1 Preamble

Our interest is to calculate the nonlinear reflection coefficient, $\mathcal{R}$. We start with equation (2) of [?]

$$\mathcal{R}_{iF} = \frac{32\pi^3\omega^2}{(n_o e)^2 c^3 \cos^2\theta} \left| T_F^{vs} T_F^{sb} (t_i^{vs} t_i^{sb})^2 r_{iF} \right|^2, \tag{1}$$

where $i = s$ or p is the incoming polarization at ω, $F = S$ or P the outgoing polarization at 2ω. θ is the angle of incidence, n_o is the electron density, e is the electron charge, and c is the speed of light. T and t are the Fresnel factors that give the transmitted fields at the vacuum–surface (vs) or the surface–bulk (sb) interfaces. They are given by

$$t_s^{vs}(\omega) = \frac{2\cos\theta}{\cos\theta + k_{zs}(\omega)}, \tag{2}$$

$$t_p^{vs}(\omega) = \frac{2\cos\theta}{\epsilon_s \cos\theta + k_{zs}(\omega)}, \tag{3}$$

$$t_s^{sb}(\omega) = \frac{2k_{zs}(\omega)}{k_{zs}(\omega) + k_{zb}(\omega)}, \tag{4}$$

$$t_p^{sb}(\omega) = \frac{2k_{zs}(\omega)}{\epsilon_b(\omega)k_{zs}(\omega) + \epsilon_s(\omega)k_{zb}(\omega)}. \tag{5}$$

where $k_{zj}(\omega) = (w/c) \times (\epsilon_j(\omega) - \sin^2\theta)^{1/2}$ for $j = s$ (surface) or b (bulk). ϵ_b (ϵ_s) is the bulk (surface) dielectric function. The Fresnel factors for the outgoing fields are $T = t(2\omega)$. Finally, the r_{iF} terms are

$$\begin{aligned} r_{pP} = {} & \sin\theta\epsilon_b(2\omega)[\sin^2\theta\epsilon_b^2(\omega)\chi_{\perp\perp\perp} + k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\perp\parallel\parallel}] \\ & +\epsilon_s(\omega)\epsilon_s(2\omega)k_{zb}(\omega)k_{zb}(2\omega)[-2\sin\theta\epsilon_b(\omega)\chi_{\parallel\parallel\perp} \\ & \qquad + k_{zb}(\omega)\epsilon_s(\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi)], \end{aligned} \tag{6}$$

$$r_{sP} = \sin\theta\epsilon_b(2\omega)\chi_{\perp\parallel\parallel} - k_{zb}(2\omega)\epsilon_s(2\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi), \tag{7}$$

$$r_{pS} = -k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\parallel\parallel\parallel}\sin(3\phi), \tag{8}$$

$$r_{sS} = \chi_{\parallel\parallel\parallel}\sin(3\phi), \tag{9}$$

where ϕ is the azimuthal angle. χ is the second-order susceptibility tensor with the following relations[1],

[1]for this symmetry group.

$$
\begin{aligned}
\chi_{\perp\perp\perp} &\equiv \chi_{zzz}, \\
\chi_{\perp\|\|} &\equiv \chi_{zxx} = \chi_{zyy}, \\
\chi_{\|\|\perp} &\equiv \chi_{xxz} = \chi_{yyz}, \\
\chi_{\|\|\|} &\equiv \chi_{xxx} = -\chi_{xyy} = -\chi_{yyx}.
\end{aligned} \tag{10}
$$

Thus, we have four different cases for $\mathcal{R}_{iF}$: $\mathcal{R}_{pP}$, $\mathcal{R}_{sP}$, $\mathcal{R}_{pS}$, and $\mathcal{R}_{sS}$. Let us derive the most explicit equations for these cases.

2 Fresnel Factors

We start with $k_{zj}(\omega)$ and substitute into the Fresnel factors. From (2),

$$
\begin{aligned}
t_s^{vs}(\omega) = \frac{2\cos\theta}{\cos\theta + k_{zs}(\omega)} &= \frac{2\cos\theta}{\cos\theta + (w/c)(\epsilon_s(\omega) - \sin^2\theta)^{1/2}} \\
&= \frac{2\cos\theta}{\cos\theta + (w/\sqrt{2}c)(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}.
\end{aligned} \tag{11}
$$

From (3),

$$
\begin{aligned}
t_p^{vs}(\omega) &= \frac{2\cos\theta}{\epsilon_s\cos\theta + k_{zs}(\omega)} \\
&= \frac{2\cos\theta}{\epsilon_s\cos\theta + (w/\sqrt{2}c)(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}.
\end{aligned} \tag{12}
$$

From (4),

$$
\begin{aligned}
t_s^{sb}(\omega) &= \frac{2k_{zs}(\omega)}{k_{zs}(\omega) + k_{zb}(\omega)} \\
&= \frac{2(\epsilon_s(\omega) - \sin^2\theta)^{1/2}}{(\epsilon_s(\omega) - \sin^2\theta)^{1/2} + (\epsilon_b(\omega) - \sin^2\theta)^{1/2}} \\
&= \frac{2(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}{(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2} + (2\epsilon_b(\omega) + \cos 2\theta + 1)^{1/2}}.
\end{aligned} \tag{13}
$$

Lastly, from (5),

$$
\begin{aligned}
t_s^{sb}(\omega) &= \frac{2k_{zs}(\omega)}{\epsilon_b(\omega)k_{zs}(\omega) + \epsilon_s(\omega)k_{zb}(\omega)} \\
&= \frac{2(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}{\epsilon_b(\omega)(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2} + \epsilon_s(\omega)(2\epsilon_b(\omega) + \cos 2\theta + 1)^{1/2}}.
\end{aligned} \tag{14}
$$

3 r_{iF} Terms

$$
\begin{aligned}
r_{pP} = \sin\theta\epsilon_b(2\omega)[\sin^2\theta\epsilon_b^2(\omega)\chi_{\perp\perp\perp} + k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\perp\|\|}] \\
+\epsilon_s(\omega)\epsilon_s(2\omega)k_{zb}(\omega)k_{zb}(2\omega)[-2\sin\theta\epsilon_b(\omega)\chi_{\|\|\perp} \\
+ k_{zb}(\omega)\epsilon_s(\omega)\chi_{\|\|\|}\cos(3\phi)],
\end{aligned}
\tag{15}
$$

$$
r_{sP} = \sin\theta\epsilon_b(2\omega)\chi_{\perp\|\|} - k_{zb}(2\omega)\epsilon_s(2\omega)\chi_{\|\|\|}\cos(3\phi), \tag{16}
$$

$$
r_{pS} = -k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\|\|\|}\sin(3\phi), \tag{17}
$$

$$
r_{sS} = \chi_{\|\|\|}\sin(3\phi), \tag{18}
$$