Optimized Software for Theoretical Optical Calculations

Sean M. Anderson

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Chapter 1

Theory

1.1 Introduction

Second harmonic generation (SHG) is a powerful spectroscopic tool for studying the optical properties of surfaces and interfaces since it has the advantage of being surface sensitive. Within the dipole approximation, inversion symmetry forbids SHG from the bulk of controsymmetric materials. SHG is allowed at the surface of these materials where the inversion symmetry is broken and should necessarily come from the localized surface region. SHG allows the study of the structural atomic arrangement and phase transitions of clean and adsorbate covered surfaces. Since it is also an optical probe it can be used out of UHV conditions and is non-invasive and non-destructive. Experimentally, new tunable high intensity laser systems have made SHG spectroscopy readily accessible and applicable to a wide range of systems.[**?**, **?**]

However, theoretical development of the field is still an ongoing subject of research. Some recent advances for the cases of semiconducting and metallic systems have appeared in the literature, where the use of theoretical models with experimental results have yielded correct physical interpretations for observed SHG spectra. [**?**, **?**, **?**, **?**, **?**, 1, 2, **?**, **?**]

In a previous article[**?**] we reviewed some of the recent results in the study of SHG using the velocity gauge for the coupling between the electromagnetic field and the electron. In particular, we demonstrated a method to systematically analyze the different contributions to the observed SHG peaks.[**?**] This approach consists of separating the different contributions to the nonlinear susceptibility according to 1ω and 2ω transitions, and the surface or bulk nature of the states among which the transitions take place.

To compliment those results, in this article we review the calculation of the nonlinear susceptibility using the longitudinal gauge. We show that it is posible to clearly obtain the "layer-by-layer" contribution for a slab scheme used for surface calculations.

1.2 Non-linear Surface Susceptibility

In this section we outline the general procedure to obtain the surface susceptibility tensor for second harmonic generation. We start with the non-linear polarization $\mathbf{P}$ written as

$$\begin{aligned} P_{\mathrm{a}}(2\omega) &= \chi_{\mathrm{abc}}(-2\omega;\omega,\omega)E_{\mathrm{b}}(\omega)E_{\mathrm{c}}(\omega) \\ &\quad + \chi_{\mathrm{abcl}}(-2\omega;\omega,\omega)E_{\mathrm{b}}(\omega)\nabla_{\mathrm{c}}E_{\mathrm{l}}(\omega) + \cdots , \end{aligned} \tag{1.1}$$

where $\chi_{\mathrm{abc}}(-2\omega;\omega,\omega)$ and $\chi_{\mathrm{abcl}}(-2\omega;\omega,\omega)$ correspond to the dipolar and quadrupolar susceptibilities. We drop the $(-2\omega;\omega,\omega)$ argument to ease on the notation. The sum continues with higher multipolar terms. If we consider a semi-infinite system with a centrosymmetric bulk, the equation above can be separated into two contributions from symmetry considerations alone; one from the surface of

the system and the other from the bulk of the system. We take

$$P_{\rm a}(\mathbf{r}) = \chi_{\rm abc} E_{\rm b}(\mathbf{r}) E_{\rm c}(\mathbf{r}) + \chi_{\rm abcl} E_{\rm b}(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}_{\rm c}} E_{\rm l}(\mathbf{r}) + \cdots , \tag{1.2}$$

as the polarization with respect to the original coordinate system, and

$$\begin{aligned} P_{\rm a}(-\mathbf{r}) &= \chi_{\rm abc} E_{\rm b}(-\mathbf{r}) E_{\rm c}(-\mathbf{r}) \\ &\quad + \chi_{\rm abcl} E_{\rm b}(-\mathbf{r}) \frac{\partial}{\partial(-\mathbf{r}_{\rm c})} E_{\rm l}(-\mathbf{r}) + \cdots , \end{aligned} \tag{1.3}$$

as the polarization in the coordinate system where inversion is taken, i.e. $\mathbf{r} \to -\mathbf{r}$. Note that we have kept the same susceptibility tensors, and they must be invariant under $\mathbf{r} \to -\mathbf{r}$ since the system is centrosymmetric. Recalling that $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ are polar vectors [**?**], we have that Eq. (1.3) reduces to

$$\begin{aligned} -P_{\rm a}(\mathbf{r}) &= \chi_{\rm abc}(-E_{\rm b}(\mathbf{r}))(-E_{\rm c}(\mathbf{r})) - \chi_{\rm abcl}(-E_{\rm b}(\mathbf{r}))(-\frac{\partial}{\partial \mathbf{r}_{\rm c}})(-E_{\rm l}(\mathbf{r})) + \cdots , \\ P_{\rm a}(\mathbf{r}) &= -\chi_{\rm abc} E_{\rm b}(\mathbf{r}) E_{\rm c}(\mathbf{r}) + \chi_{\rm abcl} E_{\rm b}(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}_{\rm c}} E_{\rm l}(\mathbf{r}) + \cdots , \end{aligned} \tag{1.4}$$

that when compared with Eq. (1.2) leads to the conclusion that

$$\chi_{\rm abc} = 0 \tag{1.5}$$

for a centrosymmetric bulk.

If we move to the surface of the semi-infinite system our assumption of centrosymmetry breaks down, and there is no restriction in $\chi_{\rm abc}$. We conclude that the leading term of the polarization in a surface region is given by

$$\int dz P_{\rm a}(\mathbf{R}, z) \approx dP_{\rm a} \equiv P_{\rm a}^S \equiv \chi_{\rm abc}^S E_{\rm b} E_{\rm c}, \tag{1.6}$$

where d is the surface region from which the dipolar signal of $\mathbf{P}$ is different from zero (see Fig. 1.1), and $\mathbf{P}^S \equiv d\mathbf{P}$ is the surface SH polarization. Then, from Eq. (1.1) we obtain that

$$\chi_{\rm abc}^S = d\chi_{\rm abc} \tag{1.7}$$

is the SH surface susceptibility. On the other hand,

$$P_{\rm a}^b(\mathbf{r}) = \chi_{\rm abcl} E_{\rm b}(\mathbf{r}) \nabla_{\rm c} E_{\rm l}(\mathbf{r}), \tag{1.8}$$

gives the bulk polarization. We immediately recognize that the surface polarization is of dipolar order while the bulk polarization is of quadrupolar order. The surface, $\chi_{\rm abc}^S$, and bulk, $\chi_{\rm abcl}$, susceptibility tensor ranks are three and four, respectively. We will only concentrate on surface SHG in this article even though bulk generated SH is also a very important optical phenomenon. Also, we leave out of this article other interesting surface SH phenomena like, electric field induced second harmonic (EFISH), which would be represented by a

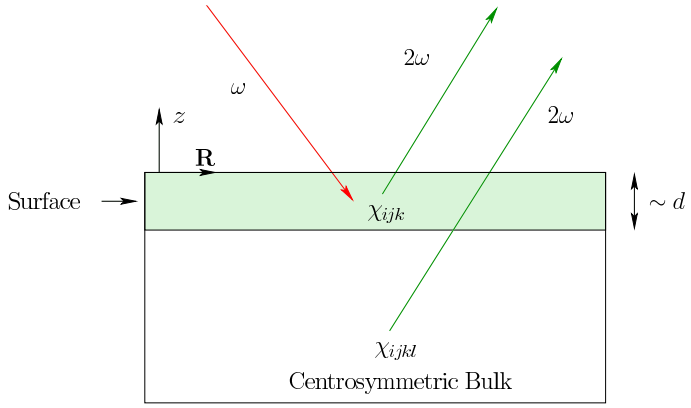

Figure 1.1: (Color Online) Sketch of the semi-infinite system with a centrosymmetric bulk. The surface region is of width $\sim d$. The incoming photon of frequency ω is represented by a downward red arrow, whereas both the surface and bulk created second harmonic photons of frequency 2ω are represented by upward green arrows. The red color suggests an incoming infrared photon with a green second harmonic photon. The dipolar ($\chi_{\rm abc}$), and quadrupolar ($\chi_{\rm abcl}$) susceptibility tensors are shown in the regions where they are different from zero. The axis has z perpendicular to the surface and $\mathbf{R}$ parallel to it.

surface susceptibility tensor of quadrupolar origin. In centrosymmetric systems for which the quadrupolar bulk response is much smaller than the dipolar surface response, SH is readily used as a very useful and powerful optical surface probe.[**?**]

In the following sections we present the theoretical approach to derive the expressions for the surface susceptibility tensor $\chi^S_{\rm abc}$.

1.3 Length Gauge

We follow the article by Aversa and Sipe[**?**] to calculate the optical properties of a given system within the longitudinal gauge. More recent derivations can also be found in Refs. [**?**, **?**]. Assuming the long-wavelength approximation which implies a position independent electric field, $\mathbf{E}(t)$, the Hamiltonian in the length gauge approximation is given by

$$\hat{H} = \hat{H}^{\sigma}_0 - e\hat{\mathbf{r}} \cdot \mathbf{E}, \tag{1.9}$$

with

$$\hat{H}^{\sigma}_0 = \hat{H}^{\rm LDA}_0 + \mathcal{S}(\mathbf{r}, \mathbf{p}), \tag{1.10}$$

as the unperturbed Hamiltonian. The LDA Hamiltonian can be expressed as follows,

$$\hat{H}_0^{\mathrm{LDA}} = \frac{\hat{p}^2}{2m_e} + \hat{V}^{\mathrm{ps}}$$
$$\hat{V}^{\mathrm{ps}} = \hat{V}^{l}(\hat{\mathbf{r}}) + \hat{V}^{\mathrm{nl}}, \tag{1.11}$$

where $\hat{V}^{l}(\hat{\mathbf{r}})$ and $\hat{V}^{\mathrm{nl}}$ are the local and the non-local parts of the crystal pseudopotential $\hat{V}^{\mathrm{ps}}$. For the latter, we have that

$$V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}') \equiv \langle \mathbf{r}|\hat{V}^{\mathrm{nl}}|\mathbf{r}'\rangle \neq 0 \quad \text{for} \quad \mathbf{r} \neq \mathbf{r}', \tag{1.12}$$

where $V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')$ is a function of $\mathbf{r}$ and $\mathbf{r}'$ representing the non-local contribution of the pseudopotential. The Schrödinger equation reads

$$\left(\frac{-\hbar^2}{2m_e}\nabla^2 + \hat{V}^{l}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}'\hat{V}^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}') = E_i\psi_{n\mathbf{k}}(\mathbf{r}), \tag{1.13}$$

where $\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r}|n\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$, are the real space representations of the Bloch states $|n\mathbf{k}\rangle$ labelled by the band index n and the crystal momentum $\mathbf{k}$, and $u_{n\mathbf{k}}(\mathbf{r})$ is cell periodic. m_e is the bare mass of the electron and Ω is the unit cell volume. The nonlocal scissors operator is given by

$$\mathcal{S}(\mathbf{r},\mathbf{p}) = \hbar\Sigma\sum_n \int d^3k'(1 - f_n(\mathbf{k}))|n\mathbf{k}'\rangle\langle n\mathbf{k}'|, \tag{1.14}$$

where $f_n(\mathbf{k})$ is the occupation number, that for $T = 0$ K, is independent of $\mathbf{k}$, and is one for filled bands and zero for unoccupied bands. For semiconductors the filled bands correspond to valence bands ($n = v$) and the unoccupied bands to conduction bands ($n = c$). We have that

$$H_0^{\mathrm{LDA}}|n\mathbf{k}\rangle = \hbar\omega_n^{\mathrm{LDA}}(\mathbf{k})|n\mathbf{k}\rangle$$
$$H_0^{\sigma}|n\mathbf{k}\rangle = \hbar\omega_n^{\sigma}(\mathbf{k})|n\mathbf{k}\rangle, \tag{1.15}$$

where

$$\hbar\omega_n^{\sigma}(\mathbf{k}) = \hbar\omega_n^{\mathrm{LDA}}(\mathbf{k}) + \hbar\Sigma(1 - f_n), \tag{1.16}$$

is the scissored energy. Here, $\hbar\Sigma$ is the value by which the conduction bands are rigidly ($\mathbf{k}$-independent) shifted upwards in energy, also known as the scissors shift. Σ could be taken to be $\mathbf{k}$ dependent, but for most calculations (like the ones presented here), a rigid shift is sufficient. We can take $\hbar\Sigma = E_g - E_g^{\mathrm{LDA}}$ where E_g could be the experimental band gap or GW band gap taken at the Γ point, i.e. $\mathbf{k} = 0$. We used the fact that $|n\mathbf{k}\rangle^{\mathrm{LDA}} \approx |n\mathbf{k}\rangle^{\sigma}$, thus negating the need to label the Bloch states with the LDA or σ superscripts. The matrix elements of $\mathbf{r}$ are split between the *intraband* ($\mathbf{r}_i$) and *interband* ($\mathbf{r}_e$) parts , where $\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e$ and[**?**, **?**, **?**]

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k} - \mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k} - \mathbf{k}')\right], \tag{1.17}$$
$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1 - \delta_{nm})\delta(\mathbf{k} - \mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}), \tag{1.18}$$

and

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i\frac{(2\pi)^3}{\Omega}\int_\Omega d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r})\nabla_{\mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}). \tag{1.19}$$

The interband part $\mathbf{r}_e$ can be obtained as follows. We start by introducing the velocity operator

$$\hat{\mathbf{v}}^\sigma = \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{H}^\sigma_0], \tag{1.20}$$

and calculating its matrix elements

$$i\hbar\langle n\mathbf{k}|\mathbf{v}^\sigma|m\mathbf{k}\rangle = \langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}^\sigma_0]|m\mathbf{k}\rangle = \langle n\mathbf{k}|\hat{\mathbf{r}}\hat{H}^\sigma_0 - \hat{H}^\sigma_0\hat{\mathbf{r}}|m\mathbf{k}\rangle = (\hbar\omega^\sigma_m(\mathbf{k}) - \hbar\omega^\sigma_n(\mathbf{k}))\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}\rangle, \tag{1.21}$$

thus defining $\omega^\sigma_{nm}(\mathbf{k}) = \omega^\sigma_n(\mathbf{k}) - \omega^\sigma_m(\mathbf{k})$ we get

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^\sigma_{nm}(\mathbf{k})}{i\omega^\sigma_{nm}(\mathbf{k})} \qquad n \notin D_m, \tag{1.22}$$

which can be identified as $\mathbf{r}_{nm} = (1-\delta_{nm})\boldsymbol{\xi}_{nm} \to \mathbf{r}_{e,nm}$. Here, D_m are all the possible degenerate m-states. When $\mathbf{r}_i$ appears in commutators we use[**?**]

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\mathcal{O}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{1.23}$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right), \tag{1.24}$$

where "$;\mathbf{k}$" denotes the generalized derivative (see Appendix **??**).

As can be seen from Eq. (1.10) and (1.11), both $\hat{S}$ and $\hat{V}^{\rm nl}$ are nonlocal potentials. Their contribution in the calculation of the optical response has to be taken in order to get reliable results.[**?**] We proceed as follows; from Eqs. (1.20), (1.10) and (1.11) we find

$$\begin{aligned}\hat{\mathbf{v}}^\sigma &= \frac{\hat{\mathbf{p}}}{m_e} + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\rm nl}(\mathbf{r},\mathbf{r}')] + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{\mathcal{S}}(\mathbf{r},\mathbf{p})] \\ &\equiv \hat{\mathbf{v}} + \hat{\mathbf{v}}^{\rm nl} + \hat{\mathbf{v}}^{\mathcal{S}} = \hat{\mathbf{v}}^{\rm LDA} + \hat{\mathbf{v}}^{\mathcal{S}},\end{aligned} \tag{1.25}$$

where we have defined

$$\begin{aligned}\hat{\mathbf{v}} &= \frac{\hat{\mathbf{p}}}{m_e} \\ \hat{\mathbf{v}}^{\rm nl} &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\rm nl}] \\ \hat{\mathbf{v}}^{\mathcal{S}} &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{S}(\mathbf{r},\mathbf{p})] \\ \hat{\mathbf{v}}^{\rm LDA} &= \hat{\mathbf{v}} + \hat{\mathbf{v}}^{\rm nl}\end{aligned} \tag{1.26}$$

with $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$ the momentum operator. Using Eq. (1.14), we obtain that the matrix elements of $\hat{\mathbf{v}}^{\mathcal{S}}$ are given by

$$\mathbf{v}^{\mathcal{S}}_{nm} = i\Sigma f_{mn}\mathbf{r}_{nm}, \tag{1.27}$$

with $f_{nm} = f_n - f_m$, where we see that $\mathbf{v}^{\mathcal{S}}_{nn} = 0$, then

$$\begin{aligned}
\mathbf{v}^{\sigma}_{nm} &= \mathbf{v}^{\mathrm{LDA}}_{nm} + i\Sigma f_{mn}\mathbf{r}_{nm} \\
&= \mathbf{v}^{\mathrm{LDA}}_{nm} + i\Sigma f_{mn}\frac{\mathbf{v}^{\sigma}_{nm}(\mathbf{k})}{i\omega^{\sigma}_{nm}(\mathbf{k})} \\
\mathbf{v}^{\sigma}_{nm}\frac{\omega^{\sigma}_{nm} - \Sigma f_{mn}}{\omega^{\sigma}_{nm}} &= \mathbf{v}^{\mathrm{LDA}}_{nm} \\
\mathbf{v}^{\sigma}_{nm}\frac{\omega^{\mathrm{LDA}}_{nm}}{\omega^{\sigma}_{nm}} &= \mathbf{v}^{\mathrm{LDA}}_{nm} \\
\frac{\mathbf{v}^{\sigma}_{nm}}{\omega^{\sigma}_{nm}} &= \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}}{\omega^{\mathrm{LDA}}_{nm}},
\end{aligned} \tag{1.28}$$

since $\omega^{\sigma}_{nm} - \Sigma f_{mn} = \omega^{\mathrm{LDA}}_{nm}$. Therefore,

$$\begin{aligned}
\mathbf{v}^{\sigma}_{nm}(\mathbf{k}) &= \frac{\omega^{\sigma}_{nm}}{\omega^{\mathrm{LDA}}_{nm}}\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}) = \left(1 + \frac{\Sigma}{\omega_c(\mathbf{k}) - \omega_v(\mathbf{k})}\right)\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}) \qquad n \notin D_m \\
\mathbf{v}^{\sigma}_{nn}(\mathbf{k}) &= \mathbf{v}^{\mathrm{LDA}}_{nn}(\mathbf{k}),
\end{aligned} \tag{1.29}$$

and Eq. (1.22) gives

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\sigma}_{nm}(\mathbf{k})}{i\omega^{\sigma}_{nm}(\mathbf{k})} = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n \notin D_m. \tag{1.30}$$

The matrix elements of $\mathbf{r}_e$ are the same whether we use the LDA or the scissored Hamiltonian and there is no need to label them with either LDA or S superscripts. Thus, we can write

$$\mathbf{r}_{e,nm} \to \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n \notin D_m, \tag{1.31}$$

which gives the interband matrix elements of the position operator in terms of the matrix elements of $\hat{\mathbf{v}}^{\mathrm{LDA}}$. These matrix elements include the matrix elements of $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k})$ which can be readily calculated[**?**] for fully separable nonlocal pseudopotentials in the Kleinman-Bylander form.[**?**, **?**, **?**] In Appendix **??** we outline how this can be accomplished.

1.4 Time-dependent Perturbation Theory

In the independent particle approximation, we use the electron density operator $\hat{\rho}$ to obtain the expectation value of any observable $\mathcal{O}$ as

$$\mathcal{O} = \mathrm{Tr}(\hat{\mathcal{O}}\hat{\rho}) = \mathrm{Tr}(\hat{\rho}\hat{\mathcal{O}}), \tag{1.32}$$

where Tr is the trace and is invariant under cyclic permutations. The dynamic equation of motion for ρ is given by

$$i\hbar\frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}], \tag{1.33}$$

where it is more convenient to work in the interaction picture. We transform all operators according to

$$\hat{\mathcal{O}}_I = \hat{U}\hat{\mathcal{O}}\hat{U}^\dagger, \tag{1.34}$$

where

$$\hat{U} = e^{i\hat{H}_0 t/\hbar}, \tag{1.35}$$

is the unitary operator that shifts us to the interaction picture. Note that $\hat{\mathcal{O}}_I$ depends on time even if $\hat{\mathcal{O}}$ does not. Then, we transform Eq. (1.33) into

$$i\hbar\frac{d\hat{\rho}_I(t)}{dt} = [-e\hat{\mathbf{r}}_I(t)\cdot\mathbf{E}(t), \hat{\rho}_I(t)], \tag{1.36}$$

that leads to

$$\hat{\rho}_I(t) = \hat{\rho}_I(t=-\infty) + \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I(t')]. \tag{1.37}$$

We assume that the interaction is switched-on adiabatically and choose a time-periodic perturbing field, to write

$$\mathbf{E}(t) = \mathbf{E}e^{-i\omega t}e^{\eta t} = \mathbf{E}e^{-i\tilde{\omega}t}, \tag{1.38}$$

with

$$\tilde{\omega} = \omega + i\eta, \tag{1.39}$$

where $\eta > 0$ assures that at $t = -\infty$ the interaction is zero and has its full strength $\mathbf{E}$ at $t = 0$. After computing the required time integrals one takes $\eta \to 0$. Also, $\hat{\rho}_I(t=-\infty)$ should be time independent and thus $[\hat{H}, \hat{\rho}]_{t=-\infty} = 0$, This implies that $\hat{\rho}_I(t=-\infty) = \hat{\rho}(t=-\infty) \equiv \hat{\rho}_0$, where $\hat{\rho}_0$ is the density matrix of the unperturbed ground state, such that

$$\langle n\mathbf{k}|\hat{\rho}_0|m\mathbf{k}'\rangle = f_n(\hbar\omega_n^\sigma(\mathbf{k}))\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{1.40}$$

with $f_n(\hbar\omega_n^\sigma(\mathbf{k})) = f_{n\mathbf{k}}$ as the Fermi-Dirac distribution function.

We solve Eq. (1.37) using the standard iterative solution, for which we write

$$\hat{\rho}_I = \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots, \tag{1.41}$$

where $\hat{\rho}_I^{(N)}$ is the density operator to order N in $\mathbf{E}(t)$. Then, Eq. (1.37) reads

$$\hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots = \hat{\rho}_0 + \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots], \tag{1.42}$$

where, by equating equal orders in the perturbation, we find

$$\hat{\rho}_I^{(0)} \equiv \hat{\rho}_0, \tag{1.43}$$

and

$$\hat{\rho}_I^{(N)}(t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I^{(N-1)}(t')]. \tag{1.44}$$

It is simple to show that matrix elements of Eq. (1.44) satisfy $\langle n\mathbf{k}|\rho_I^{(N+1)}(t)|m\mathbf{k}'\rangle = \rho_{I,nm}^{(N+1)}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')$, with

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' \langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t'), \hat{\rho}_I^{(N)}(t')]|m\mathbf{k}\rangle \cdot \mathbf{E}(t'). \tag{1.45}$$

We now work out the commutator of Eq. (1.45). Then,

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t), \hat{\rho}_I^{(N)}(t)]|m\mathbf{k}\rangle &= \langle n\mathbf{k}|[\hat{U}\hat{\mathbf{r}}\hat{U}^\dagger, \hat{U}\hat{\rho}^{(N)}(t)\hat{U}^\dagger]|m\mathbf{k}\rangle \\ &= \langle n\mathbf{k}|\hat{U}[\hat{\mathbf{r}}, \hat{\rho}^{(N)}(t)]\hat{U}^\dagger|m\mathbf{k}\rangle \\ &= e^{i\omega_{nm\mathbf{k}}^{\sigma}t}\left(\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)] + [\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle\right).\end{aligned} \tag{1.46}$$

We calculate the interband term first, so using Eq. (1.31) we obtain

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle &= \sum_{\ell}\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_e|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\rho}^{(N)}(t)|m\mathbf{k}\rangle \\ &\quad -\langle n\mathbf{k}|\hat{\rho}^{(N)}(t)|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle\Big) \\ &= \sum_{\ell\neq n,m}\Big(\mathbf{r}_{n\ell}(\mathbf{k})\rho_{\ell m}^{(N)}(\mathbf{k};t) - \rho_{n\ell}^{(N)}(\mathbf{k};t)\mathbf{r}_{\ell m}(\mathbf{k})\Big) \\ &\equiv \mathbf{R}_e^{(N)}(\mathbf{k};t),\end{aligned} \tag{1.47}$$

and from Eq. (1.23),

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\rho_{nm}^{(N)}(t))_{;\mathbf{k}} \equiv \delta(\mathbf{k}-\mathbf{k}')\mathbf{R}_i^{(N)}(\mathbf{k};t). \tag{1.48}$$

Then Eq. (1.45) becomes

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}^{\sigma}-\tilde{\omega})t'}\left[R_e^{\mathrm{b}(N)}(\mathbf{k};t') + R_i^{\mathrm{b}(N)}(\mathbf{k};t')\right]E^{\mathrm{b}}, \tag{1.49}$$

where the roman superindices $\mathrm{a}, \mathrm{b}, \mathrm{c}$ denote Cartesian components that are summed over if repeated. Starting from the linear response and proceeding from Eq. (1.40) and (1.47),

$$\begin{aligned}R_e^{\mathrm{b}(0)}(\mathbf{k};t) &= \sum_{\ell}\Big(r_{n\ell}^{\mathrm{b}}(\mathbf{k})\rho_{\ell m}^{(0)}(\mathbf{k}) - \rho_{n\ell}^{(0)}(\mathbf{k})r_{\ell m}^{\mathrm{b}}(\mathbf{k})\Big) \\ &= \sum_{\ell}\left(r_{n\ell}^{\mathrm{b}}(\mathbf{k})\delta_{\ell m}f_m(\hbar\omega_m^{\sigma}(\mathbf{k})) - \delta_{n\ell}f_n(\hbar\omega_n^{\sigma}(\mathbf{k}))r_{\ell m}^{\mathrm{b}}(\mathbf{k})\right) \\ &= f_{mn\mathbf{k}}r_{nm}^{\mathrm{b}}(\mathbf{k}),\end{aligned} \tag{1.50}$$

where $f_{mn\mathbf{k}} = f_{m\mathbf{k}} - f_{n\mathbf{k}}$. From now on, it should be clear that the matrix elements of $\mathbf{r}_{nm}$ imply $n \notin D_m$. We also have from Eq. (1.48) and Eq. (1.24) that

$$R_i^{\mathrm{b}(0)}(\mathbf{k}) = i(\rho_{nm}^{(0)})_{;k^{\mathrm{b}}} = i\delta_{nm}(f_{n\mathbf{k}})_{;k^{\mathrm{b}}} = i\delta_{nm}\nabla_{k^{\mathrm{b}}}f_{n\mathbf{k}}. \tag{1.51}$$

For a semiconductor at $T = 0$, $f_{n\mathbf{k}}$ is one if the state $|n\mathbf{k}\rangle$ is a valence state and zero if it is a conduction state; thus $\nabla_{\mathbf{k}} f_{n\mathbf{k}} = 0$ and $\mathbf{R}_i^{(0)} = 0$ and the linear response has no contribution from intraband transitions. Then,

$$\begin{aligned}\rho^{(1)}_{I,nm}(\mathbf{k};t) &= \frac{ie}{\hbar} f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k}) E^{\mathrm{b}} \int_{-\infty}^{t} dt' e^{i(\omega^{\sigma}_{nm\mathbf{k}} - \tilde{\omega})t'} \\ &= \frac{e}{\hbar} f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k}) E^{\mathrm{b}} \frac{e^{i(\omega^{\sigma}_{nm\mathbf{k}} - \tilde{\omega})t}}{\omega^{\sigma}_{nm\mathbf{k}} - \tilde{\omega}} \\ &= e^{i\omega^{\sigma}_{nm\mathbf{k}} t} B^{\mathrm{b}}_{mn}(\mathbf{k}) E^{\mathrm{b}}(t) \\ &= e^{i\omega^{\sigma}_{nm\mathbf{k}} t} \rho^{(1)}_{nm}(\mathbf{k};t), \end{aligned} \tag{1.52}$$

with

$$B^{\mathrm{b}}_{nm}(\mathbf{k},\omega) = \frac{e}{\hbar} \frac{f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k})}{\omega^{\sigma}_{nm\mathbf{k}} - \tilde{\omega}}, \tag{1.53}$$

and

$$\rho^{(1)}_{nm}(\mathbf{k};t) = B^{\mathrm{b}}_{mn}(\mathbf{k},\omega) E^{\mathrm{b}}(\omega) e^{-i\tilde{\omega}t}. \tag{1.54}$$

Now, we calculate the second-order response. Then, from Eq. (1.47)

$$\begin{aligned} R^{\mathrm{b}(1)}_{e}(\mathbf{k};t) &= \sum_{\ell} \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) \rho^{(1)}_{\ell m}(\mathbf{k};t) - \rho^{(1)}_{n\ell}(\mathbf{k};t) r^{\mathrm{b}}_{\ell m}(\mathbf{k}) \right) \\ &= \sum_{\ell} \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega) r^{\mathrm{b}}_{\ell m}(\mathbf{k}) \right) E^{\mathrm{c}}(t), \end{aligned} \tag{1.55}$$

and from Eq. (1.48)

$$R^{\mathrm{b}(1)}_{i}(\mathbf{k};t) = i(\rho^{(1)}_{nm}(t))_{;k^{\mathrm{b}}} = iE^{\mathrm{c}}(t)(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega))_{;k^{\mathrm{b}}}. \tag{1.56}$$

Using Eqs. (1.55) and (1.56) in Eq. (1.49), we obtain

$$\begin{aligned}\rho^{(2)}_{I,nm}(\mathbf{k};t) &= \frac{ie}{\hbar} \Bigg[\sum_{\ell} \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega) r^{\mathrm{b}}_{\ell m}(\mathbf{k}) \right) \\ &\quad + i(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega))_{;k^{\mathrm{b}}} \Bigg] E^{\mathrm{b}}_{\omega} E^{\mathrm{c}}_{\omega} \int_{-\infty}^{t} dt' e^{i(\omega^{\sigma}_{nm\mathbf{k}} - 2\tilde{\omega})t'} \\ &= \frac{e}{\hbar} \Bigg[\sum_{\ell} \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega) r^{\mathrm{b}}_{\ell m}(\mathbf{k}) \right) \\ &\quad + i(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega))_{;k^{\mathrm{b}}} \Bigg] E^{\mathrm{b}}_{\omega} E^{\mathrm{c}}_{\omega} \frac{e^{i(\omega^{\sigma}_{nm\mathbf{k}} - 2\tilde{\omega})t}}{\omega^{\sigma}_{nm\mathbf{k}} - 2\tilde{\omega}} \\ &= e^{i\omega^{\sigma}_{nm\mathbf{k}} t} \rho^{(2)}_{nm}(\mathbf{k};t). \end{aligned} \tag{1.57}$$

Now, we write $\rho^{(2)}_{nm}(\mathbf{k};t) = \rho^{(2)}_{nm}(\mathbf{k};2\omega) e^{-i2\tilde{\omega}t}$, with

$$\begin{aligned}\rho^{(2)}_{nm}(\mathbf{k};2\omega) &= \frac{e}{i\hbar} \frac{1}{\omega^{\sigma}_{nm\mathbf{k}} - 2\tilde{\omega}} \Bigg[- (B^{\mathrm{c}}_{nm}(\mathbf{k},\omega)_{;k^{\mathrm{b}}} \\ &\quad + i \sum_{\ell} \left(r^{\mathrm{b}}_{n\ell} B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega) r^{\mathrm{b}}_{\ell m} \right) \Bigg] E^{\mathrm{b}}(\omega) E^{\mathrm{c}}(\omega) \end{aligned} \tag{1.58}$$

where $B^{\rm a}_{\ell m}(\mathbf{k},\omega)$ are given by Eq. (1.53). We remark that $\mathbf{r}_{nm}(\mathbf{k})$ are the same whether calculated with the LDA or the scissored Hamiltonian. We chose the former in this article.

1.5 Layered Current Density

In this section, we derive the expressions for the microscopic current density of a given layer in the unit cell of the system. The approach we use to study the surface of a semi-infinite semiconductor crystal is as follows. Instead of using a semi-infinite system, we replace it by a slab (see Fig. 1.2). The slab consists of a front and back surface, and in between these two surfaces is the bulk of the system. In general the surface of a crystal reconstructs or relaxes as the atoms move to find equilibrium positions. This is due to the fact that the otherwise balanced forces are disrupted when the surface atoms do not find their partner atoms that are now absent at the surface of the slab.

To take the reconstruction or relaxation into account, we take "surface" to mean the true surface of the first layer of atoms, and some of the atomic sub-layers adjacent to it. Since the front and the back surfaces of the slab are usually identical the total slab is centrosymmetric. This implies that $\chi^{\rm slab}_{\rm abc}=0$, and thus we must find a way to bypass this characteristic of a centrosymmetric slab in order to have a finite $\chi^{s}_{\rm abc}$ representative of the surface. Even if the front and back surfaces of the slab are different, breaking the centrosymmetry and therefore giving an overall $\chi^{\rm slab}_{\rm abc}\neq 0$, we still need a procedure to extract the front surface $\chi^{f}_{\rm abc}$ and the back surface $\chi^{b}_{\rm abc}$ from the non-linear susceptibility $\chi^{\rm slab}_{\rm abc}=\chi^{f}_{\rm abc}-\chi^{b}_{\rm abc}$ of the entire slab.

A convenient way to accomplish the separation of the SH signal of either surface is to introduce a "cut function", $\mathcal{C}(z)$, which is usually taken to be unity over one half of the slab and zero over the other half.[**?**] In this case $\mathcal{C}(z)$ will give the contribution of the side of the slab for which $\mathcal{C}(z)=1$. We can generalize this simple choice for $\mathcal{C}(z)$ by a top-hat cut function $\mathcal{C}^{\ell}(z)$ that selects a given layer,

$$\mathcal{C}^{\ell}(z)=\Theta(z-z_{\ell}+\Delta^{\rm b}_{\ell})\Theta(z_{\ell}-z+\Delta^{f}_{\ell}), \tag{1.59}$$

where Θ is the Heaviside function. Here, $\Delta^{f/b}_{\ell}$ is the distance that the ℓ-th layer extends towards the front (f) or back (b) from its z_{ℓ} position. $\Delta^{f}_{\ell}+\Delta^{b}_{\ell}$ is the thickness of layer ℓ (see Fig. 1.2).

Now, we show how this "cut function" $\mathcal{C}^{\ell}(z)$ is introduced in the calculation of $\chi_{\rm abc}$. The microscopic current density is given by

$$\mathbf{j}(\mathbf{r},t)=\mathrm{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)), \tag{1.60}$$

where the operator for the electron's current is

$$\hat{\mathbf{j}}(\mathbf{r})=\frac{e}{2}\left(\hat{\mathbf{v}}^{\sigma}|\mathbf{r}\rangle\langle\mathbf{r}|+|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^{\sigma}\right), \tag{1.61}$$

where $\hat{\mathbf{v}}^\sigma$ is the electron's velocity operator to be dealt with below. We define $\hat{\mu} \equiv |\mathbf{r}\rangle\langle\mathbf{r}|$ and use the cyclic invariance of the trace to write

$$\begin{aligned}
\mathrm{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t) = \mathrm{Tr}(\hat{\rho}(t)\hat{\mathbf{j}}(\mathbf{r})) &= \frac{e}{2}\left(\mathrm{Tr}(\hat{\rho}\hat{\mathbf{v}}^\sigma\hat{\mu}) + \mathrm{Tr}(\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^\sigma)\right) \\
&= \frac{e}{2}\sum_{n\mathbf{k}}\left(\langle n\mathbf{k}|\hat{\rho}\hat{\mathbf{v}}^\sigma\hat{\mu}|n\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^\sigma|n\mathbf{k}\rangle\right) \\
&= \frac{e}{2}\sum_{nm\mathbf{k}}\langle n\mathbf{k}|\hat{\rho}|m\mathbf{k}\rangle\left(\langle m\mathbf{k}|\hat{\mathbf{v}}^\sigma|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^\sigma|n\mathbf{k}\rangle\right) \\
\mathbf{j}(\mathbf{r},t) &= \sum_{nm\mathbf{k}}\rho_{nm}(\mathbf{k};t)\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}),
\end{aligned} \tag{1.62}$$

where

$$\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}) = \frac{e}{2}\left(\langle m\mathbf{k}|\hat{\mathbf{v}}^\sigma|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^\sigma|n\mathbf{k}\rangle\right), \tag{1.63}$$

are the matrix elements of the microscopic current operator, and we have used the fact that the matrix elements between states $|n\mathbf{k}\rangle$ are diagonal in $\mathbf{k}$, i.e. proportional to $\delta(\mathbf{k}-\mathbf{k}')$.

Integrating the microscopic current $\mathbf{j}(\mathbf{r},t)$ over the entire slab gives the averaged microscopic current density. If we want the contribution from only one region of the unit cell towards the total current, we can integrate $\mathbf{j}(\mathbf{r},t)$ over the desired region. The contribution to the current density from the ℓ-th layer of the slab is given by

$$\frac{1}{\Omega}\int d^3r\, \mathcal{C}^\ell(z)\,\mathbf{j}(\mathbf{r},t) \equiv \mathbf{J}^\ell(t), \tag{1.64}$$

where $\mathbf{J}^\ell(t)$ is the microscopic current in the ℓ-th layer. Therefore we define

$$e\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{mn}(\mathbf{k}) \equiv \int d^3r\, \mathcal{C}^\ell(z)\,\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}), \tag{1.65}$$

to write

$$J_a^{(N,\ell)}(t) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{\sigma,a,\ell}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};t), \tag{1.66}$$

as the induced microscopic current of the ℓ-th layer, to order N in the external perturbation. The matrix elements of the density operator for $N=1,2$ are given by Eqs. (1.53) and (1.58) respectively. The Fourier component of microscopic current of Eq. (1.66) is given by

$$J_{\mathrm{a}}^{(N,\ell)}(\omega_3) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};\omega_3). \tag{1.67}$$

We proceed to give an explicit expression of $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{mn}(\mathbf{k})$. From Eqs. (1.65) and (1.63) we obtain

$$\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{mn}(\mathbf{k}) = \frac{1}{2}\int \mathrm{d}^3r\, \mathcal{C}^\ell(z)\Big[\langle m\mathbf{k}|\mathbf{v}^\sigma|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{v}^\sigma|n\mathbf{k}\rangle\Big], \tag{1.68}$$

and using the following property

$$\langle \mathbf{r}|\hat{\mathbf{v}}^{\sigma}(\mathbf{r},\mathbf{r}')|n\mathbf{k}\rangle = \int d^3r''\langle \mathbf{r}|\hat{\mathbf{v}}^{\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}''\rangle\langle \mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^{\sigma}(\mathbf{r},\mathbf{r}'')\int d^3r''\langle \mathbf{r}|\mathbf{r}''\rangle\langle \mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^{\sigma}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}), \tag{1.69}$$

that stems from the fact that the operator $\mathbf{v}^{\sigma}(\mathbf{r},\mathbf{r}')$ does not act on $\mathbf{r}''$, we can write

$$\begin{aligned}\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{mn}(\mathbf{k}) &= \frac{1}{2}\int \mathrm{d}^3r\,\mathcal{C}^{\ell}(z)\left[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^{\sigma *}\psi^{*}_{m\mathbf{k}}(\mathbf{r}) + \psi^{*}_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^{\sigma}\psi_{n\mathbf{k}}(\mathbf{r})\right] \\ &= \int \mathrm{d}^3r\,\psi^{*}_{m\mathbf{k}}(\mathbf{r})\left[\frac{\mathcal{C}^{\ell}(z)\mathbf{v}^{\sigma} + \mathbf{v}^{\sigma}\mathcal{C}^{\ell}(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r}) \\ &= \int \mathrm{d}^3r\,\psi^{*}_{m\mathbf{k}}(\mathbf{r})\boldsymbol{\mathcal{V}}^{\sigma,\ell}\psi_{n\mathbf{k}}(\mathbf{r}).\end{aligned} \tag{1.70}$$

We used the hermitian property of $\mathbf{v}^{\sigma}$ and defined

$$\boldsymbol{\mathcal{V}}^{\sigma,\ell} = \frac{\mathcal{C}^{\ell}(z)\mathbf{v}^{\sigma} + \mathbf{v}^{\sigma}\mathcal{C}^{\ell}(z)}{2}, \tag{1.71}$$

where the superscript ℓ is inherited from $\mathcal{C}^{\ell}(z)$ and we supress the dependance on z from the increasingly crowded notation. We see that the replacement

$$\hat{\mathbf{v}}^{\sigma} \to \hat{\boldsymbol{\mathcal{V}}}^{\sigma,\ell} = \left[\frac{\mathcal{C}^{\ell}(z)\hat{\mathbf{v}}^{\sigma} + \hat{\mathbf{v}}^{\sigma}\mathcal{C}^{\ell}(z)}{2}\right], \tag{1.72}$$

is all that is needed to change the velocity operator of the electron $\hat{\mathbf{v}}^{\sigma}$ to the new velocity operator $\boldsymbol{\mathcal{V}}^{\sigma,\ell}$ that implicitly takes into account the contribution of the region of the slab given by $\mathcal{C}^{\ell}(z)$. From Eq. (1.25),

$$\begin{aligned}\boldsymbol{\mathcal{V}}^{\sigma,\ell} &= \boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell} + \boldsymbol{\mathcal{V}}^{\mathcal{S},\ell} \\ \boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell} &= \boldsymbol{\mathcal{V}}^{\ell} + \boldsymbol{\mathcal{V}}^{\mathrm{nl},\ell} = \frac{1}{m_e}\boldsymbol{\mathcal{P}}^{\ell} + \boldsymbol{\mathcal{V}}^{\mathrm{nl},\ell}.\end{aligned} \tag{1.73}$$

We remark that the simple relationship between $\mathbf{v}^{\sigma}_{nm}(\mathbf{k})$ and $\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})$, given in Eq. (1.29), does not hold between $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k})$ and $\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$, i.e. $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k}) \neq (\omega^{\sigma}_{nm}/\omega_{nm})\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$ and $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nn}(\mathbf{k}) \neq \boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nn}(\mathbf{k})$, and thus, to calculate $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k})$ we must calculate the matrix elements of $\boldsymbol{\mathcal{V}}^{\mathcal{S},\ell}$ and $\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}$ (separately) according to the expressions of Appendix **??**. Aeroport Charles de Gaulle, Nov. 30, 2014, see Appendix **??**.

To limit the response to one surface, the equivalent of Eq. (1.71) for $\boldsymbol{\mathcal{V}}^{\ell} = \boldsymbol{\mathcal{P}}^{\ell}/m_e$ was proposed in Ref. [**?**] and later used in Refs. [1], [**?**], [**?**], and [**?**] also in the context of SHG. The layer-by-layer analysis of Refs. [**?**] and [**?**] used Eq. (1.59), limiting the current response to a particular layer of the slab and used to obtain the anisotropic linear optical response of semiconductor surfaces. However, the first formal derivation of this scheme is presented in Ref. [3] for the linear response, and here in this article, for the second harmonic optical response of semiconductors.

1.6 Microscopic surface susceptibility

In this section we obtain the expressions for the surface susceptibility tensor $\chi^S_{\rm abc}$. We start with the basic relation $\mathbf{J} = d\mathbf{P}/dt$ with $\mathbf{J}$ the current calculated in Sec. 1.5. From Eq. (1.67) we obtain

$$J^{(2,\ell)}_{\rm a}(2\omega) = -i2\tilde{\omega}P_{\rm a}(2\omega) = \frac{e}{\Omega}\sum_{mn\mathbf{k}} \mathcal{V}^{\sigma,{\rm a},\ell}_{mn}(\mathbf{k})\rho^{(2)}_{nm}(\mathbf{k};2\omega), \tag{1.74}$$

and using Eqs. (1.58) and (1.7) leads to

$$\begin{aligned}\chi^{S,\ell}_{\rm abc} &= \frac{ie}{AE^{\rm b}_1E^{\rm c}_2 2\tilde{\omega}}\sum_{mn\mathbf{k}} \mathcal{V}^{\sigma,{\rm a},\ell}_{mn}(\mathbf{k})\rho^{(2)}_{nm}(\mathbf{k};2\tilde{\omega}) \\ &= \frac{e^2}{A\hbar 2\tilde{\omega}}\sum_{mn\mathbf{k}} \frac{\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}(\mathbf{k})}{\omega^\sigma_{nm\mathbf{k}} - 2\tilde{\omega}}\Big[-(B^{\rm c}_{nm}(\mathbf{k},\omega))_{;k^{\rm b}} \\ &\quad + i\sum_\ell \left(r^{\rm b}_{n\ell}B^{\rm c}_{\ell m}(\mathbf{k},\omega) - B^{\rm c}_{n\ell}(\mathbf{k},\omega)r^{\rm b}_{\ell m}\right)\Big],\end{aligned} \tag{1.75}$$

which gives the surface-like susceptibility of ℓ-th layer, where $\boldsymbol{\mathcal{V}}^\sigma$ is given in Eq. (1.73), where $A = \Omega/d$ is the surface area of the unit cell that characterizes the surface of the system. Using Eq. (1.53) we split this equation into two contributions from the first and second terms on the right hand side,

$$\chi^{S,\ell}_{i,{\rm abc}} = -\frac{e^3}{A\hbar^2 2\tilde{\omega}}\sum_{mn\mathbf{k}} \frac{\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}}{\omega^\sigma_{nm} - 2\tilde{\omega}}\left(\frac{f_{mn}r^{\rm b}_{nm}}{\omega^\sigma_{nm} - \tilde{\omega}}\right)_{;k^{\rm c}}, \tag{1.76}$$

and

$$\chi^{S,\ell}_{e,{\rm abc}} = \frac{ie^3}{A\hbar^2 2\tilde{\omega}}\sum_{\ell mn\mathbf{k}} \frac{\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}}{\omega^\sigma_{nm} - 2\tilde{\omega}}\left(\frac{r^{\rm c}_{n\ell}r^{\rm b}_{\ell m}f_{m\ell}}{\omega^\sigma_{\ell m} - \tilde{\omega}} - \frac{r^{\rm b}_{n\ell}r^{\rm c}_{\ell m}f_{\ell n}}{\omega^\sigma_{n\ell} - \tilde{\omega}}\right), \tag{1.77}$$

where $\boldsymbol{\chi}^{S,\ell}_i$ is related to intraband transitions and $\boldsymbol{\chi}^{S,\ell}_e$ to interband transitions. For the generalized derivative in Eq. (1.76) we use the chain rule

$$\left(\frac{f_{mn}r^{\rm b}_{nm}}{\omega^\sigma_{nm} - \tilde{\omega}}\right)_{;k^{\rm c}} = \frac{f_{mn}}{\omega^\sigma_{nm} - \tilde{\omega}}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}} - \frac{f_{mn}r^{\rm b}_{nm}\Delta^{\rm c}_{nm}}{(\omega^\sigma_{nm} - \tilde{\omega})^2}, \tag{1.78}$$

and the following result shown in Appendix **??**,

$$(\omega^\sigma_{nm})_{;k^{\rm a}} = \left(\omega^{\rm LDA}_{nm}\right)_{;k^{\rm a}} = v^{{\rm LDA},{\rm a}}_{nn} - v^{{\rm LDA},{\rm a}}_{mm} \equiv \Delta^{\rm a}_{nm}. \tag{1.79}$$

In order to calculate the nonlinear susceptibility of any given layer ℓ we simply add the above terms $\boldsymbol{\chi}^{S,\ell} = \boldsymbol{\chi}^{S,\ell}_e + \boldsymbol{\chi}^{S,\ell}_i$ and then calculate the surface susceptibility as

$$\boldsymbol{\chi}^S \equiv \sum_{\ell=1}^{N}\boldsymbol{\chi}^{S,\ell}, \tag{1.80}$$

where $\ell = 1$ is the first layer right at the surface, and $\ell = N$ is the bulk-like layer (at a distance $\sim d$ from the surface as seen in Fig. 1.1), such that

$$\boldsymbol{\chi}^{S,\ell=N} = 0, \tag{1.81}$$

in accordance to Eq. (1.5) valid for a centrosymmetric environment. We note that the value of N is not universal. This means that the slab needs to have enough atomic layers for Eq. (1.81) to be satisfied and to give converged results for $\boldsymbol{\chi}^S$. We can use Eq. (1.80) for either the front or the back surface.

We can see from the prefactors of Eqs. (1.76) and (1.77) that they diverge as $\tilde{\omega} \to 0$. To remove this apparent divergence of $\boldsymbol{\chi}^{S,\ell}$, we perform a partial fraction expansion over $\tilde{\omega}$. As shown in Appendix **??**, we use time-reversal invariance to remove these divergences and obtain the following expressions for $\boldsymbol{\chi}^S$,

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\frac{1}{\omega^\sigma_{cv}}\left[\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{cl})} - \frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{lv})}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{1.82}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{(\omega^\sigma_{cv})^2}\left[\mathrm{Re}\left[\left\{r^{\mathrm{b}}_{cv}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{c}}}\right\}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\right\}\right]}{\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{1.83}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^\sigma_{cv}}\left[\sum_{v'\neq v}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{2\omega^\sigma_{cv'}-\omega^\sigma_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{2\omega^\sigma_{c'v}-\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{1.84}$$

and

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^\sigma_{cv})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\right\}\right] - \frac{2\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\right\}\right]}{\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{1.85}$$

where the limit of $\eta \to 0$ has been taken. We have split the interband and intraband 1ω and 2ω contributions. The real part of each contribution can be obtained through a Kramers-Kronig transformation,[**?**] and then $\chi^{S,\ell}_{\mathrm{abc}} = \chi^{S,\ell}_{e,\mathrm{abc},\omega} + \chi^{S,\ell}_{e,\mathrm{abc},2\omega} + \chi^{S,\ell}_{i,\mathrm{abc},\omega} + \chi^{S,\ell}_{i,\mathrm{abc},2\omega}$. To fulfill the required intrinsic permutation symmetry,[**?**] the $\{\}$ notation symmetrizes the bc Cartesian indices, i.e. $\{u^{\mathrm{b}}s^{\mathrm{c}}\} = (u^{\mathrm{b}}s^{\mathrm{c}} + u^{\mathrm{c}}s^{\mathrm{b}})/2$, and thus $\chi^{S,\ell}_{\mathrm{abc}} = \chi^{S,\ell}_{\mathrm{acb}}$. In Appendices **??** and **??** we demonstrate how to calculate the generalized derivatives of $\mathbf{r}_{nm;\mathbf{k}}$ and $\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm;\mathbf{k}}$. We find that

$$(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} = -i\mathcal{T}^{\mathrm{ab}}_{nm} + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn} + r^{\mathrm{b}}_{nm}\Delta^{\mathrm{a}}_{mn}}{\omega^{\mathrm{LDA}}_{nm}} + \frac{i}{\omega^{\mathrm{LDA}}_{nm}}\sum_{\ell}\left(\omega^{\mathrm{LDA}}_{\ell m}r^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell}r^{\mathrm{b}}_{n\ell}r^{\mathrm{a}}_{\ell m}\right), \tag{1.86}$$

where

$$\mathcal{T}^{\mathrm{ab}}_{nm} = [r^{\mathrm{a}}, v^{\mathrm{LDA,b}}] = \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm} + \mathcal{L}^{\mathrm{ab}}_{nm}, \tag{1.87}$$

and

$$\mathcal{L}^{\rm ab}_{nm} = \frac{1}{i\hbar}[r^{\rm a}, v^{\rm nl,b}]_{nm}, \tag{1.88}$$

is the contribution to the generalized derivative of $\mathbf{r}_{nm}$ coming from the nonlocal part of the pseudopotential. In Appendix **??** we calculate $\mathcal{L}^{\rm ab}_{nm}$, that is a term with very small numerical value but with a computational time at least an order of magnitude larger than for all the other terms involved in the expressions for $\chi^{s,\ell}_{\rm abc}$.[**?**] Therefore, we neglect it throughout this article and take

$$\mathcal{T}^{\rm ab}_{nm} \approx \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm}. \tag{1.89}$$

Finally, we also need the following term (Eq. (**??**))

$$\begin{aligned}(v^{\rm LDA,a}_{nn})_{;k^{\rm b}} = \nabla_{k^{\rm a}} v^{\rm LDA,b}_{nn}(\mathbf{k}) &= -i\mathcal{T}^{\rm ab}_{nn} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\left(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n} + r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\right)\\ &\approx \frac{\hbar}{m_e}\delta_{\rm ab} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\left(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n} + r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\right),\end{aligned} \tag{1.90}$$

among other quantities for $\mathcal{V}^{\sigma,{\rm a},\ell}_{nm;\mathbf{k}}$, where we also use Eq. (1.89). Above is the standard effective-mas sum rule. [**?**]

1.7 Three layer model for SHG radiation

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 [4]. 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 [5], 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. 1.3). 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. 1.3). We decompose the field into s and p polarizations, then the electric field radiated by a polarization sheet,

$$\mathcal{P}_i(2\omega) = \chi_{ijk} E_j(\omega) E_k(\omega), \tag{1.91}$$

is given by [5],

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

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. 1.3), 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. 1.3, 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,

$$\mathbf{H}_\ell = \hat{\mathbf{s}}\, T_s^{\ell v} \left(1 + R_s^{\ell b}\right) \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{\ell v} \left(\hat{\mathbf{P}}_{\ell+} + R_p^{\ell b} \hat{\mathbf{P}}_{\ell-}\right). \tag{1.92}$$

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

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

where using

$$\begin{aligned}
1 + R_s^{\ell b} &= T_s^{\ell b} \\
1 + R_p^{\ell b} &= \sqrt{\frac{\epsilon_b(2\omega)}{\epsilon_\ell(2\omega)}} T_p^{\ell b} \\
1 - R_p^{\ell b} &= \sqrt{\frac{\epsilon_\ell(2\omega)}{\epsilon_b(2\omega)}} \frac{K_b}{K_\ell} T_p^{\ell b} \\
T_p^{\ell v} &= \frac{K_\ell}{K_v} T_p^{v\ell} \\
T_s^{\ell v} &= \frac{K_\ell}{K_v} T_s^{v\ell},
\end{aligned} \tag{1.93}$$

we can write

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

where,

$$\mathbf{e}_\ell^{2\omega} = \hat{\mathbf{e}}^{\text{out}} \cdot \left[\hat{\mathbf{s}} T_s^{v\ell} T_s^{\ell b} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} \frac{T_p^{v\ell} T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega)\sin\theta_{\text{in}} \hat{\mathbf{z}} - \epsilon_\ell(2\omega) K_b \hat{\mathbf{x}}\right)\right]. \tag{1.94}$$

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

$$\mathbf{e}_v^{2\omega} = \hat{\mathbf{e}}^{\text{out}} \cdot \left[\hat{\mathbf{s}} T_s^{vb} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} \frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega)\sin\theta_{\text{in}} \hat{\mathbf{z}} - K_b \hat{\mathbf{x}}\right)\right], \tag{1.95}$$

which agrees with Eq. (3.8) of Ref. [5].

In the three layer model the nonlinear polarization is located in layer ℓ, and then we evaluate the fundamental field required in Eq. (1.91) in this layer as well, then we write

$$\mathbf{E}_\ell(\omega) = E_0\left(\hat{\mathbf{s}}t_s^{v\ell}(1+r_s^{\ell b})\hat{\mathbf{s}} + \hat{\mathbf{p}}_{\ell-}t_p^{v\ell}\hat{\mathbf{p}}_{v-} + \hat{\mathbf{p}}_{\ell+}t_p^{v\ell}r_p^{\ell b}\hat{\mathbf{p}}_{v-}\right)\cdot\hat{\mathbf{e}}^{\rm in} = E_0\mathbf{e}_\ell^\omega, \quad (1.96)$$

and following the steps that lead to Eq. (1.94), we find that

$$\mathbf{e}_\ell^\omega = \left[\hat{\mathbf{s}}t_s^{v\ell}t_s^{\ell b}\hat{\mathbf{s}} + \frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\left(\epsilon_b(\omega)\sin\theta_{\rm in}\hat{\mathbf{z}} + \epsilon_\ell(\omega)k_b\hat{\mathbf{x}}\right)\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\rm in}. \quad (1.97)$$

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

$$\mathbf{e}_b^\omega = \left[\hat{\mathbf{s}}t_s^{vb}\hat{\mathbf{s}} + \frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}}\left(\sin\theta_{\rm in}\hat{\mathbf{z}} + k_b\hat{\mathbf{x}}\right)\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\rm in}, \quad (1.98)$$

that is in agreement with Eq. (3.5) of Ref. [5].

With $\mathbf{e}^\omega$ we can write Eq. (1.91) as

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

and then from Eq. (1.7) we obtain that

$$\begin{aligned}
|E(2\omega)|^2 &= |E_0|^4\frac{16\pi^2\omega^2}{c^2K_v^2}\left|\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega\right|^2\\
\frac{c}{2\pi}|E(2\omega)|^2 &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta_{\rm in}}\left|\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega\right|^2\left(\frac{c}{2\pi}|E_0|^2\right)^2,\\
I(2\omega) &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta_{\rm in}}\left|\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega\right|^2 I^2(\omega),\\
R(2\omega) &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta_{\rm in}}\left|\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega\right|^2, \qquad (1.99)
\end{aligned}$$

as the SHG yield. At this point we mention that to recover the results of Ref. [5] which are equivalent of those of Ref. [6], we take $\mathbf{e}_\ell^{2\omega}\to\mathbf{e}_v^{2\omega}$, $\mathbf{e}_\ell^\omega\to\mathbf{e}_b^\omega$ and then

$$R(2\omega) = \frac{32\pi^3\omega^2}{c^3\cos^2\theta_{\rm in}}\left|\mathbf{e}_v^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_b^\omega\mathbf{e}_b^\omega\right|^2, \quad (1.100)$$

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,

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

1.8 $\mathcal{R}$ for different polarization cases

We obtain explicit relations for a C_{3v} symmetry characteristic of a (111) surface, for which the only components of χ_{ijk} different from zero are χ_{zzz}, $\chi_{zxx} = \chi_{zyy}$, $\chi_{xxz} = \chi_{yyz}$ and $\chi_{xxx} = -\chi_{xyy} = -\chi_{yyx}$ with $\chi_{ijk} = \chi_{ikj}$, where we have chosen the x and y axes along the [112] and [110] directions, respectively.

However, we have to remember that the plane of incidence so far was chosen to be the xz plane; the most general plane of incidence should be one that makes an angle ϕ with respect to the x axis, and so $\hat{\mathbf{x}}$ should to be replaced by a unit vector $\hat{\kappa}$ such that

$$\hat{\boldsymbol{\kappa}} = \cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}}, \tag{1.101}$$

and then

$$\hat{\mathbf{s}} = -\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}, \tag{1.102}$$

1.8.1 $\mathcal{R}_{pP}$

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 $\hat{\mathbf{e}}^{\text{in}} = \hat{\mathbf{p}}_{v-}$ in Eq. (1.97), and $\hat{\mathbf{e}}^{\text{out}} = \hat{\mathbf{P}}_{v+}$ in Eq. (1.94).

Three layer model

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

$$\begin{aligned} r_{pP}^{\ell} = {} & \epsilon_b(2\omega)\sin\theta_{\text{in}}\Big(\epsilon_b^2(\omega)\sin^2\theta_{\text{in}}\chi_{zzz} + \epsilon_\ell^2(\omega)k_b^2\chi_{zxx}\Big) \\ & - \epsilon_\ell(2\omega)\epsilon_\ell(\omega)k_bK_b\Big(2\epsilon_b(\omega)\sin\theta_{\text{in}}\chi_{xxz} + \epsilon_\ell(\omega)k_b\chi_{xxx}\cos(3\phi)\Big), \end{aligned} \tag{1.103}$$

and

$$\Gamma_{pP}^{\ell} = \frac{T_p^{\ell v}T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2. \tag{1.104}$$

Two layer model

In order to reduce above result to that of Ref. [5] and [6], 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,

$$r_{pP}^{vb} = \epsilon_b(2\omega)\sin\theta_{\text{in}}\Big(\sin^2\theta_{\text{in}}\chi_{zzz} + k_b^2 chi_{zxx}\Big) - k_b K_b\Big(2\sin\theta_{\text{in}}\chi_{xxz} + k_b\chi_{xxx}\cos(3\phi)\Big),$$

and

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

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

To evaluate the 2ω fields in the bulk, we take Eq. (1.92) considering that $\ell \to b$. We have already considered the 1ω fields in the bulk in Eq. (1.98). After some algebra, we get that

$$\mathbf{e}_b^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \Gamma_{pP}^{b} r_{pP}^{b}$$

where

$$r_{pP}^{b} = \sin^3\theta_{\text{in}}\chi_{zzz} + k_b^2\sin\theta_{\text{in}}\chi_{zxx} - 2k_b K_b\sin\theta_{\text{in}}\chi_{xxz} - k_b^2 K_b\chi_{xxx}\cos 3\phi,$$

and

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

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

To evaluate the 1ω fields in the vacuum, we take Eq. (1.96) considering that $\ell \to v$. We have already considered the 2ω fields in the vacuum in Eq. (1.95). After some algebra, we get that

$$\mathbf{e}_v^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_v^{\omega}\mathbf{e}_v^{\omega} = \Gamma_{pP}^{v} r_{pP}^{v}$$

where

$$r_{pP}^{v} = \epsilon_b^2(\omega)\epsilon_b(2\omega)\sin^3\theta_{\text{in}}\chi_{zzz} + \epsilon_b(2\omega)k_b^2\sin\theta_{\text{in}}\chi_{zxx} - 2\epsilon_b(\omega)k_b K_b\sin\theta_{\text{in}}\chi_{xxz} - k_b^2 K_b\chi_{xxx}\cos 3\phi$$

and

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

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

For this scenario, we have

$$\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi} : \mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \Gamma_{pP}^{\ell b} r_{pP}^{\ell b}$$

where

$$r_{pP}^{\ell b} = \epsilon_b(2\omega)\sin^3\theta_{\rm in}\chi_{zzz} + \epsilon_b(2\omega)k_b^2\sin\theta_{\rm in}\chi_{zxx} - 2\epsilon_\ell(2\omega)k_bK_b\sin\theta_{\rm in}\chi_{xxz} - \epsilon_\ell(2\omega)k_b^2K_b\chi_{xxx}\cos 3\phi,$$

and

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

1.8.2 $\mathcal{R}_{pS}$

To obtain $R_{pS}(2\omega)$ we use $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{p}}_{v-}$ in Eq. (1.97), and $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{S}}$ in Eq. (1.94). We also use the unit vectors defined in Eqs. (1.101) and (1.102). 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

$$r_{pS}^\ell = -\epsilon_\ell^2(\omega)k_b^2\sin 3\phi\chi_{xxx}, \tag{1.105}$$

and

$$\Gamma_{pS}^\ell = T_s^{v\ell}T_s^{\ell b}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2. \tag{1.106}$$

In order to reduce above result to that of Ref. [5] and [6], 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 $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_p^{v\ell} = t_p^{vb}$, and $t_p^{\ell b} = 1$. With these choices,

$$r_{pS}^b = -k_b^2\sin 3\phi\chi_{xxx},$$

and

$$\Gamma_{pS}^b = T_s^{vb}\left(\frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}}\right)^2.$$

1.8.3 $\mathcal{R}_{sP}$

To obtain $R_{sP}(2\omega)$ we use $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{s}}$ in Eq. (1.97), and $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{P}}_{v+}$ in Eq. (1.94). We also use the unit vectors defined in Eqs. (1.101) and (1.102). 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

$$r_{sP}^\ell = \epsilon_b(2\omega)\sin\theta_{\rm in}\chi_{zxx} + \epsilon_\ell(2\omega)K_b\chi_{xxx}\cos 3\phi, \tag{1.107}$$

and

$$\Gamma_{sP}^\ell = \frac{T_p^{\ell v}T_p^{\ell b}\left(t_s^{v\ell}t_s^{\ell b}\right)^2}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}. \tag{1.108}$$

In order to reduce above result to that of Ref. [5] and [6], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_p^{v\ell} = 1$, $T_p^{\ell b} = T_p^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_s^{v\ell} = t_s^{vb}$, and $t_s^{\ell b} = 1$. With these choices,

$$r_{sP}^b = \epsilon_b(2\omega)\sin\theta_{\text{in}}\chi_{zxx} + K_b\chi_{xxx}\cos 3\phi,$$

and

$$\Gamma_{sP}^b = \frac{T_p^{vb}(t_s^{vb})^2}{\sqrt{\epsilon_b(2\omega)}}.$$

1.8.4 $\mathcal{R}_{sS}$

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

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

where

$$r_{sS}^\ell = \chi_{xxx}\sin 3\phi, \tag{1.109}$$

and

$$\Gamma_{sS}^\ell = T_s^{v\ell}T_s^{\ell b}\left(t_s^{v\ell}t_s^{\ell b}\right)^2. \tag{1.110}$$

In order to reduce above result to that of Ref. [5] and [6], 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,

$$r_{sS}^b = \chi_{xxx}\sin 3\phi,$$

and

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

1.9 Conclusions

We have presented a complete derivation of the required elements to calculate in the independent particle approach (IPA) the microscopic surface second harmonic susceptibility tensor $\boldsymbol{\chi}^S(-2\omega;\omega,\omega)$ using a layer-by-layer approach. We have done so for semiconductors using the length gauge for the coupling of the external electric field to the electron.

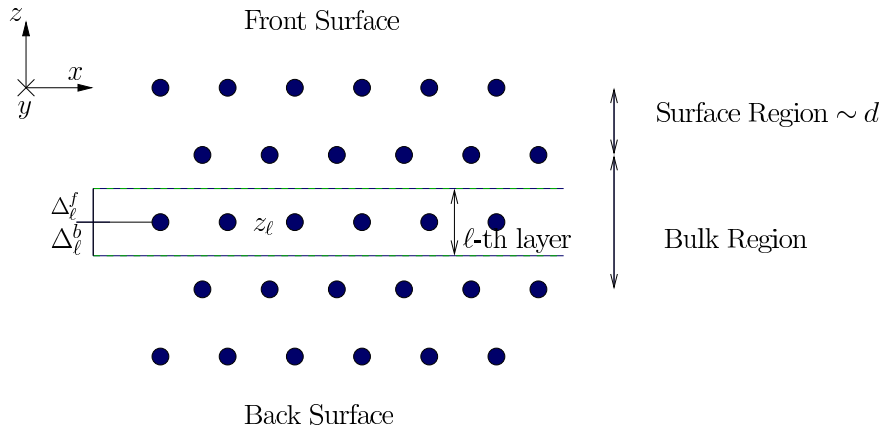

Figure 1.2: A sketch of a slab where the circles represent atoms.

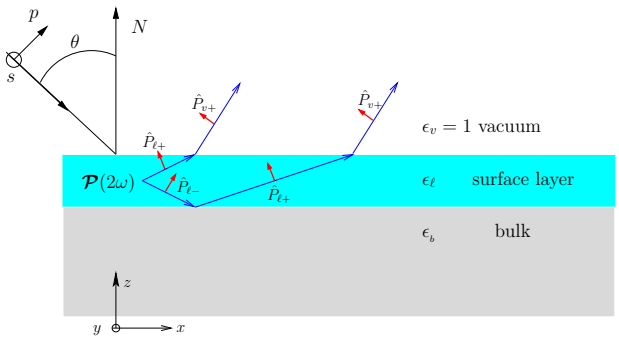

Figure 1.3: Sketch of the three layer model for SHG. Vacuum is on top with $\epsilon = 1$, the layer with nonlinear polarization $\mathbf{P}(2\omega)$ ischaracterized with $\epsilon_\ell(\omega)$ and the bulk with $\epsilon_b(\omega)$. In the dipolar approximation the bulk does not radiate SHG. The thin 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).

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