^2\phi\chi_{xxz}\\
&-k_b^2K_b\cos^3\phi\chi_{xxx}\\
&+k_b^2K_b\sin^2\phi\cos\phi\chi_{xxx}\\
&+2k_b^2K_b\sin^2\phi\cos\phi\chi_{xxx}\big),
\end{aligned}
$$

and reducing,

$$
\begin{aligned}
&= \frac{K_b}{K_v}\Gamma^b_{pP}\big(\sin^3\theta_0\chi_{zzz}\\
&\qquad\qquad + k_b^2\sin\theta_0(\sin^2\phi+\cos^2\phi)\chi_{zxx}\\
&\qquad\qquad - 2k_bK_b\sin\theta_0(\sin^2\phi+\cos^2\phi)\chi_{xxz}\\
&\qquad\qquad + k_b^2K_b(3\sin^2\phi\cos\phi-\cos^3\phi)\chi_{xxx}\big)
\end{aligned}
$$

$$
= \frac{K_b}{K_v}\Gamma^b_{pP}\big(\sin^3\theta_0\chi_{zzz} + k_b^2\sin\theta_0\chi_{zxx} - 2k_bK_b\sin\theta_0\chi_{xxz} - k_b^2K_b\chi_{xxx}\cos 3\phi\big),
$$

where,

$$
\Gamma^b_{pP} = \frac{T_p^{vb}\left(t_p^{vb}\right)^2}{\epsilon_b(\omega)\sqrt{\epsilon_b(2\omega)}}.
$$

We find the equivalent expression for $\mathcal{R}$ evaluated inside the bulk as

$$
R(2\omega) = \frac{32\pi^3\omega^2}{c^3K_b^2}\left|\mathbf{e}_b^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega}\right|^2,
$$

and we can remove the K_b/K_v factor completely and reduce to the standard form of

$$
R(2\omega) = \frac{32\pi^3\omega^2}{c^3\cos^2\theta_0}\left|\mathbf{e}_b^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega}\right|^2.
$$

B.3 Taking $\mathcal{P}(2\omega)$ and the fundamental fields in the vacuum

To consider the 1ω fields in the vacuum, we start with Eq. (1.6) but substitute $\ell \to v$, thus

$$
\mathbf{E}_v(\omega) = E_0\left[\hat{\mathbf{s}}t_s^{vv}(1+r_s^{vb})\hat{\mathbf{s}} + \hat{\mathbf{p}}_{v-}t_p^{vv}\hat{\mathbf{p}}_{v-} + \hat{\mathbf{p}}_{v+}t_p^{vv}r_p^{vb}\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\mathrm{in}},
$$

t_p^{vv} and t_s^{vv} are one, so we are left with

$$
\begin{aligned}
\mathbf{e}_v^{\omega} &= \left[\hat{\mathbf{s}}(1+r_s^{vb})\hat{\mathbf{s}} + \hat{\mathbf{p}}_{v-}\hat{\mathbf{p}}_{v-} + \hat{\mathbf{p}}_{v+}r_p^{vb}\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\mathrm{in}}\\
&= \left[\hat{\mathbf{s}}(t_s^{vb})\hat{\mathbf{s}} + (\hat{\mathbf{p}}_{v-} + \hat{\mathbf{p}}_{v+}r_p^{vb})\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\mathrm{in}}\\
&= \left[\hat{\mathbf{s}}(t_s^{vb})\hat{\mathbf{s}} + \frac{1}{\sqrt{\epsilon_v(\omega)}}\big(k_v(1-r_p^{vb})\hat{\boldsymbol{\kappa}} + \sin\theta_0(1+r_p^{vb})\hat{\mathbf{z}}\big)\hat{\mathbf{p}}_{v-}\right]\\
&= \left[\hat{\mathbf{s}}(t_s^{vb})\hat{\mathbf{s}} + \left(\frac{k_b}{\sqrt{\epsilon_b(\omega)}}t_p^{vb}\hat{\boldsymbol{\kappa}} + \sqrt{\epsilon_b(\omega)}\sin\theta_0 t_p^{vb}\hat{\mathbf{z}}\right)\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\mathrm{in}}\\
&= \left[\hat{\mathbf{s}}(t_s^{vb})\hat{\mathbf{s}} + \frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}}\left(k_b\cos\phi\hat{\mathbf{x}} + k_b\sin\phi\hat{\mathbf{y}} + \epsilon_b(\omega)\sin\theta_0\hat{\mathbf{z}}\right)\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\mathrm{in}}.
\end{aligned}
$$

For $\mathcal{R}_{pP}$ we require that $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{p}}_{v-}$, so

$$\mathbf{e}_v^\omega = \frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}} \left(k_b \cos\phi \hat{\mathbf{x}} + k_b \sin\phi \hat{\mathbf{y}} + \epsilon_b(\omega) \sin\theta_0 \hat{\mathbf{z}} \right),$$

and

$$\begin{aligned}\mathbf{e}_v^\omega \mathbf{e}_v^\omega = \left(\frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}} \right)^2 \big[& k_b^2 \cos^2\phi \hat{\mathbf{x}}\hat{\mathbf{x}} \\ & + k_b^2 \sin^2\phi \hat{\mathbf{y}}\hat{\mathbf{y}} \\ & + \epsilon_b^2(\omega) \sin^2\theta_0 \hat{\mathbf{z}}\hat{\mathbf{z}} \\ & + 2k_b^2 \sin\phi \cos\phi \hat{\mathbf{x}}\hat{\mathbf{y}} \\ & + 2\epsilon_b(\omega) k_b \sin\theta_0 \sin\phi \hat{\mathbf{y}}\hat{\mathbf{z}} \\ & + 2\epsilon_b(\omega) k_b \sin\theta_0 \cos\phi \hat{\mathbf{x}}\hat{\mathbf{z}} \big].\end{aligned}$$

We also require the 2ω fields evaluated in the vacuum, which is Eq. (1.5),

$$\mathbf{e}_v^{2\omega} = \hat{\mathbf{e}}^{\rm out} \cdot \left[\hat{\mathbf{s}} T_s^{vb} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} \frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega) \sin\theta_0 \hat{\mathbf{z}} - K_b \hat{\boldsymbol{\kappa}} \right) \right], \tag{B.1}$$

and with $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{P}}_{v+}$ we have

$$\mathbf{e}_v^{2\omega} = \frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega) \sin\theta_0 \hat{\mathbf{z}} - K_b \cos\phi \hat{\mathbf{x}} - K_b \sin\phi \hat{\mathbf{y}} \right). \tag{B.2}$$

So lastly, we have that

$$
\begin{aligned}
&\mathbf{e}_v^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_v^{\omega}\mathbf{e}_v^{\omega} = \\
&\quad\frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}}\left(\frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}}\right)^2 \big[\epsilon_b(2\omega)k_b^2\sin\theta_0\cos^2\phi\chi_{zxx} \\
&\qquad + \epsilon_b(2\omega)k_b^2\sin\theta_0\sin^2\phi\chi_{zyy} \\
&\qquad + \epsilon_b^2(\omega)\epsilon_b(2\omega)\sin^3\theta_0\chi_{zzz} \\
&\qquad + 2\epsilon_b(2\omega)k_b^2\sin\theta_0\sin\phi\cos\phi\chi_{zxy} \\
&\qquad + 2\epsilon_b(\omega)\epsilon_b(2\omega)k_b\sin^2\theta_0\sin\phi\chi_{zyz} \\
&\qquad + 2\epsilon_b(\omega)\epsilon_b(2\omega)k_b\sin^2\theta_0\cos\phi\chi_{zxz} \\
&\qquad - k_b^2K_b\cos^3\phi\chi_{xxx} \\
&\qquad - k_b^2K_b\sin^2\phi\cos\phi\chi_{xyy} \\
&\qquad - \epsilon_b^2(\omega)K_b\sin^2\theta_0\cos\phi\chi_{xzz} \\
&\qquad - 2k_b^2K_b\sin\phi\cos^2\phi\chi_{xxy} \\
&\qquad - 2\epsilon_b(\omega)k_bK_b\sin\theta_0\sin\phi\cos\phi\chi_{xyz} \\
&\qquad - 2\epsilon_b(\omega)k_bK_b\sin\theta_0\cos^2\phi\chi_{xxz} \\
&\qquad - k_b^2K_b\sin\phi\cos^2\phi\chi_{yxx} \\
&\qquad - k_b^2K_b\sin^3\phi\chi yyy \\
&\qquad - \epsilon_b^2(\omega)K_b\sin^2\theta_0\sin\phi\chi_{yzz} \\
&\qquad - 2k_b^2K_b\sin^2\phi\cos\phi\chi_{yxy} \\
&\qquad - 2\epsilon_b(\omega)k_bK_b\sin\theta_0\sin^2\phi\chi_{yyz} \\
&\qquad - 2\epsilon_b(\omega)k_bK_b\sin\theta_0\sin\phi\cos\phi\chi_{yxz}\big],
\end{aligned}
$$

and after eliminating components,

$$
\begin{aligned}
&= \Gamma_{pP}^{v}\big[\epsilon_b^2(\omega)\epsilon_b(2\omega)\sin^3\theta_0\chi_{zzz} \\
&\qquad + \epsilon_b(2\omega)k_b^2\sin\theta_0\cos^2\phi\chi_{zxx} \\
&\qquad + \epsilon_b(2\omega)k_b^2\sin\theta_0\sin^2\phi\chi_{zxx} \\
&\qquad - 2\epsilon_b(\omega)k_bK_b\sin\theta_0\cos^2\phi\chi_{xxz} \\
&\qquad - 2\epsilon_b(\omega)k_bK_b\sin\theta_0\sin^2\phi\chi_{xxz} \\
&\qquad + 3k_b^2K_b\sin^2\phi\cos\phi\chi_{xxx} \\
&\qquad - k_b^2K_b\cos^3\phi\chi_{xxx}\big]
\end{aligned}
$$

$$
\begin{aligned}
&= \Gamma_{pP}^{v}\big[\epsilon_b^2(\omega)\epsilon_b(2\omega)\sin^3\theta_0\chi_{zzz} + \epsilon_b(2\omega)k_b^2\sin\theta_0\chi_{zxx} \\
&\qquad - 2\epsilon_b(\omega)k_bK_b\sin\theta_0\chi_{xxz} - k_b^2K_b\chi_{xxx}\cos 3\phi\big],
\end{aligned}
$$

where

$$\Gamma_{pP}^{v} = \frac{T_p^{vb}\left(t_p^{vb}\right)^2}{\epsilon_b(\omega)\sqrt{\epsilon_b(2\omega)}}.$$

B.4 Taking $\mathcal{P}(2\omega)$ in ℓ and the fundamental fields in the bulk

For this scenario with $\hat{\mathbf{e}}^{\text{in}} = \hat{\mathbf{p}}_{v-}$ and $\hat{\mathbf{e}}^{\text{out}} = \hat{\mathbf{P}}_{v+}$, we obtain from Eq. (1.4),

$$\mathbf{e}_\ell^{2\omega} = \frac{T_p^{v\ell}T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}\left(\epsilon_b(2\omega)\sin\theta_0\hat{\mathbf{z}} - \epsilon_\ell(2\omega)K_b\cos\phi\hat{\mathbf{x}} - \epsilon_\ell(2\omega)K_b\sin\phi\hat{\mathbf{y}}\right),$$

and Eq. (1.8),

$$\begin{aligned}\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \frac{\left(t_p^{vb}\right)^2}{\epsilon_b(\omega)}\big(&\sin^2\theta_0\hat{\mathbf{z}}\hat{\mathbf{z}} + k_b^2\cos^2\phi\hat{\mathbf{x}}\hat{\mathbf{x}} + k_b^2\sin^2\phi\hat{\mathbf{y}}\hat{\mathbf{y}} \\ &+ 2k_b\sin\theta_0\cos\phi\hat{\mathbf{z}}\hat{\mathbf{x}} + 2k_b\sin\theta_0\sin\phi\hat{\mathbf{z}}\hat{\mathbf{y}} + 2k_b^2\sin\phi\cos\phi\hat{\mathbf{x}}\hat{\mathbf{y}}\big).\end{aligned}$$

Thus,

$$\begin{aligned}\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \frac{T_p^{v\ell}T_p^{\ell b}\left(t_p^{vb}\right)^2}{\epsilon_\ell(2\omega)\epsilon_b(\omega)\sqrt{\epsilon_b(2\omega)}}\Big[&+\epsilon_b(2\omega)\sin^3\theta_0\chi_{zzz} \\
&+\epsilon_b(2\omega)k_b^2\sin\theta_0\cos^2\phi\chi_{zxx} \\
&+\epsilon_b(2\omega)k_b^2\sin\theta_0\sin^2\phi\chi_{zyy} \\
&+2\epsilon_b(2\omega)k_b\sin^2\theta_0\cos\phi\chi_{zzx} \\
&+2\epsilon_b(2\omega)k_b\sin^2\theta_0\sin\phi\chi_{zzy} \\
&+2\epsilon_b(2\omega)k_b^2\sin\theta_0\sin\phi\cos\phi\chi_{zxy} \\
&-\epsilon_\ell(2\omega)\sin^2\theta_0K_b\cos\phi\chi_{xzz} \\
&-\epsilon_\ell(2\omega)k_b^2K_b\cos^3\phi\chi_{xxx} \\
&-\epsilon_\ell(2\omega)k_b^2K_b\sin^2\phi\cos\phi\chi_{xyy} \\
&-2\epsilon_\ell(2\omega)k_bK_b\sin\theta_0\cos^2\phi\chi_{xzx} \\
&-2\epsilon_\ell(2\omega)k_bK_b\sin\theta_0\sin\phi\cos\phi\chi_{xzy} \\
&-2\epsilon_\ell(2\omega)k_b^2K_b\sin\phi\cos^2\phi\chi_{xxy} \\
&-\epsilon_\ell(2\omega)K_b\sin^2\theta_0\sin\phi\chi_{yzz} \\
&-\epsilon_\ell(2\omega)k_b^2K_b\cos^2\phi\sin\phi\chi_{yxx} \\
&-\epsilon_\ell(2\omega)k_b^2K_b\sin^3\phi\chi_{yyy} \\
&-2\epsilon_\ell(2\omega)k_bK_b\sin\theta_0\cos\phi\sin\phi\chi_{yzx} \\
&-2\epsilon_\ell(2\omega)k_bK_b\sin\theta_0\sin^2\phi\chi_{yzy} \\
&-2\epsilon_\ell(2\omega)k_b^2K_b\sin^2\phi\cos\phi\chi_{yxy}\Big].\end{aligned}$$

We eliminate and replace components,

$$
\begin{aligned}
\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \Gamma_{pP}^{\ell b}\Big[& + \epsilon_b(2\omega)\sin^3\theta_0\chi_{zzz} \\
& + \epsilon_b(2\omega)k_b^2\sin\theta_0\cos^2\phi\chi_{zxx} \\
& + \epsilon_b(2\omega)k_b^2\sin\theta_0\sin^2\phi\chi_{zxx} \\
& - 2\epsilon_\ell(2\omega)k_bK_b\sin\theta_0\cos^2\phi\chi_{xxz} \\
& - 2\epsilon_\ell(2\omega)k_bK_b\sin\theta_0\sin^2\phi\chi_{xxz} \\
& - \epsilon_\ell(2\omega)k_b^2K_b\cos^3\phi\chi_{xxx} \\
& + \epsilon_\ell(2\omega)k_b^2K_b\sin^2\phi\cos\phi\chi_{xxx} \\
& + 2\epsilon_\ell(2\omega)k_b^2K_b\sin^2\phi\cos\phi\chi_{xxx}\Big],
\end{aligned}
$$

so lastly

$$
\begin{aligned}
\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \Gamma_{pP}^{\ell b}\Big[&\epsilon_b(2\omega)\sin^3\theta_0\chi_{zzz} + \epsilon_b(2\omega)k_b^2\sin\theta_0\chi_{zxx} \\
& - 2\epsilon_\ell(2\omega)k_bK_b\sin\theta_0\chi_{xxz} - \epsilon_\ell(2\omega)k_b^2K_b\chi_{xxx}\cos 3\phi\Big],
\end{aligned}
$$

where

$$
\Gamma_{pP}^{\ell b} = \frac{T_p^{v\ell}T_p^{\ell b}\left(t_p^{vb}\right)^2}{\epsilon_\ell(2\omega)\epsilon_b(\omega)\sqrt{\epsilon_b(2\omega)}}.
$$

Appendix C

The two layer model for SHG radiation from Sipe, Moss, and van Driel

In this treatment we follow the work of Ref. [3]. They define the following for all polarizations;

$$\begin{aligned} f_s &= \frac{\kappa}{n\tilde{\omega}} = \frac{\kappa}{\sqrt{\epsilon(\omega)}\tilde{\omega}}, \\ f_c &= \frac{w}{n\tilde{\omega}} = \frac{w}{\sqrt{\epsilon(\omega)}\tilde{\omega}}, \\ f_s^2 &+ f_c^2 = 1, \end{aligned} \tag{C.1}$$

where

$$\kappa = \tilde{\omega}\sin\theta,$$

$$w_0 = \sqrt{\tilde{\omega} - \kappa^2} = \tilde{\omega}\cos\theta, \tag{C.2}$$

$$w = \sqrt{\tilde{\omega}\epsilon(\omega) - \kappa^2} = \tilde{\omega}k_z(\omega). \tag{C.3}$$

From this point on, all capital letters and symbols indicate evaluation at 2ω. Common to all three polarization cases studied here, we require the nonzero components for the (111) face for crystals with C_{3v} symmetry,

$$\begin{aligned} \delta_{11} &= \chi^{xxx} = -\chi^{xyy} = -\chi^{yyx}, \\ \delta_{15} &= \chi^{xxz} = \chi^{yyz}, \\ \delta_{31} &= \chi^{zxx} = \chi^{zyy}, \\ \delta_{33} &= \chi^{zzz}. \end{aligned} \tag{C.4}$$

Lastly, the remaining quantities that will be needed for all three cases are

$$
\begin{aligned}
A_p &= \frac{4\pi\tilde{\Omega}\sqrt{\epsilon(2\omega)}}{W_0\epsilon(2\omega)+W}, \\
A_s &= \frac{4\pi\tilde{\Omega}}{W_0+W}.
\end{aligned}
\tag{C.5}
$$

C.1 $\mathcal{R}_{pP}$

For the (111) face ($m = 3$), we have

$$
\frac{E^{(2\omega)}(\|,\|)}{E_p^2 A_p} = a_{\|,\|} + c_{\|,\|}^{(3)} \cos 3\phi. \tag{C.6}
$$

We extract these coefficients from Table V, noting that $\Gamma = \gamma = 0$ as we are only interested in the surface contribution,

$$
\begin{aligned}
a_{\|,\|} &= i\tilde{\Omega}F_s\epsilon(2\omega)\delta_{31} + i\tilde{\Omega}\epsilon(2\omega)F_s f_s^2(\delta_{33}-\delta_{31}) - 2i\tilde{\Omega}f_s f_c F_c\delta_{15}, \\
c_{\|,\|}^{(3)} &= -i\tilde{\Omega}F_c f_c^2\delta_{11}.
\end{aligned}
$$

We substitute these in Eq. (C.6),

$$
\begin{aligned}
\frac{E^{(2\omega)}(\|,\|)}{E_p^2 A_p} = {} & i\tilde{\Omega}F_s\epsilon(2\omega)\delta_{31} + i\tilde{\Omega}\epsilon(2\omega)F_s f_s^2(\delta_{33}-\delta_{31}) \\
& - 2i\tilde{\Omega}f_s f_c F_c\delta_{15} - i\tilde{\Omega}F_c f_c^2\delta_{11}\cos 3\phi
\end{aligned}
$$

and reduce (omitting the $(\|,\|)$ notation),

$$
\begin{aligned}
\frac{E^{(2\omega)}}{E_p^2} &= A_p i\tilde{\Omega}\left[F_s\epsilon(2\omega)(\delta_{31} + f_s^2(\delta_{33}-\delta_{31})) - f_c F_c(2f_s\delta_{15} + f_c\delta_{11}\cos 3\phi)\right] \\
&= A_p i\tilde{\Omega}\left[F_s\epsilon(2\omega)(f_s^2\delta_{33} + (1-f_s^2)\delta_{31}) - f_c F_c(2f_s\delta_{15} + f_c\delta_{11}\cos 3\phi)\right] \\
&= A_p i\tilde{\Omega}\left[F_s\epsilon(2\omega)(f_s^2\delta_{33} + f_c^2\delta_{31}) - f_c F_c(2f_s\delta_{15} + f_c\delta_{11}\cos 3\phi)\right].
\end{aligned}
$$

As every term has an $f_i^2 F_i$, we can factor out the common

$$
\frac{1}{\tilde{\omega}^2\tilde{\Omega}\epsilon(\omega)\sqrt{\epsilon(2\omega)}}
$$

factor after substituting the appropriate terms from Eq. (C.1),

$$\begin{aligned}
\frac{E^{(2\omega)}}{E_p^2} &= \frac{A_p i}{\epsilon(\omega)\sqrt{\epsilon(2\omega)}\tilde{\omega}^2}\left[K\epsilon(2\omega)(\kappa^2\delta_{33} + w^2\delta_{31}) - wW(2\kappa\delta_{15} + w\delta_{11}\cos 3\phi)\right] \\
&= \frac{A_p i\tilde{\Omega}}{\epsilon(\omega)\sqrt{\epsilon(2\omega)}}\big[\sin\theta\epsilon(2\omega)(\sin^2\theta\delta_{33} + k_z^2(\omega)\delta_{31}) \\
&\qquad - k_z(\omega)k_z(2\omega)(2\sin\theta\delta_{15} + k_z(\omega)\delta_{11}\cos 3\phi)\big] \\
&= \frac{A_p i\tilde{\Omega}}{\epsilon(\omega)\sqrt{\epsilon(2\omega)}}\big[\sin\theta\epsilon(2\omega)(\sin^2\theta\chi^{zzz} + k_z^2(\omega)\chi^{zxx}) \\
&\qquad - k_z(\omega)k_z(2\omega)(2\sin\theta\chi^{xxz} + k_z(\omega)\chi^{xxx}\cos 3\phi)\big].
\end{aligned}$$

We substitute Eq. (C.5) to complete the expression,

$$\begin{aligned}
\frac{E^{(2\omega)}}{E_p^2} &= \frac{4i\pi\tilde{\Omega}^2}{\epsilon(\omega)(W_0\epsilon(2\omega) + W)}[\cdots] \\
&= \frac{4i\pi\tilde{\Omega}}{\epsilon(\omega)(\epsilon(2\omega)\cos\theta + k_z(2\omega))}[\cdots] \\
&= \frac{4i\pi\tilde{\omega}}{\cos\theta}\frac{1}{\epsilon(\omega)}\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}[\cdots].
\end{aligned}$$

However, our interest lies in $\mathcal{R}_{pP}$ which is calculated as

$$\mathcal{R}_{pP} = \frac{I_p(2\omega)}{I_p^2(\omega)} = \frac{2\pi}{c}\left|\frac{E^{(2\omega)}(\|,\|)}{E_p^2}\right|^2,$$

and we can finally complete the expression,

$$\begin{aligned}
\mathcal{R}_{pP} &= \frac{2\pi}{c}\left|\frac{4i\pi\tilde{\omega}}{\cos\theta}\frac{1}{\epsilon(\omega)}\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}r_{pP}\right|^2 \\
&= \frac{32\pi^3\tilde{\omega}^2}{c\cos^2\theta}\left|t_p(\omega)T_p(2\omega)r_{pP}\right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|t_p(\omega)T_p(2\omega)r_{pP}\right|^2,
\end{aligned} \tag{C.7}$$

where

$$\begin{aligned}
t_p(\omega) &= \frac{1}{\epsilon(\omega)}, \\
T_p(2\omega) &= \frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}, \\
r_{pP} &= \sin\theta\epsilon(2\omega)(\sin^2\theta\chi^{zzz} + k_z^2(\omega)\chi^{zxx}) \\
&\quad - k_z(\omega)k_z(2\omega)(2\sin\theta\chi^{xxz} + k_z(\omega)\chi^{xxx}\cos 3\phi).
\end{aligned}$$

C.2 $\mathcal{R}_{pS}$

We follow the same procedure as above. For the (111) face ($m = 3$),

$$\frac{E^{(2\omega)}(\|,\perp)}{E_p^2 A_s} = b^{(3)}_{\|,\perp} \sin 3\phi, \tag{C.8}$$

and we extract the relevant coefficient from Table V with $\Gamma = \gamma = 0$,

$$b^{(3)}_{\|,\perp} = i\tilde{\Omega} f_c^2 \delta_{11}.$$

Substituting this coeffecient and Eq. (C.5) into Eq. (C.8),

$$\begin{aligned}
\frac{E^{(2\omega)}(\|,\perp)}{E_p^2} &= A_s i\tilde{\Omega} f_c^2 \delta_{11} \sin 3\phi \\
&= \frac{A_s i\tilde{\Omega}}{\tilde{\omega}^2 \epsilon(\omega)} w^2 \delta_{11} \sin 3\phi \\
&= \frac{A_s i\tilde{\Omega}}{\epsilon(\omega)} k_z^2(\omega) \delta_{11} \sin 3\phi \\
&= \frac{A_s i\tilde{\Omega}}{\epsilon(\omega)} k_z^2(\omega) \chi^{xxx} \sin 3\phi \\
&= \frac{4i\pi\tilde{\Omega}^2}{W_0 + W} \frac{1}{\epsilon(\omega)} k_z^2(\omega) \chi^{xxx} \sin 3\phi \\
&= 4i\pi\tilde{\Omega} \frac{1}{\epsilon(\omega)} \frac{1}{\cos\theta + k_z(2\omega)} k_z^2(\omega) \chi^{xxx} \sin 3\phi \\
&= \frac{4i\pi\omega}{c\cos\theta} \frac{1}{\epsilon(\omega)} \frac{2\cos\theta}{\cos\theta + k_z(2\omega)} k_z^2(\omega) \chi^{xxx} \sin 3\phi
\end{aligned}$$

As before, we must calculate

$$\mathcal{R}_{pS} = \frac{2\pi}{c} \left| \frac{E^{(2\omega)}(\|,\perp)}{E_s^2} \right|^2,$$

to obtain the final expression,

$$\begin{aligned}
\mathcal{R}_{pS} &= \frac{2\pi}{c} \left| \frac{4i\pi\omega}{c\cos\theta} \frac{1}{\epsilon(\omega)} \frac{2\cos\theta}{\cos\theta + k_z(2\omega)} k_z^2(\omega) \chi^{xxx} \sin 3\phi \right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta} \left| \frac{1}{\epsilon(\omega)} \frac{2\cos\theta}{\cos\theta + k_z(2\omega)} k_z^2(\omega) \chi^{xxx} \sin 3\phi \right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta} \left| t_p(\omega) T_s(2\omega) k_z^2(\omega) r_{pS} \right|^2,
\end{aligned} \tag{C.9}$$

where

$$
\begin{aligned}
t_p(\omega) &= \frac{1}{\epsilon(\omega)}, \\
T_s(2\omega) &= \frac{2\cos\theta}{\cos\theta + k_z(2\omega)}, \\
r_{pS} &= k_z^2(\omega)\chi^{xxx}\sin 3\phi.
\end{aligned}
$$

C.3 $\mathcal{R}_{sP}$

We follow the same procedure as above for the final polarization case. For the (111) face ($m = 3$),

$$
\frac{E^{(2\omega)}(\perp, \|)}{E_s^2 A_p} = a_{\perp,\|} + c^{(3)}_{\perp,\|}\cos 3\phi, \tag{C.10}
$$

and we extract the relevant coefficients from Table V with $\Gamma = \gamma = 0$,

$$
\begin{aligned}
a_{\perp,\|} &= i\tilde{\Omega}F_s\epsilon(2\omega)\delta_{31}, \\
c^{(3)}_{\perp,\|} &= i\tilde{\Omega}F_c\delta_{11}.
\end{aligned}
$$

Substituting this coeffecient and Eq. (C.5) into Eq. (C.10),

$$
\begin{aligned}
\frac{E^{(2\omega)}(\perp, \|)}{E_s^2} &= A_p(i\tilde{\Omega}F_s\epsilon(2\omega)\delta_{31} + i\tilde{\Omega}F_c\delta_{11}\cos 3\phi) \\
&= A_p i\tilde{\Omega}(F_s\epsilon(2\omega)\delta_{31} + F_c\delta_{11}\cos 3\phi) \\
&= \frac{A_p i\tilde{\Omega}}{\sqrt{\epsilon(2\omega)}}(\sin\theta\epsilon(2\omega)\delta_{31} + k_z(2\omega)\delta_{11}\cos 3\phi) \\
&= \frac{A_p i\tilde{\Omega}}{\sqrt{\epsilon(2\omega)}}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi) \\
&= \frac{4i\pi\tilde{\Omega}^2}{W_0\epsilon(2\omega) + W}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi) \\
&= \frac{4i\pi\tilde{\Omega}}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi) \\
&= \frac{4i\pi\omega}{c\cos\theta}\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi).
\end{aligned}
$$

iF	$t_i(\omega)$	$T_F(2\omega)$	r_{iF}
pP	$\frac{1}{\epsilon(\omega)}$	$\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}$	$\sin\theta\epsilon(2\omega)(\sin^2\theta\chi^{zzz} + k_z^2(\omega)\chi^{zxx})$ $-k_z(\omega)k_z(2\omega)(2\sin\theta\chi^{xxz}+k_z(\omega)\chi^{xxx}\cos 3\phi)$
pS	$\frac{1}{\epsilon(\omega)}$	$\frac{2\cos\theta}{\cos\theta + k_z(2\omega)}$	$k_z^2(\omega)\chi^{xxx}\sin 3\phi$
sP	1	$\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}$	$\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi$

Table C.1: The necessary factors for Eq. (C.12) for each polarization case.

And we finally obtain $\mathcal{R}_{sP}$,

$$\begin{aligned}
\mathcal{R}_{sP} &= \frac{2\pi}{c}\left|\frac{E^{(2\omega)}(\perp,\|)}{E_s^2}\right|^2 \\
&= \frac{2\pi}{c}\left|\frac{4i\pi\omega}{c\cos\theta}\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi)\right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi)\right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|t_s(\omega)T_p(2\omega)r_{sP}\right|^2, \qquad \text{(C.11)}
\end{aligned}$$

where

$$\begin{aligned}
t_s(\omega) &= 1, \\
T_p(2\omega) &= \frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}, \\
r_{sP} &= \sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi.
\end{aligned}$$

C.4 Summary

We unify the final expressions for the SHG yield, Eqs. (C.7), (C.9), and (C.11), as

$$\mathcal{R}_i F = \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|t_i(\omega)T_F(2\omega)r_{iF}\right|^2. \qquad \text{(C.12)}$$

The necessary factors are summarized in Table C.1.

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