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# Chapter 1

## The Nonlinear Surface Susceptibility

### Outline

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Small intro about centrosymmetry, explaining why we must follow this procedure for a surface response. Brief intro about scissors correction, LDA vs GW. Brief intro about the procedure we will follow in general.

### 1.1 The nonlinear surface susceptibility

In this section I will outline the general procedure to obtain the surface susceptibility tensor for SHG. We start with the nonlinear polarization  $\mathbf{P}(\mathbf{r})$  of a bulk system, written as

$$P^a(\mathbf{r}, 2\omega) = \chi^{abc}(-2\omega; \omega, \omega)E^b(\mathbf{r}, \omega)E^c(\mathbf{r}, \omega) + \chi^{abcd}(-2\omega; \omega, \omega)E^b(\mathbf{r}, \omega)\nabla^c E^d(\mathbf{r}, \omega) + \dots, \quad (1.1)$$

where  $\chi^{abc}(-2\omega; \omega, \omega)$  and  $\chi^{abcd}(-2\omega; \omega, \omega)$  correspond to the dipolar and quadrupolar susceptibility tensors, and  $\mathbf{E}(\mathbf{r})$  is the incoming electric field along the different Cartesian directions denoted by the roman superscripts. For ease of notation, I will drop the  $\omega$  arguments from this point on. At this point I introduce the units of the quantities above. For simplicity, we use the MKS system of units. The units of  $\mathbf{E}(\mathbf{r})$  are  $[\mathbf{E}] = \text{V/m}$ , and the units of  $\mathbf{P}(\mathbf{r})$  are  $[\mathbf{P}] = \text{V/m}$  since  $\mathbf{P}(\mathbf{r})$  is a *bulk* polarization. Therefore, the units of the bulk  $\chi^{abc}$  are  $[\chi^{abc}] = \text{m/V}$ .

If we consider a semi-infinite system with a centrosymmetric bulk, we can obtain a bulk and a surface nonlinear polarization that differ from each other from symmetry considerations alone. To show this, we take

$$P^a(\mathbf{r}) = \chi^{abc}E^b(\mathbf{r})E^c(\mathbf{r}) + \chi^{abcd}E^b(\mathbf{r})\frac{\partial}{\partial r^c}E^d(\mathbf{r}) + \dots, \quad (1.2)$$

as the polarization with respect to the  $\mathbf{r}$  coordinate system, and

$$P^a(-\mathbf{r}) = \chi^{abc} E^b(-\mathbf{r}) E^c(-\mathbf{r}) + \chi^{abcd} E^b(-\mathbf{r}) \frac{\partial}{\partial(-\mathbf{r}^c)} E^d(-\mathbf{r}) + \dots, \quad (1.3)$$

as the polarization in the inverted coordinate system, where we take  $\mathbf{r}$  to  $-\mathbf{r}$ . Note that we have kept the same susceptibility tensors as they must be invariant under  $\mathbf{r} \rightarrow -\mathbf{r}$  since the system is centrosymmetric. Recalling that  $\mathbf{P}(\mathbf{r})$  and  $\mathbf{E}(\mathbf{r})$  are polar vectors [1], we have that Eq. (1.3) reduces to

$$\begin{aligned} -P^a(\mathbf{r}) &= \chi^{abc} (-E^b(\mathbf{r})) (-E^c(\mathbf{r})) + \chi^{abcd} (-E^b(\mathbf{r})) \left( -\frac{\partial}{\partial \mathbf{r}^c} \right) (-E^d(\mathbf{r})) + \dots, \\ P^a(\mathbf{r}) &= -\chi^{abc} E^b(\mathbf{r}) E^c(\mathbf{r}) + \chi^{abcd} E^b(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}^c} E^d(\mathbf{r}) + \dots, \end{aligned} \quad (1.4)$$

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

$$\begin{aligned} \chi^{abc} &= 0, \\ &\quad (\text{centrosymmetric bulk}) \\ \chi^{abcd} &\neq 0, \end{aligned} \quad (1.5)$$

for a centrosymmetric bulk.

The surface of a centrosymmetric system necessarily breaks the centrosymmetry; thus, there are no symmetry restrictions imposed on the  $\chi^{abc}$  produced from the surface region. Therefore, it is convenient to define the surface nonlinear polarization  $\mathbf{P}_{\text{surface}}$  as follows,

$$P_{\text{surface}}^a \equiv \chi_{\text{surface}}^{abc} E^b E^c, \quad (1.6)$$

where  $\chi_{\text{surface}}^{abc}$  is the surface nonlinear susceptibility. In this case, the units of  $[\mathbf{P}_{\text{surface}}]$  are V, and  $[\chi_{\text{surface}}^{abc}]$  are  $\text{m}^2/\text{V}$ . The contribution from  $\chi^{abcd}$  to the surface polarization is neglected as it originates from a higher order multipole. From Eq. (1.1) we have that for the bulk of a semi-infinite system,

$$P_{\text{bulk}}^a = \chi_{\text{bulk}}^{abcd} E^b \nabla^c E^d, \quad (1.7)$$

which is the bulk nonlinear polarization; in this case the dipolar contribution  $\chi_{\text{bulk}}^{abc} = 0$  since we are in the centrosymmetric bulk. Note that the surface nonlinear polarization is of dipolar electric order while the bulk polarization is of quadrupolar electric and dipolar magnetic order [2]. The surface  $\chi_{\text{surface}}^{abc}$  and bulk  $\chi_{\text{bulk}}^{abcd}$  susceptibilities are tensors of rank three and four, respectively.

In this work, we will only concentrate on SSHG, even though bulk-generated SH is also a very important optical phenomenon. To this end, we will neglect the contribution from Eq. (1.7) and only consider the surface term from Eq. (1.6). I will also exclude other interesting surface SH phenomena like, electric field induced second-harmonic (EFISH), which would be represented by a surface susceptibility tensor of quadrupolar origin. As mentioned in Chapter ??, in centrosymmetric systems for which the quadrupolar bulk response is much smaller than the dipolar surface response, SH is a very capable and powerful optical surface probe [3].

In the following sections of this chapter, we show the theoretical approach to derive the expressions for the surface susceptibility tensor  $\chi_{\text{surface}}^{abc}$ .

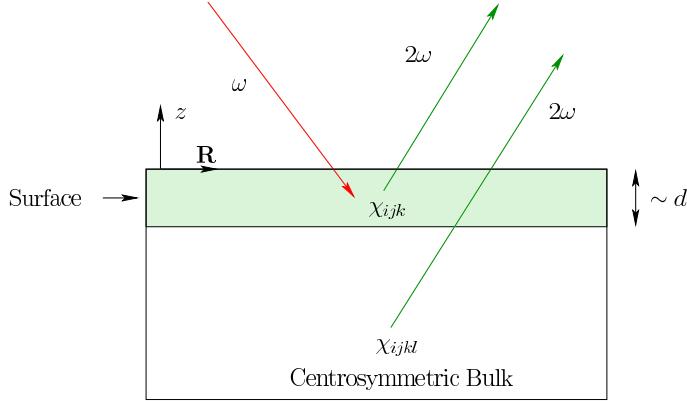


Figure 1.1: Sketch of a semi-infinite system with a centrosymmetric bulk. The surface region is of width  $\sim d$ . The incoming photon of frequency  $\omega$  is represented by a downward red arrow, whereas both the surface and bulk created second-harmonic photons of frequency  $2\omega$  are represented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

## 1.2 Length Gauge

Brief intro to work in Refs. [4] and [5] (both are bulk, aversa neglects nonlocalities while Cabellos adds nonlocal scissors)

We follow Refs. [4] and [5] to calculate  $\chi_{\text{surface}}^{\text{abc}}$  of a given system within the longitudinal gauge. We assume the long-wavelength approximation which implies a position independent electric field,  $\mathbf{E}(t)$ . The Hamiltonian in the length gauge approximation is given by

$$\hat{H} = \hat{H}_0^\Sigma - e\hat{\mathbf{r}} \cdot \mathbf{E}, \quad (1.8)$$

where  $e$  is the electron charge,  $-e\hat{\mathbf{r}} \cdot \mathbf{E}$  is the dipolar interaction,  $\mathbf{r}$  is the electron position operator, and

$$\hat{H}_0^\Sigma = \hat{H}_0^{\text{LDA}} + \mathcal{S}(\mathbf{r}, \mathbf{p}), \quad (1.9)$$

as the unperturbed, scissors-shifted Hamiltonian denoted with  $\Sigma$ , composed of the LDA ground-state Hamiltonian, and the scissors operator [6]. The LDA Hamiltonian can be expressed as follows,

$$\begin{aligned} \hat{H}_0^{\text{LDA}} &= \frac{\hat{p}^2}{2m_e} + \hat{V}^{\text{ps}}, \\ \hat{V}^{\text{ps}} &= \hat{V}^1(\hat{\mathbf{r}}) + \hat{V}^{\text{nl}}, \end{aligned} \quad (1.10)$$

where  $\hat{V}^1(\hat{\mathbf{r}})$  and  $\hat{V}^{\text{nl}}$  are the local and the nonlocal parts of the crystal pseudopotential  $\hat{V}^{\text{ps}}$ .  $m_e$  is the bare mass of the electron, and  $\hat{p}$  is the momentum operator. Make reference about why we need the nonlocal part. For the latter, we have that

$$V^{\text{nl}}(\mathbf{r}, \mathbf{r}') \equiv \langle \mathbf{r} | \hat{V}^{\text{nl}} | \mathbf{r}' \rangle \neq 0 \quad \text{for } \mathbf{r} \neq \mathbf{r}', \quad (1.11)$$

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

$$\left( \frac{-\hbar^2}{2m_e} \nabla^2 + \hat{V}^l(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) + \int \hat{V}^{\text{nl}}(\mathbf{r}, \mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}') d\mathbf{r}' = E_i \psi_{n\mathbf{k}}(\mathbf{r}), \quad (1.12)$$

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  $|n\mathbf{k}\rangle$  labeled by the band index  $n$  and the crystal momentum  $\mathbf{k}$ , and  $u_{n\mathbf{k}}(\mathbf{r})$  is cell periodic. The nonlocal scissors operator is given by

$$\mathcal{S}(\mathbf{r}, \mathbf{p}) = \hbar\Delta \sum_n \int (1 - f_n(\mathbf{k})) |n\mathbf{k}\rangle \langle n\mathbf{k}| d^3k, \quad (1.13)$$

**Check our article or cabellos to see if this has  $8\pi$  and where this equation comes from, possibly Levine** where  $f_n(\mathbf{k})$  is the occupation number that is independent of  $\mathbf{k}$  for  $T = 0$  K, and is  $f_n = 1$  for filled bands and  $f_n = 0$  for unoccupied bands. For semiconductors the filled bands correspond to valence bands ( $n = v$ ), and unoccupied bands correspond to conduction bands ( $n = c$ ). We have that **Check for reference from Pulci**

$$\begin{aligned} H_0^{\text{LDA}} |n\mathbf{k}\rangle &= \hbar\omega_n^{\text{LDA}}(\mathbf{k}) |n\mathbf{k}\rangle \\ H_0^{\Sigma} |n\mathbf{k}\rangle &= \hbar\omega_n^{\Sigma}(\mathbf{k}) |n\mathbf{k}\rangle, \end{aligned} \quad (1.14)$$

where

$$\hbar\omega_n^{\Sigma}(\mathbf{k}) = \hbar\omega_n^{\text{LDA}}(\mathbf{k}) + \hbar\Delta(1 - f_n), \quad (1.15)$$

is the scissored energy. Here,  $\hbar\Delta$  is the value by which the conduction bands are rigidly ( $\mathbf{k}$ -independent) shifted upwards in energy, also known as the scissors shift.  $\Delta$  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  $\hbar\Delta = E_g - E_g^{\text{LDA}}$  where  $E_g$  is the experimental or GW band gap taken at the  $\Gamma$  point, i.e.  $\mathbf{k} = 0$ . We used the fact that  $|n\mathbf{k}\rangle^{\text{LDA}} \approx |n\mathbf{k}\rangle^{\Sigma}$ , thus negating the need to label the Bloch states with the LDA or  $\Sigma$  superscripts. **Check for reference from Pulci** The matrix elements of  $\mathbf{r}$  are split between the *intraband* ( $\mathbf{r}_i$ ) and *interband* ( $\mathbf{r}_e$ ) parts, where  $\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e$  [7, 8], and its matrix elements are [4]

$$\langle n\mathbf{k} | \hat{\mathbf{r}}_i | m\mathbf{k}' \rangle = \delta_{nm} [\delta(\mathbf{k} - \mathbf{k}') \xi_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')], \quad (1.16)$$

$$\langle n\mathbf{k} | \hat{\mathbf{r}}_e | m\mathbf{k}' \rangle = (1 - \delta_{nm}) \delta(\mathbf{k} - \mathbf{k}') \xi_{nm}(\mathbf{k}), \quad (1.17)$$

with

$$\xi_{nm}(\mathbf{k}) \equiv i \frac{(2\pi)^3}{\Omega} \int_{\Omega} u_{n\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}) d\mathbf{r}, \quad (1.18)$$

where  $\Omega$  is the unit cell volume. The interband part,  $\mathbf{r}_e$ , can be obtained as follows. We start by introducing the velocity operator

$$\hat{\mathbf{v}}^{\Sigma} = \frac{1}{i\hbar} [\hat{\mathbf{r}}, \hat{H}_0^{\Sigma}], \quad (1.19)$$

and calculating its matrix elements

$$i\hbar \langle n\mathbf{k} | \mathbf{v}^{\Sigma} | m\mathbf{k} \rangle = \langle n\mathbf{k} | [\hat{\mathbf{r}}, \hat{H}_0^{\Sigma}] | m\mathbf{k} \rangle = \langle n\mathbf{k} | \hat{\mathbf{r}} \hat{H}_0^{\Sigma} - \hat{H}_0^{\Sigma} \hat{\mathbf{r}} | m\mathbf{k} \rangle = (\hbar\omega_m^{\Sigma}(\mathbf{k}) - \hbar\omega_n^{\Sigma}(\mathbf{k})) \langle n\mathbf{k} | \hat{\mathbf{r}} | m\mathbf{k} \rangle. \quad (1.20)$$

Defining  $\omega_{nm}^\Sigma(\mathbf{k}) = \omega_n^\Sigma(\mathbf{k}) - \omega_m^\Sigma(\mathbf{k})$ , we get

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^\Sigma(\mathbf{k})}{i\omega_{nm}^\Sigma(\mathbf{k})} \quad n \notin D_m, \quad (1.21)$$

which can be identified as  $\mathbf{r}_{nm} = (1 - \delta_{nm})\boldsymbol{\xi}_{nm} \rightarrow \mathbf{r}_{e,nm}$ . Here,  $D_m$  are all the possible degenerate  $m$ -states. When  $\mathbf{r}_i$  appears in commutators we use [4]

$$\langle n\mathbf{k}| [\hat{\mathbf{r}}_i, \hat{\mathcal{O}}] |m\mathbf{k}'\rangle = i\delta(\mathbf{k} - \mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \quad (1.22)$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})), \quad (1.23)$$

where “;  $\mathbf{k}$ ” denotes the generalized derivative (see Appendix A.1).

As can be seen from Eq. (1.9) and (1.10), both  $\mathcal{S}$  and  $\hat{V}^{\text{nl}}$  are nonlocal potentials. Their contribution in the calculation of the optical response has to be considered in order to get reliable results [9]. We proceed as follows: from Eqs. (1.19), (1.9) and (1.10) we find

$$\begin{aligned} \hat{\mathbf{v}}^\Sigma &= \frac{\hat{\mathbf{p}}}{m_e} + \frac{1}{i\hbar} [\hat{\mathbf{r}}, \hat{V}^{\text{nl}}(\mathbf{r}, \mathbf{r}')] + \frac{1}{i\hbar} [\hat{\mathbf{r}}, \hat{\mathcal{S}}(\mathbf{r}, \mathbf{p})] \\ &\equiv \hat{\mathbf{v}} + \hat{\mathbf{v}}^{\text{nl}} + \hat{\mathbf{v}}^{\mathcal{S}} = \hat{\mathbf{v}}^{\text{LDA}} + \hat{\mathbf{v}}^{\mathcal{S}}, \end{aligned} \quad (1.24)$$

where we have defined

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

with  $\hat{\mathbf{p}} = -i\hbar\nabla$  the momentum operator. Using Eq. (1.13), we obtain that the matrix elements of  $\hat{\mathbf{v}}^{\mathcal{S}}$  are given by

$$\mathbf{v}_{nm}^{\mathcal{S}} = i\Delta f_{mn} \mathbf{r}_{nm}, \quad (1.26)$$

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

$$\begin{aligned} \mathbf{v}_{nm}^\Sigma &= \mathbf{v}_{nm}^{\text{LDA}} + i\Delta f_{mn} \mathbf{r}_{nm} \\ &= \mathbf{v}_{nm}^{\text{LDA}} + i\Delta f_{mn} \frac{\mathbf{v}_{nm}^\Sigma(\mathbf{k})}{i\omega_{nm}^\Sigma(\mathbf{k})} \\ \mathbf{v}_{nm}^\Sigma \frac{\omega_{nm}^\Sigma - \Delta f_{mn}}{\omega_{nm}^\Sigma} &= \mathbf{v}_{nm}^{\text{LDA}} \\ \mathbf{v}_{nm}^\Sigma \frac{\omega_{nm}^{\text{LDA}}}{\omega_{nm}^\Sigma} &= \mathbf{v}_{nm}^{\text{LDA}} \\ \frac{\mathbf{v}_{nm}^\Sigma}{\omega_{nm}^\Sigma} &= \frac{\mathbf{v}_{nm}^{\text{LDA}}}{\omega_{nm}^{\text{LDA}}}, \end{aligned} \quad (1.27)$$

since  $\omega_{nm}^\Sigma - \Delta f_{mn} = \omega_{nm}^{\text{LDA}}$ . Therefore,

$$\mathbf{v}_{nm}^\Sigma(\mathbf{k}) = \frac{\omega_{nm}^\Sigma}{\omega_{nm}^{\text{LDA}}} \mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k}) = \left(1 + \frac{\Delta}{\omega_c(\mathbf{k}) - \omega_v(\mathbf{k})}\right) \mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k}) \quad n \notin D_m \quad (1.28)$$

$$\mathbf{v}_{nn}^\Sigma(\mathbf{k}) = \mathbf{v}_{nn}^{\text{LDA}}(\mathbf{k}),$$

and Eq. (1.21) gives

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^\Sigma(\mathbf{k})}{i\omega_{nm}^\Sigma(\mathbf{k})} = \frac{\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})}{i\omega_{nm}^{\text{LDA}}(\mathbf{k})} \quad n \notin D_m. \quad (1.29)$$

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

$$\mathbf{r}_{e,nm} \rightarrow \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})}{i\omega_{nm}^{\text{LDA}}(\mathbf{k})} \quad n \notin D_m, \quad (1.30)$$

which gives the interband matrix elements of the position operator in terms of the matrix elements of  $\hat{\mathbf{v}}^{\text{LDA}}$ . These matrix elements include the matrix elements of  $\mathbf{v}_{nm}^{\text{nl}}(\mathbf{k})$  which can be readily calculated for fully separable nonlocal pseudopotentials in the Kleinman-Bylander form [10, 11, 12]. In Appendix A.2 we outline how this is accomplished.

### 1.3 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

$$\mathcal{O} = \text{Tr}(\hat{\mathcal{O}}\hat{\rho}) = \text{Tr}(\hat{\rho}\hat{\mathcal{O}}), \quad (1.31)$$

where Tr is the trace and is invariant under cyclic permutations. The dynamic equation of motion for  $\hat{\rho}$  is given by

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}], \quad (1.32)$$

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

$$\hat{\mathcal{O}}_I = \hat{U}\hat{\mathcal{O}}\hat{U}^\dagger, \quad (1.33)$$

where

$$\hat{U} = e^{i\hat{H}_0 t/\hbar}, \quad (1.34)$$

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. (1.32) into

$$i\hbar \frac{d\hat{\rho}_I(t)}{dt} = [-e\hat{\mathbf{r}}_I(t) \cdot \mathbf{E}(t), \hat{\rho}_I(t)], \quad (1.35)$$

that leads to

$$\hat{\rho}_I(t) = \hat{\rho}_I(t = -\infty) + \frac{ie}{\hbar} \int_{-\infty}^t [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I(t')] dt'. \quad (1.36)$$

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

$$\mathbf{E}(t) = \mathbf{E}e^{-i\omega t}e^{\eta t} = \mathbf{E}e^{-i\tilde{\omega}t}, \quad (1.37)$$

with

$$\tilde{\omega} = \omega + i\eta, \quad (1.38)$$

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  $\eta \rightarrow 0$ . 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

$$\langle n\mathbf{k}|\hat{\rho}_0|m\mathbf{k}'\rangle = f_n(\hbar\omega_n^\Sigma(\mathbf{k}))\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'), \quad (1.39)$$

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

We solve Eq. (1.36) using the standard iterative solution, for which we write

$$\hat{\rho}_I = \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \dots, \quad (1.40)$$

where  $\hat{\rho}_I^{(N)}$  is the density operator to order  $N$  in  $\mathbf{E}(t)$ . Then, Eq. (1.36) reads

$$\hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \dots = \hat{\rho}_0 + \frac{ie}{\hbar} \int_{-\infty}^t dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \dots], \quad (1.41)$$

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

$$\hat{\rho}_I^{(0)} \equiv \hat{\rho}_0, \quad (1.42)$$

and

$$\hat{\rho}_I^{(N)}(t) = \frac{ie}{\hbar} \int_{-\infty}^t dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I^{(N-1)}(t')]. \quad (1.43)$$

It is simple to show that matrix elements of Eq. (1.43) 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

$$\rho_{I,nm}^{(N+1)}(\mathbf{k}; t) = \frac{ie}{\hbar} \int_{-\infty}^t dt' \langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t'), \hat{\rho}_I^{(N)}(t')]|m\mathbf{k}\rangle \cdot \mathbf{E}(t'). \quad (1.44)$$

This shows that the  $N+1$  solution is determined by the  $N$ th solution, which in turn is determined by the  $N-1$  solution, and so on. Starting from the zeroth order solution given in Eq. (1.42), we can solve for any desired order.

We now work out the commutator of Eq. (1.44). Then,

$$\begin{aligned} \langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t), \hat{\rho}_I^{(N)}(t)]|m\mathbf{k}\rangle &= \langle n\mathbf{k}|[\hat{U}\hat{\mathbf{r}}\hat{U}^\dagger, \hat{U}\hat{\rho}^{(N)}(t)\hat{U}^\dagger]|m\mathbf{k}\rangle \\ &= \langle n\mathbf{k}|[\hat{U}\hat{\mathbf{r}}, \hat{\rho}^{(N)}(t)]\hat{U}^\dagger|m\mathbf{k}\rangle \\ &= e^{i\omega_{nm\mathbf{k}}^{\Sigma}t} (\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)] + [\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle). \end{aligned} \quad (1.45)$$

We calculate the interband term first, so using Eq. (1.30) we obtain

$$\begin{aligned} \langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle &= \sum_{\ell} \left( \langle n\mathbf{k}|[\hat{\mathbf{r}}_e|\ell\mathbf{k}\rangle \langle \ell\mathbf{k}|\hat{\rho}^{(N)}(t)|m\mathbf{k}\rangle - \langle n\mathbf{k}|\hat{\rho}^{(N)}(t)|\ell\mathbf{k}\rangle \langle \ell\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle \right) \\ &= \sum_{\ell \neq n,m} \left( \mathbf{r}_{n\ell}(\mathbf{k})\rho_{\ell m}^{(N)}(\mathbf{k}; t) - \rho_{n\ell}^{(N)}(\mathbf{k}; t)\mathbf{r}_{\ell m}(\mathbf{k}) \right) \\ &\equiv \mathbf{R}_e^{(N)}(\mathbf{k}; t), \end{aligned} \quad (1.46)$$

and from Eq. (1.22),

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}'\rangle = i\delta(\mathbf{k} - \mathbf{k}')(\rho_{nm}^{(N)}(t))_{;\mathbf{k}} \equiv \delta(\mathbf{k} - \mathbf{k}')\mathbf{R}_i^{(N)}(\mathbf{k}; t). \quad (1.47)$$

Then Eq. (1.44) becomes

$$\rho_{I,nm}^{(N+1)}(\mathbf{k}; t) = \frac{ie}{\hbar} \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}}^\Sigma - \tilde{\omega})t'} [R_e^{\text{b}(N)}(\mathbf{k}; t') + R_i^{\text{b}(N)}(\mathbf{k}; t')] E^{\text{b}}, \quad (1.48)$$

where the roman superindices a, b, c denote Cartesian components that are summed over if repeated. Starting from the linear response and proceeding from Eq. (1.39) and (1.46),

$$\begin{aligned} R_e^{\text{b}(0)}(\mathbf{k}; t) &= \sum_\ell \left( r_{n\ell}^{\text{b}}(\mathbf{k}) \rho_{\ell m}^{(0)}(\mathbf{k}) - \rho_{n\ell}^{(0)}(\mathbf{k}) r_{\ell m}^{\text{b}}(\mathbf{k}) \right) \\ &= \sum_\ell \left( r_{n\ell}^{\text{b}}(\mathbf{k}) \delta_{\ell m} f_m(\hbar\omega_m^\Sigma(\mathbf{k})) - \delta_{n\ell} f_n(\hbar\omega_n^\Sigma(\mathbf{k})) r_{\ell m}^{\text{b}}(\mathbf{k}) \right) \\ &= f_{mn\mathbf{k}} r_{nm}^{\text{b}}(\mathbf{k}), \end{aligned} \quad (1.49)$$

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. (1.47) and Eq. (1.23) that

$$R_i^{\text{b}(0)}(\mathbf{k}) = i(\rho_{nm}^{(0)})_{;\mathbf{k}^{\text{b}}} = i\delta_{nm}(f_{n\mathbf{k}})_{;\mathbf{k}^{\text{b}}} = i\delta_{nm}\nabla_{k^{\text{b}}} f_{n\mathbf{k}}. \quad (1.50)$$

For a semiconductor at  $T = 0$ ,  $f_{n\mathbf{k}} = 1$  if the state  $|n\mathbf{k}\rangle$  is a valence state and  $f_{n\mathbf{k}} = 0$  if it is a conduction state. Thus,  $\nabla_{\mathbf{k}} f_{n\mathbf{k}} = 0$ ,  $\mathbf{R}_i^{(0)} = 0$  and the linear response has no contribution from the intraband transitions. Then,

$$\begin{aligned} \rho_{I,nm}^{(1)}(\mathbf{k}; t) &= \frac{ie}{\hbar} f_{mn\mathbf{k}} r_{nm}^{\text{b}}(\mathbf{k}) E^{\text{b}} \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}}^\Sigma - \tilde{\omega})t'} \\ &= \frac{e}{\hbar} f_{mn\mathbf{k}} r_{nm}^{\text{b}}(\mathbf{k}) E^{\text{b}} \frac{e^{i(\omega_{nm\mathbf{k}}^\Sigma - \tilde{\omega})t}}{\omega_{nm\mathbf{k}}^\Sigma - \tilde{\omega}} \\ &= e^{i\omega_{nm\mathbf{k}}^\Sigma t} B_{mn}^{\text{b}}(\mathbf{k}) E^{\text{b}}(t) \\ &= e^{i\omega_{nm\mathbf{k}}^\Sigma t} \rho_{nm}^{(1)}(\mathbf{k}; t), \end{aligned} \quad (1.51)$$

with

$$B_{nm}^{\text{b}}(\mathbf{k}, \omega) = \frac{e}{\hbar} \frac{f_{mn\mathbf{k}} r_{nm}^{\text{b}}(\mathbf{k})}{\omega_{nm\mathbf{k}}^\Sigma - \tilde{\omega}}, \quad (1.52)$$

and

$$\rho_{nm}^{(1)}(\mathbf{k}; t) = B_{mn}^{\text{b}}(\mathbf{k}, \omega) E^{\text{b}}(\omega) e^{-i\tilde{\omega}t}. \quad (1.53)$$

Now, we calculate the second-order response. Then, from Eq. (1.46)

$$\begin{aligned} R_e^{\text{b}(1)}(\mathbf{k}; t) &= \sum_\ell \left( r_{n\ell}^{\text{b}}(\mathbf{k}) \rho_{\ell m}^{(1)}(\mathbf{k}; t) - \rho_{n\ell}^{(1)}(\mathbf{k}; t) r_{\ell m}^{\text{b}}(\mathbf{k}) \right) \\ &= \sum_\ell \left( r_{n\ell}^{\text{b}}(\mathbf{k}) B_{\ell m}^{\text{c}}(\mathbf{k}, \omega) - B_{n\ell}^{\text{c}}(\mathbf{k}, \omega) r_{\ell m}^{\text{b}}(\mathbf{k}) \right) E^{\text{c}}(t), \end{aligned} \quad (1.54)$$

and from Eq. (1.47)

$$R_i^{b(1)}(\mathbf{k}; t) = i(\rho_{nm}^{(1)}(t))_{;k^b} = iE^c(t)(B_{nm}^c(\mathbf{k}, \omega))_{;k^b}. \quad (1.55)$$

Using Eqs. (1.54) and (1.55) in Eq. (1.48), we obtain

$$\begin{aligned} \rho_{I,nm}^{(2)}(\mathbf{k}; t) &= \frac{ie}{\hbar} \left[ \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k}, \omega) - B_{n\ell}^c(\mathbf{k}, \omega) r_{\ell m}^b(\mathbf{k}) \right) + i(B_{nm}^c(\mathbf{k}, \omega))_{;k^b} \right] E_{\omega}^b E_{\omega}^c \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}}^{\Sigma} - 2\tilde{\omega})t'} \\ &= \frac{e}{\hbar} \left[ \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k}, \omega) - B_{n\ell}^c(\mathbf{k}, \omega) r_{\ell m}^b(\mathbf{k}) \right) + i(B_{nm}^c(\mathbf{k}, \omega))_{;k^b} \right] E_{\omega}^b E_{\omega}^c \frac{e^{i(\omega_{nm\mathbf{k}}^{\Sigma} - 2\tilde{\omega})t}}{\omega_{nm\mathbf{k}}^{\Sigma} - 2\tilde{\omega}} \\ &= e^{i\omega_{nm\mathbf{k}}^{\Sigma} t} \rho_{nm}^{(2)}(\mathbf{k}; t). \end{aligned} \quad (1.56)$$

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

$$\rho_{nm}^{(2)}(\mathbf{k}; 2\omega) = \frac{e}{i\hbar} \frac{1}{\omega_{nm\mathbf{k}}^{\Sigma} - 2\tilde{\omega}} \left[ - (B_{nm}^c(\mathbf{k}, \omega))_{;k^b} + i \sum_{\ell} \left( r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega) - B_{n\ell}^c(\mathbf{k}, \omega) r_{\ell m}^b \right) \right] E^b(\omega) E^c(\omega) \quad (1.57)$$

where  $B_{\ell m}^a(\mathbf{k}, \omega)$  are given by Eq. (1.52). We remark that  $\mathbf{r}_{nm}(\mathbf{k})$  are the same whether calculated with the LDA or the scissored Hamiltonian (see Eq. (1.29)). We chose the former in this thesis.

## 1.4 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  $\chi_{\text{slab}}^{abc} = 0$ , and thus we must find a way to bypass this characteristic of a centrosymmetric slab in order to have a finite  $\chi_{\text{surface}}^{abc}$  representative of the surface. Even if the front and back surfaces of the slab are different, breaking the centrosymmetry and therefore giving an overall  $\chi_{\text{slab}}^{abc} \neq 0$ , we still need a procedure to extract the front surface  $\chi_{\text{front}}^{abc}$  and the back surface  $\chi_{\text{back}}^{abc}$  from the nonlinear susceptibility  $\chi_{\text{slab}}^{abc} = \chi_{\text{front}}^{abc} - \chi_{\text{back}}^{abc}$  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 [13]. 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  $\ell$ ,

$$\mathcal{C}^{\ell}(z) = \Theta(z - z_{\ell} + \Delta_{\ell}^b) \Theta(z_{\ell} - z + \Delta_{\ell}^f), \quad (1.58)$$

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

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

$$\mathbf{j}(\mathbf{r}, t) = \text{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)), \quad (1.59)$$

where the operator for the electron’s current is

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{e}{2} (\hat{\mathbf{v}}^\Sigma |\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^\Sigma), \quad (1.60)$$

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

$$\begin{aligned} \text{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)) &= \text{Tr}(\hat{\rho}(t)\hat{\mathbf{j}}(\mathbf{r})) = \frac{e}{2} (\text{Tr}(\hat{\rho}\hat{\mathbf{v}}^\Sigma\hat{\mu}) + \text{Tr}(\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^\Sigma)) \\ &= \frac{e}{2} \sum_{n\mathbf{k}} (\langle n\mathbf{k}|\hat{\rho}\hat{\mathbf{v}}^\Sigma\hat{\mu}|n\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^\Sigma|n\mathbf{k}\rangle) \\ &= \frac{e}{2} \sum_{nm\mathbf{k}} \langle n\mathbf{k}|\hat{\rho}|m\mathbf{k}\rangle (\langle m\mathbf{k}|\hat{\mathbf{v}}^\Sigma|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^\Sigma|n\mathbf{k}\rangle) \\ \mathbf{j}(\mathbf{r}, t) &= \sum_{nm\mathbf{k}} \rho_{nm}(\mathbf{k}; t) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}), \end{aligned} \quad (1.61)$$

where

$$\mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}) = \frac{e}{2} (\langle m\mathbf{k}|\hat{\mathbf{v}}^\Sigma|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^\Sigma|n\mathbf{k}\rangle), \quad (1.62)$$

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

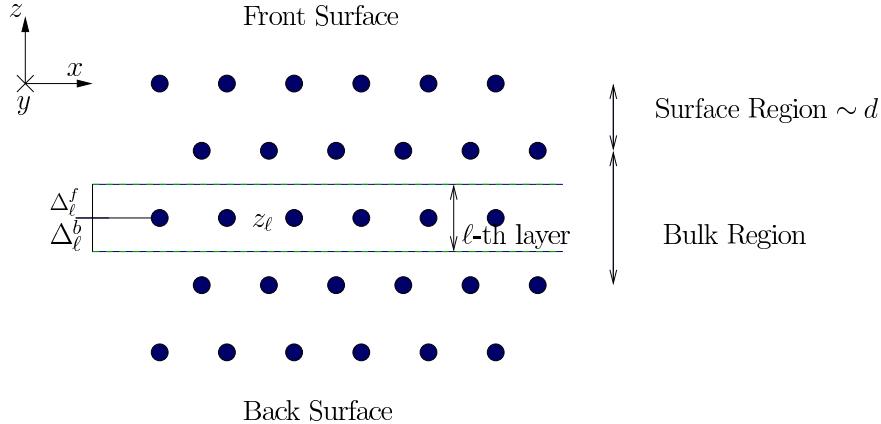


Figure 1.2: A sketch of a slab where the circles represent atoms.

from the  $\ell$ -th layer of the slab is given by  $\Omega \rightarrow A$ ?

$$\frac{1}{\Omega} \int d^3r \mathcal{C}^\ell(z) \mathbf{j}(\mathbf{r}, t) \equiv \mathbf{J}^\ell(t), \quad (1.63)$$

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

$$e\mathcal{V}_{mn}^{\Sigma,\ell}(\mathbf{k}) \equiv \int d^3r \mathcal{C}^\ell(z) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}), \quad (1.64)$$

to write

$$J_a^{(N,\ell)}(t) = \frac{e}{\Omega} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k}) \rho_{nm}^{(N)}(\mathbf{k}; t), \quad (1.65)$$

as the induced microscopic current of the  $\ell$ -th layer, to order  $N$  in the external perturbation. The matrix elements of the density operator for  $N = 1, 2$  are given by Eqs. (1.52) and (1.57) respectively. The Fourier component of microscopic current of Eq. (1.65) is given by

$$J_a^{(N,\ell)}(\omega_3) = \frac{e}{\Omega} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k}) \rho_{nm}^{(N)}(\mathbf{k}; \omega_3). \quad (1.66)$$

We proceed to give an explicit expression of  $\mathcal{V}_{mn}^{\Sigma,\ell}(\mathbf{k})$ . From Eqs. (1.64) and (1.62) we obtain

$$\mathcal{V}_{mn}^{\Sigma,\ell}(\mathbf{k}) = \frac{1}{2} \int d^3r \mathcal{C}^\ell(z) \left[ \langle m\mathbf{k} | \mathbf{v}^\Sigma | \mathbf{r} \rangle \langle \mathbf{r} | n\mathbf{k} \rangle + \langle m\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{v}^\Sigma | n\mathbf{k} \rangle \right], \quad (1.67)$$

and using the following property

$$\langle \mathbf{r} | \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}') | n\mathbf{k} \rangle = \int d^3r'' \langle \mathbf{r} | \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}') | \mathbf{r}'' \rangle \langle \mathbf{r}'' | n\mathbf{k} \rangle = \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}'') \int d^3r'' \langle \mathbf{r} | \mathbf{r}'' \rangle \langle \mathbf{r}'' | n\mathbf{k} \rangle = \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}), \quad (1.68)$$

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

$$\begin{aligned} \mathcal{V}_{mn}^{\Sigma,\ell}(\mathbf{k}) &= \frac{1}{2} \int d^3r \mathcal{C}^\ell(z) \left[ \psi_{n\mathbf{k}}(\mathbf{r}) \hat{\mathbf{v}}^{\Sigma*} \psi_{m\mathbf{k}}^*(\mathbf{r}) + \psi_{m\mathbf{k}}^*(\mathbf{r}) \hat{\mathbf{v}}^\Sigma \psi_{n\mathbf{k}}(\mathbf{r}) \right] \\ &= \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \left[ \frac{\mathcal{C}^\ell(z) \mathbf{v}^\Sigma + \mathbf{v}^\Sigma \mathcal{C}^\ell(z)}{2} \right] \psi_{n\mathbf{k}}(\mathbf{r}) \\ &= \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \mathcal{V}^{\Sigma,\ell} \psi_{n\mathbf{k}}(\mathbf{r}). \end{aligned} \quad (1.69)$$

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

$$\mathcal{V}^{\Sigma,\ell} = \frac{\mathcal{C}^\ell(z) \mathbf{v}^\Sigma + \mathbf{v}^\Sigma \mathcal{C}^\ell(z)}{2}, \quad (1.70)$$

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

$$\hat{\mathbf{v}}^\Sigma \rightarrow \hat{\mathbf{V}}^{\Sigma,\ell} = \left[ \frac{\mathcal{C}^\ell(z) \hat{\mathbf{v}}^\Sigma + \hat{\mathbf{v}}^\Sigma \mathcal{C}^\ell(z)}{2} \right], \quad (1.71)$$

is all that is needed to change the velocity operator of the electron  $\hat{\mathbf{v}}^\Sigma$  to the new velocity operator  $\mathcal{V}^{\Sigma,\ell}$  that implicitly takes into account the contribution of the region of the slab given by  $\mathcal{C}^\ell(z)$ . From Eq. (1.24),

$$\begin{aligned}\mathcal{V}^{\Sigma,\ell} &= \mathcal{V}^{\text{LDA},\ell} + \mathcal{V}^{\mathcal{S},\ell} \\ \mathcal{V}^{\text{LDA},\ell} &= \mathcal{V}^\ell + \mathcal{V}^{\text{nl},\ell} = \frac{1}{m_e} \mathcal{P}^\ell + \mathcal{V}^{\text{nl},\ell}.\end{aligned}\quad (1.72)$$

**Add  $\ell$  to app:voila** As shown in Appendix A.9, Eq. (1.27) is generalized to  $\mathcal{V}_{nm}^{\Sigma,\ell} = (\omega_{nm}^\Sigma / \omega_{nm}^{\text{LDA}}) \mathcal{V}_{nm}^{\text{LDA},\ell}$  from which  $\mathcal{V}_{nm}^{\Sigma,\ell}$  can be readily calculated. As a consistency test we have calculated the matrix elements of  $\mathcal{V}^{\text{LDA},\ell}$  and  $\mathcal{V}^{\mathcal{S},\ell}$  separately, according to the derivation presented in Appendix A.4, and confirm that both approaches yield identical results for  $\chi_{\text{surface}}^{abc}$ .

To limit the response to one surface, the equivalent of Eq. (1.70) for  $\mathcal{V}^\ell = \mathcal{P}^\ell / m_e$  was proposed in Ref. [13] and later used in Refs. [14], [15], [16], and [17] also in the context of SHG. The layer-by-layer analysis of Refs. [18] and [19] used Eq. (1.58), 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. [20] for the linear response, and here in this thesis, for the second harmonic optical response of semiconductors.

## 1.5 Microscopic surface susceptibility

In this section we obtain the expressions for the surface susceptibility tensor  $\chi_{\text{surface}}^{abc}$ . We start with the basic relation  $\mathbf{J} = d\mathbf{P}/dt$  with  $\mathbf{J}$  the current calculated in Sec. 1.4. From Eq. (1.66) we obtain

$$J^{(2,\ell)a}(2\omega) = -i2\tilde{\omega}P^a(2\omega) = \frac{e}{\Omega} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k}; 2\omega), \quad (1.73)$$

and using Eqs. (1.57) leads to

$$\begin{aligned}\chi^{abc,\ell} &= \frac{ie}{AE_1^b E_2^c 2\tilde{\omega}} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k}; 2\tilde{\omega}) \\ &= \frac{e^2}{A\hbar 2\tilde{\omega}} \sum_{mn\mathbf{k}} \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k})}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \left[ -(B_{nm}^c(\mathbf{k}, \omega))_{;k^b} + i \sum_\ell \left( r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega) - B_{n\ell}^c(\mathbf{k}, \omega) r_{\ell m}^b \right) \right],\end{aligned}\quad (1.74)$$

which gives the susceptibility of the  $\ell$ -th layer, where  $\mathcal{V}^\Sigma$  is given in Eq. (1.72), where **Remark about the normalization of the calculated  $\chi$  in results**  $A = \Omega/d$  is the surface area of the unit cell that characterizes the surface of the system. Using Eq. (1.52) we split this equation into two contributions from the first and second terms on the right hand side, **!!!!CHECK THAT  $\ell$  IS NOT USED AS INDEX, AND SWITCH  $l$ !!!**

$$\chi_i^{abc,\ell} = -\frac{e^3}{A\hbar^2 2\tilde{\omega}} \sum_{mn\mathbf{k}} \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \left( \frac{f_{mn} r_{nm}^b}{\omega_{nm}^\Sigma - \tilde{\omega}} \right)_{;k^c}, \quad (1.75)$$

and

$$\chi_e^{abc,\ell} = \frac{ie^3}{A\hbar^2 2\tilde{\omega}} \sum_{\ell mn\mathbf{k}} \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \left( \frac{r_{n\ell}^c r_{\ell m}^b f_{ml}}{\omega_{\ell m}^\Sigma - \tilde{\omega}} - \frac{r_{n\ell}^b r_{\ell m}^c f_{ln}}{\omega_{n\ell}^\Sigma - \tilde{\omega}} \right), \quad (1.76)$$

where  $\chi_i^\ell$  is related to intraband transitions and  $\chi_e^\ell$  to interband transitions. For the generalized derivative in Eq. (1.75) we use the chain rule and the following result shown in Appendix A.5,

$$\left(\omega_{nm}^\Sigma\right)_{;k^a} = \left(\omega_{nm}^{\text{LDA}}\right)_{;k^a} = v_{nn}^{\text{LDA},a} - v_{mm}^{\text{LDA},a} \equiv \Delta_{nm}^a, \quad (1.77)$$

to show that

$$\left(\frac{f_{mn}r_{nm}^b}{\omega_{nm}^\Sigma - \tilde{\omega}}\right)_{;k^c} = \frac{f_{mn}}{\omega_{nm}^\Sigma - \tilde{\omega}} \left(r_{nm}^b\right)_{;k^c} - \frac{f_{mn}r_{nm}^b \Delta_{nm}^c}{(\omega_{nm}^\Sigma - \tilde{\omega})^2}. \quad (1.78)$$

In order to calculate the nonlinear susceptibility of any given layer  $\ell$  we simply add the above terms  $\chi^\ell = \chi_e^\ell + \chi_i^\ell$  and then calculate the surface susceptibility as

$$\chi_{\text{surface}} \equiv \sum_{\ell=1}^N \chi^\ell, \quad (1.79)$$

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

$$\chi^{\ell=N} = 0, \quad (1.80)$$

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. (1.80) to be satisfied and to give converged results for  $\chi_{\text{surface}}$ . We can use Eq. (1.79) for either the front or the back surface.

We can see from the prefactors of Eqs. (1.75) and (1.76) that they diverge as  $\tilde{\omega} \rightarrow 0$ . To remove this apparent divergence of  $\chi^\ell$ , we perform a partial fraction expansion over  $\tilde{\omega}$ . As shown in Appendix A.6, we use time-reversal invariance to remove these divergences and obtain the following expressions for  $\chi^\ell$ ,

$$\text{Im}[\chi_{e,\omega}^{abc,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vc} \sum_{q \neq (v,c)} \frac{1}{\omega_{cv}^\Sigma} \left[ \frac{\text{Im}[\mathcal{V}_{qc}^{\Sigma,a,\ell}\{r_{cv}^b r_{vq}^c\}]}{(2\omega_{cv}^\Sigma - \omega_{cq}^\Sigma)} - \frac{\text{Im}[\mathcal{V}_{vq}^{\Sigma,a,\ell}\{r_{qc}^c r_{cv}^b\}]}{(2\omega_{cv}^\Sigma - \omega_{qv}^\Sigma)} \right] \delta(\omega_{cv}^\Sigma - \omega), \quad (1.81a)$$

$$\text{Im}[\chi_{i,\omega}^{abc,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{cv} \frac{1}{(\omega_{cv}^\Sigma)^2} \left[ \text{Re} \left[ \left\{ r_{cv}^b \left( \mathcal{V}_{vc}^{\Sigma,a,\ell} \right)_{;k^c} \right\} \right] + \frac{\text{Re} [\mathcal{V}_{vc}^{\Sigma,a,\ell} \{r_{cv}^b \Delta_{cv}^c\}]}{\omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - \omega), \quad (1.81b)$$

$$\text{Im}[\chi_{e,2\omega}^{abc,\ell}] = -\frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vc} \frac{4}{\omega_{cv}^\Sigma} \left[ \sum_{v' \neq v} \frac{\text{Im}[\mathcal{V}_{vc}^{\Sigma,a,\ell}\{r_{cv'}^b r_{v'v}^c\}]}{2\omega_{cv'}^\Sigma - \omega_{cv}^\Sigma} - \sum_{c' \neq c} \frac{\text{Im}[\mathcal{V}_{vc}^{\Sigma,a,\ell}\{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v}^\Sigma - \omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - 2\omega), \quad (1.81c)$$

$$\text{Im}[\chi_{i,2\omega}^{abc,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vc} \frac{4}{(\omega_{cv}^\Sigma)^2} \left[ \text{Re} \left[ \mathcal{V}_{vc}^{\Sigma,a,\ell} \left\{ \left(r_{cv}^b\right)_{;k^c} \right\} \right] - \frac{2\text{Re} [\mathcal{V}_{vc}^{\Sigma,a,\ell} \{r_{cv}^b \Delta_{cv}^c\}]}{\omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - 2\omega), \quad (1.81d)$$

where the limit of  $\eta \rightarrow 0$  has been taken. We have split the interband and intraband  $1\omega$  and  $2\omega$  contributions. The real part of each contribution can be obtained through a Kramers-Kronig transformation,[21] and then  $\chi^{abc,\ell} = \chi_{e,\omega}^{abc,\ell} + \chi_{e,2\omega}^{abc,\ell} + \chi_{i,\omega}^{abc,\ell} + \chi_{i,2\omega}^{abc,\ell}$ . To fulfill the required intrinsic permutation symmetry,[22] the  $\{\}$  notation symmetrizes the bc Cartesian indices, i.e.  $\{u^b s^c\} =$

$(u^b s^c + u^c s^b)/2$ , and thus  $\chi^{abc,\ell} = \chi^{acb,\ell}$ . In Appendices A.7 and A.4 we demonstrate how to calculate the generalized derivatives of  $(\mathbf{r})_{nm;\mathbf{k}}$  and  $(\mathcal{V}_{nm}^{\Sigma,a,\ell})_{;\mathbf{k}}$ . From Appendix A.7 we find that  $\mathcal{T}_{nm}^{ab}$ , given by

$$\mathcal{T}_{nm}^{ab} = [r^a, v^{\text{LDA},b}] = \frac{i\hbar}{m_e} \delta_{ab} \delta_{nm} + \mathcal{L}_{nm}^{ab}, \quad (1.82)$$

with

$$\mathcal{L}_{nm}^{ab} = \frac{1}{i\hbar} [r^a, v^{\text{nl},b}]_{nm}, \quad (1.83)$$

is the contribution to the generalized derivatives  $(\mathbf{r}_{nm})_{;\mathbf{k}}$ , and  $(\mathcal{V}_{nm}^{\Sigma,a,\ell})_{;\mathbf{k}}$  coming from the nonlocal part of the pseudopotential,  $\mathbf{v}^{\text{nl}}$ . In Appendix A.8 we calculate  $\mathcal{L}_{nm}^{ab}$ , that as shown in Ref. [23], is a term with a 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  $\chi^{abc,\ell}$ . Therefore, we neglect it throughout this thesis and take

$$\mathcal{T}_{nm}^{ab} \approx \frac{i\hbar}{m_e} \delta_{ab} \delta_{nm}. \quad (1.84)$$

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  $\chi_{\text{surface}}$  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.

## Chapter 2

# Surface Second-Harmonic Generation Yield

## Outline

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In Chapter 1 we derived the expressions for the nonlinear surface susceptibility tensor including three features not previously found in a single formulation: (i) the scissors correction, (ii) the contribution of the nonlocal part of the pseudopotentials, and (iii) the cut function used to extract the surface response, all within the independent particle approximation. There are, of course, several other theoretical formalisms that describe the SHG process for surfaces with different approximations and varying levels of difficulty [6, 14, 24, 15, 25, 16, 17, 26]. However, I consider that this newly developed framework, with the inclusion of these three contributions opens the possibility

to study SSHG with more versatility and accuracy than was previously available at this level of approximation.

In this chapter, I will walk the reader through the considerations for developing the three layer (3-layer) model for the SSHG yield, that considers that the SH conversion takes place in a thin layer just below the surface that lies under the vacuum region and above the bulk of the material. We will then derive explicit expressions for each of the four polarization configurations for the incoming and outgoing fields. These expressions will be simplified by taking into account the symmetry relations for the (111), (110), and (001) surfaces. I have also included Appendix B that contains a wealth of supplementary derivations for all the work contained in this chapter.

## 2.1 The three layer model for the SSHG yield

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

$$\mathcal{R}(\omega) = \frac{I(2\omega)}{I^2(\omega)}, \quad (2.1)$$

with the intensity given by [27, 28]

$$I(\omega) = \begin{cases} \frac{c}{2\pi} n(\omega) |E(\omega)|^2 & (\text{CGS units}) \\ 2\epsilon_0 c n(\omega) |E(\omega)|^2 & (\text{MKS units}) \end{cases}, \quad (2.2)$$

where  $n(\omega) = \sqrt{\epsilon(\omega)}$  is the index of refraction with  $\epsilon(\omega)$  as the dielectric function,  $\epsilon_0$  is the vacuum permittivity, and  $c$  the speed of light in vacuum.

There are several ways to calculate  $R$ , one of which is the procedure followed by Cini [29]. This approach calculates the nonlinear susceptibility and at the same time the radiated fields. However, I present an alternative derivation based on the work of Mizrahi and Sipe [30], since the derivation of the 3-layer model is straightforward. In this scheme, the surface is represented by three regions or layers. The first layer is the vacuum region (denoted by  $v$ ) with a dielectric function  $\epsilon_v(\omega) = 1$  from where the fundamental electric field  $\mathbf{E}_v(\omega)$  impinges on the material. The second layer is a thin layer (denoted by  $\ell$ ) of thickness  $d$  characterized by a dielectric function  $\epsilon_\ell(\omega)$ . It is in this layer where the SHG takes place. The third layer is the bulk region denoted by  $b$  and characterized by  $\epsilon_b(\omega)$ . Both the vacuum and bulk layers are semi-infinite (see Fig. 2.1).

To model the electromagnetic response of the 3-layer model, we follow Ref. [30] and assume a polarization sheet of the form **Decide if layered P (in previous chapter) should have calligraphic P or not**

$$\mathbf{P}(\mathbf{r}, t) = \mathcal{P} e^{i\kappa \cdot \mathbf{R}} e^{-i\omega t} \delta(z - z_\beta) + \text{c.c.}, \quad (2.3)$$

where  $\mathbf{R} = (x, y)$ ,  $\kappa$  is the component of the wave vector  $\nu_\beta$  parallel to the surface, and  $z_\beta$  is the position of the sheet within medium  $\beta$ , and  $\mathcal{P}$  is the position independent polarization. Ref. [31] demonstrates that the solution of the Maxwell equations for the radiated fields  $E_{\beta,p\pm}$ , and  $E_{\beta,s}$  with  $\mathbf{P}(\mathbf{r}, t)$  as a source at points  $z \neq 0$ , can be written as

$$(E_{\beta,p\pm}, E_{\beta,s}) = \left( \frac{\gamma i \tilde{\omega}^2}{\tilde{w}_\beta} \hat{\mathbf{p}}_{\beta\pm} \cdot \mathcal{P}, \frac{\gamma i \tilde{\omega}^2}{\tilde{w}_\beta} \hat{\mathbf{s}} \cdot \mathcal{P} \right), \quad (2.4)$$

where  $\gamma = 2\pi$  in CGS units or  $\gamma = 1/2\epsilon_0$  in MKS units, and  $\tilde{\omega} = \omega/c$ . Also,  $\hat{\mathbf{s}}$  and  $\hat{\mathbf{p}}_{\beta\pm}$  are the unitary vectors for the  $s$  and  $p$  polarizations of the radiated field, respectively. The  $\pm$  refers to upward (+) or downward (-) direction of propagation within medium  $\beta$ , as shown in Fig. 2.1. Also,  $\tilde{w}_\beta(\omega) = \tilde{\omega}w_\beta$ , where

$$\hat{\mathbf{p}}_{\beta\pm}(\omega) = \frac{\kappa(\omega)\hat{\mathbf{z}} \mp \tilde{w}_\beta(\omega)\hat{\boldsymbol{\kappa}}}{\tilde{\omega}n_\beta(\omega)} = \frac{\sin\theta_0\hat{\mathbf{z}} \mp w_\beta(\omega)\hat{\boldsymbol{\kappa}}}{n_\beta(\omega)}, \quad (2.5)$$

with

$$w_\beta(\omega) = (\epsilon_\beta(\omega) - \sin^2\theta_0)^{1/2}, \quad (2.6)$$

$\theta_0$  is the angle of incidence of  $\mathbf{E}_v(\omega)$ ,  $\kappa(\omega) = |\boldsymbol{\kappa}| = \tilde{\omega}\sin\theta_0$ ,  $n_\beta(\omega) = \sqrt{\epsilon_\beta(\omega)}$  is the index of refraction of medium  $\beta$ , and  $z$  is the direction perpendicular to the surface that points towards the vacuum. If we consider the plane of incidence along the  $\boldsymbol{\kappa}z$  plane, then

$$\hat{\boldsymbol{\kappa}} = \cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}}, \quad (2.7)$$

and

$$\hat{\mathbf{s}} = -\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}, \quad (2.8)$$

where  $\phi$  is the azimuthal angle with respect to the  $x$  axis.

In the 3-layer model the nonlinear polarization responsible for the SHG is immersed in the thin layer ( $\beta = \ell$ ), and is given by

$$\mathcal{P}_{\ell,i}(2\omega) = \begin{cases} \chi_{\text{surface}}^{abc}(-2\omega;\omega,\omega)E^b(\omega)E^c(\omega) & (\text{CGS units}) \\ \epsilon_0\chi_{\text{surface}}^{abc}(-2\omega;\omega,\omega)E^b(\omega)E^c(\omega) & (\text{MKS units}) \end{cases}, \quad (2.9)$$

where  $\chi_{\text{surface}}(-2\omega;\omega,\omega)$  is the dipolar surface nonlinear susceptibility tensor that we derived in Chapter 1, and the Cartesian indices  $a, b, c$  are summed over if repeated. As we mentioned before,  $\chi^{abc}(-2\omega;\omega,\omega) = \chi^{acb}(-2\omega;\omega,\omega)$  is the intrinsic permutation symmetry due to the fact that SHG is degenerate in  $E_j(\omega)$  and  $E_k(\omega)$ . As in Ref. [30], we consider the polarization sheet (Eq. (2.3)) to be oscillating at some frequency  $\omega$  in order to properly express Eqs. (2.4)-(2.8). However, in the following we find it convenient to use  $\omega$  exclusively to denote the fundamental frequency and  $\boldsymbol{\kappa}$  to denote the component of the incident wave vector parallel to the surface. The generated nonlinear polarization is oscillating at  $\Omega = 2\omega$  and will be characterized by a wave vector parallel to the surface  $\mathbf{K} = 2\boldsymbol{\kappa}$ . We can carry over Eqs. (2.3)-(2.8) simply by replacing the lowercase symbols  $(\omega, \tilde{\omega}, \boldsymbol{\kappa}, n_\beta, \tilde{w}_\beta, w_\beta, \hat{\mathbf{p}}_{\beta\pm}, \hat{\mathbf{s}})$  with uppercase symbols  $(\Omega, \tilde{\Omega}, \mathbf{K}, N_\beta, \tilde{W}_\beta, W_\beta, \hat{\mathbf{P}}_{\beta\pm}, \hat{\mathbf{S}})$ , all evaluated at  $2\omega$ . Of course, we always have that  $\hat{\mathbf{S}} = \hat{\mathbf{s}}$ .

From Fig. 2.1, we observe the propagation of the SH field as it is refracted at the layer-vacuum interface ( $\ell v$ ), and reflected multiple times from the layer-bulk ( $\ell b$ ) and layer-vacuum ( $\ell v$ ) interfaces. Thus, we can define

$$\mathbf{T}^{\ell v} = \hat{\mathbf{s}}T_s^{\ell v}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}T_p^{\ell v}\hat{\mathbf{P}}_{\ell+}, \quad (2.10)$$

as the transmission tensor for the  $\ell v$  interface,

$$\mathbf{R}^{\ell b} = \hat{\mathbf{s}}R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell+}R_p^{\ell b}\hat{\mathbf{P}}_{\ell-}, \quad (2.11)$$

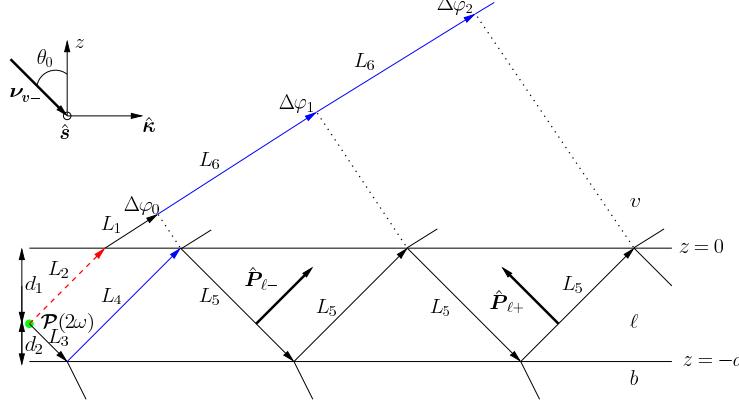


Figure 2.1: Sketch of the three layer model for SHG. The vacuum region ( $v$ ) is on top with  $\epsilon_v = 1$ ; the layer  $\ell$  of thickness  $d = d_1 + d_2$ , is characterized with  $\epsilon_\ell(\omega)$ , and it is where the SH polarization sheet  $\mathcal{P}_\ell(2\omega)$  is located at  $z_\ell = d_1$ . The bulk  $b$  is described with  $\epsilon_b(\omega)$ . The arrows point along the direction of propagation, and the  $p$ -polarization unit vector,  $\hat{\mathbf{P}}_{\ell- (+)}$ , along the downward (upward) direction is denoted with a thick arrow. The  $s$ -polarization unit vector  $\hat{\mathbf{s}}$ , points out of the page. The fundamental field  $\mathbf{E}(\omega)$  is incident from the vacuum side along the  $\kappa\hat{z}$ -plane, with  $\theta_0$  its angle of incidence and  $\nu_{v-}$  its wave vector.  $\Delta\varphi_i$  denotes the phase difference between the multiple reflected beams and the first layer-vacuum transmitted beam, denoted by the dashed-red arrow (of length  $L_2$ ) followed by the solid black arrow (of length  $L_1$ ). The dotted lines in the vacuum region are perpendicular to the beam extended from the solid black arrow (denoted by solid blue arrows of length  $L_6$ ).

as the reflection tensor for the  $\ell b$  interface, and

$$\mathbf{R}^{\ell v} = \hat{\mathbf{s}} R_s^{\ell v} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell-} R_p^{\ell v} \hat{\mathbf{P}}_{\ell+}, \quad (2.12)$$

as the reflection tensor for the  $\ell v$  interface. The Fresnel factors in uppercase letters,  $T_{s,p}^{ij}$  and  $R_{s,p}^{ij}$ , are evaluated at  $2\omega$  from the following well known formulas [1]

$$\begin{aligned} t_s^{ij}(\omega) &= \frac{2w_i(\omega)}{w_i(\omega) + w_j(\omega)}, & t_p^{ij}(\omega) &= \frac{2w_i(\omega)\sqrt{\epsilon_i(\omega)\epsilon_j(\omega)}}{w_i(\omega)\epsilon_j(\omega) + w_j(\omega)\epsilon_i(\omega)}, \\ r_s^{ij}(\omega) &= \frac{w_i(\omega) - w_j(\omega)}{w_i(\omega) + w_j(\omega)}, & r_p^{ij}(\omega) &= \frac{w_i(\omega)\epsilon_j(\omega) - w_j\epsilon_i(\omega)}{w_i(\omega)\epsilon_j(\omega) + w_j(\omega)\epsilon_i(\omega)}. \end{aligned} \quad (2.13)$$

With these expressions we easily derive the following useful relations,

$$\begin{aligned} 1 + r_s^{\ell b} &= t_s^{\ell b}, \\ 1 + r_p^{\ell b} &= \frac{n_b}{n_\ell} t_p^{\ell b}, \\ 1 - r_p^{\ell b} &= \frac{n_\ell}{n_b} \frac{w_b}{w_\ell} t_p^{\ell b}, \\ t_p^{\ell v} &= \frac{w_\ell}{w_v} t_p^{v\ell}, \\ t_s^{\ell v} &= \frac{w_\ell}{w_v} t_s^{v\ell}. \end{aligned} \quad (2.14)$$

### 2.1.1 Multiple SHG reflections

The SH field  $\mathbf{E}(2\omega)$  radiated by the SH polarization  $\mathcal{P}_\ell(2\omega)$  will radiate directly into the vacuum and the bulk, where it will be reflected back at the layer-bulk interface into the thin layer. This beam will be transmitted and reflected multiple times, as shown in Fig. 2.1. As the two beams propagate, a phase difference will develop between them according to

$$\begin{aligned} \Delta\varphi_m &= \tilde{\Omega}\left((L_3 + L_4 + 2mL_5)N_\ell - (L_2N_\ell + (L_1 + mL_6)N_v)\right) \\ &= \delta_0 + m\delta \quad m = 0, 1, 2, \dots, \end{aligned} \quad (2.15)$$

where

$$\delta_0 = 8\pi \left(\frac{d_2}{\lambda_0}\right) W_\ell, \quad (2.16)$$

and

$$\delta = 8\pi \left(\frac{d}{\lambda_0}\right) W_\ell, \quad (2.17)$$

where  $\lambda_0$  is the wavelength of the fundamental field in the vacuum,  $d$  is the thickness of layer  $\ell$ , and  $d_2$  is the distance of  $\mathcal{P}_\ell(2\omega)$  from the  $\ell b$  interface (see Fig. 2.1). We see that  $\delta_0$  is the phase difference of the first and second transmitted beams, and  $m\delta$  that of the first and third ( $m = 1$ ), first and fourth ( $m = 2$ ), and so on. Note that the thickness  $d$  of the layer  $\ell$  enters through the phase  $\delta$ , and the position  $d_2$  of the nonlinear polarization sheet  $\mathbf{P}(\mathbf{r}, t)$  (Eq. (2.3)) enters through  $\delta_0$ . In particular,  $d_2$  could be used as a variable to study the effects of multiple reflections on the SSHG yield  $\mathcal{R}(2\omega)$ .

To take into account the multiple reflections of the generated SH field in the layer  $\ell$ , we proceed as follows. I include the algebra for the  $p$ -polarized SH field, and the  $s$ -polarized field could be worked out along the same steps. The  $p$ -polarized  $\mathbf{E}_{\ell,p}(2\omega)$  field reflected multiple times is given by

$$\begin{aligned} \mathbf{E}_{\ell,p}(2\omega) &= E_{\ell,p+}(2\omega) \mathbf{T}^{\ell v} \cdot \hat{\mathbf{P}}_{\ell+} + E_{\ell,p-}(2\omega) \mathbf{T}^{\ell v} \cdot \mathbf{R}^{\ell b} \cdot \hat{\mathbf{P}}_{\ell-} e^{i\Delta\varphi_0} \\ &\quad + E_{\ell,p-}(2\omega) \mathbf{T}^{\ell v} \cdot \mathbf{R}^{\ell b} \cdot \mathbf{R}^{\ell v} \cdot \mathbf{R}^{\ell b} \cdot \hat{\mathbf{P}}_{\ell-} e^{i\Delta\varphi_1} \\ &\quad + E_{\ell,p-}(2\omega) \mathbf{T}^{\ell v} \cdot \mathbf{R}^{\ell b} \cdot \mathbf{R}^{\ell v} \cdot \mathbf{R}^{\ell b} \cdot \mathbf{R}^{\ell v} \cdot \mathbf{R}^{\ell b} \cdot \hat{\mathbf{P}}_{\ell-} e^{i\Delta\varphi_2} + \dots \\ &= E_{\ell,p+}(2\omega) \mathbf{T}^{\ell v} \cdot \hat{\mathbf{P}}_{\ell+} + E_{\ell,p-}(2\omega) \mathbf{T}^{\ell v} \cdot \sum_{m=0}^{\infty} (\mathbf{R}^{\ell b} \cdot \mathbf{R}^{\ell v} e^{i\delta})^m \cdot \mathbf{R}^{\ell b} \cdot \hat{\mathbf{P}}_{\ell-} e^{i\delta_0}. \end{aligned} \quad (2.18)$$

From Eqs. (2.10) - (2.12) it is easy to show that

$$\mathbf{T}^{\ell v} \cdot (\mathbf{R}^{\ell b} \cdot \mathbf{R}^{\ell v})^n \cdot \mathbf{R}^{\ell b} = \hat{\mathbf{s}} T_s^{\ell v} (R_s^{\ell b} R_s^{\ell v})^n R_s^{\ell b} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{\ell v} (R_p^{\ell b} R_p^{\ell v})^n R_p^{\ell b} \hat{\mathbf{P}}_{\ell-},$$

then,

$$\mathbf{E}_{\ell,p}(2\omega) = \hat{\mathbf{P}}_{\ell+} T_p^{\ell v} (E_{\ell,p+}(2\omega) + \frac{R_p^{\ell b} e^{i\delta_0}}{1 + R_p^{v\ell} R_p^{\ell b} e^{i\delta}} E_{\ell,p-}(2\omega)), \quad (2.19)$$

where we used  $R_{s,p}^{ij} = -R_{s,p}^{ji}$ . Using Eq. (2.4) and (2.14), we can readily write

$$\mathbf{E}_{\ell,p}(2\omega) = \frac{\gamma i \tilde{\Omega}}{W_\ell} \mathbf{H}_\ell \cdot \mathcal{P}_\ell(2\omega), \quad (2.20)$$

where

$$\mathbf{H}_\ell = \frac{W_\ell}{W_v} [\hat{\mathbf{s}} T_s^{v\ell} (1 + R_s^M) \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{v\ell} (\hat{\mathbf{P}}_{\ell+} + R_p^M \hat{\mathbf{P}}_{\ell-})], \quad (2.21)$$

and

$$R_i^M \equiv \frac{R_i^{\ell b} e^{i\delta_0}}{1 + R_i^{v\ell} R_i^{\ell b} e^{i\delta}}, \quad i = s, p, \quad (2.22)$$

is defined as the multiple ( $M$ ) reflection coefficient. This coefficient depends on the thickness  $d$  of layer  $\ell$ , and most importantly on the position  $d_2$  of  $\mathcal{P}_\ell(2\omega)$  within this layer. The final results will depend on both  $d$  and  $d_2$ . However, using Eq. (2.16) we can also define an average  $\bar{R}_i^M$  as

$$\bar{R}_i^M \equiv \frac{1}{d} \int_0^d \frac{R_i^{\ell b} e^{i(8\pi W_\ell / \lambda_0)x}}{1 + R_i^{v\ell} R_i^{\ell b} e^{i\delta}} dx = \frac{R_i^{\ell b} e^{i\delta/2}}{1 + R_i^{v\ell} R_i^{\ell b} e^{i\delta}} \text{sinc}(\delta/2), \quad (2.23)$$

that only depends on  $d$  through the  $\delta$  term from Eq. (2.17).

To connect with the work in Ref. [30], where  $\mathcal{P}(2\omega)$  is located on top of the vacuum-surface interface and only the vacuum radiated beam and the first (and only) reflected beam need be considered, we take  $\ell = v$  and  $d_2 = 0$ , then  $T^{\ell v} = 1$ ,  $R^{v\ell} = 0$  and  $\delta_0 = 0$ , with which  $R_i^M = R_i^{vb}$ . Thus, Eq. (2.21) coincides with Eq. (3.8) of Ref. [30].

### 2.1.2 Multiple reflections for the linear field

For a more complete formulation, we must also consider the multiple reflections of the fundamental field  $\mathbf{E}_\ell(\omega)$  inside the thin  $\ell$  layer. In Fig. 2.2 I present the situation where  $\mathbf{E}_v(\omega)$  impinges from the vacuum side with an angle of incidence  $\theta_0$ . As the first transmitted beam is multiply reflected from the  $\ell b$  and the  $\ell v$  interfaces, it accumulates a phase difference of  $n\phi$ , with  $n = 1, 2, 3, \dots$ , given by

$$\begin{aligned} \varphi &= \frac{\omega}{c} (2L_1 n_\ell - L_2 n_v) \\ &= 4\pi \left( \frac{d}{\lambda_0} \right) w_\ell, \end{aligned} \quad (2.24)$$

where  $n_v = 1$ . Besides the equivalent of Eqs. (2.11) and (2.12) for  $\omega$ , we also need

$$\mathbf{t}^{v\ell} = \hat{\mathbf{s}} t_s^{v\ell} \hat{\mathbf{s}} + \hat{\mathbf{p}}_{\ell-} t_p^{v\ell} \hat{\mathbf{p}}_{v-}, \quad (2.25)$$

to write

$$\begin{aligned}
\mathbf{E}(\omega) &= E_0 \left[ \mathbf{t}^{v\ell} + \mathbf{r}^{\ell b} \cdot \mathbf{t}^{v\ell} e^{i\varphi} + \mathbf{r}^{\ell b} \cdot \mathbf{r}^{\ell v} \cdot \mathbf{r}^{\ell b} \cdot \mathbf{t}^{v\ell} e^{i2\varphi} + \mathbf{r}^{\ell b} \cdot \mathbf{r}^{\ell v} \cdot \mathbf{r}^{\ell b} \cdot \mathbf{r}^{\ell v} \cdot \mathbf{r}^{\ell b} \cdot \mathbf{t}^{v\ell} e^{i3\varphi} + \dots \right] \cdot \hat{\mathbf{e}}^i \\
&= E_0 \left[ 1 + \left( 1 + \mathbf{r}^{\ell b} \cdot \mathbf{r}^{\ell v} e^{i\varphi} + (\mathbf{r}^{\ell b} \cdot \mathbf{r}^{\ell v})^2 e^{i2\varphi} + \dots \right) \cdot \mathbf{r}^{\ell b} e^{i\varphi} \right] \cdot \mathbf{t}^{v\ell} \cdot \hat{\mathbf{e}}^i \\
&= E_0 \left[ \hat{\mathbf{s}} t_s^{v\ell} (1 + r_s^M) \hat{\mathbf{s}} + t_p^{v\ell} \left( \hat{\mathbf{p}}_{\ell-} + \hat{\mathbf{p}}_{\ell+} r_p^M \right) \hat{\mathbf{p}}_{v-} \right] \cdot \hat{\mathbf{e}}^i,
\end{aligned} \tag{2.26}$$

where  $E_0$  is the intensity of the fundamental field, and  $\hat{\mathbf{e}}^i$  is the unit vector of the incoming polarization, with  $i = s, p$ , and then,  $\hat{\mathbf{e}}^s = \hat{\mathbf{s}}$  and  $\hat{\mathbf{e}}^p = \hat{\mathbf{p}}_{v-}$ . Also,

$$r_i^M \equiv \frac{r_i^{\ell b} e^{i\varphi}}{1 + r_i^{v\ell} r_i^{\ell b} e^{i\varphi}}, \quad i = s, p. \tag{2.27}$$

$r_i^M$  is defined as the multiple (M) reflection coefficient for the fundamental field. We define  $\mathbf{E}_\ell^i(\omega) \equiv E_0 \mathbf{e}_\ell^{\omega, i}$  ( $i = s, p$ ), where

$$\mathbf{e}_\ell^{\omega, i} = \left[ \hat{\mathbf{s}} t_s^{v\ell} (1 + r_s^M) \hat{\mathbf{s}} + t_p^{v\ell} \left( \hat{\mathbf{p}}_{\ell-} + \hat{\mathbf{p}}_{\ell+} r_p^M \right) \hat{\mathbf{p}}_{v-} \right] \cdot \hat{\mathbf{e}}^i, \tag{2.28}$$

and using Eq. (2.5) we obtain that

$$\mathbf{e}_\ell^{\omega, p} = \frac{t_p^{v\ell}}{n_\ell} \left( r_p^{M+} \sin \theta_0 \hat{\mathbf{z}} + r_p^{M-} w_\ell \hat{\boldsymbol{\kappa}} \right), \tag{2.29}$$

for  $p$ -input polarization with  $\hat{\mathbf{e}}^i = \hat{\mathbf{p}}_{v-}$ , and

$$\mathbf{e}_\ell^{\omega, s} = t_s^{v\ell} r_s^{M+} \hat{\mathbf{s}}, \tag{2.30}$$

for  $s$ -input polarization with  $\hat{\mathbf{e}}^i = \hat{\mathbf{s}}$ , where

$$r_i^{M\pm} = 1 \pm r_i^M, \quad i = s, p. \tag{2.31}$$

### 2.1.3 Deriving the SSHG yield

The magnitude of the radiated field is given by  $E(2\omega) = \hat{\mathbf{e}}^F \cdot \mathbf{E}_\ell(2\omega)$ , where  $\hat{\mathbf{e}}^F$  is the unit vector of the final,  $S$  or  $P$  SH polarization with  $F = S, P$ , where  $\hat{\mathbf{e}}^S = \hat{\mathbf{s}}$  and  $\hat{\mathbf{e}}^P = \hat{\mathbf{P}}_{v+}$ . We expand the rightmost term in parenthesis of Eq. (2.21) as

$$\begin{aligned}
\hat{\mathbf{P}}_{\ell+} + R_p^M \hat{\mathbf{P}}_{\ell-} &= \frac{\sin \theta_0 \hat{\mathbf{z}} - W_\ell \hat{\boldsymbol{\kappa}}}{N_\ell} + R_p^M \frac{\sin \theta_0 \hat{\mathbf{z}} + W_\ell \hat{\boldsymbol{\kappa}}}{N_\ell} \\
&= \frac{1}{N_\ell} \left( \sin \theta_0 R_p^{M+} \hat{\mathbf{z}} - W_\ell R_p^{M-} \hat{\boldsymbol{\kappa}} \right),
\end{aligned} \tag{2.32}$$

where

$$R_i^{M\pm} \equiv 1 \pm R_i^M, \quad i = s, p. \tag{2.33}$$

Using Eq. (2.14) we write Eq. (2.20) as

$$E(2\omega) = \frac{2\gamma i\omega}{cW_\ell} \hat{\mathbf{e}}^F \cdot \mathbf{H}_\ell \cdot \mathcal{P}_\ell(2\omega) = \frac{2\gamma i\omega}{cW_v} \mathbf{e}_\ell^{2\omega, F} \cdot \mathcal{P}_\ell(2\omega), \tag{2.34}$$

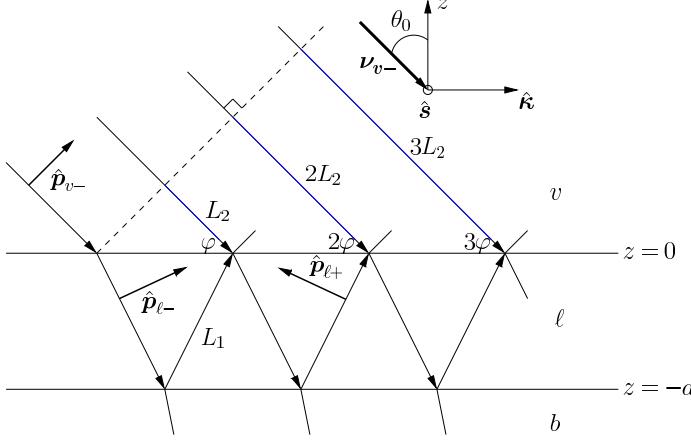


Figure 2.2: Sketch for the multiple reflected fundamental field  $\mathbf{E}(\omega)$ , which impinges from the vacuum side along the  $\hat{\kappa}z$ -plane.  $\theta_0$  and  $\nu_{v-}$  are the angle of incidence and wave vector, respectively. The arrows point along the direction of propagation. The  $p$ -polarization unit vectors  $\hat{\mathbf{p}}_{\beta\pm}$ , point along the downward ( $-$ ) or upward ( $+$ ) directions and are denoted with thick arrows, where  $\beta = v$  or  $\ell$ . The  $s$ -polarization unit vector  $\hat{\mathbf{s}}$  points out of the page.  $(1, 2, 3, \dots)\varphi$  denotes the phase difference for the multiple reflected beams with respect to the incident field, where the dotted line is perpendicular to this beam.

where

$$\mathbf{e}_\ell^{2\omega, F} = \hat{\mathbf{e}}^F \cdot \left[ \hat{\mathbf{s}} T_s^{v\ell} R_s^{M+} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} \frac{T_p^{v\ell}}{N_\ell} (\sin \theta_0 R_p^{M+} \hat{\mathbf{z}} - W_\ell R_p^{M-} \hat{\kappa}) \right]. \quad (2.35)$$

Replacing  $\mathbf{E}(\omega) \rightarrow E_0 \mathbf{e}_\ell^{\omega,i}$ , in Eq. (2.9), we obtain that

$$\mathcal{P}_\ell(2\omega) = \begin{cases} E_0^2 \chi_{\text{surface}} : \mathbf{e}_\ell^{\omega,i} \mathbf{e}_\ell^{\omega,i} & (\text{CGS units}) \\ \epsilon_0 E_0^2 \chi_{\text{surface}} : \mathbf{e}_\ell^{\omega,i} \mathbf{e}_\ell^{\omega,i} & (\text{MKS units}) \end{cases}, \quad (2.36)$$

where  $\mathbf{e}_\ell^{\omega,i}$  is given by Eq. (2.28), and thus Eq. (2.34) reduces to ( $W_v = \cos \theta_0$ )

$$E_\ell(2\omega) = \frac{2\eta i \omega}{c \cos \theta_0} \mathbf{e}_\ell^{2\omega, F} \cdot \chi_{\text{surface}} : \mathbf{e}_\ell^{\omega,i} \mathbf{e}_\ell^{\omega,i}, \quad (2.37)$$

where  $\eta = 2\pi$  in CGS units and  $\eta = 1/2$  in MKS units. For ease of notation, we define

$$\Upsilon_{iF} \equiv \mathbf{e}_\ell^{2\omega, F} \cdot \chi_{\text{surface}} : \mathbf{e}_\ell^{\omega,i} \mathbf{e}_\ell^{\omega,i}, \quad (2.38)$$

where  $i$  stands for the incoming polarization of the fundamental electric field given by  $\hat{\mathbf{e}}^i$  in Eq. (2.28), and  $F$  for the outgoing polarization of the SH electric field given by  $\hat{\mathbf{e}}^F$  in Eq. (2.35). I purposely omitted the full  $\chi(-2\omega; \omega, \omega)$  notation, and will do so from this point on.

From Eqs. (2.1) and (2.2) we obtain that in CGS units ( $\eta = 2\pi$ ),

$$\begin{aligned} |E(2\omega)|^2 &= |E_0|^4 \frac{16\pi^2\omega^2}{c^2 W_v^2} |\Upsilon_{iF}|^2 \\ \frac{c}{2\pi} |\sqrt{N_v} E(2\omega)|^2 &= \frac{32\pi^3\omega^2}{c^3 \cos^2 \theta_0} \left| \frac{\sqrt{N_v}}{n_\ell^2} \Upsilon_{iF} \right|^2 \left( \frac{c}{2\pi} |\sqrt{n_\ell} E_0|^2 \right)^2 \\ I(2\omega) &= \frac{32\pi^3\omega^2}{c^3 \cos^2 \theta_0} \left| \frac{\sqrt{N_v}}{n_\ell^2} \Upsilon_{iF} \right|^2 I^2(\omega) \\ \mathcal{R}_{iF}(2\omega) &= \frac{32\pi^3\omega^2}{c^3 \cos^2 \theta_0} \left| \frac{1}{n_\ell} \Upsilon_{iF} \right|^2, \end{aligned} \quad (2.39)$$

and in MKS units ( $\eta = 1/2$ ),

$$\begin{aligned} |E(2\omega)|^2 &= |E_0|^4 \frac{\omega^2}{c^2 W_v^2} \\ 2\epsilon_0 c |\sqrt{N_v} E(2\omega)|^2 &= \frac{2\epsilon_0 \omega^2}{c \cos^2 \theta_0} \left| \frac{\sqrt{N_v}}{n_\ell^2} \Upsilon_{iF} \right|^2 \frac{1}{4\epsilon_0^2 c^2} (2\epsilon_0 c |\sqrt{n_\ell} E_0|^2)^2 \\ I(2\omega) &= \frac{\omega^2}{2\epsilon_0 c^3 \cos^2 \theta_0} \left| \frac{\sqrt{N_v}}{n_\ell^2} \Upsilon_{iF} \right|^2 I^2(\omega) \\ \mathcal{R}_{iF}(2\omega) &= \frac{\omega^2}{2\epsilon_0 c^3 \cos^2 \theta_0} \left| \frac{1}{n_\ell} \Upsilon_{iF} \right|^2. \end{aligned} \quad (2.40)$$

Finally, we condense these results and establish the SHHG yield as

$$\mathcal{R}_{iF}(2\omega) \begin{cases} \frac{32\pi^3\omega^2}{c^3 \cos^2 \theta_0} \left| \frac{1}{n_\ell} \Upsilon_{iF} \right|^2 & (\text{CGS units}) \\ \frac{\omega^2}{2\epsilon_0 c^3 \cos^2 \theta_0} \left| \frac{1}{n_\ell} \Upsilon_{iF} \right|^2 & (\text{MKS units}) \end{cases}, \quad (2.41)$$

where  $N_v = 1$  and  $W_v = \cos \theta_0$ . As mentioned in Chapter (1),  $\chi_{\text{surface}}$  is given in  $\text{m}^2/\text{V}$  in the MKS unit system, since it is a surface second order nonlinear susceptibility, and  $\mathcal{R}_{iF}$  is given in  $\text{m}^2/\text{W}$ .

## 2.2 $\mathcal{R}_{iF}$ for different polarization cases

We now have everything we need to derive explicit expressions for  $\mathcal{R}_{iF}$ , Eq. (2.41), for the most commonly used polarizations of incoming and outgoing fields ( $iF=pP, pS, sP$ , and  $sS$ ). For this, we must expand  $\Upsilon_{iF}$  from Eq. (2.38) for each case. By substituting Eqs. (2.7) and (2.8) into Eq. (2.35), we obtain

$$\mathbf{e}_\ell^{2\omega, P} = \frac{T_p^{v\ell}}{N_\ell} (\sin \theta_0 R_p^{M+} \hat{\mathbf{z}} - W_\ell R_p^{M-} \cos \phi \hat{\mathbf{x}} - W_\ell R_p^{M-} \sin \phi \hat{\mathbf{y}}), \quad (2.42)$$

for  $P$  ( $\hat{\mathbf{e}}^F = \hat{\mathbf{P}}_{v+}$ ) outgoing polarization, and

$$\mathbf{e}_\ell^{2\omega, S} = T_s^{v\ell} R_s^{M+} (-\sin \phi \hat{\mathbf{x}} + \cos \phi \hat{\mathbf{y}}). \quad (2.43)$$

Case	$\hat{\mathbf{e}}^F$	$\hat{\mathbf{e}}^i$	$\mathbf{e}_\ell^{2\omega,F}$	$\mathbf{e}_\ell^{\omega,i}\mathbf{e}_\ell^{\omega,i}$
$\mathcal{R}_{pP}$	$\hat{\mathbf{P}}_{v+}$	$\hat{\mathbf{p}}_{v-}$	Eq. (2.42)	Eq. (2.44)
$\mathcal{R}_{pS}$	$\hat{\mathbf{S}}$	$\hat{\mathbf{p}}_{v-}$	Eq. (2.43)	Eq. (2.44)
$\mathcal{R}_{sP}$	$\hat{\mathbf{P}}_{v+}$	$\hat{\mathbf{s}}$	Eq. (2.42)	Eq. (2.45)
$\mathcal{R}_{sS}$	$\hat{\mathbf{S}}$	$\hat{\mathbf{s}}$	Eq. (2.43)	Eq. (2.45)

Table 2.1: Polarization unit vectors for  $\hat{\mathbf{e}}^F$  and  $\hat{\mathbf{e}}^i$ , and equations describing  $\mathbf{e}_\ell^{2\omega,F}$  and  $\mathbf{e}_\ell^{\omega,i}\mathbf{e}_\ell^{\omega,i}$  for each polarization case.

for  $S$  ( $\hat{\mathbf{e}}^F = \hat{\mathbf{s}}$ ) outgoing polarization.

Following a similar procedure, we use Eqs. (2.7) and (2.8) with Eq. (2.29), and obtain

$$\begin{aligned} \mathbf{e}_\ell^{\omega,p}\mathbf{e}_\ell^{\omega,p} &= \left(\frac{t_p^{\ell}}{n_\ell}\right)^2 \left( (r_p^{M-})^2 w_\ell^2 \cos^2 \phi \hat{\mathbf{x}}\hat{\mathbf{x}} + 2(r_p^{M-})^2 w_\ell^2 \sin \phi \cos \phi \hat{\mathbf{x}}\hat{\mathbf{y}} \right. \\ &\quad + 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \cos \phi \hat{\mathbf{x}}\hat{\mathbf{z}} + (r_p^{M-})^2 w_\ell^2 \sin^2 \phi \hat{\mathbf{y}}\hat{\mathbf{y}} \\ &\quad \left. + 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \hat{\mathbf{y}}\hat{\mathbf{z}} + (r_p^{M+})^2 \sin^2 \theta_0 \hat{\mathbf{z}}\hat{\mathbf{z}} \right), \end{aligned} \quad (2.44)$$

for  $p$  incoming polarization ( $\hat{\mathbf{e}}^i = \hat{\mathbf{p}}_{v-}$ ), and with Eq. (2.30),

$$\mathbf{e}_\ell^{\omega,s}\mathbf{e}_\ell^{\omega,s} = \left(t_s^{\ell} r_s^{M+}\right)^2 (\sin^2 \phi \hat{\mathbf{x}}\hat{\mathbf{x}} + \cos^2 \phi \hat{\mathbf{y}}\hat{\mathbf{y}} - 2 \sin \phi \cos \phi \hat{\mathbf{x}}\hat{\mathbf{y}}). \quad (2.45)$$

for  $s$  incoming polarization ( $\hat{\mathbf{e}}^i = \hat{\mathbf{s}}$ ).

I have summarized the combination of equations needed to derive the expressions for all four polarization cases of  $\mathcal{R}_{iF}$  in Table 2.1. In the following subsections we will derive the explicit expressions for  $\Upsilon_{iF}$  for the most general case where the surface has no symmetry other than that of noncentrosymmetry. We will then develop these expressions for particular cases of the most commonly investigated surfaces, the (111), (001), and (110) crystallographic faces. For ease of writing we split  $\Upsilon_{iF}$  as

$$\Upsilon_{iF} = \Gamma_{iF} r_{iF}. \quad (2.46)$$

Lastly, in Table 2.2 I list the nonzero components of  $\chi_{\text{surface}}$  for each surface symmetry [32, 33]. From this point on, I will omit the “surface” subscript for the  $\chi^{abc}$  components for ease of notation.

I have provided the full, step-by-step derivation for all of these expressions in Appendix B, with and without the effects of multiple reflections. The avid reader should refer to that chapter if interested in deriving any of the expressions listed below.

### 2.2.1 $\mathcal{R}_{pP}$ ( $p$ -in, $P$ -out)

Per Table 2.1,  $\mathcal{R}_{pP}$  requires Eqs. (2.42) and (2.44). After some algebra, we obtain that

$$\Gamma_{pP} = \frac{T_p^{\ell}}{N_\ell} \left(\frac{t_p^{\ell}}{n_\ell}\right)^2, \quad (2.47)$$

(111)- $C_{3v}$	(110)- $C_{2v}$	(001)- $C_{4v}$
$\chi^{zzz}$ $\chi^{zxx} = \chi^{zyy}$ $\chi^{xxz} = \chi^{yyz}$ $\chi^{xxx} = -\chi^{xyy} = -\chi^{yyx}$	$\chi^{zzz}$ $\chi^{zxx} \neq \chi^{zyy}$ $\chi^{xxz} \neq \chi^{yyz}$	$\chi^{zzz}$ $\chi^{zxx} = \chi^{zyy}$ $\chi^{xxz} = \chi^{yyz}$

Table 2.2: Components of  $\chi$  for the (111), (110) and (001) crystallographic faces, belonging to the  $C_{3v}$ ,  $C_{2v}$ , and  $C_{4v}$ , symmetry groups, respectively. For the (111) surface we choose the  $x$  and  $y$  axes along the  $[1\bar{1}\bar{2}]$  and  $[1\bar{1}0]$  directions, respectively. For the (110) and (001) we consider the  $y$  axis perpendicular to the plane of symmetry.[32] We remark that in general  $\chi^{(111)} \neq \chi^{(110)} \neq \chi^{(001)}$ .

and

$$\begin{aligned}
r_{pP} = & -R_p^{M-} \left(r_p^{M-}\right)^2 w_\ell^2 W_\ell \cos^3 \phi \chi^{xxx} - 2R_p^{M-} \left(r_p^{M-}\right)^2 w_\ell^2 W_\ell \sin \phi \cos^2 \phi \chi^{xxy} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \cos^2 \phi \chi^{xxz} - R_p^{M-} \left(r_p^{M-}\right)^2 w_\ell^2 W_\ell \sin^2 \phi \cos \phi \chi^{xyy} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xyz} - R_p^{M-} \left(r_p^{M+}\right)^2 W_\ell \sin^2 \theta_0 \cos \phi \chi^{xzz} \\
& - R_p^{M-} \left(r_p^{M-}\right)^2 w_\ell^2 W_\ell \sin \phi \cos^2 \phi \chi^{yxx} - 2R_p^{M-} \left(r_p^{M-}\right)^2 w_\ell^2 W_\ell \sin^2 \phi \cos \phi \chi^{yxy} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{yxz} - R_p^{M-} \left(r_p^{M-}\right)^2 w_\ell^2 W_\ell \sin^3 \phi \chi^{yyy} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin^2 \phi \chi^{yyz} - R_p^{M-} \left(r_p^{M+}\right)^2 W_\ell \sin^2 \theta_0 \sin \phi \chi^{yzz} \\
& + R_p^{M+} \left(r_p^{M-}\right)^2 w_\ell^2 \sin \theta_0 \cos^2 \phi \chi^{zxx} + 2R_p^{M+} r_p^{M+} r_p^{M-} w_\ell \sin^2 \theta_0 \cos \phi \chi^{zxz} \\
& + 2R_p^{M+} \left(r_p^{M-}\right)^2 w_\ell^2 \sin \theta_0 \sin \phi \cos \phi \chi^{zxy} + R_p^{M+} \left(r_p^{M-}\right)^2 w_\ell^2 \sin \theta_0 \sin^2 \phi \chi^{zyy} \\
& + 2R_p^{M+} r_p^{M+} r_p^{M-} w_\ell \sin^2 \theta_0 \sin \phi \chi^{zzy} + R_p^{M+} \left(r_p^{M+}\right)^2 \sin^3 \theta_0 \chi^{zzz},
\end{aligned} \tag{2.48}$$

where all 18 independent components of  $\chi$  for a surface with no symmetries, contribute to  $\mathcal{R}_{pP}$ . Recall that  $\chi^{abc} = \chi^{acb}$ . We will derive the expressions for each of the three surfaces being considered here, referring to Table 2.2. For the (111) surface we obtain

$$\begin{aligned}
r_{pP}^{(111)} = & R_p^{M+} \sin \theta_0 \left[ \left(r_p^{M+}\right)^2 \sin^2 \theta_0 \chi^{zzz} + \left(r_p^{M-}\right)^2 w_\ell^2 \chi^{xxx} \right] \\
& - R_p^{M-} w_\ell W_\ell \left[ 2r_p^{M+} r_p^{M-} \sin \theta_0 \chi^{xxz} + \left(r_p^{M-}\right)^2 w_\ell \chi^{xxx} \cos 3\phi \right],
\end{aligned} \tag{2.49}$$

where the three-fold azimuthal symmetry of the SHG signal that is typical of the  $C_{3v}$  symmetry group, is seen in the  $3\phi$  argument of the cosine function. For the (110) surface, we have that

$$\begin{aligned}
r_{pP}^{(110)} = & R_p^{M+} \sin \theta_0 \left[ \left(r_p^{M+}\right)^2 \sin^2 \theta_0 \chi^{zzz} + \left(r_p^{M-}\right)^2 w_\ell^2 \left( \frac{\chi^{zyy} + \chi^{zxx}}{2} + \frac{\chi^{zyy} - \chi^{zxx}}{2} \cos 2\phi \right) \right] \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \left( \frac{\chi^{yyz} + \chi^{xxz}}{2} + \frac{\chi^{yyz} - \chi^{xxz}}{2} \cos 2\phi \right).
\end{aligned} \tag{2.50}$$

The two-fold azimuthal symmetry of the SHG signal that is typical of the  $C_{2v}$  symmetry group, is seen in the  $2\phi$  argument of the cosine function. For the (001) surface we simply make  $\chi^{zxx} = \chi^{zyy}$  and  $\chi^{xxz} = \chi^{yyz}$  as seen in Table 2.2, and the previous expression reduces to

$$\begin{aligned} r_{sP}^{(001)} &= R_p^{M+} \sin \theta_0 \left[ \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} + \left( r_p^{M-} \right)^2 w_\ell^2 \chi^{zxx} \right] \\ &\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \chi^{xxz}. \end{aligned} \quad (2.51)$$

This time, the azimuthal  $4\phi$  symmetry for the  $C_{4v}$  group of the (001) surface is absent in this expression since this contribution is only related to the bulk nonlinear quadrupolar SH term, Eq. (1.7) [32], that we neglect in this work.

### 2.2.2 $\mathcal{R}_{sP}$ (*s*-in, *P*-out)

Per Table 2.1,  $\mathcal{R}_{sP}$  requires Eqs. (2.42) and (2.45). After some algebra, we obtain that

$$\Gamma_{sP} = \frac{T_p^{v\ell}}{N_\ell} \left( t_s^{v\ell} r_s^{M+} \right)^2, \quad (2.52)$$

and

$$\begin{aligned} r_{sP} &= R_p^{M-} W_\ell (-\sin^2 \phi \cos \phi \chi^{xxx} + 2 \sin \phi \cos^2 \phi \chi^{xxy} - \cos^3 \phi \chi^{xyy}) \\ &\quad R_p^{M-} W_\ell (-\sin^3 \phi \chi^{yxx} + 2 \sin^2 \phi \cos \phi \chi^{yxy} - \sin \phi \cos^2 \phi \chi^{yyy}) \\ &\quad R_p^{M+} \sin \theta_0 (\sin^2 \phi \chi^{zxx} - 2 \sin \phi \cos \phi \chi^{zxy} + \cos^2 \phi \chi^{zyy}). \end{aligned} \quad (2.53)$$

In this case, 9 out of the 18 components of  $\chi$  for a surface with no symmetries, contribute to  $\mathcal{R}_{sP}$ . This is because there is no  $E_z(\omega)$  component, as the incoming polarization is *s*. From Table 2.2 we get,

$$r_{sP}^{(111)} = R_p^{M+} \sin \theta_0 \chi^{zxx} + R_p^{M-} W_\ell \chi^{xxx} \cos 3\phi, \quad (2.54)$$

for the (111) surface,

$$r_{sP}^{(110)} = R_p^{M+} \sin \theta_0 \left( \frac{\chi^{zxx} + \chi^{zyy}}{2} + \frac{\chi^{zyy} - \chi^{zxx}}{2} \cos 2\phi \right), \quad (2.55)$$

for the (110) surface, and

$$r_{sP}^{(001)} = R_p^{M+} \sin \theta_0 \chi^{zxx}, \quad (2.56)$$

for the (001) surface.

### 2.2.3 $\mathcal{R}_{pS}$ (*p*-in, *S*-out)

Per Table 2.1,  $\mathcal{R}_{pS}$  requires Eqs. (2.43) and (2.44). After some algebra, we obtain that

$$\Gamma_{pS} = T_s^{v\ell} R_s^{M+} \left( \frac{t_p^{v\ell}}{n_\ell} \right)^2, \quad (2.57)$$

and

$$\begin{aligned}
r_{pS} = & - \left( r_p^{M-} \right)^2 w_\ell^2 \sin \phi \cos^2 \phi \chi^{xxx} - 2 \left( r_p^{M-} \right)^2 w_\ell^2 \sin^2 \phi \cos \phi \chi^{xxy} \\
& - 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xxz} - \left( r_p^{M-} \right)^2 w_\ell^2 \sin^3 \phi \chi^{xyy} \\
& - 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin^2 \phi \chi^{xzy} - \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \sin \phi \chi^{xzz} \\
& + \left( r_p^{M-} \right)^2 w_\ell^2 \cos^3 \phi \chi^{yxx} + 2 \left( r_p^{M-} \right)^2 w_\ell^2 \sin \phi \cos^2 \phi \chi^{yxy} \\
& + 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \cos^2 \phi \chi^{yxz} + \left( r_p^{M-} \right)^2 w_\ell^2 \sin^2 \phi \cos \phi \chi^{yyy} \\
& + 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{yzx} + \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \cos \phi \chi^{yzz}.
\end{aligned} \tag{2.58}$$

In this case, 12 out of the 18 components of  $\chi$  for a surface with no symmetries, contribute to  $\mathcal{R}_{pS}$ . This is because there is no  $\mathcal{P}_z(2\omega)$  component, as the outgoing polarization is  $S$ . From Table 2.2 we obtain,

$$r_{pS}^{(111)} = - \left( r_p^{M-} \right)^2 w_\ell^2 \chi^{xxx} \sin 3\phi, \tag{2.59}$$

for the (111) surface,

$$r_{sP}^{(110)} = r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 (\chi^{yyz} - \chi^{xxz}) \sin 2\phi, \tag{2.60}$$

for the (110) surface, finally,

$$r_{pS}^{(001)} = 0, \tag{2.61}$$

for the (001) surface, where the zero value is only surface related as we neglect the bulk nonlinear quadrupolar contribution [32].

#### 2.2.4 $\mathcal{R}_{sS}$ (*s*-in, *S*-out)

Per Table 2.1,  $\mathcal{R}_{sS}$  requires Eqs. (2.43) and (2.45). After some algebra, we obtain that

$$\Gamma_{sS} = T_s^{v\ell} R_s^{M+} \left( t_s^{v\ell} r_s^{M+} \right)^2, \tag{2.62}$$

and

$$\begin{aligned}
r_{sS} = & - \sin^3 \phi \chi^{xxx} + 2 \sin^2 \phi \cos \phi \chi^{xxy} - \sin \phi \cos^2 \phi \chi^{xyy} \\
& + \sin^2 \phi \cos \phi \chi^{yxx} + \cos^3 \phi \chi^{yyy} - 2 \sin \phi \cos^2 \phi \chi^{yxy}.
\end{aligned} \tag{2.63}$$

In this case, only 6 out of the 18 components of  $\chi$  for a surface with no symmetries, contribute to  $\mathcal{R}_{sS}$ . This is because there is neither an  $E_z(\omega)$  component as the incoming polarization is  $s$ , nor a  $\mathcal{P}_z(2\omega)$  component as the outgoing polarization is  $S$ . From Table 2.2, we get

$$r_{sS}^{(111)} = \chi^{xxx} \sin 3\phi, \tag{2.64}$$

for the (111) surface,

$$r_{sS}^{(110)} = 0, \tag{2.65}$$

and

$$r_{sS}^{(001)} = 0, \tag{2.66}$$

for the (110) and (001) surfaces, respectively, both being zero as the bulk nonlinear quadrupolar contribution is not considered here [32].

Label	$\mathcal{P}(2\omega)$	$\mathbf{E}(\omega)$
3-layer	$\ell$	$\ell$
3-layer-hybrid	$\ell$	$b$
2-layer-bulk	$b$	$b$
2-layer-fresnel	$v$	$b$
2-layer-vacuum	$v$	$v$

Table 2.3: Summary of the SSHG yield models used throughout this work. “Label” is the name used in subsequent figures, while the remaining columns show in which medium we will consider the specified quantity.  $\ell$  is the thin layer below the surface of the material,  $v$  is the vacuum region, and  $b$  is the bulk region of the material. We use the following convention for the labels. Models with “3-layer” consider the presence of the thin layer  $\ell$ , while “2-layer” models do not. The “fresnel”, “bulk”, “vacuum”, and “hybrid” tags refers to the configuration in which we evaluate the specific quantities. For instance, the 3-layer-hybrid model evaluates  $\mathcal{P}(2\omega)$  in the thin layer  $\ell$ , while the fundamental fields are evaluated in the bulk region  $b$ .

## 2.3 Some scenarios of interest

In this section we present five different scenarios for placing the nonlinear polarization  $\mathcal{P}(2\omega)$  and the fundamental electric field  $\mathbf{E}(\omega)$ , which are alternatives to the three-layer model presented above. In what follows, we confine ourselves only to the (111) surface and the  $p$ -in  $P$ -out combination polarizations. This is the case where the proposed scenarios differ the most as the SSHG yield depends on all the finite  $\chi^{abc}$  components for this surface. However, the other  $pS$ ,  $sP$ , and  $sS$  polarization cases, or the (110) or (001) surfaces could be worked out along the same lines described below. For all the scenarios we omit the multiple SH reflections by taking  $R_p^{M\pm} \rightarrow 1 \pm R_p^{\ell b}$  (Eq. (2.33)) and the linear multiple reflections by taking  $r_p^{M\pm} \rightarrow 1 \pm r_p^{\ell b}$  (Eq. (2.31)). Using the expressions in Eq. (2.14), we obtain the following useful relationships

$$\begin{aligned} r_p^{M+} &\rightarrow \frac{n_b}{n_\ell} t_p^{\ell b} \\ r_p^{M-} &\rightarrow \frac{n_\ell}{n_b} \frac{w_b}{w_\ell} t_p^{\ell b}, \end{aligned} \tag{2.67}$$

which will come in handy for expressing  $\Gamma_{pP}$  and  $r_{pP}^{(111)}$  in the forms presented below. Recall that these expressions are valid for the  $2\omega$  terms by simply capitalizing the relevant quantities as explained in Sec. 2.1. We summarize these scenarios in Table 2.3 for quick reference.

### 2.3.1 The 3-layer model without multiple reflections

Using Eq. (2.67) in Eq. (2.49) with Eq. (2.47), we obtain

$$\Gamma_{pP} = \frac{T_p^{\ell v} T_p^{\ell b}}{N_\ell^2 N_b} \left( \frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b} \right)^2, \tag{2.68}$$

and

$$\begin{aligned} r_{pP}^{(111)} &= N_b^2 \sin \theta_0 \left( n_b^4 \sin^2 \theta_0 \chi^{zzz} + n_\ell^4 w_b^2 \chi^{zxx} \right) \\ &\quad - N_\ell^2 n_\ell^2 w_b W_b \left( 2n_b^2 \sin \theta_0 \chi^{xxz} + n_\ell^2 w_b \chi^{xxx} \cos(3\phi) \right). \end{aligned} \quad (2.69)$$

Now that we have neglected multiple SH reflections, we can use these two expressions for  $\Gamma_{pP}$  and  $r_{pP}$  to obtain the next four scenarios by using the choices described in each subsection below. Note that by neglecting the multiple reflections, the thickness  $d$  of layer  $\ell$  disappears from the formulation, and the location of the nonlinear polarization sheet  $\mathbf{P}(\mathbf{r}, t)$  (Eq. (2.3)) at  $d_2$  (see Fig. 2.1) is immaterial.

### 2.3.2 The two layer, or Fresnel (2-layer-fresnel) model

Historically, this is the model most used in the literature. In Chap. 3, we will see how the 3-layer model, presented in the previous sections, offers a significant improvement over this model.

In the 2-layer-fresnel model, we consider that  $\mathcal{P}(2\omega)$  is evaluated in the vacuum region, while the fundamental fields are evaluated in the bulk region [32, 30]. To do this, we evaluate the  $2\omega$  radiations factors in the vacuum by taking  $\ell = v$ , thus  $\epsilon_\ell(2\omega) = 1$ ,  $T_p^{\ell v} = 1$ , and  $T_p^{\ell b} = T_p^{vb}$ . We also evaluate 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, Eqs. (2.68) and (2.69) reduce to

$$\Gamma_{pP} = \frac{T_p^{vb} (t_p^{vb})^2}{n_b^2 N_b}, \quad (2.70)$$

and

$$r_{pP}^{(111)} = N_b^2 \sin \theta_0 \left( \sin^2 \theta_0 \chi^{zzz} + w_b^2 \chi^{zxx} \right) - w_b W_b \left( 2 \sin \theta_0 \chi^{xxz} + w_b \chi^{xxx} \cos(3\phi) \right). \quad (2.71)$$

These expressions are in perfect agreement with Refs. [32] and [30].

### 2.3.3 The 2-layer-bulk model: evaluating $\mathcal{P}(2\omega)$ and $\mathbf{E}(\omega)$ in the bulk

We follow the same procedure as above considering that both the  $2\omega$  and  $1\omega$  terms will be evaluated in the bulk, by taking  $\ell = b$ . Thus,  $\epsilon_\ell(2\omega) = \epsilon_b(2\omega)$ ,  $T_p^{v\ell} = T_p^{vb}$ ,  $T_p^{\ell b} = 1$ , and  $\epsilon_\ell(\omega) = \epsilon_b(\omega)$ ,  $t_p^{v\ell} = t_p^{vb}$ , and  $t_p^{\ell b} = 1$ . With these choices Eqs. (2.68) and (2.69) reduce to

$$\Gamma_{pP} = \frac{T_p^{vb} (t_p^{vb})^2}{n_b^2 N_b}, \quad (2.72)$$

and

$$r_{pP}^{(111)} = \sin^3 \theta_0 \chi^{zzz} + w_b^2 \sin \theta_0 \chi^{zxx} - 2w_b W_b \sin \theta_0 \chi^{xxz} - w_b^2 W_b \chi^{xxx} \cos 3\phi. \quad (2.73)$$

### 2.3.4 The 2-layer-vacuum model: evaluating $\mathcal{P}(2\omega)$ and $\mathbf{E}(\omega)$ in the vacuum

We consider both  $\mathcal{P}(2\omega)$  and the fundamental fields to be evaluated in the vacuum. We take  $\ell = v$ , thus  $\epsilon_\ell(2\omega) = 1$ ,  $T_p^{\ell v} = 1$ ,  $T_p^{\ell b} = T_p^{vb}$ , and  $\epsilon_\ell(\omega) = 1$ ,  $t_p^{v\ell} = 1$ , and  $t_p^{\ell b} = t_p^{vb}$ . With these choices Eqs.

(2.68) and (2.69) reduce to

$$\Gamma_{pP} = \frac{T_p^{vb} \left( t_p^{vb} \right)^2}{n_b^2 N_b}, \quad (2.74)$$

and

$$r_{pP}^{(111)} = n_b^4 N_b^2 \sin^3 \theta_0 \chi^{zzz} + N_b^2 w_b^2 \sin \theta_0 \chi^{zxx} - 2n_b^2 w_b W_b \sin \theta_0 \chi^{xxz} - w_b^2 W_b \chi^{xxx} \cos 3\phi. \quad (2.75)$$

### 2.3.5 The 3-layer-hybrid model: evaluating $\mathcal{P}(2\omega)$ in $\ell$ and $\mathbf{E}(\omega)$ in the bulk

Again, we follow the same procedure as above considering that  $2\omega$  terms are evaluated in the thin layer  $\ell$ , and the  $1\omega$  terms will be evaluated in the bulk 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 Eqs. (2.68) and (2.69) reduce to

$$\Gamma_{pP}^{\ell b} = \frac{T_p^{v\ell} T_p^{\ell b} \left( t_p^{vb} \right)^2}{N_\ell^2 n_b^2 N_b}, \quad (2.76)$$

and

$$r_{pP}^{(111)} = N_b^2 \sin^3 \theta_0 \chi^{zzz} + N_b^2 k_b^2 \sin \theta_0 \chi^{zxx} - 2N_\ell^2 w_b W_b \sin \theta_0 \chi^{xxz} - N_\ell^2 w_b^2 W_b \chi^{xxx} \cos 3\phi. \quad (2.77)$$

## 2.4 Conclusions

In this chapter, we derived the complete expressions for the SSHG radiation using the three layer model to describe the radiating system. Our derivation yields the full expressions for the radiation that include all required components of  $\chi^{abc}$ , regardless of symmetry considerations. Thus, these expressions can be applied to any surface symmetry. We also reduce them according to the most commonly used surface symmetries, the (111), (110), and (100) cases.

In the next chapter, I will present the results obtained from using the theory developed here and in Chapter 1 applied to the Si(001)(2×1) and the Si(111)(1×1):H surfaces. In particular, we will compare the theoretical SSHG yield for the latter surface with experimental data from several sources. This is an excellent way to test the validity of this approach, and will provide a benchmark for future calculations using the theory developed here.

# Chapter 3

# Results

## Outline

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In this chapter, I will present the results for the calculation of the nonlinear susceptibility,  $\chi_{\text{surface}}$ , and the SSHG yield,  $\mathcal{R}_{\text{iF}}$ , for the Si(001)(2×1) and the Si(111)(1×1):H surfaces. These results are the direct product of all the theory derived in Chapters 1 and 2. These example surfaces provide the perfect testbed for the theory developed in this work, and the resulting spectra yield insight into the various key aspects of the theory.

The first part focuses on using the Si(001)(2×1) surface to review and compare the enhancements that we have added to the framework for calculating  $\chi$ . This surface is presented in a special configuration that allows us to test each improvement made on the theory; namely, the use of the cut function for extracting the surface susceptibility, the effect of the scissors operator, and the addition of  $\mathbf{v}^{\text{nl}}$ . I will also present a very brief overview of the calculated SSHG yield, but with no comparison to experimental data as there is very little available for this surface.

The second part features the Si(111)(1×1):H, which is experimentally well-characterized, and thus provides an excellent platform with which to test our robust formulation for the SSHG yield. We will first compare the calculated  $\chi^{xxx}$  component with experimental data from Ref. [34]. This will provide a nice confirmation of everything we learned from the Si(001)(2×1) surface. We will then review the calculated spectra for different polarization cases of the incoming fields, and compare them to experimental data from Refs. [35, 25, 36], over a wide energy range covering both the E<sub>1</sub> and E<sub>2</sub> critical point transitions for bulk Si. We will find that this new formalism, that is developed from the 3-layer model and includes the effect of multiple reflections in the material, compares quite favorably with the experimental data. The quality of these calculations affords us some insight into how the SSHG spectrum can be affected by several physical factors.

### 3.1 Results for the Si(001)(2×1) surface

In this section, let us review the characteristics of the Si(001)(2×1) surface we will be using for the subsequent calculations. This surface provides an excellent test case to check the consistency of our approach for calculating  $\chi$  with the new elements described in Chap. 1. For this, I have selected a clean Si(001) surface with a 2×1 surface reconstruction. The slab for such a surface could be made centrosymmetric by creating the front and back surfaces with the same 2×1 reconstruction. However, this particular slab has the lower surface terminated with hydrogen, producing a terminated, “ideal” bulk Si surface. The H atoms saturate the dangling bonds of the bulk-like Si atoms at the surface, as seen in Fig. 3.1. Consider the  $z$  coordinate pointing out of the surface with the  $x$  coordinate along the crystallographic [011] direction, parallel to the dimers.

The self-consistent ground state and the Kohn-Sham states were calculated in the DFT-LDA framework using the plane-wave ABINIT code [37, 38], using Troullier-Martins pseudopotentials [39] that are fully separable nonlocal pseudopotentials in the Kleinman-Bylander form [11]. The contribution of  $\mathbf{v}^{\text{nl}}$  and  $\mathcal{V}^{\text{nl}}$  to Eq. (1.81) was carried out using the DP code [40], which is implemented in our in the TINIBA code [41] developed at the Centro de Investigaciones en Óptica, A.C. The surface was studied with the experimental lattice constant of 5.43 Å. Structural optimizations were also performed with the ABINIT code. The geometry optimization was carried out in slabs of 12 atomic layers, where the central four layers were fixed at the bulk positions. The structures were relaxed until the Cartesian force components were less than 5 meV/Å. The geometry optimization for the clean surface gives a dimer buckling of 0.721 Å, and a dimer length of 2.301 Å. For the dihydride surface, the obtained Si-H bond distance was 1.48 Å. These results are in good agreement with previous theoretical studies [42, 20]. The vacuum size is equivalent to one quarter the size of the slab, avoiding the effects produced by possible wave-function tunneling from the contiguous surfaces of the full crystal formed by the repeated super-cell scheme [20]. Note that all spectra for  $\chi^{xxx}$  presented in this section were calculated with a Gaussian broadening of 0.15 eV.

Spin-orbit, local field, and electron-hole attraction [43] effects on the SHG process are all neglected. Although these are important factors in the optical response of a semiconductor, their efficient calculation is still theoretically and numerically challenging and under debate. This merits further study but is beyond the scope of this thesis. For a given slab size, I found the converged spectra to obtain the relevant parameters. The most important of these are: an energy cutoff of 10 Ha for the 16, 24, and 32 layered slabs and 13 Ha for the 40 layer slab, an equal number of conduction and valence bands, and a set of 244  $\mathbf{k}$  points in the irreducible Brillouin zone, which are equivalent to 1058  $\mathbf{k}$  points when disregarding symmetry relations. The  $\mathbf{k}$  points are used for

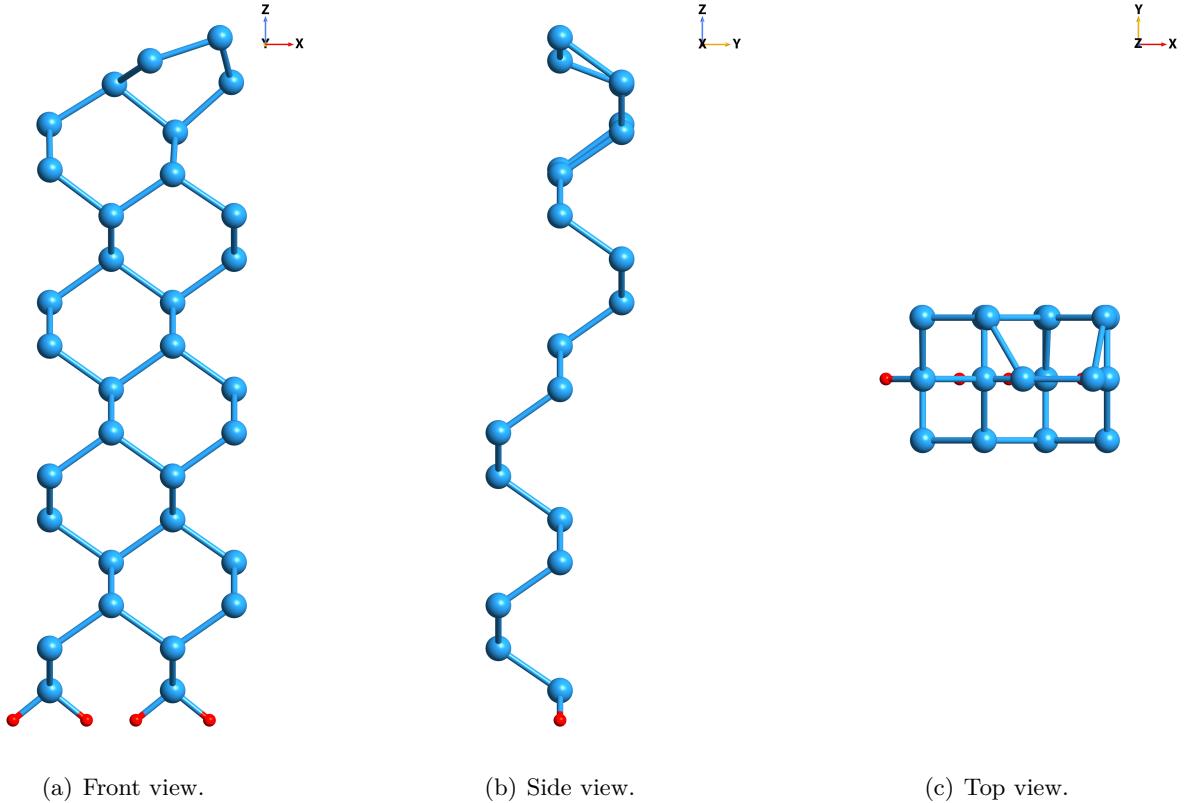


Figure 3.1: Several views of the slab used to represent the Si(001)(2×1) surface. This particular slab has 16 Si atomic layers (large blue balls) with two H atomic layers (small red balls).

the linear analytic tetrahedron method for evaluating the 3D Brillouin Zone (BZ) integrals, where special care was taken to examine the double resonances of Eq. (1.81) [44]. Note that the Brillouin zone for the slab geometry collapses to a 2D-zone, with only one  $\mathbf{k}$ -point along the  $z$ -axis.

### 3.1.1 Calculating $\chi_{\text{surface}}^{xxx}(-2\omega; \omega, \omega)$

The idea behind the special slab configuration, pictured in Fig. 3.2, is that the crystalline symmetry of the H terminated surface imposes that  $\chi_{\text{H}}^{xxx} = 0$ . The 2×1 surface has no such restrictions, so naturally  $\chi_{2\times 1}^{xxx} \neq 0$ . This is due to the fact that along the  $y$  direction there is a mirror plane for the H-saturated surface (causing centrosymmetry), whereas for the 2×1 surface this mirror is lost as the dimers are asymmetric along  $x$ . Thus, calculating  $\chi^{xxx}$  for the full-slab, or the upper half-slab containing the 2×1 surface [45] should yield the same result, since the contribution from the H saturated surface is zero either way. The following relationship must be satisfied for this particular slab,

$$\chi_{\text{half-slab}}^{xxx} = \chi_{\text{full-slab}}^{xxx},$$

where  $\chi_{\text{half-slab}}^{xxx}$  is calculated using  $\mathcal{C}(z) = 1$  for the upper half containing the 2×1 surface reconstruction (see Fig. 3.2), and  $\chi_{\text{full-slab}}^{xxx}$  is calculated using  $\mathcal{C}(z) = 1$  for the entire slab. Again, the

$2\times 1$  reconstruction  $\Rightarrow \chi_{2\times 1}^{xxx} \neq 0$

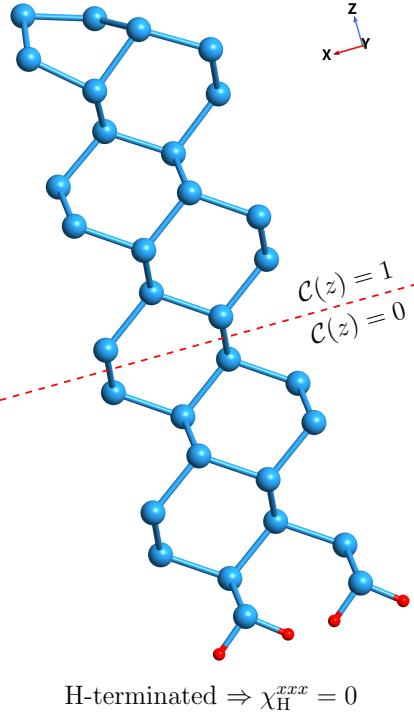


Figure 3.2: The slab for the Si(001)( $2\times 1$ ) surface. The front (upper) surface is in a  $2\times 1$ , clean reconstruction, and the rear (lower) surfaces is H-terminated, with “ideal” bulk-like atomic positions. The dangling bonds are H-saturated.

dihydride surface on the lower half of the slab must have  $\chi_{\text{half-slab}}^{xxx} = 0$ .

### 3.1.1.1 Full-slab results

Fig. 3.3 shows  $|\chi_{\text{full-slab}}^{xxx}|$  for the slab with 16, 24, 32, and 40 Si atomic layers, without the contribution of  $\mathbf{v}^{\text{nl}}$ , and with no scissors correction. Since the clean Si(001) surface is in a  $2\times 1$  reconstruction there are two atoms per atomic layer. Thus, the total number of atoms per slab is twice the number of atomic layers of the slab. The slabs were extended in the  $z$  directions in steps of 8 layers of bulk-like atomic positions. Note that the response differs substantially for 16 and 24 layers but is quite similar for 32 and 40 layers. As explained above, the calculation of the  $\mathbf{v}^{\text{nl}}$  contribution is computationally expensive, so it is crucial to minimize the number of atoms in the calculation. I consider a slab with 32 Si atomic layers as a good compromise between the convergence of  $\chi_{\text{full-slab}}^{xxx}$  as a function of the number of layers in the slab, and the computational expense.

### 3.1.1.2 Half-slab vs full-slab

Now that we have established an adequate number of layers to attain convergence, we can proceed to study the spectra produced from the slab with 32 atomic layers. Fig. 3.4 presents a comparison

between  $\chi_{\text{half-slab}}^{xxx}$  and  $\chi_{\text{full-slab}}^{xxx}$  for four different scenarios: with and without the effects of  $\mathbf{v}^{\text{nl}}$ , and with two values for the scissors correction,  $\hbar\Delta$ . I have chosen a scissors value of  $\hbar\Delta = 0.5$  eV, that is the GW gap reported in Refs. [46, 47]. This is justified by the fact that the surface states from the clean  $2\times 1$  surface are rigidly shifted and maintain their dispersion relation with respect to the LDA value, according to the GW calculations of Ref. [46].

We can appreciate that the difference between the half-slab and full-slab responses is quite small for all four scenarios. Indeed, when the value  $|\chi^{xxx}|$  is large, the difference between the two is quite small; when  $|\chi^{xxx}|$  is small, the difference increases slightly but the spectra is so close to zero that it is negligible. Of course, the difference between the two would decrease as the number of atomic layers increases. Note how 32 layers in the slab is more than enough to confirm that the extraction of the surface second-harmonic susceptibility from the  $2\times 1$  surface is readily possible using the formalism contained in Eq. (1.81). Calculating the response from the lower half of the slab substantiates that  $|\chi_{\text{half-slab}}^{xxx}| \approx 0$  for the dihydride surface (not shown). **Show this motherfucking bitch**

This confirms the validity of the theory developed in Chapter 1 and is an important result of this work. Through the proposed layer formalism, we can calculate the surface  $\chi^{\text{abc}}$  component including the contribution from the nonlocal part of the pseudopotentials, and part of the many-body effects through the scissors correction. Therefore, this scheme is robust and versatile and should work for any crystalline surface.

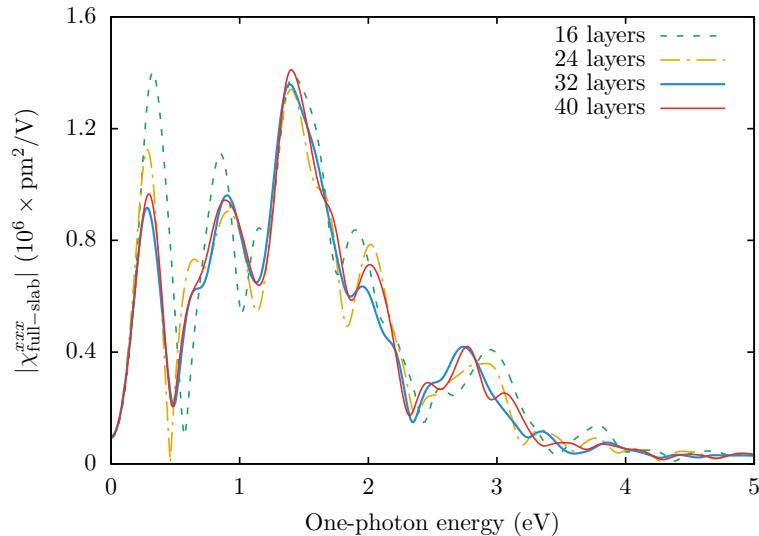


Figure 3.3:  $|\chi_{\text{full-slab}}^{xxx}|$  vs  $\hbar\omega$  for the slab with 16, 24, 32, and 40 atomic Si layers. Adequate convergence is achieved after 32 layers. The spectra presented here use a scissors value of  $\hbar\Delta = 0$  eV, and do not include the contribution from  $\mathbf{v}^{\text{nl}}$ .

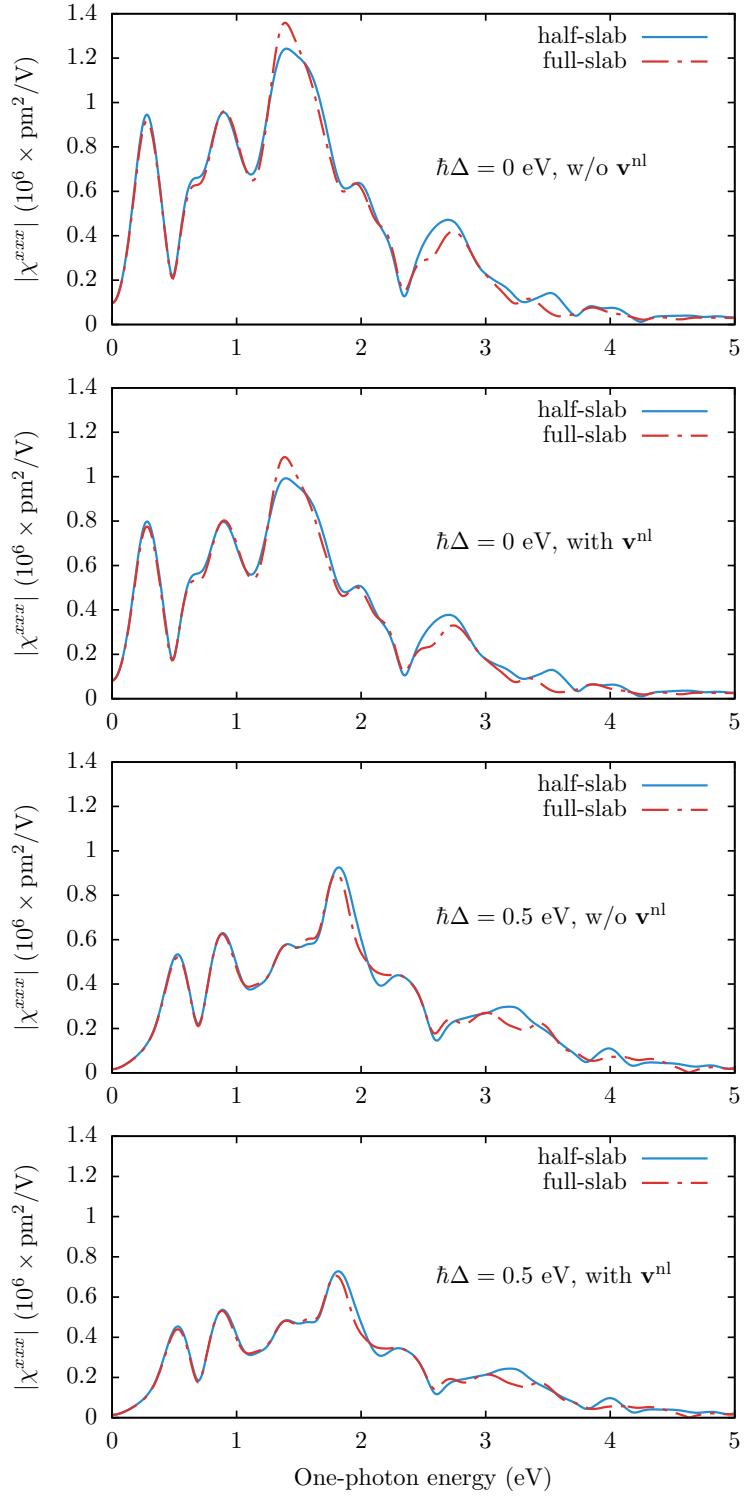


Figure 3.4:  $\chi_{\text{half-slab}}^{xxx}$  and  $\chi_{\text{full-slab}}^{xxx}$  vs  $\hbar\omega$  for four different combinations: with and without the effects of  $\mathbf{v}^{\text{nl}}$ , and with two values for the scissors correction,  $\hbar\Delta$ .

### 3.1.1.3 Half-slab results

I proceed to explain some of the features seen in  $|\chi_{\text{half-slab}}^{xxx}|$  that is obtained when setting  $\mathcal{C}(z) = 1$  for the upper half containing the  $2 \times 1$  surface reconstruction, as seen in Fig. 3.2. From Fig. 3.4, we note a series of resonances that derive from the  $1\omega$  and  $2\omega$  terms in Eq. (1.81). Notice that the  $2\omega$  resonances start below  $E_g/2$ , where  $E_g$  is the band gap (0.53 eV for LDA, and 1.03 eV if the scissor is used with  $\hbar\Delta = 0.5$  eV). These resonances come from the electronic states of the  $2 \times 1$  surface, that lie inside the bulk band gap of Si and are the well known electronic surface states [46].

Fig. 3.5 shows that the inclusion of  $\mathbf{v}^{\text{nl}}$  reduces the value of  $|\chi_{\text{half-slab}}^{xxx}|$  by 15-20%. This demonstrates the importance of this contribution for a fully correct SHHG calculation. This is in agreement with the analysis for bulk semiconductors [48]. However, the inclusion of  $\mathbf{v}^{\text{nl}}$  does not change the spectral shape of  $|\chi_{\text{half-slab}}^{xxx}|$ . We can confirm that this is not unique for this specific scissors shift, as we can appreciate from the upper two panels of Fig. 3.4, with  $\hbar\Delta = 0$  eV.

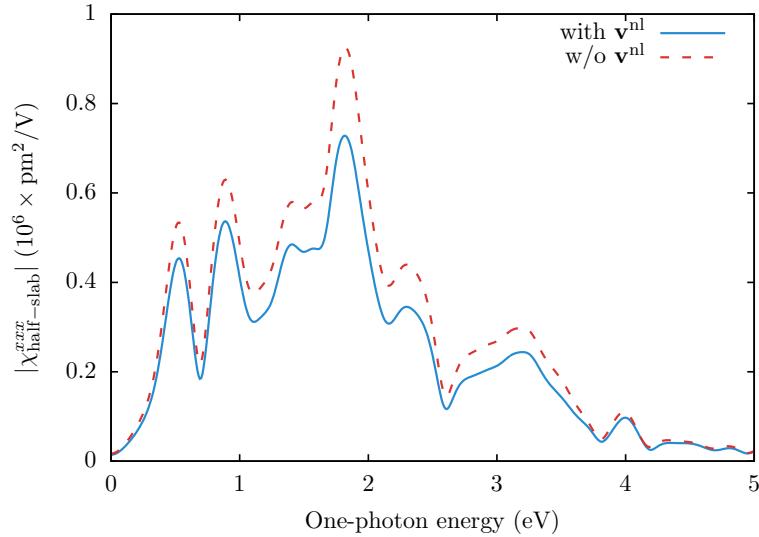


Figure 3.5:  $\chi_{\text{half-slab}}^{xxx}$  vs  $\hbar\omega$ , with and without the contribution from  $\mathbf{v}^{\text{nl}}$ . This spectrum has a scissors value of  $\hbar\Delta = 0.5$  eV.

To demonstrate the effect of the scissors correction, I considered two different finite values for  $\hbar\Delta$ . The first, with a value of  $\hbar\Delta = 0.5$  eV that is used in the previous results, is the “average” GW gap taken from Ref. [46] that is in agreement with Ref. [47]. The second, with a value of  $\hbar\Delta = 0.63$  eV is the “average” gap taken from Ref. [49], where more  $\mathbf{k}$  points in the Brillouin zone were used to calculate the GW value. Fig. 3.6 shows that the scissors correction shifts the spectra from its LDA value to higher energies, as expected. However, contrary to the case of linear optics [5], the shift introduced by the scissors correction is not rigid, which is consistent with the work of Ref. [44]. This is because the second-harmonic optical response mixes  $1\omega$  and  $2\omega$  transitions (see Eq. (1.81)), and accounts for the non-rigid shift. The reduction of the spectral strength is in agreement with previous calculations for bulk systems [44, 50, 51]. When comparing  $|\chi_{\text{half-slab}}^{xxx}|$  for the two finite values of  $\hbar\Delta$ , it is clear that the first two peaks are almost rigidly shifted with a small difference in height while the rest of the peaks are modified substantially. This behavior comes from the fact that the first two peaks are almost exclusively related to the  $2\omega$  resonances of

Eq. (1.81). The other peaks are a combination of  $1\omega$  and  $2\omega$  resonances and yield a more varied spectrum. Note that for large-gap materials the  $1\omega$  and  $2\omega$  resonances would be split, producing a small interference effect. The  $2\omega$  resonances would still strongly depend on the surface states. Thus, small changes in the scissors shift can affect the SSH susceptibility spectrum quite dramatically. In Ref. [52], the authors already noted that the nonlinear optical response of bulk materials is more influenced by the electronic structure of the material than the linear case. For the case of semiconductor surfaces, the problem is even more intricate due to the presence of electronic surface states.

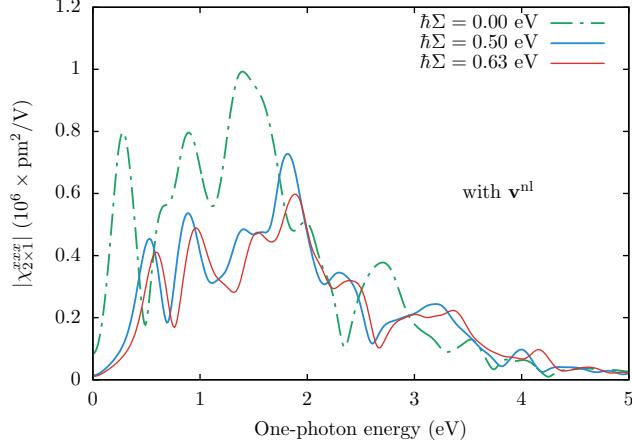


Figure 3.6:  $\chi_{\text{half-slab}}^{xxx}$  vs  $\hbar\omega$  for a slab with 32 atomic Si layers plus one H layer, for three different values of the scissors correction,  $\hbar\Delta$ .

The high sensitivity of SSHG to the energy position of surface states, as seen in Fig. 3.6, makes SSHG a good benchmark tool for spectroscopically testing the validity of the inclusion of many-body effects, and in particular the quasi-particle correction to the electronic states. Although local fields are neglected, in principle they should be quite small parallel to the interface as the electric field is continuous.  $\chi^{xxx}$  should have a relatively small influence from these local fields. Excitonic effects should also be explored, but their efficient calculation is theoretically and numerically challenging [43] and far beyond the scope of this work. Unfortunately the experimental measurement of the  $\chi^{xxx}$  component is difficult as the SH radiated intensity would be proportional not only to this component but also to the other components of  $\chi$ . However, I will present this comparison later on in Sec. 3.2.1 for the Si(111)(1×1):H surface.

### 3.1.2 Overview of the calculated $\mathcal{R}$ spectra

In Figs. 3.7 and 3.8, I present the results for the calculation of the SSHG yield for our test surface. The  $2\times 1$  surface reconstruction yields a Class 1, primitive triclinic system with all 18 components independent from each other [33]. We cannot take advantage of any symmetry relations for this surface. However, this is no problem for the robust formulation we derived in Chapter 2 that can accommodate all 18 components disregarding any surface symmetries. Calculating all 18 components is obviously more time consuming, but this calculation can be parallelized in order to calculate all components at once, so very little time is actually lost.

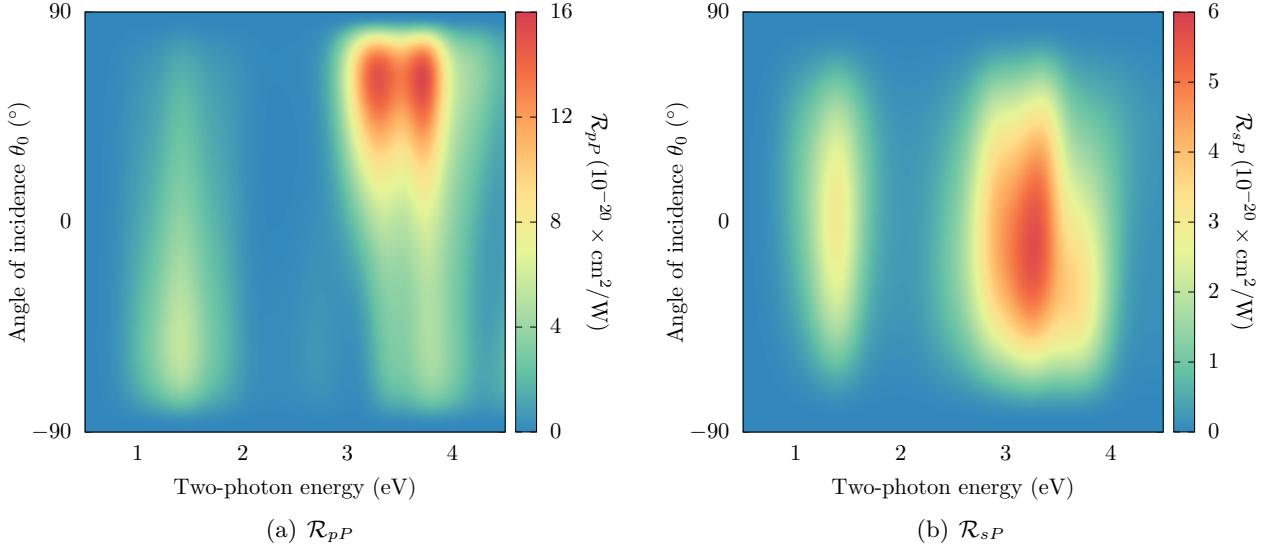


Figure 3.7:  $\mathcal{R}$  for outgoing  $P$  polarization, versus the angle of incidence ( $\theta_0$ ) for the Si(001)(2×1) surface. The scissor shift used was  $\hbar\Delta = 0.5$  eV. Both figures consider an azimuthal angle of  $\phi = 45^\circ$ .

Fig. 3.7 presents the results for the SSHG yield with outgoing  $P$  polarization. I set a fixed azimuthal angle of  $\phi = 45^\circ$  and then varied the incoming angle  $\theta_0$  from  $-90^\circ$  to  $90^\circ$ . We can clearly see that the surface states associated with the  $2\times 1$  reconstruction produce significant intensity between 1-2 eV in the two-photon energy range. This is consistent with the findings presented in the previous section and in Ref. [53]. The intensity of the peak related to the surface states is significantly lower than the peaks produced in the 2.5-4 eV two-photon energy range. The spectrum for  $\mathcal{R}_{pP}$  is very consistent with other calculations of this type [54], and even with some limited experimental data [55].

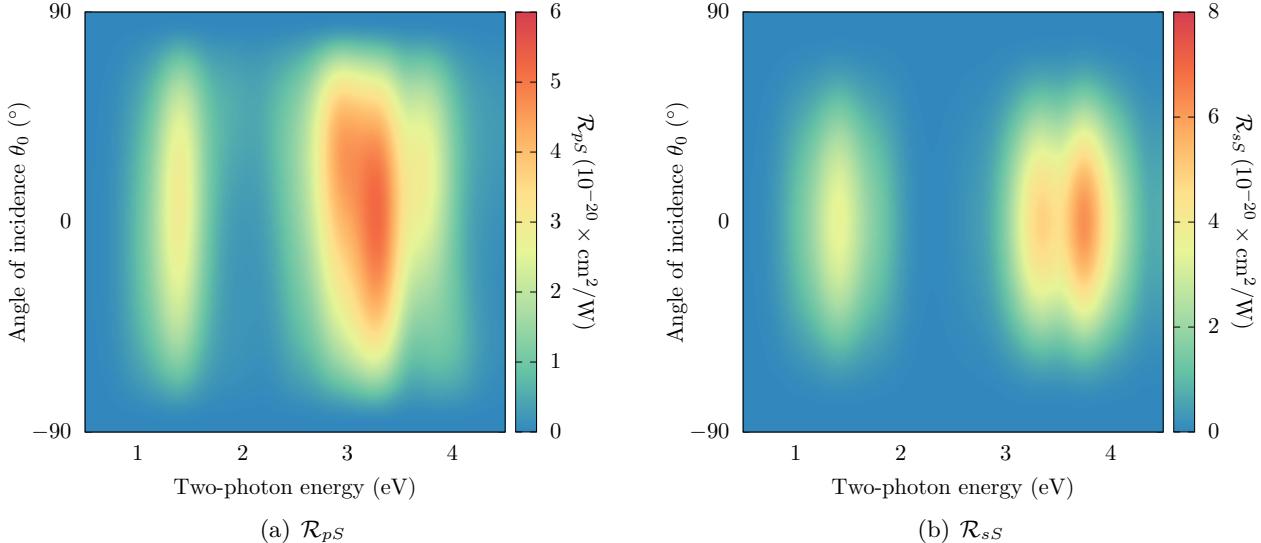


Figure 3.8:  $\mathcal{R}$  for outgoing  $S$  polarized fields, versus the angle of incidence ( $\theta_0$ ) for the Si(001)(2×1) surface. The scissor shift used was  $\hbar\Delta = 0.5$  eV. Both figures consider an azimuthal angle of  $\phi = 45^\circ$ .

Fig. 3.8 presents the results for the SSHG yield with outgoing  $S$  polarization. They are quite similar to what we observed in Fig. 3.7, with a peak related to the surface states between 1-2 eV, and a larger set of peaks between 2.4-4 eV in the two-photon energy range. These spectra have a clear maxima around  $\theta_0 = 0^\circ$ . These plots are presented for mainly illustrative purposes, as there is little experimental data to compare with the theoretical spectrum. However, these kinds of plots will be quite useful to the experimentalist interested in this kind of spectroscopy. Excellent intensity for all polarization cases can be obtained for small beam angles, such as  $\theta_0 = 30^\circ$ .

## 3.2 Results for the Si(111)(1×1):H surface

We will now focus our attention on the Si(111)(1×1):H surface. This surface is a  $C_{3v}$ , primitive hexagonal system with only 4 nonzero components independent from each other, as shown in Table 2.2 [33, 32, 30]. It is composed of stacked layers with one Si atom each, with one H atom terminating each surface. The added H saturates the surface Si dangling bonds and eliminates any surface-related electronic states in the band gap. Here, the top and bottom surfaces are mirror images (see Fig. 3.9); this provides the centrosymmetry that necessitates the use of the cut function to extract the nonzero surface response. In Sec. 3.2.1 we will compare the spectrum produced by using relaxed and unrelaxed coordinates, so it is worth reviewing this concept here. The specifics of this process are as follows.

The relaxation process was done by my colleague, Nicolas Tancogne-Dejean [54]. The structure was initially constructed with the experimental lattice constant of 5.43 Å, and then performed structural optimizations with the ABINIT [37, 38] code. It was then relaxed until the Cartesian force components were less than 5 meV/Å, yielding a final Si-H bond distance of 1.50 Å. The energy cutoff used was 20 Ha, and Troullier-Martin LDA pseudopotentials were used [39]. The resulting

atomic positions are in good agreement with previous theoretical studies [56, 57, 58, 59, 25], as well as the experimental value for the Si-H distance [60].

I also evaluated the number of layers required for convergence (like Sec. 3.1.1.1) and settled on a slab with 48 atomic Si planes. The geometric optimizations mentioned above are therefore carried out on slabs of 48 atomic layers without fixing any atoms to the bulk positions. Fig. 3.9 depicts a sample slab with 16 layers of Si. The surface susceptibilities must be extracted from only half of the slab. This encompasses 24 layers of Si and the single layer of H that terminates the top surface. The vacuum size is equivalent to one quarter the size of the slab, avoiding the effects produced by possible wave-function tunneling from the contiguous surfaces of the full crystal formed by the repeated super-cell scheme [20].

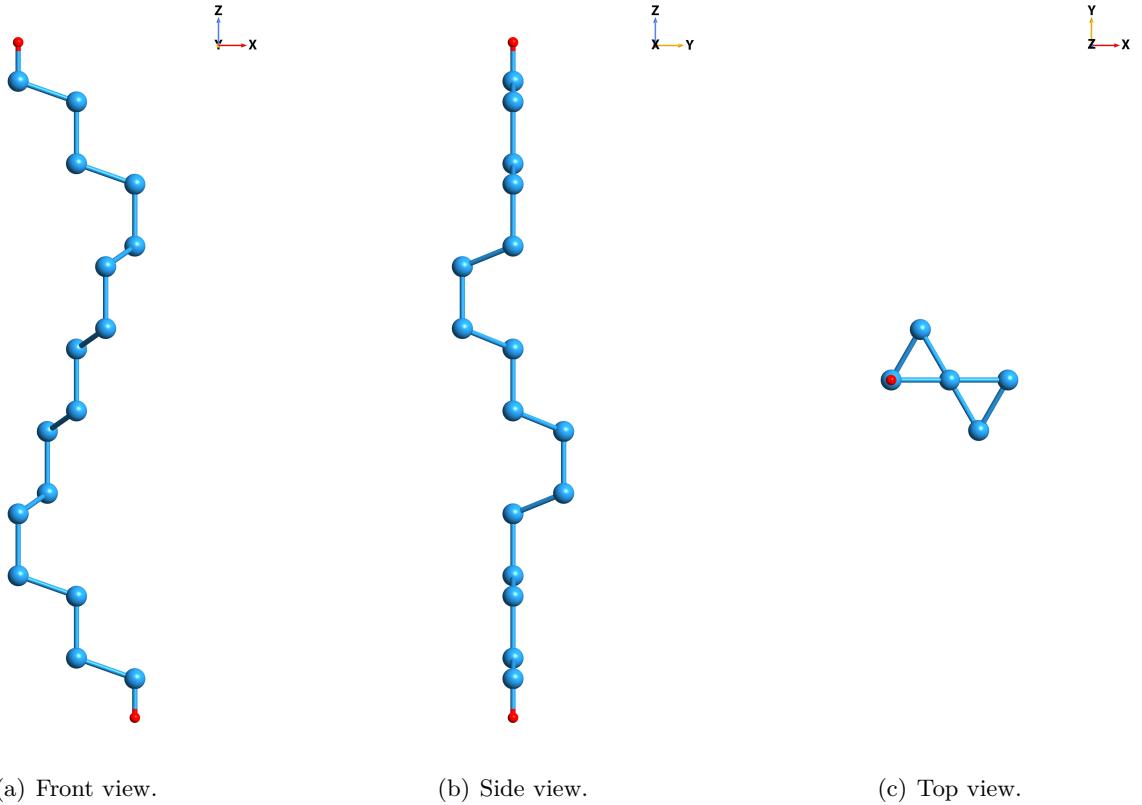


Figure 3.9: Several views of the slab used to represent the Si(111)(1×1):H surface. This particular slab has 16 Si atomic layers (large blue balls) with two H atomic layers (small red balls).

The electronic wave-functions,  $\psi_{n\mathbf{k}}(\mathbf{r})$ , were also calculated with the ABINIT code using a planewave basis set with an energy cutoff of 15 Hartrees.  $\chi^{\text{abc}_{\text{surface}}}$  was properly converged with 576  $\mathbf{k}$  points in the irreducible Brillouin zone, which are equivalent to 1250  $\mathbf{k}$  points when disregarding symmetry relations. The contribution of  $\mathbf{v}^{\text{nl}}$  in Eq. (1.81) was carried out using the DP [40] code implemented in TINIBA [41], with a basis set of 3000 planewaves. Convergence for the number of bands was achieved at 200, which includes 97 occupied bands and 103 unoccupied bands. All spectra were produced using a scissors value of 0.7 eV in the  $\chi^{\text{abc}_{\text{surface}}}$  and  $\epsilon_\ell(\omega)$  calculations.

This value was obtained from Ref. [61], in which the authors carry out a  $G_0W_0$  calculation on this surface for increasing numbers of layers. They calculated the LDA and  $G_0W_0$  band gaps, and found that the difference between the two tends towards  $\sim 0.7$  eV as more layers are added, culminating in a value of 0.68 eV for bulk Si. This calculation is completely *ab-initio*, so I consider 0.7 eV to be a very reasonable value for the scissors correction.

It is important to mention that we must also calculate the bulk and surface dielectric functions,  $\epsilon_b(\omega)$  and  $\epsilon_\ell(\omega)$ . For this, we follow the method presented in Ref. [20]. For the bulk, the tensor components are equal in all three directions due to the cubic symmetry,

$$\varepsilon_b(\omega) = \epsilon_b^{xx}(\omega) = \epsilon_b^{yy}(\omega) = \epsilon_b^{zz}(\omega).$$

For the purpose of this calculation, we introduce the average value for the surface dielectric function,  $\varepsilon_\ell(\omega)$ . This entails that  $\epsilon_\ell^{xx}(\omega) = \epsilon_\ell^{yy}(\omega) \approx \epsilon_\ell^{zz}(\omega)$ , since symmetry is broken in the  $zz$  direction because of the surface. We find the average in the conventional way,

$$\varepsilon_\ell(\omega) = \frac{\epsilon_\ell^{xx}(\omega) + \epsilon_\ell^{yy}(\omega) + \epsilon_\ell^{zz}(\omega)}{3},$$

and use that quantity in the equations for the SSHG yield. In order to obtain a result which does not depend on the size of the vacuum region [62], we have normalized the surface dielectric function to the volume of the slab, instead of the volume of the super-cell. We remark that we could calculate  $\epsilon_{\text{half-slab}}^{\text{ab}}(\omega)$  using  $\mathcal{C}(z) = 1$  for the upper half of our slab and normalize to the volume of the half-slab. Nevertheless,  $\epsilon_\ell^{\text{ab}}(\omega)$  and  $\epsilon_{\text{half-slab}}^{\text{ab}}(\omega)$  give the same result [18, 19, 62].

### 3.2.1 Calculating $\chi_{\text{surface}}^{xxx}(-2\omega; \omega, \omega)$

The pioneering work presented in Ref. [25] showed the effect of artificially moving the atomic position on the resulting SSHG spectra. In this section, I will address the more practical and relevant case of atomic relaxation. More precisely, I compare the fully relaxed structure described above with an unrelaxed structure where all the Si atoms are at the ideal bulk positions. Note that in both cases, the Si-H bond distance is the same 1.5 Å. The unrelaxed coordinates use the same parameters mentioned above. Fortunately, there exists experimental data that can be compared to the calculated  $\chi_{\text{surface}}^{xxx}$  for this surface, taken from Ref. [34]. This data provides an excellent point of comparison as it was presented in absolute units and was measured at a very low temperature of 80 K.

Fig. 3.10 depicts the spectra from the relaxed and unrelaxed coordinates compared to experiment. The theoretical curves were calculated with a scissors shift of  $\hbar\Delta = 0.7$  eV, as mentioned in the previous section. The relaxed coordinates have a peak position that is very slightly blueshifted with respect to the experimental peak near 1.7 eV. In contrast, the unrelaxed coordinates have a peak that is redshifted close to 0.05 eV from experiment. There is also a feature between 1.5 eV and 1.6 eV that appears in the relaxed spectrum that coincides partially with the experimental data. Both theoretical curves have half the intensity of the experimental peak. It is important to note that this data was taken at low temperature (80 K); this further favors the comparison, as the theory neglects the effects of temperature. As is shown in Ref. [34], the peaks in the spectrum redshift as the temperature increases. Intensity for both the relaxed and unrelaxed curves are roughly half the intensity of the experimental spectrum. I have converted the units of the experimental data from CGS to MKS units for easier comparison.

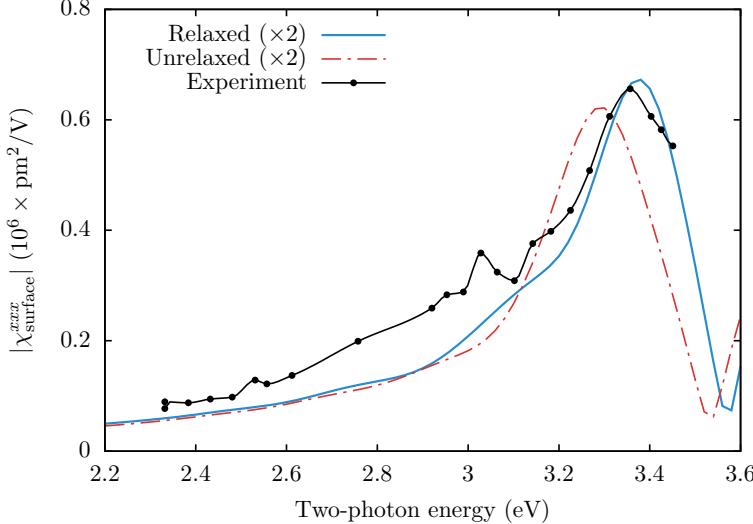


Figure 3.10: Comparison of  $\chi_{\text{surface}}^{xxx}$  calculated using relaxed and unrelaxed atomic positions, with the experimental data presented in Ref. [34]. The theoretical curves were calculated with a scissors shift of  $\hbar\Delta = 0.7$  eV, and are broadened with  $\sigma = 0.075$  eV. Experimental data was taken at 80 K.

We can conclude that the most accurate theoretical results are produced by using relaxed atomic positions for the calculation of  $\chi_{\text{surface}}$ . Although this process can be very time consuming for large numbers of atoms, this should be considered a crucial step. This also further demonstrates that SSHG is very sensitive to the surface atomic positions. In particular, these results show that a correct value of the Si-H bond length is not enough to obtain the most accurate SSHG spectra, and that a full relaxation of the structure is required. Additionally, it seems that the theory may coincide better with experiments that are conducted under very low temperature conditions.

### 3.2.2 Comparing the theoretical $\mathcal{R}$ to experiment

All calculations presented from this point on were done using the relaxed atomic positions described in the previous section. I will now present the theoretical SSHG yield for the Si(111)(1×1):H surface compared to experiments from Refs. [36, 25, 35]. These comparisons are good benchmarks to test the complete formalism for calculating the SSHG yield.

The method of calculation is as follows. I first calculated  $\varepsilon_b(\omega)$ ,  $\varepsilon_\ell(\omega)$ , and then  $\chi_{\text{surface}}^{\text{abc}}$  from Eq. (1.81). I used these for the Fresnel factors and in Eqs. (2.49), (2.59), and (2.54), and finally, those into Eq. (2.41) to obtain the theoretical SSHG yield for different polarizations that can then be compared with the experimental data. Remember that a scissors shift of  $\hbar\Delta = 0.7$  eV is used for all the  $\chi_{\text{surface}}^{\text{abc}}$  components. These components and the calculated  $\mathcal{R}$  spectra were also broadened with a Gaussian broadening of  $\sigma = 0.075$  eV. These values were selected so that the theoretical calculation best represents the lineshape of the experimental spectrum.

#### 3.2.2.1 Overview of the calculated $\mathcal{R}$ spectra

We will carefully explain and compare the calculated  $\mathcal{R}$  for each different polarization case in the following sections. However, I first want to present a general overview of the theoretical SSHG

yield, as I did in Sec. 3.1.2. In Figs. 3.11 and 3.12, I present these results over a two-photon energy range of 2.5-5 eV. This range corresponds to the experimental measurements featured in Refs. [25] and [35]. Note that the SSHG yield drops to zero very rapidly before for energy values under 3 eV. This is because of the lack of surface states due to the surface H-saturation.

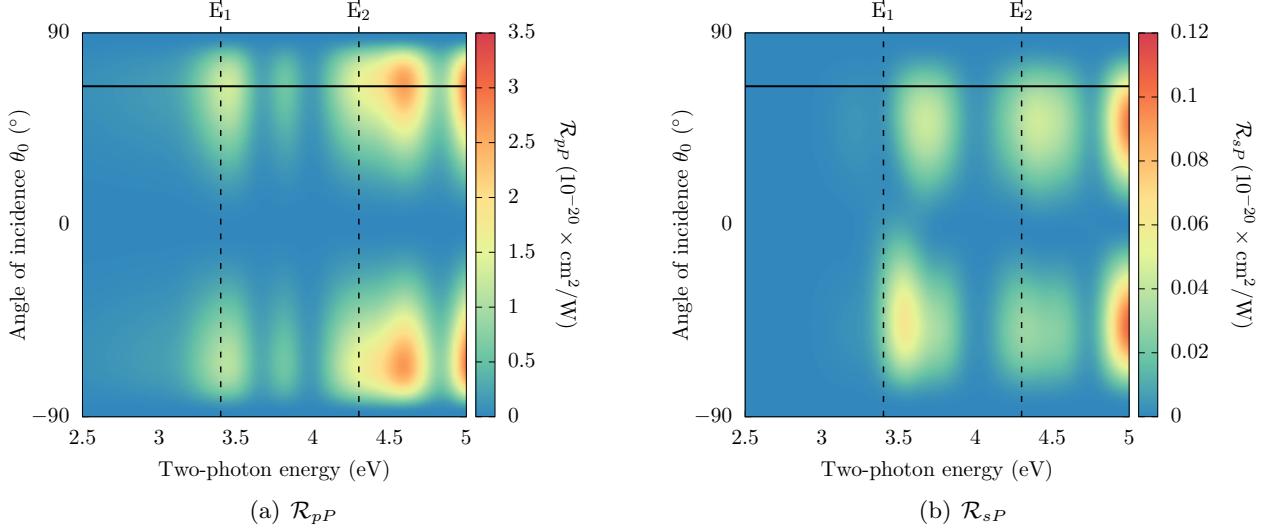


Figure 3.11:  $\mathcal{R}$  for outgoing  $P$  polarization, versus the angle of incidence ( $\theta_0$ ) for the Si(111)(1×1):H surface. A scissors shift of  $\hbar\Delta = 0.7$  eV is applied. The solid line represents  $\theta_0 = 65^\circ$ , and the dotted lines represent the  $E_1$  and  $E_2$  Si critical points. Both figures consider an azimuthal angle of  $\phi = 30^\circ$ .

I have included some helpful markers in these figures. First, the solid black line represents an angle incidence of  $\theta_0 = 65^\circ$ . This is one of two angles that we will consider for the remainder of this chapter; in particular, this is the angle used in the experiment from Ref. Refs. [25]. It is clear that they chose this particular angle to maximize the  $\mathcal{R}_{pP}$  output. Second, the dashed black lines represent the  $E_1 = 3.4$  eV and  $E_2 = 4.3$  eV critical points of bulk Si [63]. For the outgoing  $P$  polarization in Fig. 3.11, we can see that the calculated SSHG yield does have peaks around those energy values. We will review this in much further detail below. We see similar characteristics, for Fig. 3.12 with the outgoing  $S$  polarization cases. Indeed, the theoretical peak values seem to match quite well with the critical points. Again, we will review these findings in much more detail below. Note that I will omit  $\mathcal{R}_{sS}$  from this point forward, as I do not have any experimental data to compare it with.

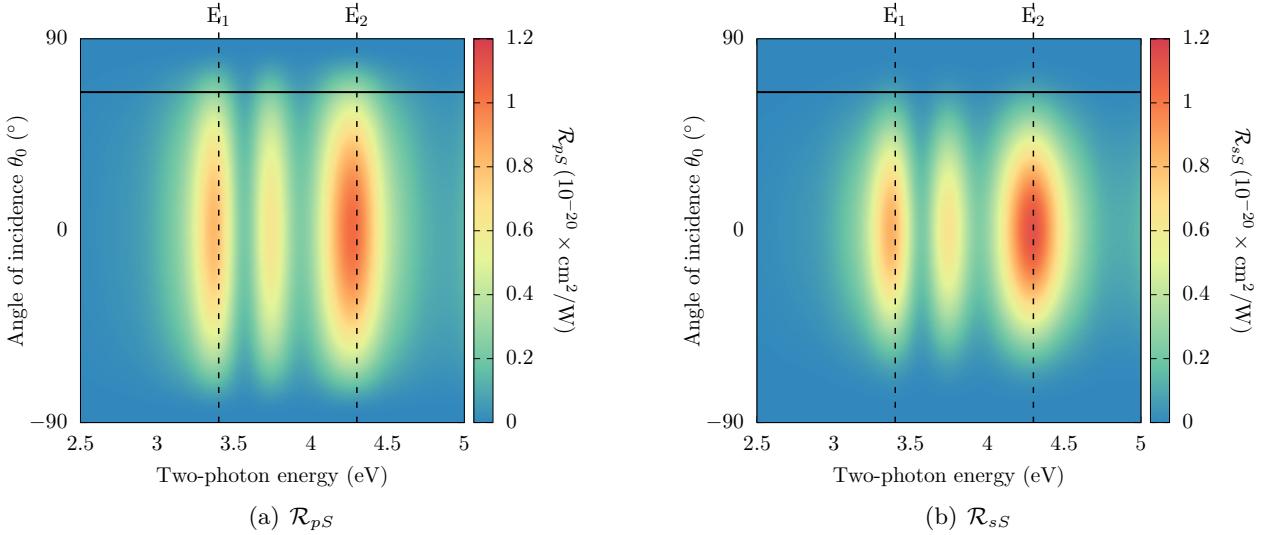


Figure 3.12:  $\mathcal{R}$  for outgoing  $S$  polarized fields, versus the angle of incidence ( $\theta_0$ ) for the Si(111)(1×1):H surface. A scissors shift of  $\hbar\Delta = 0.7$  eV is applied. The solid line represents  $\theta_0 = 65^\circ$ , and the dotted lines represent the  $E_1$  and  $E_2$  Si critical points. Both figures consider an azimuthal angle of  $\phi = 30^\circ$ .

### 3.2.2.2 $\mathcal{R}_{pP}$ ( $p$ -in, $P$ -out)

We first analyze how the inclusion of multiple reflections affects the calculated SSHG yield. I will conduct this study for  $\mathcal{R}_{pP}$  as it is typically associated with the strongest signal output. It is also by far the most involved calculation out of the four different polarization cases, since it includes all four nonzero components. We are interested in finding the thickness of the layer  $\ell$  where  $\chi_{\text{surface}}^{\text{abc}} \neq 0$ . As mentioned above, we found reasonable converged results for this surface using a slab of 48 atomic layers. This corresponds to a thickness of  $\sim 5$  nm, that is equivalent to the 24 atomic sheets of Si along the (111) direction, corresponding to the half-slab. As this represents only the upper half of the slab, we find it reasonable to choose the thickness of the layer  $\ell$  to be between  $d \sim 5 - 10$  nm, as in this range of values  $\chi_{\text{surface}}^{\text{abc}}$  will be well converged.

We begin our comparisons in Fig. 3.13, in which we compare the theoretical results for the SHG radiation with the experimental results from Ref. [25]. First, we note that the experimental spectrum shows two very well defined resonances which come from electronic transitions from the valence to the conduction bands around the well known  $E_1 \sim 3.4$  eV and  $E_2 \sim 4.3$  eV critical points of Si [63]. We mention that the experimental results were produced with an angle of incidence of  $\theta = 65^\circ$ , and an azimuthal angle of  $\phi = 30^\circ$ , which eliminates the contribution from  $\chi_{\text{surface}}^{xxx}$  from Eq. (2.49). The theoretical curves that include multiple reflections are featured with the average value  $\bar{R}_p^M$ , Eq. (2.23), with two values for the total thickness,  $d$ , and Eqs. (2.47) and (2.49). We contrast these with the standard three layer model excluding the effects of multiple reflections from Sec. 2.3.1. We see that the  $E_2$  peak is blueshifted by around 0.3 eV, and the yield does not go to zero after 4.75 eV. We can attribute these shortcomings to the fact that both  $\chi_{\text{surface}}^{zzz}$  and  $\chi_{\text{surface}}^{xxz}$  include out-of-plane incoming fields. These are affected by local field effects that can change both intensity and peak position [54]. Including these effects is computationally very expensive and is beyond the scope of this work. We speculate that the components of  $\chi_{\text{surface}}^{\text{abc}}$

necessary for  $\mathcal{R}_{pP}$  require the proper inclusion of these effects in order to accurately describe the experimental peaks. Additionally, Ref. [64] shows that low temperature measurements of  $\mathcal{R}_{pP}$  will blueshift the spectrum away from room temperature measurements such as those shown in Figs. 3.16 and 3.18, and towards the theoretical results.

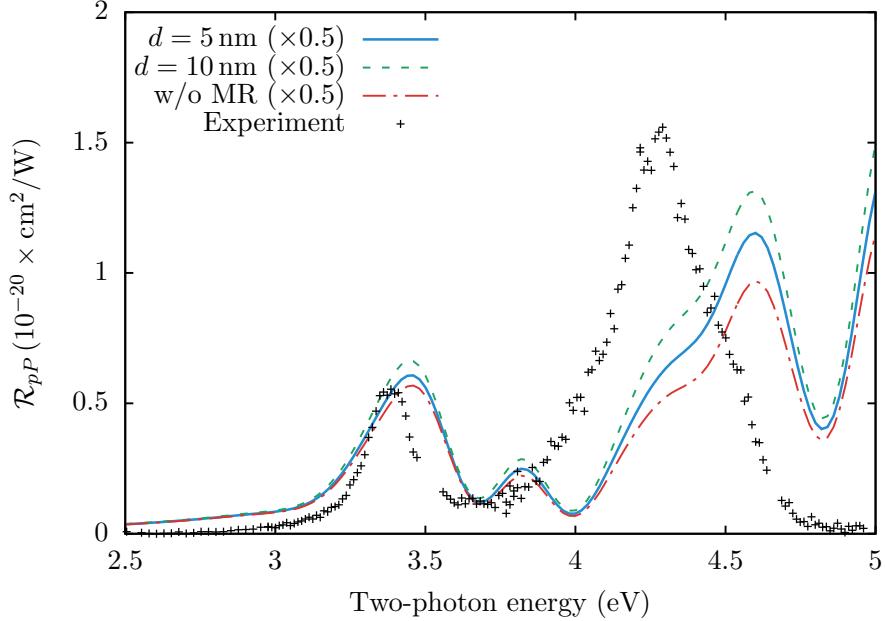


Figure 3.13: Comparison between the three layer model with the effects of multiple reflections for two different values of the total layer thickness  $d$ , with the standard three layer model without the effects of multiple reflections, and the experimental data from Ref. [25]. We take  $\theta = 65^\circ$ ,  $\phi = 30^\circ$ , and a scissors value of  $\hbar\Delta = 0.7 \text{ eV}$ .

We can see that including the effects of multiple reflections enhances the  $E_2$  peak significantly, and that the enhancement increases with the thickness  $d$  of the thin layer  $\ell$ . This should be quite obvious from 2.1; as the layer thickness increases, so does the total contribution from the multiple reflections. Since we have already established that using a layer thickness of 10 nm is reasonable for this surface, I will use this value from this point on.

In Fig. 3.14, I present the results from calculating the spectra with and without the multiple reflections from the  $1\omega$  fields. The difference between the two lines is almost negligible for energies below 4 eV. After 4 eV, the spectrum without the  $1\omega$  multiple reflections is less intense. The difference in intensity between the two curves is most noticeable at  $E_2$ . We can conclude that the  $1\omega$  multiple reflections contribute only slightly to the region around  $E_2$ , and are almost negligible elsewhere. This is clear since the phase shift of Eq. (2.24) is not only a factor of 2 smaller than that of Eqs. (2.16) and (2.17), but also  $w_\ell < W_\ell$ . However, including them is indeed necessary in order to have the most complete formulation, and calculating  $r_p^M$  comes at no additional computational expense.

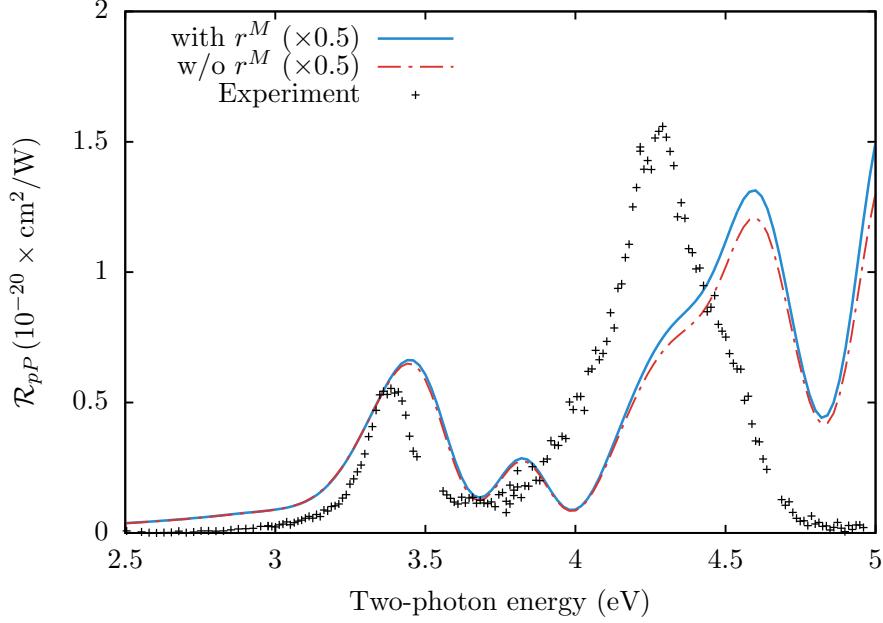


Figure 3.14: Comparison between including or neglecting the effects of multiple reflections for the fundamental fields. The theoretical spectra were produced for a layer thickness of  $d = 10$  nm using the average value of  $\bar{R}_p^M$ .

We can analyze the effects of moving the polarization sheet to different depths within the layer  $\ell$  in Fig. 3.15. As mentioned above, we consider a layer thickness of  $d = 10$  nm. We compare the theoretical SSHG yield for  $d_2 = 0$  nm and  $d_2 = 10$  nm, with the SSHG yield that neglects multiple reflections. When  $d_2 = 0$  nm, we have placed the polarization sheet at the bottom of the layer region. This minimizes the effect of the multiple reflections, and thus the curve is very similar to the three layer model that neglects multiple reflections entirely. When  $d_2 = 10$  nm, the polarization sheet is placed at the top of the layer region. This maximizes the effect of the multiple reflections and therefore leads to the largest yield. We also notice that the average value obtained by using  $\bar{R}_p^M$  (Eq. (2.23)) is intermediate between  $d_2 = 0$  and  $d_2 = 10$  nm, as expected. This is very similar to selecting  $d_2 = d/2$ , which can be interpreted as placing the nonlinear polarization sheet  $\mathbf{P}(\mathbf{r}, t)$  at the middle of the thin layer  $\ell$ .

As before, these enhancements are larger for  $E_2$  than for  $E_1$ . This can be understood from the fact that the corresponding  $\lambda_0$  for  $E_1$  is larger than that of  $E_2$ . From Eqs. (2.16), (2.17), and (2.24), we see that the phase shifts are larger for  $E_2$  than for  $E_1$ , producing a larger enhancement of the SSHG yield at  $E_2$  from the multiple reflections. As the phase shifts grow with  $d$ , so does the enhancement caused by the multiple reflections. From this figure, it becomes evident that the inclusion of multiple reflections is crucial to obtain a better agreement between the theoretical SSHG yield and the experimental spectrum. This is particularly true for larger energies, such as  $E_2$ , as  $\lambda_0$  becomes smaller and the multiple reflection effects become more noticeable. The selected value for  $d \ll \lambda_0$ , that comes naturally from the *ab initio* calculation of  $\chi_{\text{surface}}^{\text{abc}}$  is thus very reasonable in order to model a thin surface layer below the vacuum region where the nonlinear SH conversion takes place. From this point on, we will always include the effects of multiple reflections in the 3-layer model, with a layer thickness of  $d = 10$  nm and the average value of  $\bar{R}_p^M$ .

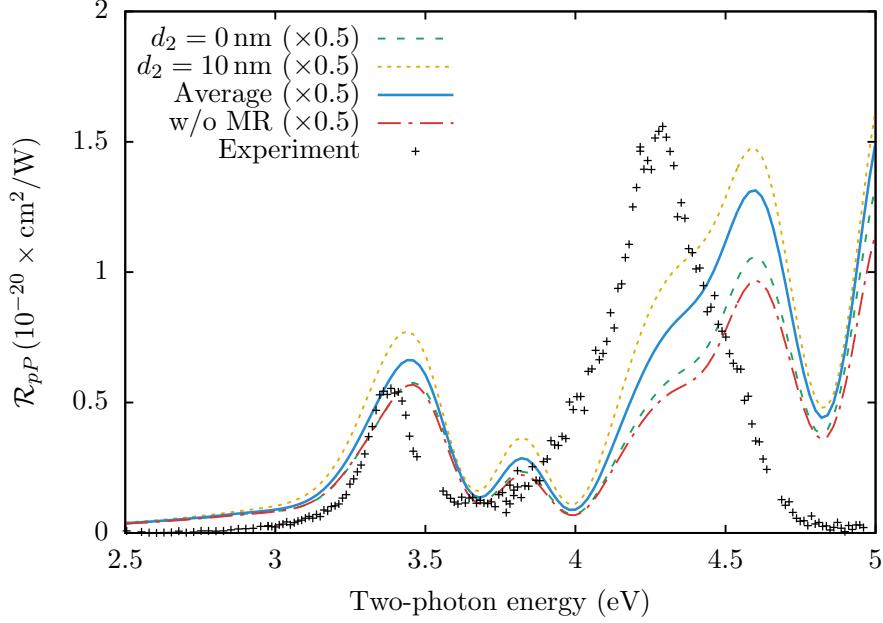


Figure 3.15: Comparison between the three layer model with the effects of multiple reflections for two different values of  $d_2$ , and the average value  $\bar{R}_p^M$ . All curves that include multiple reflections consider a layer  $\ell$  thickness of  $d = 10$  nm.

I will now present an overview of the different models from Sec. 2.3, and summarized in Table 2.3. Namely, we will compare the 3-layer model with multiple reflections, the 2-layer-fresnel, 2-layer-bulk, 2-layer-vacuum, and 3-layer hybrid models. In Fig. 3.16, I present a comparison between the 3-layer, 3-layer-hybrid, and 2-layer-bulk models with experiment. The peak position for the 3-layer model compares quite nicely to the experimental peaks, with an overall intensity that is only two times larger. The 2-layer-bulk model is almost identical in lineshape to the 3-layer model, but with four times less intensity than the experiment. The 3-layer-hybrid model is also similar in lineshape with a less pronounced E<sub>2</sub> peak, and is half as intense as the experiment. All these observations are consistent as  $\epsilon_b$  and  $\epsilon_\ell$  differ mostly in intensity; each model is screened with either  $\epsilon_b$  (2-layer-bulk),  $\epsilon_\ell$  (3-layer), or a combination of the two (3-layer-hybrid). Ultimately, the 3-layer model has better peak proportions and good intensity, but the other two models are interesting alternatives.

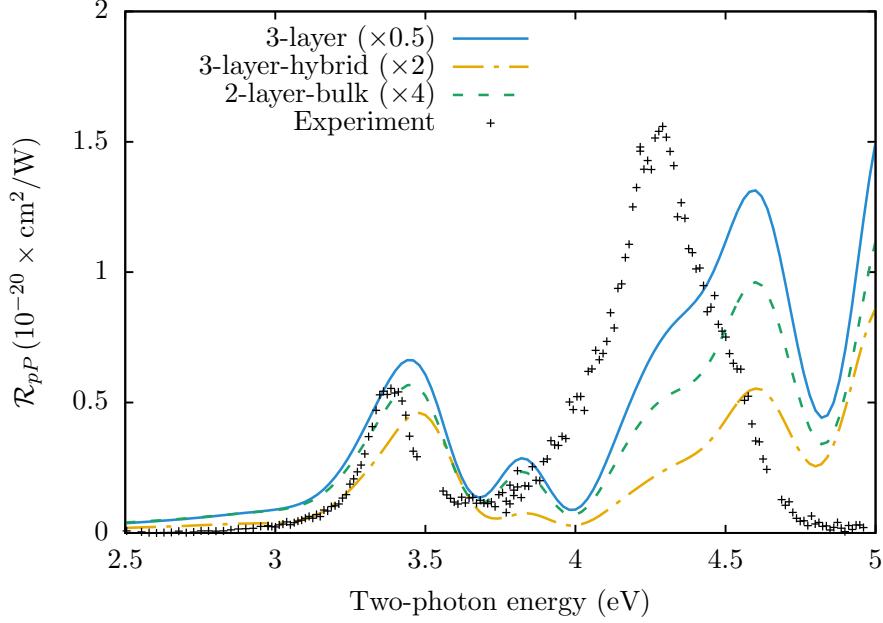


Figure 3.16: Comparison between theoretical models (see Table 2.3) and experiment for  $\mathcal{R}_{pP}$ , for  $\theta = 65^\circ$ , and a scissors value of  $\hbar\Delta = 0.7 \text{ eV}$ . Experimental data taken from Ref. [25], measured at room temperature.

The two remaining models from Sec. 2.3 are presented in Fig. 3.17. The 2-layer-fresnel model produces a spectrum with peak positions that are close to the experiment, but are around 40 times more intense. The calculated E<sub>2</sub> peak is similar, but the E<sub>1</sub> peak lacks the sharpness present in the experiment, with poor proportional intensity between the peaks. On the other hand, the 2-layer-vacuum model has the most extreme intensity difference with the experiment, over 5 orders of magnitude higher. The lineshape reproduces the E<sub>2</sub> peak quite well, but lacks a sharp E<sub>1</sub> peak with poor peak position. Clearly, the screening provided by  $\epsilon_b$  and  $\epsilon_\ell$  are necessary for accurate results. From Eq. (2.49), it is clear that  $\mathcal{R}_{pP}$  has several  $2\omega$  terms that will change between models; this will have a deep effect on the lineshape. Additionally,  $\Gamma_{pP}^\ell$  also has  $\epsilon_\ell(2\omega)$  in the denominator, and so we have a significant difference in both lineshape and intensity between these models and the rest.

From this point forward, we will only consider the 3-layer (with multiple reflections), the 2-layer-fresnel (the historically popular model), and the 2-layer bulk models. These three models give an interesting overview of the different possibilities available and add some insight into the physics behind the SSHG yield.

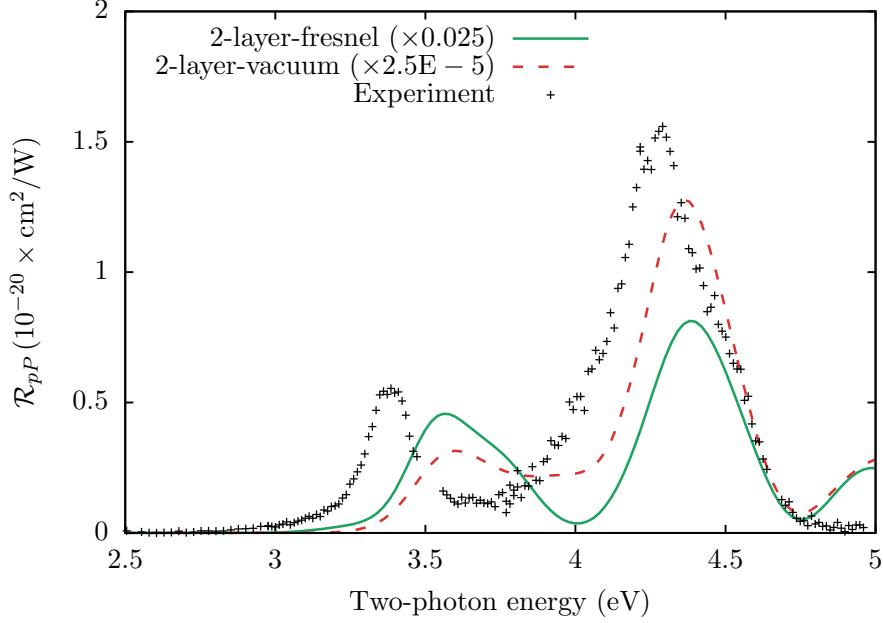


Figure 3.17: Comparison between the 2-layer-fresnel and 2-layer-vacuum models (see Table 2.3) and experiment for  $\mathcal{R}_{pP}$ , for  $\theta = 65^\circ$ , and a scissors value of  $\hbar\Delta = 0.7 \text{ eV}$ . Experimental data taken from Ref. [25], measured at room temperature.

In Fig. 3.18, I compare the theoretical spectra to results from Ref. [36]. The 3-layer model is, as before, close to the experiment in both peak position and intensity. Intensity is almost the same the experimental value. This provides a more compelling argument against the 2-layer-fresnel model than Fig. 3.16. The 2-layer-fresnel model is 20 times more intense and blueshifted by around 0.1 eV. As mentioned above, this surface is of very high quality with measurements taken shortly after surface preparation. The 2-layer-bulk model is intermediate between the other two models in both intensity and lineshape. Under these conditions, the 3-layer model very accurately reproduces the E<sub>1</sub> peak over the 2-layer-fresnel and 2-layer-bulk models.

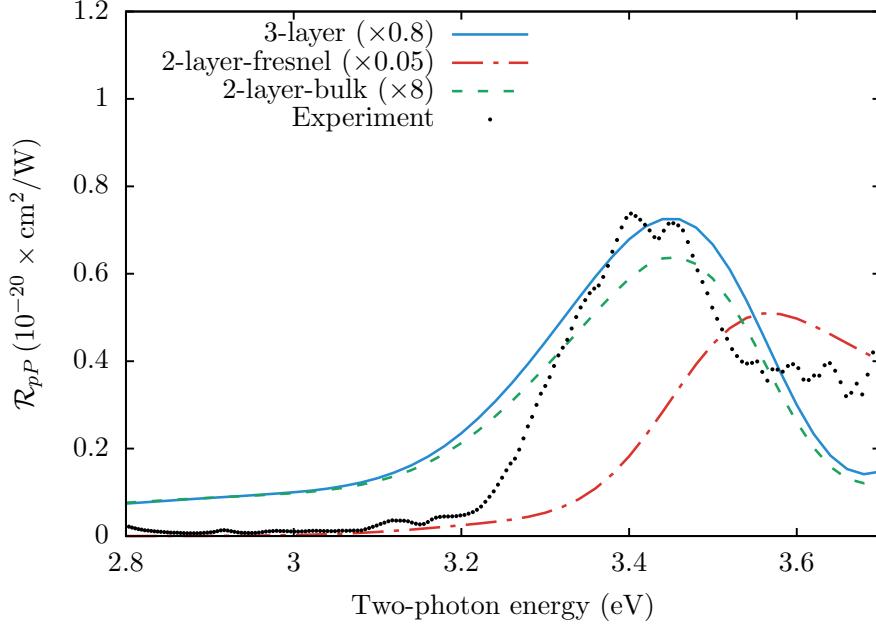


Figure 3.18: Comparison between theoretical models (see Table 2.3) and experiment for  $\mathcal{R}_{pP}$ , for  $\theta = 45^\circ$ , and a scissors value of  $\hbar\Delta = 0.7$  eV. Experimental data taken from Ref. [36], measured at room temperature.

### 3.2.2.3 Calculated $\mathcal{R}_{sP}$ compared to experiment

Next, we will compare the calculated  $\mathcal{R}_{sP}$  spectra with experimental data from Ref. [25]. The calculation adheres to the experimental setup by taking an angle of incidence  $\theta = 65^\circ$  and an azimuthal angle  $\phi = 30^\circ$ . As seen in Fig. 3.19, the overall intensity of  $\mathcal{R}_{sP}$  is one order of magnitude lower than  $\mathcal{R}_{pS}$ . The experimental data is far noisier than in the other cases but the E<sub>1</sub> and E<sub>2</sub> peaks are still discernible. As with the previous comparisons, the 3-layer model is the closest match in both intensity and lineshape to the experimental spectrum. It produces a curve that is very close to the experimental intensity with good proportional heights for the calculated E<sub>1</sub> and E<sub>2</sub> peaks. In contrast, the 2-layer-fresnel model is 100 times more intense than experiment and produces an enlarged E<sub>2</sub> peak. The 2-layer-bulk model is ten times smaller with a very similar lineshape to the 3-layer model.

The differences between the 2-layer-fresnel and 2-layer-bulk models are not derived from Eq. (2.54), as the  $\varepsilon_b(2\omega)$  does not change and the second term vanishes for this azimuthal angle of  $\phi = 30$ . However,  $\Gamma_{sP}^\ell$  does cause a significant change in the intensity as there is an  $\varepsilon_\ell(2\omega)$  term in the denominator. This will become  $\varepsilon_v(2\omega) = 1$  for the 2-layer-fresnel model, and  $\varepsilon_b(2\omega)$  in the bulk model. This accounts for the significant difference between the intensity of the two models, while the lineshape remains mostly consistent. At higher energies, the theoretical curve is blueshifted as compared to the experiment. The best explanation for this is the inclusion of the scissor operator, which does not adequately correct the transitions occurring at these higher energies. A full GW calculation would be well suited for this task, but is well beyond the scope of this work.

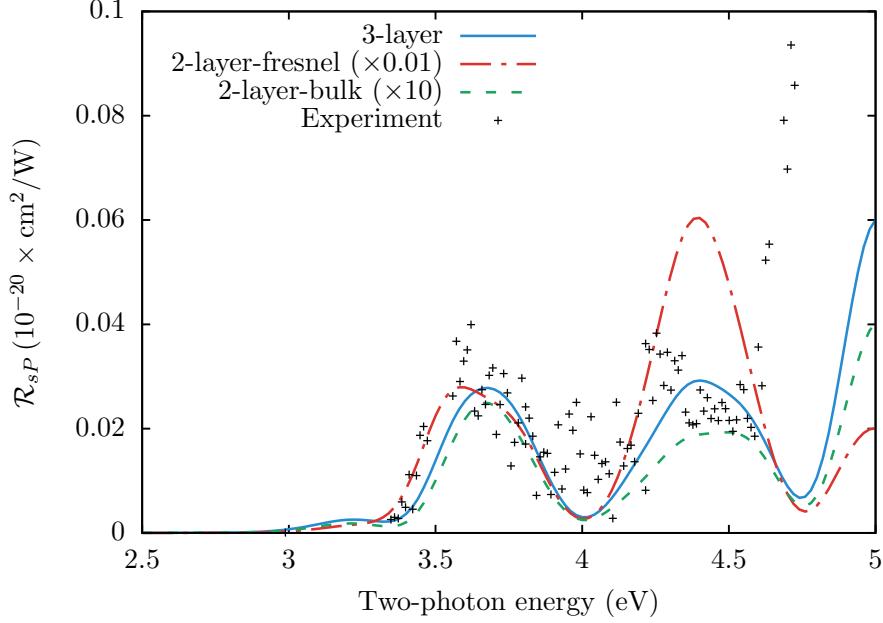


Figure 3.19: Comparison between theoretical models (see Table 2.3) and experiment for  $\mathcal{R}_{sp}$ , for  $\theta = 65^\circ$ , and a scissors value of  $\hbar\Delta = 0.7$  eV. Experimental data taken from Ref. [25], measured at room temperature.

### 3.2.2.4 Calculated $\mathcal{R}_{ps}$ compared to experiment

We will now compare the  $\mathcal{R}_{ps}$  spectra with room temperature experimental data from Ref. [25]. Adhering to the experimental setup, I set an angle of incidence  $\theta = 65^\circ$  and an azimuthal angle of  $\phi = 30^\circ$  with respect to the  $x$ -axis. This azimuthal angle maximizes  $r_{ps}$ , as shown in Eq. (2.59). Fig. 3.20, shows that all three models reproduce the lineshape of the experimental spectrum which includes the peaks corresponding to both the  $E_1$  and  $E_2$  critical points of bulk silicon, and a smaller feature at around 3.8 eV. The calculated  $E_1$  and  $E_2$  peaks are redshifted by 0.1 eV and 0.06 eV, respectively, compared with the experimental peaks. The proportional peak intensity is quite good and compares favorably with the experimental peaks. Any minor discrepancy in the peak intensity could be due to the effects of oxidation on the surface. Ref. [35] features similar data to those of Ref. [25] but focuses on the effects of surface oxidation. From Ref. [35] it is clear that as time passes during the experiment, the surface becomes more oxidized and the  $E_1$  peak diminishes substantially, as shown by the experimental data taken 5 hours after initial H-termination. This may be enough time to slightly reduce the  $E_1$  peak intensity in the experimental data.

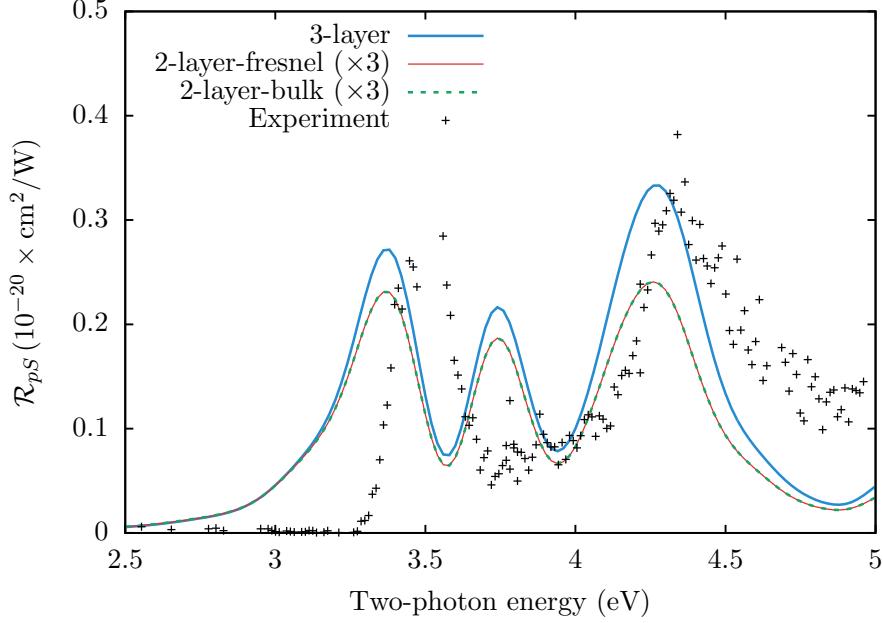


Figure 3.20: Comparison between theoretical models (see Table 2.3) and experiment for  $\mathcal{R}_{pS}$ , for  $\theta = 65^\circ$ , and a scissors value of  $\hbar\Delta = 0.7 \text{ eV}$ . Experimental data taken from Ref. [25], measured at room temperature.

In Fig. 3.21, I compare the theoretical  $\mathcal{R}_{pS}$  with experimental data from Ref. [36]. This calculation uses an angle of incidence  $\theta = 45^\circ$  and an azimuthal angle  $\phi = 30^\circ$  to match the experimental conditions. As in the previous comparison, the E<sub>1</sub> peak is slightly redshifted compared to experiment. The intensity of the theoretical yield is smaller than the experimental yield for all three models. The measurements presented in Ref. [36] were taken very shortly after the surface had been prepared, and the surface itself was prepared with a high degree of quality and measured at room temperature. Peak position compared to theory is slightly improved under these conditions. As before, the 3-layer model is closer in intensity to the experimental spectrum.

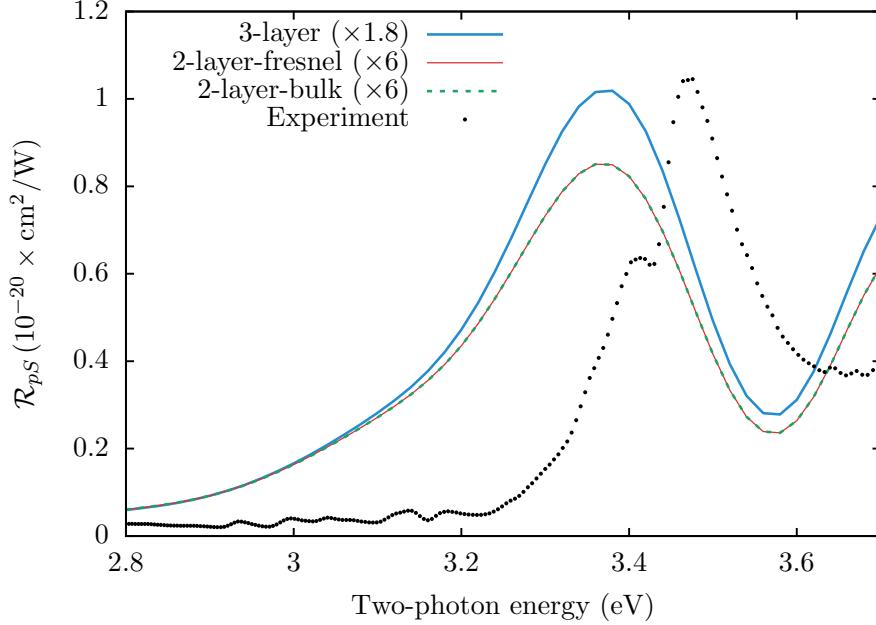


Figure 3.21: Comparison between theoretical models (see Table 2.3) and experiment for  $\mathcal{R}_{pS}$ , for  $\theta = 45^\circ$ . We use a scissors value of  $\hbar\Delta = 0.7$  eV. Experimental data taken from Ref. [36], measured at room temperature.

From Fig. 3.10, I presented that our calculation for  $\chi_{\text{surface}}^{xxx}$  coincides with the measurement taken at a low temperature of 80 K. It is well known that temperature causes shifting in the peak position of SSHG spectra [64]. As  $\mathcal{R}_{pS}$  only depends on this component (see Eq. (2.59)), the position of the theoretical peak should be correct in Figs. 3.20 and 3.21. Thus, the difference in peak position should stem from the higher temperature at which the experiments were measured.

Both the 2-layer-fresnel and 2-layer-bulk models are identical and roughly three times smaller than the experiment. It is clear from Eq. (2.59) that  $\mathcal{R}_{pS}$  only has  $1\omega$  terms ( $\varepsilon_\ell(\omega)$  and  $k_b$ ). For both of these models, the fundamental fields are evaluated in the bulk, which means that the only change to Eq. (2.59) is that  $\varepsilon_\ell(\omega) \rightarrow \varepsilon_b(\omega)$ . Additionally,  $\Gamma_{pS}^\ell$  also remains identical between the two models and has no  $2\omega$  terms in the denominator. Therefore,  $r_{pS}$  is identical between these two models. Ultimately, the intensity of the 3-layer model is the closest to the experiment.

Per Eq. (2.59), the intensity of  $\mathcal{R}_{pS}$  depends only on  $\chi_{\text{surface}}^{xxx}$ , which is not affected by local field effects [54]. These effects are neglected in this calculation, but  $\mathcal{R}_{pS}$  maintains an accurate lineshape and provides a good quantitative description of the experimental SSHG yield. Note that both the calculated and experimental spectra show two-photon resonances at the energies corresponding to the critical point transitions of bulk Si. Note also that the SSHG yield drops rapidly to zero below  $E_1$ , which is consistent with the absence of surface states due to the H saturation on the surface. This observation holds true for all three polarization cases studied for this surface.

In Fig. 3.22 I provide an overview of the different levels of approximation proposed in this article. All curves here were calculated using the 3-layer model. The long dashed line depicts the effect of excluding the contribution from the nonlocal part of the pseduopotentials. This is consistent with the results reported in Ref. [53], where the exclusion of this term increases the intensity of the components of  $\chi_{\text{surface}}$  by approximately 15% to 20%. Note that the  $E_1$  peak is

larger than the  $E_2$  peak, contrasting with the experiment, where the  $E_1$  peak is smaller than  $E_2$ . The thin solid line depicts the full calculation with a scissors value of  $\hbar\Delta = 0$ . The spectrum is almost rigidly redshifted as this H-saturated surface has no electronic surface states [53], in contrast to the Si(001)(2×1) surface presented in the first part of this chapter. Thus, this demonstrates the importance of including the scissors correction to accurately reproduce the experimental spectrum. In summary, the inclusion of the contribution from the nonlocal part of the pseudopotentials and the scissors operator on top of the 3-layer model produces spectra with a lineshape and intensity that compare favorably with the experimental data.

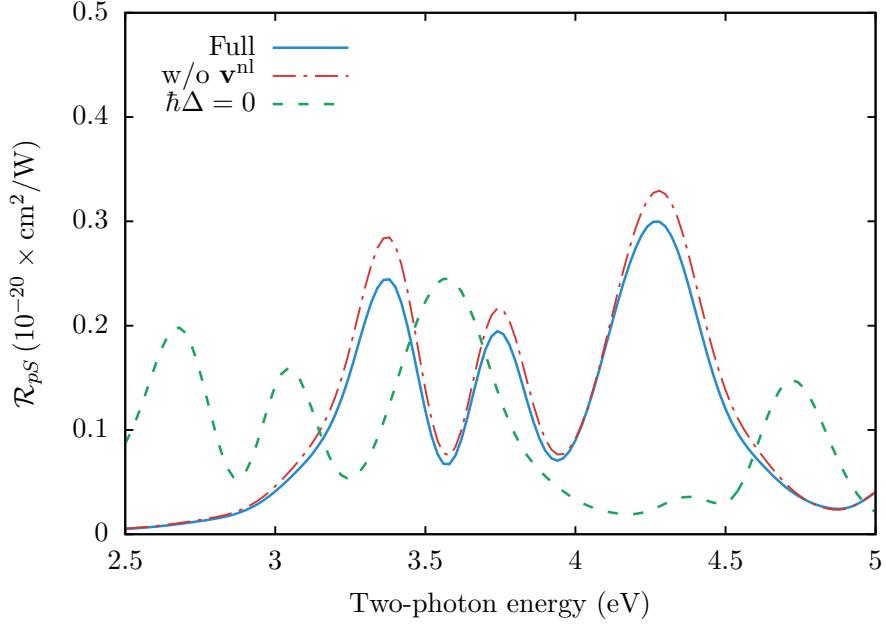


Figure 3.22: Calculated results for  $\mathcal{R}_{pS}$  for the different levels of approximation proposed in this article. All curves were calculated using the 3-layer model. We take  $\theta = 65^\circ$  for this plot. See text for full details.

Lastly,  $GW$  transition energies are needed for linear optics and SHG. Doing a Bethe-Salpeter calculation for SSHG will undoubtedly improve the position and the amplitude of the peaks, but is far beyond current capabilities [65]. I kept the scissors shift constant throughout these calculations as I want to keep this calculation at the *ab initio* level. Remember that the choice of  $\hbar\Delta = 0.7$  eV for the scissors shift comes from a  $GW$  calculation [61]. I have checked that it is not possible to have a single scissors value that can reproduce the energy positions of both the  $E_1$  and the  $E_2$  peaks. Of course, the experimental temperature at which the spectra is measured should be taken into account in a more complete formulation. However, these calculations are always restricted to  $T = 0$  K. As mentioned before, it is important to consider the local field effects on the components of  $\chi_{\text{surface}}^{abc}$ . For this surface in particular,  $\chi_{\text{surface}}^{zzz}$  and  $\chi_{\text{surface}}^{xxz}$  include out-of-plane incoming fields. These are affected by local field effects [54] that reveal the inhomogeneities in the material, which are much more prevalent perpendicular to the surface than in the surface plane. This can be evidenced for Si, as Reflectance Anisotropy Spectroscopy (RAS) measurements are well described by *ab initio* calculations neglecting local field effects [66, 67]. It is therefore expected that the out-

of-plane components will be more sensitive to the inclusion of local fields. These will not change the transition energies, only their relative weights of the resonant peaks [54]. Including these effects is challenging to compute [62], and beyond the scope of this thesis. These effects would mostly affect  $\mathcal{R}_{pP}$  since it includes all four nonzero components. We speculate that  $\mathcal{R}_{pP}$  requires the proper inclusion of these effects in order to accurately describe the experimental peaks.

### 3.3 Conclusion

We have used the formulation to calculate the surface nonlinear susceptibility tensor  $\chi_{\text{surface}}(-2\omega; \omega, \omega)$ , using the length gauge formalism and within the independent particle approximation (IPA). It includes on equal footing: (i) the scissors correction, (ii) the contribution of the non-local part of the pseudopotentials, and (iii) the cut function. We have used a Si(001) $2 \times 1$  surface to confirm that our scheme correctly obtains the surface response as we confirm that  $\chi_{\text{half-slab}}^{xxx}(-2\omega; \omega, \omega) \approx \chi_{\text{full-slab}}^{xxx}(-2\omega; \omega, \omega)$ . Although one can in principle increase the number of atomic layers,  $\mathbf{k}$ -points, etc. to improve even further on the similarity of the half-slab and full-slab results, we have chosen a good compromise between accuracy and the burden and time of the computations. We describe the effect of the independent inclusion of the three effects mentioned above in the calculation of  $\chi(-2\omega; \omega, \omega)$ . The scissors correction shifts the spectrum to higher energies though the shifting is not rigid and mixes the  $1\omega$  and  $2\omega$  resonances, and has a strong influence in the line-shape, as for the case of bulk semiconductors.[68, 50, 51] The cut function allows us to extract unequivocally  $\chi_{2 \times 1}^{xxx}(-2\omega; \omega, \omega)$ . The effects of the nonlocal part of the pseudopotentials keeps the same line-shape of  $|\chi_{2 \times 1}^{xxx}(-2\omega; \omega, \omega)|$ , but reduces the value of by 15-20%. The  $xxx$  component of  $\chi_{2 \times 1}(-2\omega; \omega, \omega)$ , can not be experimentally isolated, however in a forthcoming publication we will compare our formulation against experimental results. We have neglected local field and excitonic effects. Although these are important factors in the optical response of a semiconductor, their efficient calculation is theoretically and numerically challenging and still under debate [43]. This merits further study but is beyond the scope of this paper. Nevertheless, the inclusion of aforementioned contributions in our scheme opens the unprecedented possibility to study SSHG with more versatility and more accurate results.

We also revised the 3-layer model for the SSHG yield where the nonlinear polarization,  $\mathcal{P}(2\omega)$ , and the fundamental fields are taken within a small layer  $\ell$  below the surface of the material. This model reproduces key spectral features and yields an intensity closer to the experiment for all cases of  $\mathcal{R}_{iF}$ . We consider it an upgrade over the much reviewed 2-layer model[30], and it comes with very little added computational expense. Additionally, we have compared these to other models that change the placement of  $\mathcal{P}(2\omega)$  and the fundamental fields. Ultimately we consider that the 3-layer model offers the closest comparison to experiment.

This study affords us an interesting view of both the theoretical and experimental aspects of SSHG studies. On the theoretical side, we have shown the importance of using relaxed atomic positions to more accurately calculate the nonlinear susceptibility tensor. The intensity of these spectra is greatly improved when compared to previous works.[25] We also postulate that the lack of local field effects in the theory is a serious shortcoming, but in this case, it only affects two of the  $\chi(-2\omega; \omega, \omega)$  components. Concerning the experiments, we show that surface preparation and quality are important for better results. The approach for calculating the SSHG yield presented here finds closer agreement with surfaces that are freshly prepared with little or no oxidation, and with measurements taken at low temperatures. Overall, this newly implemented framework

for calculating  $\chi_{\text{surface}}(-2\omega; \omega, \omega)$  and  $\mathcal{R}$  focused on the Si(001)2  $\times$  1 and Si(111)(1  $\times$  1):H surfaces provides a compelling benchmark for SSHG studies. We are confident that this work can be applied directly to many other surfaces of interest.

## Appendix A

# Supplementary Derivations for the Nonlinear Surface Susceptibility

## Outline

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### A.1 $\mathbf{r}_e$ and $\mathbf{r}_i$

In this appendix, we derive the expressions for the matrix elements of the electron position operator  $\mathbf{r}$ . The  $r$  representation of the Bloch states is given by

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | n\mathbf{k} \rangle = \sqrt{\frac{\Omega}{8\pi^3}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (\text{A.1})$$

where  $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$  is cell periodic, and

$$\int_{\Omega} u_{n\mathbf{k}}^*(\mathbf{r}) u_{m\mathbf{k}'}(\mathbf{r}) d^3r = \delta_{nm} \delta_{\mathbf{k}, \mathbf{k}'}, \quad (\text{A.2})$$

and  $\Omega$  is the unit cell volume.

The key ingredient in the calculation are the matrix elements of the position operator  $\mathbf{r}$ . We start from the basic relation

$$\langle n\mathbf{k}|m\mathbf{k}' \rangle = \delta_{nm} \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.3})$$

and take its derivative with respect to  $\mathbf{k}$  as follows. On one hand,

$$\frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k}|m\mathbf{k}' \rangle = \delta_{nm} \frac{\partial}{\partial \mathbf{k}} \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.4})$$

and on the other,

$$\frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k}|m\mathbf{k}' \rangle = \frac{\partial}{\partial \mathbf{k}} \int \langle n\mathbf{k}|\mathbf{r} \rangle \langle \mathbf{r}|m\mathbf{k}' \rangle d\mathbf{r} = \int \left( \frac{\partial}{\partial \mathbf{k}} \psi_{n\mathbf{k}}^*(\mathbf{r}) \right) \psi_{m\mathbf{k}'}(\mathbf{r}) d\mathbf{r}. \quad (\text{A.5})$$

The derivative of the wavefunction is simply given by

$$\frac{\partial}{\partial \mathbf{k}} \psi_{n\mathbf{k}}^*(\mathbf{r}) = \sqrt{\frac{\Omega}{8\pi^3}} \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) e^{-i\mathbf{k}\cdot\mathbf{r}} - i\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r}). \quad (\text{A.6})$$

Substituting into Eq. (A.5), we obtain

$$\begin{aligned} \frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k}|m\mathbf{k}' \rangle &= \sqrt{\frac{\Omega}{8\pi^3}} \int \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) e^{-i\mathbf{k}\cdot\mathbf{r}} \psi_{m\mathbf{k}'}(\mathbf{r}) d\mathbf{r} - i \int \psi_{n\mathbf{k}}^*(\mathbf{r}) \mathbf{r} \psi_{m\mathbf{k}'}(\mathbf{r}) d\mathbf{r} \\ &= \frac{\Omega}{8\pi^3} \int e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) u_{m\mathbf{k}'}(\mathbf{r}) d\mathbf{r} - i \langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}' \rangle. \end{aligned} \quad (\text{A.7})$$

Restricting  $\mathbf{k}$  and  $\mathbf{k}'$  to the first Brillouin zone, we use the following result that is valid for any periodic function  $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$ ,

$$\int e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) d^3r = \frac{8\pi^3}{\Omega} \delta(\mathbf{q} - \mathbf{k}) \int_{\Omega} f(\mathbf{r}) d^3r, \quad (\text{A.8})$$

to finally write [8]

$$\frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k}|m\mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}') \int_{\Omega} \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) u_{m\mathbf{k}}(\mathbf{r}) d\mathbf{r} - i \langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}' \rangle. \quad (\text{A.9})$$

From

$$\int_{\Omega} u_{m\mathbf{k}} u_{n\mathbf{k}}^* d\mathbf{r} = \delta_{nm}, \quad (\text{A.10})$$

we easily find that

$$\int_{\Omega} \left( \frac{\partial}{\partial \mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}) \right) u_{n\mathbf{k}}^*(\mathbf{r}) d\mathbf{r} = - \int_{\Omega} u_{m\mathbf{k}}(\mathbf{r}) \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) d\mathbf{r}. \quad (\text{A.11})$$

Therefore, we define

$$\xi_{nm}(\mathbf{k}) \equiv i \int_{\Omega} u_{n\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}) d\mathbf{r}, \quad (\text{A.12})$$

with  $\nabla_{\mathbf{k}} = \partial/\partial\mathbf{k}$ . Now, from Eqs. (A.4), (A.7), and (A.12), we have that the matrix elements of the position operator of the electron are given by

$$\langle n\mathbf{k} | \hat{\mathbf{r}} | m\mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}') \xi_{nm}(\mathbf{k}) + i \delta_{nm} \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.13})$$

Then, from Eq. (A.13) and writing  $\hat{\mathbf{r}} = \hat{\mathbf{r}}_e + \hat{\mathbf{r}}_i$ , with  $\hat{\mathbf{r}}_e$  ( $\hat{\mathbf{r}}_i$ ) the interband (intraband) part, we obtain that

$$\langle n\mathbf{k} | \hat{\mathbf{r}}_i | m\mathbf{k}' \rangle = \delta_{nm} [\delta(\mathbf{k} - \mathbf{k}') \xi_{nn}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')], \quad (\text{A.14})$$

$$\langle n\mathbf{k} | \hat{\mathbf{r}}_e | m\mathbf{k}' \rangle = (1 - \delta_{nm}) \delta(\mathbf{k} - \mathbf{k}') \xi_{nm}(\mathbf{k}). \quad (\text{A.15})$$

To proceed, we relate Eq. (A.15) to the matrix elements of the momentum operator as follows. For the intraband part, we derive the following general result,

$$\begin{aligned} \langle n\mathbf{k} | [\hat{\mathbf{r}}_i, \hat{O}] | m\mathbf{k}' \rangle &= \sum_{\ell, \mathbf{k}''} \left( \langle n\mathbf{k} | \hat{\mathbf{r}}_i | \ell\mathbf{k}'' \rangle \langle \ell\mathbf{k}'' | \hat{O} | m\mathbf{k}' \rangle - \langle n\mathbf{k} | \hat{O} | \ell\mathbf{k}'' \rangle \langle \ell\mathbf{k}'' | \hat{\mathbf{r}}_i | m\mathbf{k}' \rangle \right) \\ &= \sum_{\ell} \left( \langle n\mathbf{k} | \hat{\mathbf{r}}_i | \ell\mathbf{k}' \rangle \mathcal{O}_{\ell m}(\mathbf{k}') - \mathcal{O}_{n\ell}(\mathbf{k}) \langle \ell\mathbf{k} | \hat{\mathbf{r}}_i | m\mathbf{k}' \rangle \right), \end{aligned} \quad (\text{A.16})$$

where we have taken  $\langle n\mathbf{k} | \hat{O} | \ell\mathbf{k}'' \rangle = \delta(\mathbf{k} - \mathbf{k}'') \mathcal{O}_{n\ell}(\mathbf{k})$ . We substitute Eq. (A.14) to obtain

$$\begin{aligned} \sum_{\ell} &(\delta_{n\ell} [\delta(\mathbf{k} - \mathbf{k}') \xi_{nn}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')] \mathcal{O}_{\ell m}(\mathbf{k}') - \mathcal{O}_{n\ell}(\mathbf{k}) \delta_{\ell m} [\delta(\mathbf{k} - \mathbf{k}') \xi_{mm}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')]) \\ &= ([\delta(\mathbf{k} - \mathbf{k}') \xi_{nn}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')] \mathcal{O}_{nm}(\mathbf{k}') - \mathcal{O}_{nm}(\mathbf{k}) [\delta(\mathbf{k} - \mathbf{k}') \xi_{mm}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')]) \\ &= \delta(\mathbf{k} - \mathbf{k}') \mathcal{O}_{nm}(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})) + i \mathcal{O}_{nm}(\mathbf{k}') \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') + i \delta(\mathbf{k} - \mathbf{k}') \nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i \mathcal{O}_{nm}(\mathbf{k}') \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') \\ &= i \delta(\mathbf{k} - \mathbf{k}') (\nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i \mathcal{O}_{nm}(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k}))) \\ &\equiv i \delta(\mathbf{k} - \mathbf{k}') (\mathcal{O}_{nm})_{;\mathbf{k}}. \end{aligned} \quad (\text{A.17})$$

Then,

$$\langle n\mathbf{k} | [\hat{\mathbf{r}}_i, \hat{O}] | m\mathbf{k}' \rangle = i \delta(\mathbf{k} - \mathbf{k}') (\mathcal{O}_{nm})_{;\mathbf{k}}, \quad (\text{A.18})$$

where

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i \mathcal{O}_{nm}(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})), \quad (\text{A.19})$$

is the generalized derivative of  $\mathcal{O}_{nm}$  with respect to  $\mathbf{k}$ . Note that the highly singular term  $\nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')$  cancels in Eq. (A.17), thus giving a well defined commutator of the intraband position operator with any arbitrary operator  $\hat{O}$ .

## A.2 Matrix elements of $\mathbf{v}_{nm}^{\text{nl}}(\mathbf{k})$ and $\mathcal{V}_{nm}^{\text{nl},\ell}(\mathbf{k})$

From Eq. (1.25), we have that

$$\begin{aligned} \mathbf{v}_{nm}^{\text{nl}}(\mathbf{k}) &= \langle n\mathbf{k} | \hat{\mathbf{v}}^{\text{nl}} | m\mathbf{k}' \rangle = \frac{i}{\hbar} \langle n\mathbf{k} | [\hat{V}^{\text{nl}}, \hat{\mathbf{r}}] | m\mathbf{k}' \rangle \\ &= \frac{i}{\hbar} \int \langle n\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | [\hat{V}^{\text{nl}}, \hat{\mathbf{r}}] | \mathbf{r}' \rangle \langle \mathbf{r}' | m\mathbf{k}' \rangle d\mathbf{r} d\mathbf{r}' \\ &= \frac{i}{\hbar} \delta(\mathbf{k} - \mathbf{k}') \int \psi_{n\mathbf{k}}^*(\mathbf{r}) \langle \mathbf{r} | [\hat{V}^{\text{nl}}, \hat{\mathbf{r}}] | \mathbf{r}' \rangle \psi_{m\mathbf{k}'}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \end{aligned} \quad (\text{A.20})$$

where  $\mathbf{k} = \mathbf{k}'$  due to the fact that the integrand is periodic in real space, and  $\mathbf{k}$  is restricted to the Brillouin Zone. Now,

$$\begin{aligned}\langle \mathbf{r} | [\hat{V}^{\text{nl}}, \hat{\mathbf{r}}] | \mathbf{r}' \rangle &= \langle \mathbf{r} | \hat{V}^{\text{nl}} \hat{\mathbf{r}} - \hat{\mathbf{r}} \hat{V}^{\text{nl}} | \mathbf{r}' \rangle = \langle \mathbf{r} | \hat{V}^{\text{nl}} \hat{\mathbf{r}} | \mathbf{r}' \rangle - \langle \mathbf{r} | \hat{\mathbf{r}} \hat{V}^{\text{nl}} | \mathbf{r}' \rangle \\ &= \langle \mathbf{r} | \hat{V}^{\text{nl}} \mathbf{r}' | \mathbf{r}' \rangle - \langle \mathbf{r} | \mathbf{r}' \hat{V}^{\text{nl}} | \mathbf{r}' \rangle = \langle \mathbf{r} | \hat{V}^{\text{nl}} | \mathbf{r}' \rangle (\mathbf{r}' - \mathbf{r}) = V^{\text{nl}}(\mathbf{r}, \mathbf{r}') (\mathbf{r}' - \mathbf{r}),\end{aligned}\quad (\text{A.21})$$

where we used  $\hat{r} \langle \mathbf{r} | = r \langle \mathbf{r} |$ ,  $\langle \mathbf{r}' | \hat{r} = \langle \mathbf{r}' | r'$ , and  $V^{\text{nl}}(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \hat{V}^{\text{nl}} | \mathbf{r}' \rangle$  (Eq. (1.11)). Also, we have the following identity which will be used shortly,

$$\begin{aligned}(\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) \frac{1}{\Omega} \int e^{-i\mathbf{K} \cdot \mathbf{r}} V^{\text{nl}}(\mathbf{r}, \mathbf{r}') e^{i\mathbf{K}' \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}' &= -i \frac{1}{\Omega} \int e^{-i\mathbf{K} \cdot \mathbf{r}} \left( \mathbf{r} V^{\text{nl}}(\mathbf{r}, \mathbf{r}') - V^{\text{nl}}(\mathbf{r}, \mathbf{r}') \mathbf{r}' \right) e^{i\mathbf{K}' \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}' \\ (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) \langle \mathbf{K} | V^{\text{nl}} | \mathbf{K}' \rangle &= \frac{i}{\Omega} \int e^{-i\mathbf{K} \cdot \mathbf{r}} V^{\text{nl}}(\mathbf{r}, \mathbf{r}') (\mathbf{r}' - \mathbf{r}) e^{i\mathbf{K}' \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}',\end{aligned}\quad (\text{A.22})$$

where  $\Omega$  is the volume of the unit cell, and we defined

$$V^{\text{nl}}(\mathbf{K}, \mathbf{K}') \equiv \langle \mathbf{K} | V^{\text{nl}} | \mathbf{K}' \rangle = \frac{1}{\Omega} \int e^{-i\mathbf{K} \cdot \mathbf{r}} V^{\text{nl}}(\mathbf{r}, \mathbf{r}') e^{i\mathbf{K}' \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}',\quad (\text{A.23})$$

where  $V^{\text{nl}}(\mathbf{K}', \mathbf{K}) = V^{\text{nl}*}(\mathbf{K}, \mathbf{K}')$ , since  $V^{\text{nl}}(\mathbf{r}', \mathbf{r}) = V^{\text{nl}*}(\mathbf{r}, \mathbf{r}')$  due to the fact that  $\hat{V}^{\text{nl}}$  is a hermitian operator. Using the plane wave expansion

$$\langle \mathbf{r} | n\mathbf{k} \rangle = \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{K} \cdot \mathbf{r}},\quad (\text{A.24})$$

with  $\mathbf{K} = \mathbf{k} + \mathbf{G}$ , we obtain from Eq. (A.20) and Eq. (A.22), that

$$\begin{aligned}\mathbf{v}_{nm}^{\text{nl}}(\mathbf{k}) &= \frac{i}{\hbar} \delta(\mathbf{k} - \mathbf{k}') \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}) A_{m\mathbf{k}'}(\mathbf{G}') \frac{1}{\Omega} \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{K} \cdot \mathbf{r}} \langle \mathbf{r} | [\hat{V}^{\text{nl}}, \hat{\mathbf{r}}] | \mathbf{r}' \rangle e^{i\mathbf{K}' \cdot \mathbf{r}'} \\ &= \frac{1}{\hbar} \delta(\mathbf{k} - \mathbf{k}') \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}) A_{m\mathbf{k}'}(\mathbf{G}') \frac{i}{\Omega} \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{K} \cdot \mathbf{r}} V^{\text{nl}}(\mathbf{r}, \mathbf{r}') (\mathbf{r}' - \mathbf{r}) e^{i\mathbf{K}' \cdot \mathbf{r}'} \\ &= \frac{1}{\hbar} \delta(\mathbf{k} - \mathbf{k}') \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}) A_{m\mathbf{k}'}(\mathbf{G}') (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) V^{\text{nl}}(\mathbf{K}, \mathbf{K}').\end{aligned}\quad (\text{A.25})$$

For fully separable pseudopotentials in the Kleinman-Bylander (KB) form,[10, 11, 12] the matrix elements  $\langle \mathbf{K} | V^{\text{nl}} | \mathbf{K}' \rangle = V^{\text{nl}}(\mathbf{K}, \mathbf{K}')$  can be readily calculated. [10] Indeed, the Fourier representation assumes the form,[12, 69, 70]

$$\begin{aligned}V_{\text{KB}}^{\text{nl}}(\mathbf{K}, \mathbf{K}') &= \sum_s e^{i(\mathbf{K} - \mathbf{K}') \cdot \boldsymbol{\tau}_s} \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l F_{lm}^s(\mathbf{K}) F_{lm}^{s*}(\mathbf{K}') \\ &= \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l f_{lm}^s(\mathbf{K}) f_{lm}^{s*}(\mathbf{K}'),\end{aligned}\quad (\text{A.26})$$

with  $f_{lm}^s(\mathbf{K}) = e^{i\mathbf{K} \cdot \boldsymbol{\tau}_s} F_{lm}^s(\mathbf{K})$ , and

$$F_{lm}^s(\mathbf{K}) = \int d\mathbf{r} e^{-i\mathbf{K} \cdot \mathbf{r}} \delta V_l^S(\mathbf{r}) \Phi_{lm}^{\text{ps}}(\mathbf{r}).\quad (\text{A.27})$$

Here  $\delta V_l^S(\mathbf{r})$  is the non-local contribution of the ionic pseudopotential centered at the atomic position  $\boldsymbol{\tau}_s$  located in the unit cell,  $\Phi_{lm}^{\text{ps}}(\mathbf{r})$  is the pseudo-wavefunction of the corresponding atom, while  $E_l$  is the so called Kleinman-Bylander energy. Further details can be found in Ref. [70]. From Eq. (A.26) we find

$$\begin{aligned} (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'})V_{\text{KB}}^{\text{nl}}(\mathbf{K}, \mathbf{K}') &= \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) f_{lm}^s(\mathbf{K}) f_{lm}^{s*}(\mathbf{K}') \\ &= \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l ([\nabla_{\mathbf{K}} f_{lm}^s(\mathbf{K})] f_{lm}^{s*}(\mathbf{K}') + f_{lm}^s(\mathbf{K}) [\nabla_{\mathbf{K}'} f_{lm}^{s*}(\mathbf{K}')]), \end{aligned} \quad (\text{A.28})$$

and using this in Eq. (A.25) leads to

$$\begin{aligned} \mathbf{v}_{nm}^{\text{nl}}(\mathbf{k}) &= \frac{1}{\hbar} \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l \sum_{\mathbf{G}\mathbf{G}'} A_{n,\vec{k}}^*(\mathbf{G}) A_{n',\vec{k}}(\mathbf{G}') \times (\nabla_{\mathbf{K}} f_{lm}^s(\mathbf{K}) f_{lm}^{s*}(\mathbf{K}') + f_{lm}^s(\mathbf{K}) \nabla_{\mathbf{K}'} f_{lm}^{s*}(\mathbf{K}')) \\ &= \frac{1}{\hbar} \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l \left[ \left( \sum_{\mathbf{G}} A_{n,\vec{k}}^*(\mathbf{G}) \nabla_{\mathbf{K}} f_{lm}^s(\mathbf{K}) \right) \left( \sum_{\mathbf{G}'} A_{n',\vec{k}}(\mathbf{G}') f_{lm}^{s*}(\mathbf{K}') \right) \right. \\ &\quad \left. + \left( \sum_{\mathbf{G}} A_{n,\vec{k}}^*(\mathbf{G}) f_{lm}^s(\mathbf{K}) \right) \left( \sum_{\mathbf{G}'} A_{n',\vec{k}}(\mathbf{G}') \nabla_{\mathbf{K}'} f_{lm}^{s*}(\mathbf{K}') \right) \right], \end{aligned} \quad (\text{A.29})$$

where there are only single sums over  $\mathbf{G}$ . The above equation is implemented in the DP code [40].

Now we derive  $\mathbf{v}_{nm}^{\text{nl},\ell}(\mathbf{k})$ . First we prove that

$$\sum_{\mathbf{G}} |\mathbf{k} + \mathbf{G}\rangle \langle \mathbf{k} + \mathbf{G}| = 1. \quad (\text{A.30})$$

Proof:

$$\langle n\mathbf{k}|1|n'\mathbf{k}\rangle = \delta_{nn'}, \quad (\text{A.31})$$

take

$$\begin{aligned} \sum_{\mathbf{G}} \langle n\mathbf{k}||\mathbf{k} + \mathbf{G}\rangle \langle \mathbf{k} + \mathbf{G}||n'\mathbf{k}\rangle &= \int d\mathbf{r} d\mathbf{r}' \sum_{\mathbf{G}} \langle n\mathbf{k}||\mathbf{r}\rangle \langle \mathbf{r}||\mathbf{k} + \mathbf{G}\rangle \langle \mathbf{k} + \mathbf{G}||\mathbf{r}'\rangle \langle \mathbf{r}'||n'\mathbf{k}\rangle \\ &= \int d\mathbf{r} d\mathbf{r}' \sum_{\mathbf{G}} \psi_{n\mathbf{k}}^*(\mathbf{r}) \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \frac{1}{\sqrt{\Omega}} e^{-i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}'} \psi_{m\mathbf{k}}(\mathbf{r}') \\ &= \int d\mathbf{r} d\mathbf{r}' \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{k}}(\mathbf{r}') \frac{1}{V} \sum_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot (\mathbf{r}-\mathbf{r}')} \\ &= \int d\mathbf{r} d\mathbf{r}' \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{k}}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') = \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{k}}(\mathbf{r}) = \delta_{nn'}, \end{aligned} \quad (\text{A.32})$$

and thus Eq. (A.30) follows. We used

$$\langle \mathbf{r}|\mathbf{k} + \mathbf{G}\rangle = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}. \quad (\text{A.33})$$

From Eq. (1.70), we would like to calculate

$$\mathcal{V}_{nm}^{\text{nl},\ell}(\mathbf{k}) = \frac{1}{2} \langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\text{nl}} + \mathbf{v}^{\text{nl}}C^\ell(z)|m\mathbf{k}\rangle. \quad (\text{A.34})$$

We work out the first term on the right hand side,

$$\begin{aligned} \langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\text{nl}}|m\mathbf{k}\rangle &= \sum_{\mathbf{G}} \langle n\mathbf{k}|C^\ell(z)|\mathbf{k} + \mathbf{G}\rangle \langle \mathbf{k} + \mathbf{G}|\mathbf{v}^{\text{nl}}|m\mathbf{k}\rangle \\ &= \sum_{\mathbf{G}} \int d\mathbf{r} \int d\mathbf{r}' \langle n\mathbf{k}|\mathbf{r}\rangle \langle \mathbf{r}|C^\ell(z)|\mathbf{r}'\rangle \langle \mathbf{r}'|\mathbf{k} + \mathbf{G}\rangle \times \int d\mathbf{r}'' \int d\mathbf{r}''' \langle \mathbf{k} + \mathbf{G}|\mathbf{r}''\rangle \langle \mathbf{r}''|\mathbf{v}^{\text{nl}}|\mathbf{r}'''\rangle \langle \mathbf{r}'''|m\mathbf{k}\rangle \\ &= \sum_{\mathbf{G}} \int d\mathbf{r} \int d\mathbf{r}' \langle n\mathbf{k}|\mathbf{r}\rangle C^\ell(z) \delta(\mathbf{r} - \mathbf{r}') \langle \mathbf{r}'|\mathbf{k} + \mathbf{G}\rangle \times \int d\mathbf{r}'' \int d\mathbf{r}''' \langle \mathbf{k} + \mathbf{G}|\mathbf{r}''\rangle \langle \mathbf{r}''|\mathbf{v}^{\text{nl}}|\mathbf{r}'''\rangle \langle \mathbf{r}'''|m\mathbf{k}\rangle \\ &= \sum_{\mathbf{G}} \int d\mathbf{r} \langle n\mathbf{k}|\mathbf{r}\rangle C^\ell(z) \langle \mathbf{r}|\mathbf{k} + \mathbf{G}\rangle \times \frac{i}{\hbar} \int d\mathbf{r}'' \int d\mathbf{r}''' \langle \mathbf{k} + \mathbf{G}|\mathbf{r}''\rangle V^{\text{nl}}(\mathbf{r}'', \mathbf{r}''') (\mathbf{r}''' - \mathbf{r}'') \langle \mathbf{r}'''|m\mathbf{k}\rangle, \end{aligned} \quad (\text{A.35})$$

where we used Eq. (A.21) and (1.25). We use Eq. (A.24), (A.33) and (A.22) to obtain

$$\begin{aligned} \langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\text{nl}}|m\mathbf{k}\rangle &= \sum_{\mathbf{G}} \sum_{\mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') \frac{1}{\Omega} \int d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} C^\ell(z) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\ &\quad \times \sum_{\mathbf{G}''} A_{m\mathbf{k}}(\mathbf{G}'') \frac{i}{\hbar\Omega} \int d\mathbf{r}'' \int d\mathbf{r}''' e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}''} V^{\text{nl}}(\mathbf{r}'', \mathbf{r}''') (\mathbf{r}''' - \mathbf{r}'') e^{i(\mathbf{k}+\mathbf{G}'')\cdot\mathbf{r}'''} \\ &= \frac{1}{\hbar} \sum_{\mathbf{G}} \sum_{\mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') \delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel} f_\ell(\mathbf{G}_\perp - \mathbf{G}'_\perp) \sum_{\mathbf{G}''} A_{m\mathbf{k}}(\mathbf{G}'') (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) V^{\text{nl}}(\mathbf{K}, \mathbf{K}''), \end{aligned} \quad (\text{A.36})$$

where

$$\frac{1}{\Omega} \int d\mathbf{r} C^\ell(z) e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} = \delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel} f_\ell(\mathbf{G}_\perp - \mathbf{G}'_\perp), \quad (\text{A.37})$$

and

$$f_\ell(g) = \frac{1}{L} \int_{z_\ell - \Delta_\ell^b}^{z_\ell + \Delta_\ell^f} e^{igz} dz, \quad (\text{A.38})$$

where  $f^*(g) = f(-g)$ . We define

$$\mathcal{F}_{n\mathbf{k}}^\ell(\mathbf{G}) = \sum_{\mathbf{G}'} A_{n\mathbf{k}}(\mathbf{G}') \delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel} f_\ell(\mathbf{G}'_\perp - \mathbf{G}_\perp), \quad (\text{A.39})$$

and

$$\mathcal{H}_{n\mathbf{k}}(\mathbf{G}) = \sum_{\mathbf{G}'} A_{n\mathbf{k}}(\mathbf{G}') (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) V^{\text{nl}}(\mathbf{K}, \mathbf{K}'), \quad (\text{A.40})$$

thus we can compactly write,

$$\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\text{nl}}|m\mathbf{k}\rangle = \frac{1}{\hbar} \sum_{\mathbf{G}} \mathcal{F}_{n\mathbf{k}}^{\ell*}(\mathbf{G}) \mathcal{H}_{m\mathbf{k}}(\mathbf{G}). \quad (\text{A.41})$$

Now, the second term of Eq. (A.34)

$$\begin{aligned}
\langle n\mathbf{k}|\mathbf{v}^{\text{nl}}C^\ell(z)|m\mathbf{k}\rangle &= \sum_{\mathbf{G}} \langle n\mathbf{k}|\mathbf{v}^{\text{nl}}|\mathbf{k} + \mathbf{G}\rangle \langle \mathbf{k} + \mathbf{G}|C^\ell(z)|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}} \int d\mathbf{r}'' \int d\mathbf{r}''' \langle n\mathbf{k}||\mathbf{r}''\rangle \langle \mathbf{r}''|\mathbf{v}^{\text{nl}}|\mathbf{r}'''\rangle \langle \mathbf{r}'''||\mathbf{k} + \mathbf{G}\rangle \\
&\quad \times \int d\mathbf{r} \int d\mathbf{r}' \langle \mathbf{k} + \mathbf{G}||\mathbf{r}\rangle \langle \mathbf{r}|C^\ell(z)|\mathbf{r}'\rangle \langle \mathbf{r}'||m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}} \frac{i}{\hbar} \int d\mathbf{r}'' \int d\mathbf{r}''' \langle n\mathbf{k}|\mathbf{r}''\rangle V^{\text{nl}}(\mathbf{r}'', \mathbf{r}''') (\mathbf{r}''' - \mathbf{r}'') \langle \mathbf{r}'''||\mathbf{k} + \mathbf{G}\rangle \\
&\quad \times \int d\mathbf{r} \langle \mathbf{k} + \mathbf{G}|\mathbf{r}\rangle C^\ell(z) \langle \mathbf{r}|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}} \sum_{\mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') \frac{i}{\hbar\Omega} \int d\mathbf{r}'' \int d\mathbf{r}''' e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}''} V^{\text{nl}}(\mathbf{r}'', \mathbf{r}''') (\mathbf{r}''' - \mathbf{r}'') e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}'''} \\
&\quad \times \sum_{\mathbf{G}''} A_{m\mathbf{k}}(\mathbf{G}'') \frac{1}{\Omega} \int d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} C^\ell(z) e^{i(\mathbf{k}+\mathbf{G}'')\cdot\mathbf{r}} \\
&= \frac{1}{\hbar} \sum_{\mathbf{G}} \sum_{\mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) V^{\text{nl}}(\mathbf{K}', \mathbf{K}) \\
&\quad \times \sum_{\mathbf{G}''} A_{m\mathbf{k}}(\mathbf{G}'') \delta_{\mathbf{G}_{\parallel} \mathbf{G}''_{\parallel}} f_\ell(\mathbf{G}''_{\perp} - \mathbf{G}_{\perp}) \\
&= \frac{1}{\hbar} \sum_{\mathbf{G}} \mathcal{H}_{n\mathbf{k}}^*(\mathbf{G}) \mathcal{F}_{m\mathbf{k}}^\ell(\mathbf{G}). \tag{A.42}
\end{aligned}$$

Therefore Eq. (A.34) is compactly given by

$$\mathcal{V}_{nm}^{\text{nl},\ell}(\mathbf{k}) = \frac{1}{2\hbar} \sum_{\mathbf{G}} \left( \mathcal{F}_{n\mathbf{k}}^*(\mathbf{G}) \mathcal{H}_{m\mathbf{k}}(\mathbf{G}) + \mathcal{H}_{n\mathbf{k}}^*(\mathbf{G}) \mathcal{F}_{m\mathbf{k}}^\ell(\mathbf{G}) \right). \tag{A.43}$$

For fully separable pseudopotentials in the Kleinman-Bylander (KB) form [10, 11, 12], we can use Eq. (A.28) and evaluate above expression, that we have implemented in the DP code [40]. Explicitly,

$$\begin{aligned}
\mathcal{V}_{nm}^{\text{nl},\ell}(\mathbf{k}) &= \frac{1}{2\hbar} \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l \\
&\quad \left[ \left( \sum_{\mathbf{G}''} \nabla_{\mathbf{G}''} f_{lm}^s(\mathbf{G}'') \sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) \delta_{\mathbf{G}_{\parallel} \mathbf{G}''_{\parallel}} f_\ell(G_z - G_z'') \right) \left( \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') f_{lm}^{s*}(\mathbf{K}') \right) \right. \\
&\quad + \left( \sum_{\mathbf{G}''} f_{lm}^s(\mathbf{G}'') \sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) \delta_{\mathbf{G}_{\parallel} \mathbf{G}''_{\parallel}} f_\ell(G_z - G_z'') \right) \left( \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') \nabla_{\mathbf{K}'} f_{lm}^{s*}(\mathbf{K}') \right) \\
&\quad + \left( \sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) \nabla_{\mathbf{G}} f_{lm}^s(\mathbf{G}) \right) \left( \sum_{\mathbf{G}''} f_{lm}^{s*}(\mathbf{G}'') \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') \delta_{\mathbf{G}'_{\parallel} \mathbf{G}''_{\parallel}} f_\ell(G_z'' - G_z') \right) \\
&\quad \left. + \left( \sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) f_{lm}^s(\mathbf{G}) \right) \left( \sum_{\mathbf{G}''} \nabla_{\mathbf{G}''} f_{lm}^{s*}(\mathbf{G}'') \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') \delta_{\mathbf{G}'_{\parallel} \mathbf{G}''_{\parallel}} f_\ell(G_z'' - G_z') \right) \right]. \tag{A.44}
\end{aligned}$$

For a full slab calculation, equivalent to a bulk calculation,  $C^\ell(z) = 1$  and then  $f_\ell(g) = \delta_{g0}$ , and Eq. (A.44) reduces to Eq. (A.29).

### A.3 Explicit expressions for $\mathcal{V}_{nm}^{a,\ell}(\mathbf{k})$ and $\mathcal{C}_{nm}^\ell(\mathbf{k})$

Expanding the wave function in planewaves, we obtain

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}, \quad (\text{A.45})$$

where  $\{\mathbf{G}\}$  are the reciprocal basis vectors satisfying  $e^{\mathbf{R} \cdot \mathbf{G}} = 1$ ,  $\{\mathbf{R}\}$  are the translation vectors in real space, and  $A_{n\mathbf{k}}(\mathbf{G})$  are the expansion coefficients. Using  $m_e \mathbf{v} = -i\hbar \nabla$  into Eqs. (1.71) and (1.69) we obtain [20],

$$\mathcal{V}_{nm}^\ell(\mathbf{k}) = \frac{\hbar}{2m_e} \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') A_{m\mathbf{k}}(\mathbf{G}) (2\mathbf{k} + \mathbf{G} + \mathbf{G}') \delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp), \quad (\text{A.46})$$

with

$$f_\ell(g) = \frac{1}{L} \int_{z_\ell - \Delta_\ell^b}^{z_\ell + \Delta_\ell^f} e^{igz} dz, \quad (\text{A.47})$$

where the reciprocal lattice vectors  $\mathbf{G}$  are decomposed into components parallel to the surface  $\mathbf{G}_\parallel$ , and perpendicular to the surface  $G_\perp \hat{z}$ , so that  $\mathbf{G} = \mathbf{G}_\parallel + G_\perp \hat{z}$ . Likewise we obtain that

$$\begin{aligned} \mathcal{C}_{nm}(\mathbf{k}) &= \int \psi_{n\mathbf{k}}^*(\mathbf{r}) f(z) \psi_{m\mathbf{k}}(\mathbf{r}) d\mathbf{r} \\ &= \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') A_{m\mathbf{k}}(\mathbf{G}) \int f(z) e^{-i(\mathbf{G}-\mathbf{G}') \cdot \mathbf{r}} d\mathbf{r} \\ &= \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') A_{m\mathbf{k}}(\mathbf{G}) \underbrace{\int e^{-i(\mathbf{G}_\parallel - \mathbf{G}'_\parallel) \cdot \mathbf{R}_\parallel} d\mathbf{R}_\parallel}_{\delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel}} \underbrace{\int e^{-i(g-g')z} f(z) dz}_{f_\ell(G_\perp - G'_\perp)} \end{aligned}$$

which we can express compactly as,

$$\mathcal{C}_{nm}^\ell(\mathbf{k}) = \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') A_{m\mathbf{k}}(\mathbf{G}) \delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp). \quad (\text{A.48})$$

The double summation over the  $\mathbf{G}$  vectors can be efficiently done by creating a pointer array to identify all the plane-wave coefficients associated with the same  $G_\parallel$ . We take  $z_\ell$  at the center of an atom that belongs to layer  $\ell$ , so the equations above give the  $\ell$ -th atomic-layer contribution to the optical response [20].

If  $\mathcal{C}^\ell(z) = 1$  from Eqs. (A.46) and (A.48), we recover the well known results

$$\begin{aligned} v_{nm}(\mathbf{k}) &= \frac{\hbar}{m_e} \sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) A_{m\mathbf{k}}(\mathbf{G}) (\mathbf{k} + \mathbf{G}), \\ \mathcal{C}_{nm}^\ell &= \delta_{nm}, \end{aligned} \quad (\text{A.49})$$

since for this case,  $f_\ell(g) = \delta_{g0}$ .

### A.3.1 Time-reversal relations

The following relations hold for time-reversal symmetry.

$$\begin{aligned}
A_{n\mathbf{k}}^*(\mathbf{G}) &= A_{n-\mathbf{k}}(\mathbf{G}), \\
\mathbf{P}_{n\ell}(-\mathbf{k}) &= \hbar \sum_{\mathbf{G}} A_{n-\mathbf{k}}^*(\mathbf{G}) A_{\ell-\mathbf{k}}(\mathbf{G})(-\mathbf{k} + \mathbf{G}), \\
(\mathbf{G} \rightarrow -\mathbf{G}) &= -\hbar \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G}) A_{\ell\mathbf{k}}^*(\mathbf{G})(\mathbf{k} + \mathbf{G}) = -\mathbf{P}_{\ell n}(\mathbf{k}), \\
\mathcal{C}_{nm}(L; -\mathbf{k}) &= \sum_{\mathbf{G}_{\parallel}, g, g'} A_{n-\mathbf{k}}^*(\mathbf{G}_{\parallel}, g) A_{m-\mathbf{k}}(\mathbf{G}_{\parallel}, g') f_{\ell}(g - g') \\
&= \sum_{\mathbf{G}_{\parallel}, g, g'} A_{n\mathbf{k}}(\mathbf{G}_{\parallel}, g) A_{m\mathbf{k}}^*(\mathbf{G}_{\parallel}, g') f_{\ell}(g - g') \\
&= \mathcal{C}_{mn}(L; \mathbf{k}).
\end{aligned}$$

### A.4 $\mathcal{V}_{nm}^{\Sigma, a, \ell}$ and $(\mathcal{V}_{nm}^{\Sigma, a, \ell})_{;k^b}$

From Eq. (1.72)

$$(\mathcal{V}_{nm}^{\Sigma, a, \ell})_{;k^b} = (\mathcal{V}_{nm}^{\text{LDA}, a, \ell})_{;k^b} + (\mathcal{V}_{nm}^{\mathcal{S}, a, \ell})_{;k^b}. \quad (\text{A.50})$$

For the LDA term we have

$$\mathcal{V}_{nm}^{\text{LDA}, a, \ell} = \frac{1}{2} (v^{\text{LDA}, a} \mathcal{C}^{\ell} + \mathcal{C}^{\ell} v^{\text{LDA}, a})_{nm} = \frac{1}{2} \sum_q (v_{nq}^{\text{LDA}, a} \mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell} v_{qm}^{\text{LDA}, a}) \quad (\text{A.51})$$

and

$$\begin{aligned}
(\mathcal{V}_{nm}^{\text{LDA}, a})_{;k^b} &= \frac{1}{2} \sum_q (v_{nq}^{\text{LDA}, a} \mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell} v_{qm}^{\text{LDA}, a})_{;k^b} \\
&= \frac{1}{2} \sum_q ((v_{nq}^{\text{LDA}, a})_{;k^b} \mathcal{C}_{qm}^{\ell} + v_{nq}^{\text{LDA}, a} (\mathcal{C}_{qm}^{\ell})_{;k^b} + (\mathcal{C}_{nq}^{\ell})_{;k^b} v_{qm}^{\text{LDA}, a} + \mathcal{C}_{nq}^{\ell} (v_{qm}^{\text{LDA}, a})_{;k^b}),
\end{aligned} \quad (\text{A.52})$$

where we omit the  $\mathbf{k}$  argument in all terms. From Eq. (A.25) we know that  $\mathbf{v}_{nm}^{\text{nl}}(\mathbf{k})$  can be readily calculated, and from Sec. A.3, both  $v_{nm}^a$  and  $\mathcal{C}_{nm}^{\ell}$  are also known quantities. Thus,  $\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})$  is known, and in turn  $\mathcal{V}_{nm}^{\text{LDA}, a, \ell}$  is also known. For the generalized derivative  $(\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k}))_{;\mathbf{k}}$  we use Eq. (1.30) to write

$$\begin{aligned}
(v_{nm}^{\text{LDA}, a})_{;k^b} &= i m_e (\omega_{nm}^{\text{LDA}} r_{nm}^a)_{;k^b} \\
&= i m_e (\omega_{nm}^{\text{LDA}})_{;k^b} r_{nm}^a + i m_e \omega_{nm}^{\text{LDA}} (r_{nm}^a)_{;k^b} \\
&= i m_e \Delta_{nm}^b r_{nm}^a + i m_e \omega_{nm}^{\text{LDA}} (r_{nm}^a)_{;k^b} \quad \text{for } n \neq m,
\end{aligned} \quad (\text{A.53})$$

where we used Eq (1.77) and  $(r_{nm}^a)_{;k^b}$ , from Eq. (A.103).

Likewise for the scissored term,

$$\mathcal{V}_{nm}^{\mathcal{S}, a, \ell} = \frac{1}{2} (v^{\mathcal{S}, a} \mathcal{C}^{\ell} + \mathcal{C}^{\ell} v^{\mathcal{S}, a})_{nm} = \frac{1}{2} \sum_q (v_{nq}^{\mathcal{S}, a} \mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell} v_{qm}^{\mathcal{S}, a}) \quad (\text{A.54})$$

and

$$\begin{aligned} (\mathcal{V}_{nm}^{\mathcal{S},a})_{;k^b} &= \frac{1}{2} \sum_q \left( v_{nq}^{\mathcal{S},a} \mathcal{C}_{qm}^\ell + \mathcal{C}_{nq}^\ell v_{qm}^{\mathcal{S},a} \right)_{;k^b} \\ &= \frac{1}{2} \sum_q \left( (v_{nq}^{\mathcal{S},a})_{;k^b} \mathcal{C}_{qm}^\ell + v_{nq}^{\mathcal{S},a} (\mathcal{C}_{qm}^\ell)_{;k^b} + (\mathcal{C}_{nq}^\ell)_{;k^b} v_{qm}^{\mathcal{S},a} + \mathcal{C}_{nq}^\ell (v_{qm}^{\mathcal{S},a})_{;k^b} \right), \end{aligned} \quad (\text{A.55})$$

where  $v_{nm}^{\mathcal{S},a}(\mathbf{k})$  is given in Eq. (1.26) and  $(v_{nm}^{\mathcal{S},a})_{;k^b}$  is given in Eq. (A6) of Ref. [5] as

$$(v_{nm}^{\mathcal{S},a})_{;k^b} = i\Delta f_{mn}(r_{nm}^a)_{;k^b}. \quad (\text{A.56})$$

To evaluate  $(\mathcal{C}_{nm}^\ell)_{;k^a}$ , we use the fact that as  $\mathcal{C}^\ell(z)$  is only a function of the  $z$  coordinate, its commutator with  $\mathbf{r}$  is zero. Then,

$$\langle n\mathbf{k}| [r_e^a, \mathcal{C}^\ell(z)] |m\mathbf{k}'\rangle = \langle n\mathbf{k}| [r_e^a, \mathcal{C}^\ell(z)] |m\mathbf{k}'\rangle + \langle n\mathbf{k}| [r_i^a, \mathcal{C}^\ell(z)] |m\mathbf{k}'\rangle = 0. \quad (\text{A.57})$$

The interband part reduces to,

$$\begin{aligned} [r_e^a, \mathcal{C}^\ell(z)]_{nm} &= \sum_{q\mathbf{k}''} \left( \langle n\mathbf{k}| r_e^a |q\mathbf{k}''\rangle \langle q\mathbf{k}''| \mathcal{C}^\ell(z) |m\mathbf{k}'\rangle - \langle n\mathbf{k}| \mathcal{C}^\ell(z) |q\mathbf{k}''\rangle \langle q\mathbf{k}''| r_e^a |m\mathbf{k}'\rangle \right) \\ &= \sum_{q\mathbf{k}''} \delta(\mathbf{k} - \mathbf{k}'') \delta(\mathbf{k}' - \mathbf{k}'') \left( (1 - \delta_{qn}) \xi_{nq}^a \mathcal{C}_{qm}^\ell - (1 - \delta_{qm}) \mathcal{C}_{nq}^\ell \xi_{qm}^a \right) \\ &= \delta(\mathbf{k} - \mathbf{k}') \left( \sum_q \left( \xi_{nq}^a \mathcal{C}_{qm}^\ell - \mathcal{C}_{nq}^\ell \xi_{qm}^a \right) + \mathcal{C}_{nm}^\ell (\xi_{mm}^a - \xi_{nn}^a) \right), \end{aligned} \quad (\text{A.58})$$

where we used Eq. (A.15), and the  $\mathbf{k}$  and  $z$  dependence is implicitly understood. From Eq. (A.18) the intraband part is,

$$\langle n\mathbf{k}| [\hat{\mathbf{r}}_i, \mathcal{C}^\ell(z)] |m\mathbf{k}'\rangle = i\delta(\mathbf{k} - \mathbf{k}') (\mathcal{C}_{nm}^\ell)_{;\mathbf{k}}, \quad (\text{A.59})$$

then from Eq. (A.57)

$$\left( (\mathcal{C}_{nm}^\ell)_{;\mathbf{k}} - i \sum_q \left( \xi_{nq}^a \mathcal{C}_{qm}^\ell - \mathcal{C}_{nq}^\ell \xi_{qm}^a \right) - i\mathcal{C}_{nm}^\ell (\xi_{mm}^a - \xi_{nn}^a) \right) i\delta(\mathbf{k} - \mathbf{k}') = 0, \quad (\text{A.60})$$

which we can simplify,

$$\begin{aligned} (\mathcal{C}_{nm}^\ell)_{;\mathbf{k}} &= i \sum_q \left( \xi_{nq}^a \mathcal{C}_{qm}^\ell - \mathcal{C}_{nq}^\ell \xi_{qm}^a \right) + i\mathcal{C}_{nm}^\ell (\xi_{mm}^a - \xi_{nn}^a) \\ &= i \sum_{q \neq nm} \left( \xi_{nq}^a \mathcal{C}_{qm}^\ell - \mathcal{C}_{nq}^\ell \xi_{qm}^a \right) + i \left( \xi_{nn}^a \mathcal{C}_{nm}^\ell - \mathcal{C}_{nn}^\ell \xi_{nm}^a \right)_{q=n} + i \left( \xi_{nm}^a \mathcal{C}_{mm}^\ell - \mathcal{C}_{nm}^\ell \xi_{mm}^a \right)_{q=m} + i\mathcal{C}_{nm}^\ell (\xi_{mm}^a - \xi_{nn}^a) \\ &= i \sum_{q \neq nm} \left( \xi_{nq}^a \mathcal{C}_{qm}^\ell - \mathcal{C}_{nq}^\ell \xi_{qm}^a \right) + i\xi_{nm}^a (\mathcal{C}_{mm}^\ell - \mathcal{C}_{nn}^\ell) \\ &= i \sum_{q \neq nm} \left( r_{nq}^a \mathcal{C}_{qm}^\ell - \mathcal{C}_{nq}^\ell r_{qm}^a \right) + ir_{nm}^a (\mathcal{C}_{mm}^\ell - \mathcal{C}_{nn}^\ell) \\ &= i \left( \sum_{q \neq n} r_{nq}^a \mathcal{C}_{qm}^\ell - \sum_{q \neq m} \mathcal{C}_{nq}^\ell r_{qm}^a \right) + ir_{nm}^a (\mathcal{C}_{mm}^\ell - \mathcal{C}_{nn}^\ell), \end{aligned} \quad (\text{A.61})$$

since in  $\xi_{nm}^a$  we have that  $n \neq m$ , and we can replace it with  $r_{nm}^a$ . The matrix elements  $\mathcal{C}_{nm}^\ell(\mathbf{k})$  are calculated in Sec. A.3.

For the general case of

$$\langle n\mathbf{k}| [\hat{r}^a, \hat{\mathcal{G}}(\mathbf{r}, \mathbf{p})] |m\mathbf{k}'\rangle = \mathcal{U}_{nm}(\mathbf{k}), \quad (\text{A.62})$$

we can generalize our result to a more general expression,

$$(\mathcal{G}_{nm}(\mathbf{k}))_{;k^a} = \mathcal{U}_{nm}(\mathbf{k}) + i \sum_{q \neq (nm)} \left( r_{nq}^a(\mathbf{k}) \mathcal{G}_{qm}(\mathbf{k}) - \mathcal{G}_{nq}(\mathbf{k}) r_{qm}^a(\mathbf{k}) \right) + ir_{nm}^a(\mathbf{k}) (\mathcal{G}_{mm}(\mathbf{k}) - \mathcal{G}_{nn}(\mathbf{k})). \quad (\text{A.63})$$

## A.5 Generalized derivative $(\omega_n(\mathbf{k}))_{;\mathbf{k}}$

We obtain the generalized derivative  $(\omega_n(\mathbf{k}))_{;\mathbf{k}}$ . We start from

$$\langle n\mathbf{k}| \hat{H}_0^\Sigma |m\mathbf{k}'\rangle = \delta_{nm} \delta(\mathbf{k} - \mathbf{k}') \hbar \omega_m^\Sigma(\mathbf{k}), \quad (\text{A.64})$$

then for  $n = m$ , Eq. (A.19) yields

$$\begin{aligned} (H_{0,nn}^\Sigma)_{;\mathbf{k}} &= \nabla_{\mathbf{k}} H_{0,nn}^\Sigma(\mathbf{k}) - i H_{0,nn}^\Sigma(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{nn}(\mathbf{k})) \\ &= \hbar \nabla_{\mathbf{k}} \omega_m^\Sigma(\mathbf{k}), \end{aligned} \quad (\text{A.65})$$

and from Eq. (A.18),

$$\langle n\mathbf{k}| [\hat{\mathbf{r}}_i, \hat{H}_0] |m\mathbf{k}\rangle = i \delta_{nm} \hbar (\omega_m^\Sigma(\mathbf{k}))_{;\mathbf{k}} = i \delta_{nm} \hbar \nabla_{\mathbf{k}} \omega_m^\Sigma(\mathbf{k}), \quad (\text{A.66})$$

so

$$(\omega_n^\Sigma(\mathbf{k}))_{;\mathbf{k}} = \nabla_{\mathbf{k}} \omega_n^\Sigma(\mathbf{k}). \quad (\text{A.67})$$

From Eq. (1.19),

$$\langle n\mathbf{k}| [\hat{\mathbf{r}}, \hat{H}_0^\Sigma] |m\mathbf{k}\rangle = i \hbar \mathbf{v}_{nm}^\Sigma(\mathbf{k}), \quad (\text{A.68})$$

and substituting Eqs. (A.66) and (A.68) into

$$\langle n\mathbf{k}| [\hat{\mathbf{r}}, \hat{H}_0^\Sigma] |m\mathbf{k}\rangle = \langle n\mathbf{k}| [\hat{\mathbf{r}}_i, \hat{H}_0^\Sigma] |m\mathbf{k}\rangle + \langle n\mathbf{k}| [\hat{\mathbf{r}}_e, \hat{H}_0^\Sigma] |m\mathbf{k}\rangle, \quad (\text{A.69})$$

we get

$$i \hbar \mathbf{v}_{nm}^\Sigma(\mathbf{k}) = i \delta_{nm} \hbar \nabla_{\mathbf{k}} \omega_m^\Sigma(\mathbf{k}) + \omega_{mn}^\Sigma \mathbf{r}_{e,nm}(\mathbf{k}). \quad (\text{A.70})$$

For  $m = n$ , we have that

$$\begin{aligned} \nabla_{\mathbf{k}} \omega_n^\Sigma(\mathbf{k}) &= \mathbf{v}_{nn}^\Sigma(\mathbf{k}) \\ \nabla_{\mathbf{k}} (\omega^{\text{LDA}}_n(\mathbf{k}) + \frac{\Sigma}{\hbar} (1 - f_n)) &= \nabla_{\mathbf{k}} \omega^{\text{LDA}}_n(\mathbf{k}) \\ \nabla_{\mathbf{k}} \omega^{\text{LDA}}_n(\mathbf{k}) &= \mathbf{v}_{nn}^\Sigma(\mathbf{k}), \end{aligned} \quad (\text{A.71})$$

where we use Eq. (1.15). However, from Eq. (1.26),  $v_{nn}^\Sigma = 0$  so  $\mathbf{v}_{nn}^\Sigma = v^{\text{LDA}}_{nn}$ . Thus, from Eq. (A.67)

$$(\omega_n^\Sigma(\mathbf{k}))_{;k^a} = (\omega^{\text{LDA}}_n(\mathbf{k}))_{;k^a} = v_{nn}^{\text{LDA},a}(\mathbf{k}), \quad (\text{A.72})$$

which is the same for the LDA and scissored Hamiltonians;  $\mathbf{v}_{nn}^{\text{LDA}}(\mathbf{k})$  are the LDA velocities of the electron in state  $|n\mathbf{k}\rangle$ .

## A.6 Expressions for $\chi_{\text{surface}}^{\text{abc}}$ in terms of $\mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell}$

The prefactor of Eqs. (1.75) and (1.76) diverges as  $\tilde{\omega} \rightarrow 0$ . To remove this apparent divergence of  $\chi$ , we perform a partial fraction expansion in  $\tilde{\omega}$ .

### A.6.1 Intraband Contributions

For the intraband term of Eq. (1.75), we obtain

$$I = C \left[ -\frac{1}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} + \frac{2}{(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} + \frac{1}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\tilde{\omega}} \right] \\ - D \left[ -\frac{3}{2(\omega_{nm}^\Sigma)^3} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} + \frac{4}{(\omega_{nm}^\Sigma)^3} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} + \frac{1}{2(\omega_{nm}^\Sigma)^3} \frac{1}{\tilde{\omega}} - \frac{1}{2(\omega_{nm}^\Sigma)^2} \frac{1}{(\omega_{nm}^\Sigma - \tilde{\omega})^2} \right], \quad (\text{A.73})$$

where  $C = f_{mn} \mathcal{V}_{mn}^{\Sigma,\mathbf{a}}(r_{nm}^{\text{LDA,b}})_{;k^c}$ , and  $D = f_{mn} \mathcal{V}_{mn}^{\Sigma,\mathbf{a}} r_{nm}^b \Delta_{nm}^c$ .

Time-reversal symmetry leads to the following relationships:

$$\begin{aligned} \mathbf{r}_{mn}(\mathbf{k})|_{-\mathbf{k}} &= \mathbf{r}_{nm}(\mathbf{k})|_{\mathbf{k}}, \\ (\mathbf{r}_{mn})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (-\mathbf{r}_{nm})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \\ \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell}(\mathbf{k})|_{-\mathbf{k}} &= -\mathcal{V}_{nm}^{\Sigma,\mathbf{a},\ell}(\mathbf{k})|_{\mathbf{k}}, \\ (\mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (\mathcal{V}_{nm}^{\Sigma,\mathbf{a},\ell})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \\ \omega_{mn}^\Sigma(\mathbf{k})|_{-\mathbf{k}} &= \omega_{mn}^\Sigma(\mathbf{k})|_{\mathbf{k}}, \\ \Delta_{nm}^a(\mathbf{k})|_{-\mathbf{k}} &= -\Delta_{nm}^a(\mathbf{k})|_{\mathbf{k}}. \end{aligned} \quad (\text{A.74})$$

For a clean, cold semiconductor,  $f_n = 1$  for an occupied or valence ( $n = v$ ) band, and  $f_n = 0$  for an empty or conduction ( $n = c$ ) band independent of  $\mathbf{k}$ , and  $f_{nm} = -f_{mn}$ . Using the relationships above, we can show that the  $1/\omega$  terms cancel each other out. Therefore, all the remaining nonzero terms in expressions (A.73) are simple  $\omega$  and  $2\omega$  resonant denominators that are well behaved at  $\omega = 0$ .

To apply time-reversal invariance, we notice that the energy denominators are invariant under  $\mathbf{k} \rightarrow -\mathbf{k}$ , so we only need to review the numerators. So,

$$\begin{aligned} C &\rightarrow f_{mn} \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell} \left( r_{nm}^{\text{LDA,b}} \right)_{;k^c} |_{\mathbf{k}} + f_{mn} \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell} \left( r_{nm}^{\text{LDA,b}} \right)_{;k^c} |_{-\mathbf{k}} \\ &= f_{mn} \left[ \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell} \left( r_{nm}^{\text{LDA,b}} \right)_{;k^c} |_{\mathbf{k}} + \left( -\mathcal{V}_{nm}^{\Sigma,\mathbf{a},\ell} \right) \left( -r_{mn}^{\text{LDA,b}} \right)_{;k^c} |_{\mathbf{k}} \right] \\ &= f_{mn} \left[ \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell} \left( r_{nm}^{\text{LDA,b}} \right)_{;k^c} + \mathcal{V}_{nm}^{\Sigma,\mathbf{a},\ell} \left( r_{mn}^{\text{LDA,b}} \right)_{;k^c} \right] \\ &= f_{mn} \left[ \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell} \left( r_{nm}^{\text{LDA,b}} \right)_{;k^c} + \left( \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell} \left( r_{nm}^{\text{LDA,b}} \right)_{;k^c} \right)^* \right] \\ &= 2f_{mn} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell} \left( r_{nm}^{\text{LDA,b}} \right)_{;k^c} \right], \end{aligned} \quad (\text{A.75})$$

and likewise,

$$\begin{aligned}
D \rightarrow f_{mn} \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \Delta_{nm}^c |_{\mathbf{k}} + f_{mn} \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \Delta_{nm}^c |_{-\mathbf{k}} \\
= f_{mn} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \Delta_{nm}^c |_{\mathbf{k}} + (-\mathcal{V}_{nm}^{\Sigma,a,\ell}) r_{mn}^{\text{LDA},b} (-\Delta_{nm}^c) |_{\mathbf{k}} \right] \\
= f_{mn} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} + \mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b} \right] \Delta_{nm}^c \\
= f_{mn} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} + (\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b})^* \right] \Delta_{nm}^c \\
= 2f_{mn} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \right] \Delta_{nm}^c. \tag{A.76}
\end{aligned}$$

The last term in the second line of Eq. (A.73) is dealt with as follows,

$$\begin{aligned}
\frac{D}{2(\omega_{nm}^{\Sigma})^2} \frac{1}{(\omega_{nm}^{\Sigma} - \tilde{\omega})^2} &= \frac{f_{mn}}{2} \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{(\omega_{nm}^{\Sigma})^2} \frac{\Delta_{nm}^c}{(\omega_{nm}^{\Sigma} - \tilde{\omega})^2} = -\frac{f_{mn}}{2} \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{(\omega_{nm}^{\Sigma})^2} \left( \frac{1}{\omega_{nm}^{\Sigma} - \tilde{\omega}} \right)_{;k^c} \\
&= \frac{f_{mn}}{2} \left( \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{(\omega_{nm}^{\Sigma})^2} \right)_{;k^c} \frac{1}{\omega_{nm}^{\Sigma} - \tilde{\omega}}, \tag{A.77}
\end{aligned}$$

where we used Eq. (1.77). For the last line, we performed an integration by parts over the Brillouin zone where the contribution from the edges vanishes [71]. Now, we apply the chain rule, to get

$$\left( \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^{\Sigma})^2} \right)_{;k^c} = \frac{r_{nm}^{\text{LDA},b}}{(\omega_{nm}^{\Sigma})^2} \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \right)_{;k^c} + \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{(\omega_{nm}^{\Sigma})^2} \left( r_{nm}^{\text{LDA},b} \right)_{;k^c} - \frac{2\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^{\Sigma})^3} \left( \omega_{nm}^{\Sigma} \right)_{;k^c}, \tag{A.78}$$

and work the time-reversal on each term. The first term is reduced to

$$\begin{aligned}
\frac{r_{nm}^{\text{LDA},b}}{(\omega_{nm}^{\Sigma})^2} \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \right)_{;k^c} |_{\mathbf{k}} + \frac{r_{nm}^{\text{LDA},b}}{(\omega_{nm}^{\Sigma})^2} \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \right)_{;k^c} |_{-\mathbf{k}} &= \frac{r_{nm}^{\text{LDA},b}}{(\omega_{nm}^{\Sigma})^2} \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \right)_{;k^c} |_{\mathbf{k}} + \frac{r_{mn}^{\text{LDA},b}}{(\omega_{nm}^{\Sigma})^2} \left( \mathcal{V}_{nm}^{\Sigma,a,\ell} \right)_{;k^c} |_{\mathbf{k}} \\
&= \frac{1}{(\omega_{nm}^{\Sigma})^2} \left[ r_{nm}^{\text{LDA},b} \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \right)_{;k^c} + \left( r_{nm}^{\text{LDA},b} \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \right)_{;k^c} \right)^* \right] \\
&= \frac{2}{(\omega_{nm}^{\Sigma})^2} \operatorname{Re} \left[ r_{nm}^{\text{LDA},b} \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \right)_{;k^c} \right], \tag{A.79}
\end{aligned}$$

the second term is reduced to

$$\begin{aligned}
\frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{(\omega_{nm}^{\Sigma})^2} \left( r_{nm}^{\text{LDA},b} \right)_{;k^c} |_{\mathbf{k}} + \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{(\omega_{nm}^{\Sigma})^2} \left( r_{nm}^{\text{LDA},b} \right)_{;k^c} |_{-\mathbf{k}} &= \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{(\omega_{nm}^{\Sigma})^2} \left( r_{nm}^{\text{LDA},b} \right)_{;k^c} |_{\mathbf{k}} + \frac{\mathcal{V}_{nm}^{\Sigma,a,\ell}}{(\omega_{nm}^{\Sigma})^2} \left( r_{mn}^{\text{LDA},b} \right)_{;k^c} |_{\mathbf{k}} \\
&= \frac{1}{(\omega_{nm}^{\Sigma})^2} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} \left( r_{nm}^{\text{LDA},b} \right)_{;k^c} + \left( \mathcal{V}_{mn}^{\Sigma,a,\ell} \left( r_{nm}^{\text{LDA},b} \right)_{;k^c} \right)^* \right] \\
&= \frac{2}{(\omega_{nm}^{\Sigma})^2} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} \left( r_{nm}^{\text{LDA},b} \right)_{;k^c} \right], \tag{A.80}
\end{aligned}$$

and by using (1.77), the third term is reduced to

$$\begin{aligned}
& \frac{2\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^3} (\omega_{nm}^\Sigma)_{;k^c} |_{\mathbf{k}} + \frac{2\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^3} (\omega_{nm}^\Sigma)_{;k^c} |_{-\mathbf{k}} = \frac{2\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^3} \Delta_{nm}^c |_{\mathbf{k}} + \frac{2\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^3} \Delta_{nm}^c |_{-\mathbf{k}} \\
& = \frac{2\mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^3} \Delta_{nm}^c |_{\mathbf{k}} + \frac{2\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^3} \Delta_{nm}^c |_{\mathbf{k}} \\
& = \frac{2}{(\omega_{nm}^\Sigma)^3} [\mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b} + (\mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b})^*] \Delta_{nm}^c \\
& = \frac{4}{(\omega_{nm}^\Sigma)^3} \operatorname{Re} [\mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b}] \Delta_{nm}^c. \quad (\text{A.81})
\end{aligned}$$

Combining the results from (A.79), (A.80), and (A.81) into (A.78),

$$\begin{aligned}
& \frac{f_{mn}}{2} \left[ \left( \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^2} \right)_{;k^c} |_{\mathbf{k}} + \left( \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}}{(\omega_{nm}^\Sigma)^2} \right)_{;k^c} |_{-\mathbf{k}} \right] \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} = \\
& \left( 2 \operatorname{Re} [r_{nm}^{\text{LDA},b} (\mathcal{V}_{mn}^{\Sigma,a,\ell})_{;k^c}] + 2 \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c}] - \frac{4}{\omega_{nm}^\Sigma} \operatorname{Re} [\mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b}] \Delta_{nm}^c \right) \frac{f_{mn}}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}}. \quad (\text{A.82})
\end{aligned}$$

We substitute (A.75), (A.76), and (A.82) in (A.73),

$$\begin{aligned}
I = & \left[ -\frac{2f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c}]}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} + \frac{4f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c}]}{(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \right] \\
& + \left[ \frac{6f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}] \Delta_{nm}^c}{2(\omega_{nm}^\Sigma)^3} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} - \frac{8f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}] \Delta_{nm}^c}{(\omega_{nm}^\Sigma)^3} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \right. \\
& \left. + \frac{f_{mn} \left( 2 \operatorname{Re} [r_{nm}^{\text{LDA},b} (\mathcal{V}_{mn}^{\Sigma,a,\ell})_{;k^c}] + 2 \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c}] - \frac{4}{\omega_{nm}^\Sigma} \operatorname{Re} [\mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b}] \Delta_{nm}^c \right)}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} \right].
\end{aligned}$$

If we simplify,

$$\begin{aligned}
I = & -\frac{2f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c}]}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} + \frac{4f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c}]}{(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \\
& + \frac{6f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}] \Delta_{nm}^c}{2(\omega_{nm}^\Sigma)^3} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} - \frac{8f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b}] \Delta_{nm}^c}{(\omega_{nm}^\Sigma)^3} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \\
& + \frac{2f_{mn} \operatorname{Re} [r_{nm}^{\text{LDA},b} (\mathcal{V}_{mn}^{\Sigma,a,\ell})_{;k^c}]}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} \\
& + \frac{2f_{mn} \operatorname{Re} [\mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c}]}{2(\omega_{nm}^\Sigma)^2} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} \\
& - \frac{4f_{mn} \operatorname{Re} [\mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b}] \Delta_{nm}^c}{2(\omega_{nm}^\Sigma)^3} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}}, \quad (\text{A.83})
\end{aligned}$$

we conveniently collect the terms in columns of  $\omega$  and  $2\omega$ . We can now express the susceptibility in terms of  $\omega$  and  $2\omega$ . Separating the  $2\omega$  terms and substituting in the equation above,

$$\begin{aligned} I_{2\omega} &= -\frac{e^3}{\hbar^2} \sum_{mn\mathbf{k}} \left[ \frac{4f_{mn} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c} \right]}{(\omega_{nm}^\Sigma)^2} - \frac{8f_{mn} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \right] \Delta_{nm}^c}{(\omega_{nm}^\Sigma)^3} \right] \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \\ &= -\frac{e^3}{\hbar^2} \sum_{mn\mathbf{k}} \frac{4f_{mn}}{(\omega_{nm}^\Sigma)^2} \left[ \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c} \right] - \frac{2 \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \right] \Delta_{nm}^c}{\omega_{nm}^\Sigma} \right] \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}}. \quad (\text{A.84}) \end{aligned}$$

We can express the energies in terms of transitions between bands. Therefore,  $\omega_{nm}^\Sigma = \omega_{cv}^\Sigma$  for transitions between conduction and valence bands. To take the limit  $\eta \rightarrow 0$ , we use

$$\lim_{\eta \rightarrow 0} \frac{1}{x \pm i\eta} = P \frac{1}{x} \mp i\pi\delta(x), \quad (\text{A.85})$$

and can finally rewrite (A.84) in the desired form,

$$\operatorname{Im}[\chi_{i,a,\ell bc,2\omega}^{s,\ell}] = -\frac{\pi|e|^3}{2\hbar^2} \sum_{vc\mathbf{k}} \frac{4}{(\omega_{cv}^\Sigma)^2} \left( \operatorname{Re} \left[ \mathcal{V}_{vc}^{\Sigma,a,\ell} (r_{cv}^{\text{LDA},b})_{;k^c} \right] - \frac{2 \operatorname{Re} \left[ \mathcal{V}_{vc}^{\Sigma,a,\ell} r_{cv}^{\text{LDA},b} \right] \Delta_{cv}^c}{\omega_{cv}^\Sigma} \right) \delta(\omega_{cv}^\Sigma - 2\omega). \quad (\text{A.86})$$

where we added a  $1/2$  from the sum over  $\mathbf{k} \rightarrow -\mathbf{k}$ . We do the same for the  $\tilde{\omega}$  terms in (A.83) to obtain

$$\begin{aligned} I_\omega &= -\frac{e^3}{2\hbar^2} \sum_{nm\mathbf{k}} \left[ -\frac{2f_{mn} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c} \right]}{(\omega_{nm}^\Sigma)^2} + \frac{6f_{mn} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \right] \Delta_{nm}^c}{(\omega_{nm}^\Sigma)^3} \right. \\ &\quad \left. + \frac{2f_{mn} \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} (r_{nm}^{\text{LDA},b})_{;k^c} \right]}{(\omega_{nm}^\Sigma)^2} - \frac{4f_{mn} \operatorname{Re} \left[ \mathcal{V}_{nm}^{\Sigma,a,\ell} r_{mn}^{\text{LDA},b} \right] \Delta_{nm}^c}{(\omega_{nm}^\Sigma)^3} \right. \\ &\quad \left. + \frac{2f_{mn} \operatorname{Re} \left[ r_{nm}^{\text{LDA},b} (\mathcal{V}_{mn}^{\Sigma,a,\ell})_{;k^c} \right]}{(\omega_{nm}^\Sigma)^2} \right] \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}}. \quad (\text{A.87}) \end{aligned}$$

We reduce in the same way as (A.84),

$$I_\omega = -\frac{e^3}{2\hbar^2} \sum_{nm\mathbf{k}} \frac{f_{mn}}{(\omega_{nm}^\Sigma)^2} \left[ 2 \operatorname{Re} \left[ r_{nm}^{\text{LDA},b} (\mathcal{V}_{mn}^{\Sigma,a,\ell})_{;k^c} \right] + \frac{2 \operatorname{Re} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nm}^{\text{LDA},b} \right] \Delta_{nm}^c}{\omega_{nm}^\Sigma} \right] \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}}, \quad (\text{A.88})$$

and using (A.85) we obtain our final form,

$$\operatorname{Im}[\chi_{i,a,\ell bc,\omega}^{s,\ell}] = -\frac{\pi|e|^3}{2\hbar^2} \sum_{cv} \frac{1}{(\omega_{cv}^\Sigma)^2} \left( \operatorname{Re} \left[ r_{cv}^{\text{LDA},b} (\mathcal{V}_{vc}^{\Sigma,a,\ell})_{;k^c} \right] + \frac{\operatorname{Re} \left[ \mathcal{V}_{vc}^{\Sigma,a,\ell} r_{cv}^{\text{LDA},b} \right] \Delta_{cv}^c}{\omega_{cv}^\Sigma} \right) \delta(\omega_{cv}^\Sigma - \omega), \quad (\text{A.89})$$

where again we added a  $1/2$  from the sum over  $\mathbf{k} \rightarrow -\mathbf{k}$ .

### A.6.2 Interband Contributions

We follow an equivalent procedure for the interband contribution. From Eq. (1.76) we have

$$E = A \left[ -\frac{1}{2\omega_{lm}^\Sigma(2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{lm}^\Sigma - \tilde{\omega}} + \frac{2}{\omega_{nm}^\Sigma(2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} + \frac{1}{2\omega_{lm}^\Sigma \omega_{nm}^\Sigma} \frac{1}{\tilde{\omega}} \right] \\ - B \left[ -\frac{1}{2\omega_{nl}^\Sigma(2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nl}^\Sigma - \tilde{\omega}} + \frac{2}{\omega_{nm}^\Sigma(2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} + \frac{1}{2\omega_{nl}^\Sigma \omega_{nm}^\Sigma} \frac{1}{\tilde{\omega}} \right], \quad (\text{A.90})$$

where  $A = f_{ml} \mathcal{V}_{mn}^{\Sigma,a} r_{nl}^c r_{lm}^b$  and  $B = f_{ln} \mathcal{V}_{mn}^{\Sigma,a} r_{nl}^b r_{lm}^c$ .

Just as above, the  $\frac{1}{\tilde{\omega}}$  terms cancel out. We multiply out the  $A$  and  $B$  terms,

$$E = \left[ -\frac{A}{2\omega_{lm}^\Sigma(2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{lm}^\Sigma - \tilde{\omega}} + \frac{2A}{\omega_{nm}^\Sigma(2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \right] \\ + \left[ \frac{B}{2\omega_{nl}^\Sigma(2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nl}^\Sigma - \tilde{\omega}} - \frac{2B}{\omega_{nm}^\Sigma(2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \right]. \quad (\text{A.91})$$

As before, we notice that the energy denominators are invariant under  $\mathbf{k} \rightarrow -\mathbf{k}$  so we need only to review the numerators. Starting with  $A$ ,

$$A \rightarrow f_{ml} \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b |_{\mathbf{k}} + f_{ml} \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b |_{-\mathbf{k}} \\ = f_{ml} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b |_{\mathbf{k}} + (-\mathcal{V}_{nm}^{\Sigma,a,\ell}) r_{ln}^c r_{ml}^b |_{\mathbf{k}} \right] \\ = f_{ml} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b - \mathcal{V}_{nm}^{\Sigma,a,\ell} r_{ln}^c r_{ml}^b \right] \\ = f_{ml} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b - (\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b)^* \right] \\ = -2f_{ml} \text{Im} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b \right],$$

then  $B$ ,

$$B \rightarrow f_{ln} \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c |_{\mathbf{k}} + f_{ln} \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c |_{-\mathbf{k}} \\ = f_{ln} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c |_{\mathbf{k}} + (-\mathcal{V}_{nm}^{\Sigma,a,\ell}) r_{ln}^b r_{ml}^c |_{\mathbf{k}} \right] \\ = f_{ln} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c - \mathcal{V}_{nm}^{\Sigma,a,\ell} r_{ln}^b r_{ml}^c \right] \\ = f_{ln} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c - (\mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c)^* \right] \\ = -2f_{ln} \text{Im} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c \right].$$

We then substitute in (A.91),

$$E = \left[ \frac{2f_{ml} \text{Im} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b \right]}{2\omega_{lm}^\Sigma(2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{lm}^\Sigma - \tilde{\omega}} - \frac{4f_{ml} \text{Im} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^c r_{lm}^b \right]}{\omega_{nm}^\Sigma(2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \right. \\ \left. - \frac{2f_{ln} \text{Im} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c \right]}{2\omega_{nl}^\Sigma(2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nl}^\Sigma - \tilde{\omega}} + \frac{4f_{ln} \text{Im} \left[ \mathcal{V}_{mn}^{\Sigma,a,\ell} r_{nl}^b r_{lm}^c \right]}{\omega_{nm}^\Sigma(2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \right].$$

We manipulate indices and simplify,

$$\begin{aligned}
E &= \left[ \frac{f_{ml} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} r_{nl}^c r_{lm}^b]}{\omega_{lm}^\Sigma (2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{lm}^\Sigma - \tilde{\omega}} - \frac{f_{ln} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} r_{nl}^b r_{lm}^c]}{\omega_{nl}^\Sigma (2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma)} \frac{1}{\omega_{nl}^\Sigma - \tilde{\omega}} \right] \\
&\quad + \left[ \frac{f_{ln} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} r_{nl}^b r_{lm}^c]}{2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma} - \frac{f_{ml} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} r_{nl}^c r_{lm}^b]}{2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma} \right] \frac{4}{\omega_{nm}^\Sigma} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}} \\
&= \left[ \frac{f_{mn} \operatorname{Im} [\mathcal{V}_{ml}^{\Sigma, a, \ell} r_{ln}^c r_{nm}^b]}{2\omega_{nm}^\Sigma - \omega_{lm}^\Sigma} - \frac{f_{mn} \operatorname{Im} [\mathcal{V}_{ln}^{\Sigma, a, \ell} r_{nm}^b r_{ml}^c]}{2\omega_{nm}^\Sigma - \omega_{nl}^\Sigma} \right] \frac{1}{\omega_{nm}^\Sigma} \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} \\
&\quad + \left[ \frac{f_{ln} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} r_{nl}^b r_{lm}^c]}{2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma} - \frac{f_{ml} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} r_{nl}^c r_{lm}^b]}{2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma} \right] \frac{4}{\omega_{nm}^\Sigma} \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}},
\end{aligned}$$

and substitute in (1.76),

$$\begin{aligned}
I &= -\frac{e^3}{2\hbar^2} \sum_{nm} \frac{1}{\omega_{nm}^\Sigma} \left[ \frac{f_{mn} \operatorname{Im} [\mathcal{V}_{ml}^{\Sigma, a, \ell} \{r_{ln}^c r_{nm}^b\}]}{2\omega_{nm}^\Sigma - \omega_{lm}^\Sigma} - \frac{f_{mn} \operatorname{Im} [\mathcal{V}_{ln}^{\Sigma, a, \ell} \{r_{nm}^b r_{ml}^c\}]}{2\omega_{nm}^\Sigma - \omega_{nl}^\Sigma} \right] \frac{1}{\omega_{nm}^\Sigma - \tilde{\omega}} \\
&\quad + 4 \left[ \frac{f_{ln} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} \{r_{nl}^b r_{lm}^c\}]}{2\omega_{nl}^\Sigma - \omega_{nm}^\Sigma} - \frac{f_{ml} \operatorname{Im} [\mathcal{V}_{mn}^{\Sigma, a, \ell} \{r_{nl}^c r_{lm}^b\}]}{2\omega_{lm}^\Sigma - \omega_{nm}^\Sigma} \right] \frac{1}{\omega_{nm}^\Sigma - 2\tilde{\omega}}.
\end{aligned}$$

Finally, we take  $n = c$ ,  $m = v$ , and  $l = q$  and substitute,

$$\begin{aligned}
I &= -\frac{e^3}{2\hbar^2} \sum_{cv} \frac{1}{\omega_{cv}^\Sigma} \left( \left[ \frac{f_{vc} \operatorname{Im} [\mathcal{V}_{vq}^{\Sigma, a, \ell} \{r_{qc}^c r_{cv}^b\}]}{2\omega_{cv}^\Sigma - \omega_{qv}^\Sigma} - \frac{f_{vc} \operatorname{Im} [\mathcal{V}_{qc}^{\Sigma, a, \ell} \{r_{cv}^b r_{vq}^c\}]}{2\omega_{cv}^\Sigma - \omega_{cq}^\Sigma} \right] \frac{1}{\omega_{cv}^\Sigma - \tilde{\omega}} \right. \\
&\quad \left. + 4 \left[ \frac{f_{qc} \operatorname{Im} [\mathcal{V}_{vc}^{\Sigma, a, \ell} \{r_{cq}^b r_{qv}^c\}]}{2\omega_{cq}^\Sigma - \omega_{cv}^\Sigma} - \frac{f_{vq} \operatorname{Im} [\mathcal{V}_{vc}^{\Sigma, a, \ell} \{r_{cq}^c r_{qv}^b\}]}{2\omega_{qv}^\Sigma - \omega_{cv}^\Sigma} \right] \frac{1}{\omega_{cv}^\Sigma - 2\tilde{\omega}} \right) \\
&= \frac{e^3}{2\hbar^2} \sum_{cv} \frac{1}{\omega_{cv}^\Sigma} \left( \left[ \frac{\operatorname{Im} [\mathcal{V}_{qc}^{\Sigma, a, \ell} \{r_{cv}^b r_{vq}^c\}]}{2\omega_{cv}^\Sigma - \omega_{cq}^\Sigma} - \frac{\operatorname{Im} [\mathcal{V}_{vq}^{\Sigma, a, \ell} \{r_{qc}^c r_{cv}^b\}]}{2\omega_{cv}^\Sigma - \omega_{qv}^\Sigma} \right] \frac{1}{\omega_{cv}^\Sigma - \tilde{\omega}} \right. \\
&\quad \left. - 4 \left[ \frac{f_{qc} \operatorname{Im} [\mathcal{V}_{vc}^{\Sigma, a, \ell} \{r_{cq}^b r_{qv}^c\}]}{2\omega_{cq}^\Sigma - \omega_{cv}^\Sigma} - \frac{f_{vq} \operatorname{Im} [\mathcal{V}_{vc}^{\Sigma, a, \ell} \{r_{cq}^c r_{qv}^b\}]}{2\omega_{qv}^\Sigma - \omega_{cv}^\Sigma} \right] \frac{1}{\omega_{cv}^\Sigma - 2\tilde{\omega}} \right).
\end{aligned}$$

Add appendix A from article and modify the I terms to be chis to present the final chis from the article We use (A.85),

$$\begin{aligned}
I &= \frac{\pi |e^3|}{2\hbar^2} \sum_{cv} \frac{1}{\omega_{cv}^\Sigma} \left( \left[ \frac{\operatorname{Im} [\mathcal{V}_{qc}^{\Sigma, a, \ell} \{r_{cv}^b r_{vq}^c\}]}{2\omega_{cv}^\Sigma - \omega_{cq}^\Sigma} - \frac{\operatorname{Im} [\mathcal{V}_{vq}^{\Sigma, a, \ell} \{r_{qc}^c r_{cv}^b\}]}{2\omega_{cv}^\Sigma - \omega_{qv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - \omega) \right. \\
&\quad \left. - 4 \left[ \frac{f_{qc} \operatorname{Im} [\mathcal{V}_{vc}^{\Sigma, a, \ell} \{r_{cq}^b r_{qv}^c\}]}{2\omega_{cq}^\Sigma - \omega_{cv}^\Sigma} - \frac{f_{vq} \operatorname{Im} [\mathcal{V}_{vc}^{\Sigma, a, \ell} \{r_{cq}^c r_{qv}^b\}]}{2\omega_{qv}^\Sigma - \omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - 2\omega) \right),
\end{aligned}$$

and recognize that for the  $1\omega$  terms,  $q \neq (v, c)$ , and for the  $2\omega$  q can have two distinct values such that,

$$I = \frac{\pi|e^3|}{2\hbar^2} \sum_{cv} \frac{1}{\omega_{cv}^\Sigma} \left( \sum_{q \neq (v,c)} \left[ \frac{\text{Im} [\mathcal{V}_{qc}^{\Sigma,a,\ell} \{r_{cv}^b r_{vq}^c\}]}{2\omega_{cv}^\Sigma - \omega_{cq}^\Sigma} - \frac{\text{Im} [\mathcal{V}_{vq}^{\Sigma,a,\ell} \{r_{qc}^c r_{cv}^b\}]}{2\omega_{cv}^\Sigma - \omega_{qv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - \omega) \right. \\ \left. - 4 \left[ \sum_{v' \neq v} \frac{\text{Im} [\mathcal{V}_{vc}^{\Sigma,a,\ell} \{r_{cv'}^b r_{v'v}^c\}]}{2\omega_{cv'}^\Sigma - \omega_{cv}^\Sigma} - \sum_{c' \neq c} \frac{\text{Im} [\mathcal{V}_{vc}^{\Sigma,a,\ell} \{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v}^\Sigma - \omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - 2\omega) \right).$$

## A.7 Generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$ for nonlocal potentials

We will derive the generalized derivative  $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$  for the case of a nonlocal potential in the Hamiltonian. We start from Eq. (1.25),

$$[r^a, v^{\text{LDA},b}] = [r^a, v^b] + [r^a, v^{\text{nl},b}] = \frac{i\hbar}{m_e} \delta_{ab} + [r^a, v^{\text{nl},b}] \equiv \tau^{ab}, \quad (\text{A.92})$$

where we used the fact that  $[r^a, p^b] = i\hbar \delta_{ab}$ . Then,

$$\langle n\mathbf{k}|[r^a, v^{\text{LDA},b}]|m\mathbf{k}'\rangle = \langle n\mathbf{k}|\tau^{ab}|m\mathbf{k}'\rangle = \tau_{nm}^{ab}(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.93})$$

so

$$\langle n\mathbf{k}|[r_i^a, v^{\text{LDA},b}]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|[r_e^a, v^{\text{LDA},b}]|m\mathbf{k}'\rangle = \tau_{nm}^{ab}(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.94})$$

where the matrix elements of  $\tau_{nm}^{ab}(\mathbf{k})$  are calculated in Sec. A.8. From Eq. (A.18) and (A.19)

$$\langle n\mathbf{k}|[r_i^a, v^{\text{LDA}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k} - \mathbf{k}') (v_{nm}^{\text{LDA},b})_{;k^a} \quad (\text{A.95})$$

$$(v_{nm}^{\text{LDA},b})_{;k^a} = \nabla_{k^a} v_{nm}^{\text{LDA},b}(\mathbf{k}) - iv_{nm}^{\text{LDA},b}(\mathbf{k}) (\xi_{nn}^a(\mathbf{k}) - \xi_{mm}^a(\mathbf{k})), \quad (\text{A.96})$$

and

$$\begin{aligned} \langle n\mathbf{k}|[r_e^a, v^{\text{LDA},b}]|m\mathbf{k}'\rangle &= \sum_{\ell\mathbf{k}''} \left( \langle n\mathbf{k}|r_e^a|\ell\mathbf{k}''\rangle \langle \ell\mathbf{k}''|v^{\text{LDA},b}|m\mathbf{k}'\rangle - \langle n\mathbf{k}|v^{\text{LDA},b}|\ell\mathbf{k}''\rangle \langle \ell\mathbf{k}''|r_e^a|m\mathbf{k}'\rangle \right) \\ &= \sum_{\ell\mathbf{k}''} \left( (1 - \delta_{n\ell})\delta(\mathbf{k} - \mathbf{k}'')\xi_{n\ell}^a \delta(\mathbf{k}'' - \mathbf{k}') v_{\ell m}^{\text{LDA},b} - \delta(\mathbf{k} - \mathbf{k}'')v_{n\ell}^{\text{LDA},b}(1 - \delta_{\ell m})\delta(\mathbf{k}'' - \mathbf{k}')\xi_{\ell m}^a \right) \\ &= \delta(\mathbf{k} - \mathbf{k}') \sum_{\ell} \left( (1 - \delta_{n\ell})\xi_{n\ell}^a v_{\ell m}^{\text{LDA},b} - (1 - \delta_{\ell m})v_{n\ell}^{\text{LDA},b}\xi_{\ell m}^a \right) \\ &= \delta(\mathbf{k} - \mathbf{k}') \left( \sum_{\ell} \left( \xi_{n\ell}^a v_{\ell m}^{\text{LDA},b} - v_{n\ell}^{\text{LDA},b}\xi_{\ell m}^a \right) + v_{nm}^{\text{LDA},b}(\xi_{mm}^a - \xi_{nn}^a) \right). \end{aligned} \quad (\text{A.97})$$

Using Eqs. (A.95) and (A.97) into Eq. (A.94) gives

$$i\delta(\mathbf{k} - \mathbf{k}') \left( (v_{nm}^{\text{LDA},b})_{;k^a} - i \sum_{\ell} \left( \xi_{n\ell}^a v_{\ell m}^{\text{LDA},b} - v_{n\ell}^{\text{LDA},b}\xi_{\ell m}^a \right) - iv_{nm}^{\text{LDA},b}(\xi_{mm}^a - \xi_{nn}^a) \right) = \tau_{nm}^{ab}(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.98})$$

then

$$(v_{nm}^{\text{LDA,b}})_{;k^a} = -i\tau_{nm}^{ab} + i \sum_{\ell} \left( \xi_{n\ell}^a v_{\ell m}^{\text{LDA,b}} - v_{n\ell}^{\text{LDA,b}} \xi_{\ell m}^a \right) + iv_{nm}^{\text{LDA,b}} (\xi_{mm}^a - \xi_{nn}^a), \quad (\text{A.99})$$

and from Eq. (A.96),

$$\nabla_{k^a} v_{nm}^{\text{LDA,b}} = -i\tau_{nm}^{ab} + i \sum_{\ell} \left( \xi_{n\ell}^a v_{\ell m}^{\text{LDA,b}} - v_{n\ell}^{\text{LDA,b}} \xi_{\ell m}^a \right). \quad (\text{A.100})$$

Now, there are two cases. We use Eq. (1.30).

### A.7.1 Case $n = m$

$$\begin{aligned} \nabla_{k^a} v_{nn}^{\text{LDA,b}} &= -i\tau_{nn}^{ab} + i \sum_{\ell} \left( \xi_{n\ell}^a v_{\ell n}^{\text{LDA,b}} - v_{n\ell}^{\text{LDA,b}} \xi_{\ell n}^a \right) \\ &= -i\tau_{nn}^{ab} - \sum_{\ell \neq n} \left( r_{n\ell}^a \omega_{\ell n}^{\text{LDA}} r_{\ell n}^b - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^b r_{\ell n}^a \right) \\ &= -i\tau_{nn}^{ab} - \sum_{\ell \neq n} \omega_{\ell n}^{\text{LDA}} \left( r_{n\ell}^a r_{\ell n}^b - r_{n\ell}^b r_{\ell n}^a \right), \end{aligned} \quad (\text{A.101})$$

since the  $\ell = n$  cancels out. This would give the generalization for the inverse effective mass tensor  $(m_n^{-1})_{ab}$  for nonlocal potentials. Indeed, if we neglect the commutator of  $\mathbf{v}^{\text{nl}}$  in Eq. (A.92), we obtain  $-i\tau_{nn}^{ab} = \hbar/m_e \delta_{ab}$  thus obtaining the familiar expression of  $(m_n^{-1})_{ab}$  [71].

### A.7.2 Case $n \neq m$

$$\begin{aligned} (v_{nm}^{\text{LDA,b}})_{;k^a} &= -i\tau_{nm}^{ab} + i \sum_{\ell \neq m \neq n} \left( \xi_{n\ell}^a v_{\ell m}^{\text{LDA,b}} - v_{n\ell}^{\text{LDA,b}} \xi_{\ell m}^a \right) + i \left( \xi_{nm}^a v_{mm}^{\text{LDA,b}} - v_{nm}^{\text{LDA,b}} \xi_{mm}^a \right) \\ &\quad + i \left( \xi_{nn}^a v_{nm}^{\text{LDA,b}} - v_{nn}^{\text{LDA,b}} \xi_{nm}^a \right) + iv_{nm}^{\text{LDA,b}} (\xi_{mm}^a - \xi_{nn}^a) \\ &= -i\tau_{nm}^{ab} - \sum_{\ell} \left( \omega_{\ell m}^{\text{LDA}} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^b r_{\ell m}^a \right) + i\xi_{nm}^a (v_{mm}^{\text{LDA,b}} - v_{nn}^{\text{LDA,b}}) \\ &= -i\tau_{nm}^{ab} - \sum_{\ell} \left( \omega_{\ell m}^{\text{LDA}} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^b r_{\ell m}^a \right) + ir_{nm}^a \Delta_{mn}^b, \end{aligned} \quad (\text{A.102})$$

where we use  $\Delta_{mn}^a$  of Eq. (1.77). Now, for  $n \neq m$ , Eqs. (1.30), (A.72) and (A.102) and the chain rule, give

$$\begin{aligned}
(r_{nm}^b)_{;k^a} &= \left( \frac{v_{nm}^{\text{LDA},b}}{i\omega_{nm}^{\text{LDA}}} \right)_{;k^a} = \frac{1}{i\omega_{nm}^{\text{LDA}}} (v_{nm}^{\text{LDA},b})_{;k^a} - \frac{v_{nm}^{\text{LDA},b}}{i(\omega_{nm}^{\text{LDA}})^2} (\omega_{nm}^{\text{LDA}})_{;k^a} \\
&= -i\tau_{nm}^{ab} + \frac{i}{\omega_{nm}^{\text{LDA}}} \sum_{\ell} \left( \omega_{\ell m}^{\text{LDA}} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^b r_{\ell m}^a \right) + \frac{r_{nm}^a \Delta_{mn}^b}{\omega_{nm}^{\text{LDA}}} - \frac{r_{nm}^b}{\omega_{nm}^{\text{LDA}}} (\omega_{nm}^{\text{LDA}})_{;k^a} \\
&= -i\tau_{nm}^{ab} + \frac{i}{\omega_{nm}^{\text{LDA}}} \sum_{\ell} \left( \omega_{\ell m}^{\text{LDA}} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^b r_{\ell m}^a \right) + \frac{r_{nm}^a \Delta_{mn}^b}{\omega_{nm}^{\text{LDA}}} - \frac{r_{nm}^b}{\omega_{nm}^{\text{LDA}}} \frac{v_{nn}^{\text{LDA},a} - v_{mm}^{\text{LDA},a}}{m_e} \\
&= -i\tau_{nm}^{ab} + \frac{r_{nm}^a \Delta_{mn}^b + r_{nm}^b \Delta_{mn}^a}{\omega_{nm}^{\text{LDA}}} + \frac{i}{\omega_{nm}^{\text{LDA}}} \sum_{\ell} \left( \omega_{\ell m}^{\text{LDA}} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^b r_{\ell m}^a \right), \quad (\text{A.103})
\end{aligned}$$

where the  $-i\tau_{nm}^{ab}$  term, generalizes the usual expresion of  $\mathbf{r}_{nm;\mathbf{k}}$  for local Hamiltonians,[4, 44, 5, 22] to the case of a nonlocal potential in the Hamiltonian.

### A.7.3 Layer Case

To obtain the generalized derivative expressions for the case of the layered matrix elements ar required by Eq. (1.70), we could start form Eq. (A.92) again, and replace  $\hat{\mathbf{v}}^{\text{LDA}}$  by  $\mathbf{V}^{\text{LDA}}$ , to obtain the equivalent of Eqs. (A.101) and (A.102), for which we need to calculate the new  $\tau_{nm}^{ab}$ , that is given by

$$\begin{aligned}
\mathcal{T}_{nm}^{ab} &= [r^a, \mathcal{V}^{\text{LDA},b}]_{nm} = [r^a, \mathcal{V}^b]_{nm} + [r^a, \mathcal{V}^{\text{nl},b}]_{nm} \\
&= \frac{1}{2} [r^a, v^b C^\ell(z) + C^\ell(z) v^b]_{nm} + \frac{1}{2} [r^a, v^{\text{nl},b} C^\ell(z) + C^\ell(z) v^{\text{nl},b}]_{nm} \\
&= ([r^a, v^b] C^\ell(z))_{nm} + ([r^a, v^{\text{nl},b}] C^\ell(z))_{nm} \\
&= \sum_p [r^a, v^b]_{np} C_{pm}^\ell + \sum_p [r^a, v^{\text{nl},b}]_{np} C_{pm}^\ell \\
&= \frac{i\hbar}{m_e} \delta_{ab} C_{nm}^\ell + \sum_p [r^a, v^{\text{nl},b}]_{np} C_{pm}^\ell. \quad (\text{A.104})
\end{aligned}$$

For a full-slab calculation, that would correspondo to a bulk calculation as well,  $C^\ell(z) = 1$  and then,  $C_{nm}^\ell = \delta_{nm}$ , and from above expression  $\mathcal{T}_{nm}^{ab} \rightarrow \tau_{nm}^{ab}$ . Thus, the layered expression for  $\mathcal{V}_{nm}^{\text{LDA},a}$  becomes

$$(\mathcal{V}_{nm}^{\text{LDA},a})_{;k^b} = \frac{\hbar}{m_e} \delta_{ab} C_{nm}^\ell - i \sum_p [r^b, v^{\text{nl},a}]_{np} C_{pm}^\ell + i \sum_\ell \left( r_{n\ell}^b \mathcal{V}_{\ell m}^{\text{LDA},a} - \mathcal{V}_{n\ell}^{\text{LDA},a} r_{\ell m}^b \right) + i r_{nm}^b \tilde{\Delta}_{mn}^a, \quad (\text{A.105})$$

where

$$\tilde{\Delta}_{mn}^a = \mathcal{V}_{nn}^{\text{LDA},a} - \mathcal{V}_{mm}^{\text{LDA},a}. \quad (\text{A.106})$$

As mentioned before, the term  $[r^b, v^{\text{nl},a}]_{nm}$  calculated in Sec. A.8, is small compared to the other terms, thus we neglect it throwout this work.[23] The expression for  $C_{nm}^\ell$  is calculated in Sec. A.3.

## A.8 Matrix elements of $\tau_{nm}^{ab}(\mathbf{k})$

To calculate  $\tau_{nm}^{ab}$ , we first need to calculate

$$\mathcal{L}_{nm}^{ab}(\mathbf{k}) = \frac{1}{i\hbar} \langle n\mathbf{k} | [\hat{r}^a, \hat{v}^{nl,b}] | m\mathbf{k}' \rangle \delta(\mathbf{k} - \mathbf{k}') = \frac{1}{\hbar^2} \langle n\mathbf{k} | [\hat{r}^a, [\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^b]] | m\mathbf{k}' \rangle \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.107})$$

for which we need the following triple commutator

$$[\hat{r}^a, [\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^b]] = [\hat{r}^b, [\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^a]], \quad (\text{A.108})$$

where the right hand side follows from the Jacobi identity, since  $[\hat{r}^a, \hat{r}^b] = 0$ . We expand the triple commutator as

$$\begin{aligned} [\hat{r}^a, [\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^b]] &= [\hat{r}^a, \hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\hat{r}^b] - [\hat{r}^a, \hat{r}^b\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')] \\ &= [\hat{r}^a, \hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')] \hat{r}^b - \hat{r}^b [\hat{r}^a, \hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')] \\ &= \hat{r}^a \hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}') \hat{r}^b - \hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}') \hat{r}^a \hat{r}^b - \hat{r}^b \hat{r}^a \hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}') + \hat{r}^b \hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}') \hat{r}^a. \end{aligned} \quad (\text{A.109})$$

Then,

$$\begin{aligned} \frac{1}{\hbar^2} \langle n\mathbf{k} | [\hat{r}^a, [\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^b]] | m\mathbf{k}' \rangle &= \frac{1}{\hbar^2} \int \langle n\mathbf{k} | |\mathbf{r}\rangle \langle \mathbf{r}| [\hat{r}^a, [\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^b]] | \mathbf{r}' \rangle \langle \mathbf{r}' | m\mathbf{k}' \rangle \delta(\mathbf{k} - \mathbf{k}') d\mathbf{r} d\mathbf{r}' \\ &= \frac{1}{\hbar^2} \int \psi_{n\mathbf{k}}^*(\mathbf{r}) \left( r^a V^{nl}(\mathbf{r}, \mathbf{r}') r'^b - V^{nl}(\mathbf{r}, \mathbf{r}') r'^a r'^b - r^b r^a V^{nl}(\mathbf{r}, \mathbf{r}') + r^b V^{nl}(\mathbf{r}, \mathbf{r}') r'^a \right) \psi_{m\mathbf{k}}(\mathbf{r}') \delta(\mathbf{k} - \mathbf{k}') d\mathbf{r} d\mathbf{r}' \\ &= \frac{1}{\hbar^2 \Omega} \sum_{\mathbf{K}, \mathbf{K}'} C_{n\mathbf{k}}^*(\mathbf{K}) C_{m\mathbf{k}}(\mathbf{K}') \int e^{-i\mathbf{K} \cdot \mathbf{r}} \left( r^a V^{nl}(\mathbf{r}, \mathbf{r}') r'^b - V^{nl}(\mathbf{r}, \mathbf{r}') r'^a r'^b - r^b r^a V^{nl}(\mathbf{r}, \mathbf{r}') + r^b V^{nl}(\mathbf{r}, \mathbf{r}') r'^a \right) e^{i\mathbf{K}' \cdot \mathbf{r}'} \delta(\mathbf{k} - \mathbf{k}') d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (\text{A.110})$$

We use the following identity,

$$\begin{aligned} \left( \frac{\partial^2}{\partial K^a \partial K'^b} + \frac{\partial^2}{\partial K'^a \partial K'^b} + \frac{\partial^2}{\partial K^a \partial K^b} + \frac{\partial^2}{\partial K^b \partial K'^a} \right) \int e^{-i\mathbf{K} \cdot \mathbf{r}} V^{nl}(\mathbf{r}, \mathbf{r}') e^{i\mathbf{K}' \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}' \\ = \int e^{-i\mathbf{K} \cdot \mathbf{r}} \left( r^a V^{nl}(\mathbf{r}, \mathbf{r}') r'^b - V^{nl}(\mathbf{r}, \mathbf{r}') r'^a r'^b - r^b r^a V^{nl}(\mathbf{r}, \mathbf{r}') + r^b V^{nl}(\mathbf{r}, \mathbf{r}') r'^a \right) e^{i\mathbf{K}' \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}' \\ = \left( \frac{\partial^2}{\partial K^a \partial K'^b} + \frac{\partial^2}{\partial K'^a \partial K'^b} + \frac{\partial^2}{\partial K^a \partial K^b} + \frac{\partial^2}{\partial K^b \partial K'^a} \right) \langle \mathbf{K} | V^{nl} | \mathbf{K}' \rangle, \end{aligned} \quad (\text{A.111})$$

to write

$$\mathcal{L}_{nm}^{ab}(\mathbf{k}) = \frac{1}{\hbar^2 \Omega} \sum_{\mathbf{K}, \mathbf{K}'} C_{n\mathbf{k}}^*(\mathbf{K}) C_{m\mathbf{k}}(\mathbf{K}') \left( \frac{\partial^2}{\partial K^a \partial K'^b} + \frac{\partial^2}{\partial K'^a \partial K'^b} + \frac{\partial^2}{\partial K^a \partial K^b} + \frac{\partial^2}{\partial K^b \partial K'^a} \right) \langle \mathbf{K} | V^{nl} | \mathbf{K}' \rangle. \quad (\text{A.112})$$

The double derivatives with respect to  $\mathbf{K}$  and  $\mathbf{K}'$  can be worked out as shown in Sec. A.2, to obtain the matrix elements of  $[\hat{V}^{nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^b]$  [72]. Therefore, we can obtain the value of the matrix elements of the triple commutator [23].

With above results we can proceed to evaluate the matrix elements  $\tau_{nm}(\mathbf{k})$ . From Eq. (A.92)

$$\begin{aligned}\langle n\mathbf{k}|\tau^{ab}|m\mathbf{k}'\rangle &= \langle n\mathbf{k}|\frac{i\hbar}{m_e}\delta_{ab}|m\mathbf{k}'\rangle + \langle n\mathbf{k}|\frac{1}{i\hbar}\left[r^a, v^{nl,b}\right]|m\mathbf{k}'\rangle \\ \mathcal{L}_{nm}^{ab}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}') &= \delta(\mathbf{k}-\mathbf{k}')\left(\frac{i\hbar}{m_e}\delta_{ab}\delta_{nm} + \mathcal{L}_{nm}^{ab}(\mathbf{k})\right) \\ \tau_{nm}^{ab}(\mathbf{k}) = \tau_{nm}^{ba}(\mathbf{k}) &= \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm} + \mathcal{L}_{nm}^{ab}(\mathbf{k}),\end{aligned}\tag{A.113}$$

which is an explicit expression that can be numerically calculated.

## A.9 Scissors renormalization for $\mathcal{V}_{nm}^\Sigma$

add some motherfuckin text yo

$$\begin{aligned}\langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle(E_m^\Sigma - E_n^\Sigma) &= \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r})\mathcal{C}(z)\mathbf{r}(E_m^\Sigma - E_n^\Sigma)\psi_{m\mathbf{k}}(\mathbf{r}) \\ &= \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r})\mathcal{C}(z)[\mathbf{r}, H^\Sigma]\psi_{m\mathbf{k}}(\mathbf{r}) \\ &= -i \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r})\mathcal{C}(z)\mathbf{v}^\Sigma\psi_{m\mathbf{k}}(\mathbf{r}) \rightarrow \mathcal{V}_{nm}^\Sigma \\ \langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle &\rightarrow \frac{\mathcal{V}_{nm}^\Sigma}{\omega_{nm}^\Sigma} \\ \langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle(E_m^{\text{LDA}} - E_n^{\text{LDA}}) &= \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r})\mathcal{C}(z)\mathbf{r}(E_m^{\text{LDA}} - E_n^{\text{LDA}})\psi_{m\mathbf{k}}(\mathbf{r}) \\ &= \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r})\mathcal{C}(z)[\mathbf{r}, H^{\text{LDA}}]\psi_{m\mathbf{k}}(\mathbf{r}) \\ &= -i \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r})\mathcal{C}(z)\mathbf{v}^{\text{LDA}}\psi_{m\mathbf{k}}(\mathbf{r}) \rightarrow \mathcal{V}_{nm}^{\text{LDA}} \\ \langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle &\rightarrow \frac{\mathcal{V}_{nm}^{\text{LDA}}}{\omega_{nm}^{\text{LDA}}} \\ \mathcal{V}_{nm}^\Sigma &= \frac{\omega_{nm}^\Sigma}{\omega_{nm}^{\text{LDA}}} \mathcal{V}_{nm}^{\text{LDA}} \quad \text{voila!!!.}\end{aligned}\tag{A.114}$$

## Appendix B

# Complete Derivations for the SSHG yield

## Outline

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## B.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  $\kappa z$  plane, and define

$$\hat{\kappa} = \cos \phi \hat{\mathbf{x}} + \sin \phi \hat{\mathbf{y}}, \quad (\text{B.1})$$

and

$$\hat{\mathbf{s}} = -\sin \phi \hat{\mathbf{x}} + \cos \phi \hat{\mathbf{y}}, \quad (\text{B.2})$$

where  $\phi$  the angle with respect to the  $x$  axis.

### B.1.1 $2\omega$ terms

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

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

and neglecting the multiple reflections reduces this expression to

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

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

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

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

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

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

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

If we wish to neglect the effects from the multiple reflections, we do the exact same for Eq. (B.4), and get the following term for  $\hat{\mathbf{P}}_{v+}$ ,

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

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

$$\mathbf{e}_\ell^{2\omega} = T_s^{v\ell} T_s^{\ell b} [-\sin \phi \hat{\mathbf{x}} + \cos \phi \hat{\mathbf{y}}]. \quad (\text{B.8})$$

### B.1.2 $1\omega$ terms

We have that the  $\mathbf{e}_\ell^\omega$  term is

$$\mathbf{e}_\ell^\omega = \left[ \hat{\mathbf{s}} t_s^{v\ell} r_s^{M+} \hat{\mathbf{s}} + \frac{t_p^{v\ell}}{n_\ell} \left( r_p^{M+} \sin \theta_0 \hat{\mathbf{z}} + r_p^{M-} w_\ell \hat{\boldsymbol{\kappa}} \right) \hat{\mathbf{p}}_{v-} \right] \cdot \hat{\mathbf{e}}^{\text{in}}.$$

We are interested in finding  $\mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega$  for both polarizations. For  $\hat{\mathbf{e}}^{\text{in}} = \hat{\mathbf{p}}_{v-}$  we have

$$\mathbf{e}_\ell^\omega = \frac{t_p^{v\ell}}{n_\ell} \left( r_p^{M+} \sin \theta_0 \hat{\mathbf{z}} + r_p^{M-} w_\ell \cos \phi \hat{\mathbf{x}} + r_p^{M-} w_\ell \sin \phi \hat{\mathbf{y}} \right),$$

so

$$\begin{aligned} \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega &= \left( \frac{t_p^{v\ell}}{n_\ell} \right)^2 \left( \left( r_p^{M-} \right)^2 w_\ell^2 \cos^2 \phi \hat{\mathbf{x}} \hat{\mathbf{x}} + 2 \left( r_p^{M-} \right)^2 w_\ell^2 \sin \phi \cos \phi \hat{\mathbf{x}} \hat{\mathbf{y}} \right. \\ &\quad + 2 r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \cos \phi \hat{\mathbf{x}} \hat{\mathbf{z}} + \left( r_p^{M-} \right)^2 w_\ell^2 \sin^2 \phi \hat{\mathbf{y}} \hat{\mathbf{y}} \\ &\quad \left. + 2 r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \hat{\mathbf{z}} \hat{\mathbf{y}} + \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \hat{\mathbf{z}} \hat{\mathbf{z}} \right), \end{aligned} \quad (\text{B.9})$$

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

$$\mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega = \left( t_s^{v\ell} r_s^{M+} \right)^2 \left( \sin^2 \phi \hat{\mathbf{x}} \hat{\mathbf{x}} + \cos^2 \phi \hat{\mathbf{y}} \hat{\mathbf{y}} - 2 \sin \phi \cos \phi \hat{\mathbf{x}} \hat{\mathbf{y}} \right). \quad (\text{B.10})$$

Neglecting the effects of the multiple reflections for the  $\mathbf{e}_\ell^\omega$  term yields

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

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  $\hat{\mathbf{e}}^{\text{in}} = \hat{\mathbf{p}}_{v-}$ ,

$$\begin{aligned} \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega &= \left( \frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b} \right)^2 \left( n_\ell^4 w_b^2 \cos^2 \phi \hat{\mathbf{x}} \hat{\mathbf{x}} + 2 n_\ell^4 w_b^2 \sin \phi \cos \phi \hat{\mathbf{x}} \hat{\mathbf{y}} \right. \\ &\quad + 2 n_\ell^2 n_b^2 w_b \sin \theta_0 \cos \phi \hat{\mathbf{x}} \hat{\mathbf{z}} + n_\ell^4 w_b^2 \sin^2 \phi \hat{\mathbf{y}} \hat{\mathbf{y}} \\ &\quad \left. + 2 n_\ell^2 n_b^2 w_b \sin \theta_0 \sin \phi \hat{\mathbf{y}} \hat{\mathbf{z}} + n_b^4 \sin^2 \theta_0 \hat{\mathbf{z}} \hat{\mathbf{z}} \right), \end{aligned} \quad (\text{B.11})$$

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

$$\mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega = \left( t_s^{v\ell} t_s^{\ell b} \right)^2 \left( \sin^2 \phi \hat{\mathbf{x}} \hat{\mathbf{x}} + \cos^2 \phi \hat{\mathbf{y}} \hat{\mathbf{y}} - 2 \sin \phi \cos \phi \hat{\mathbf{x}} \hat{\mathbf{y}} \right). \quad (\text{B.12})$$

We summarize these expressions in Table B.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  $\chi(-2\omega; \omega, \omega)$ .

### B.1.3 Nonzero components of $\chi(-2\omega; \omega, \omega)$

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

$$\begin{aligned}\chi^{xxx} &= -\chi^{xyy} = -\chi^{yyx}, \\ \chi^{xxz} &= \chi^{yyz}, \\ \chi^{zxx} &= \chi^{zyy}, \\ \chi^{zzz}.\end{aligned}\tag{B.13}$$

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

$$\chi^{xxz}, \chi^{yyz}, \chi^{zxx}, \chi^{zyy}, \chi^{zzz}.\tag{B.14}$$

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

$$\begin{aligned}\chi^{xxz} &= \chi^{yyz}, \\ \chi^{zxx} &= \chi^{zyy}, \\ \chi^{zzz}.\end{aligned}\tag{B.15}$$

Case	$\hat{\mathbf{e}}^{\text{out}}$	$\hat{\mathbf{e}}^{\text{in}}$	$\mathbf{e}_\ell^{2\omega}$	$\mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega$
$\mathcal{R}_{pP}$	$\hat{\mathbf{P}}_{v+}$	$\hat{\mathbf{p}}_{v-}$	Eq. (B.5) or (B.7)	Eq. (B.9) or Eq. (B.11)
$\mathcal{R}_{pS}$	$\hat{\mathbf{s}}$	$\hat{\mathbf{p}}_{v-}$	Eq. (B.6) or (B.8)	Eq. (B.9) or Eq. (B.11)
$\mathcal{R}_{sP}$	$\hat{\mathbf{P}}_{v+}$	$\hat{\mathbf{s}}$	Eq. (B.5) or (B.7)	Eq. (B.10) or Eq. (B.12)
$\mathcal{R}_{sS}$	$\hat{\mathbf{s}}$	$\hat{\mathbf{s}}$	Eq. (B.6) or (B.8)	Eq. (B.10) or Eq. (B.12)

Table B.1: Polarization unit vectors for  $\hat{\mathbf{e}}^{\text{out}}$  and  $\hat{\mathbf{e}}^{\text{in}}$ , 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.

## B.2 $\mathcal{R}_{pP}$

Per Table B.1,  $\mathcal{R}_{pP}$  requires Eqs. (B.5) and (B.9). After some algebra, we obtain that

$$\begin{aligned}
\Upsilon_{pP}^{\text{MR}} = \Gamma_{pP}^{\text{MR}} & \left[ -R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \cos^3 \phi \chi^{xxx} \right. \\
& - 2R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \sin \phi \cos^2 \phi \chi^{xxy} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \cos^2 \phi \chi^{xxz} \\
& - R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \sin^2 \phi \cos \phi \chi^{xyy} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xyz} \\
& - R_p^{M-} \left( r_p^{M+} \right)^2 W_\ell \sin^2 \theta_0 \cos \phi \chi^{xzz} \\
& - R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \sin \phi \cos^2 \phi \chi^{yxx} \\
& - 2R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \sin^2 \phi \cos \phi \chi^{yxy} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{yxz} \\
& - R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \sin^3 \phi \chi^{yyg} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin^2 \phi \chi^{yyz} \\
& - R_p^{M-} \left( r_p^{M+} \right)^2 W_\ell \sin^2 \theta_0 \sin \phi \chi^{yzz} \\
& + R_p^{M+} \left( r_p^{M-} \right)^2 w_\ell^2 \sin \theta_0 \cos^2 \phi \chi^{zxx} \\
& + 2R_p^{M+} r_p^{M+} r_p^{M-} w_\ell \sin^2 \theta_0 \cos \phi \chi^{zxz} \\
& + 2R_p^{M+} \left( r_p^{M-} \right)^2 w_\ell^2 \sin \theta_0 \sin \phi \cos \phi \chi^{zxy} \\
& + R_p^{M+} \left( r_p^{M-} \right)^2 w_\ell^2 \sin \theta_0 \sin^2 \phi \chi^{zyy} \\
& + 2R_p^{M+} r_p^{M+} r_p^{M-} w_\ell \sin^2 \theta_0 \sin \phi \chi^{zzy} \\
& \left. + R_p^{M+} \left( r_p^{M+} \right)^2 \sin^3 \theta_0 \chi^{zzz} \right], \tag{B.16}
\end{aligned}$$

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

$$\Gamma_{pP}^{\text{MR}} = \frac{T_p^{v\ell}}{N_\ell} \left( \frac{t_p^{v\ell}}{n_\ell} \right)^2. \tag{B.17}$$

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

$$\begin{aligned}
\Upsilon_{pP} = \Gamma_{pP} & \left[ -N_\ell^2 W_b \left( + n_\ell^4 w_b^2 \cos^3 \phi \chi^{xxx} + 2n_\ell^4 w_b^2 \sin \phi \cos^2 \phi \chi^{xxy} \right. \right. \\
& + 2n_b^2 n_\ell^2 w_b \sin \theta_0 \cos^2 \phi \chi^{xxz} + n_\ell^4 w_b^2 \sin^2 \phi \cos \phi \chi^{xyy} \\
& \left. \left. + 2n_b^2 n_\ell^2 w_b \sin \theta_0 \sin \phi \cos \phi \chi^{xyz} + n_b^4 \sin^2 \theta_0 \cos \phi \chi^{xzz} \right) \right. \\
& - N_\ell^2 W_b \left( + n_\ell^4 w_b^2 \sin \phi \cos^2 \phi \chi^{yxx} + 2n_\ell^4 w_b^2 \sin^2 \phi \cos \phi \chi^{yxy} \right. \\
& + 2n_b^2 n_\ell^2 w_b \sin \theta_0 \sin \phi \cos \phi \chi^{yxz} + n_\ell^4 w_b^2 \sin^3 \phi \chi^{yyy} \\
& \left. \left. + 2n_b^2 n_\ell^2 w_b \sin \theta_0 \sin^2 \phi \chi^{yyz} + n_b^4 \sin^2 \theta_0 \sin \phi \chi^{yzz} \right) \right. \\
& + N_b^2 \sin \theta_0 \left( + n_\ell^4 w_b^2 \cos^2 \phi \chi^{zxx} + 2n_\ell^4 w_b^2 \sin \phi \cos \phi \chi^{zxy} \right. \\
& + n_\ell^4 w_b^2 \sin^2 \phi \chi^{zyy} + 2n_\ell^2 n_b^2 w_b \sin \theta_0 \cos \phi \chi^{zxx} \\
& \left. \left. + 2n_\ell^2 n_b^2 w_b \sin \theta_0 \sin \phi \chi^{zzy} + n_b^4 \sin^2 \theta_0 \chi^{zzz} \right) \right], \tag{B.18}
\end{aligned}$$

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

$$\Gamma_{pP} = \frac{T_p^{v\ell} T_p^{\ell b}}{N_\ell^2 N_b} \left( \frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b} \right)^2. \tag{B.19}$$

### B.2.1 For the (111) surface

We take Eqs. (B.16) and (B.13), eliminate the components that do not contribute, and apply the symmetry relations as follows,

$$\begin{aligned}
\Upsilon_{pP}^{\text{MR},(111)} = \Gamma_{pP}^{\text{MR}} & \left[ -R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \cos^3 \phi \chi^{xxx} \right. \\
& + R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \sin^2 \phi \cos \phi \chi^{xxx} \\
& + 2R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell \sin^2 \phi \cos \phi \chi^{xxx} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \cos^2 \phi \chi^{xxz} \\
& - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin^2 \phi \chi^{xxz} \\
& + R_p^{M+} \left( r_p^{M-} \right)^2 w_\ell^2 \sin \theta_0 \cos^2 \phi \chi^{zxx} \\
& + R_p^{M+} \left( r_p^{M-} \right)^2 w_\ell^2 \sin \theta_0 \sin^2 \phi \chi^{zxx} \\
& \left. + R_p^{M+} \left( r_p^{M+} \right)^2 \sin^3 \theta_0 \chi^{zzz} \right].
\end{aligned}$$

We reduce terms,

$$\begin{aligned}
\Upsilon_{pP}^{\text{MR},(111)} &= \Gamma_{pP}^{\text{MR}} \left[ R_p^{M-} \left( r_p^{M-} \right)^2 w_\ell^2 W_\ell (3 \sin^2 \phi \cos \phi - \cos^3 \phi) \chi^{xxx} \right. \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 (\sin^2 \phi + \cos^2 \phi) \chi^{xxz} \\
&\quad + R_p^{M+} \left( r_p^{M+} \right)^2 w_\ell^2 \sin \theta_0 (\sin^2 \phi + \cos^2 \phi) \chi^{zxx} \\
&\quad \left. + R_p^{M+} \left( r_p^{M+} \right)^2 \sin^3 \theta_0 \chi^{zzz} \right] \\
&= \Gamma_{pP}^{\text{MR}} \left[ R_p^{M+} \sin \theta_0 \left( \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} + \left( r_p^{M-} \right)^2 w_\ell^2 \chi^{zxx} \right) \right. \\
&\quad \left. - R_p^{M-} w_\ell W_\ell \left( 2r_p^{M+} r_p^{M-} \sin \theta_0 \chi^{xxz} + \left( r_p^{M-} \right)^2 w_\ell \chi^{xxx} \cos 3\phi \right) \right] \\
&= \Gamma_{pP}^{\text{MR}} r_{pP}^{\text{MR},(111)},
\end{aligned}$$

where

$$\begin{aligned}
r_{pP}^{\text{MR},(111)} &= R_p^{M+} \sin \theta_0 \left( \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} + \left( r_p^{M-} \right)^2 w_\ell^2 \chi^{zxx} \right) \\
&\quad - R_p^{M-} w_\ell W_\ell \left( 2r_p^{M+} r_p^{M-} \sin \theta_0 \chi^{xxz} + \left( r_p^{M-} \right)^2 w_\ell \chi^{xxx} \cos 3\phi \right). \tag{B.20}
\end{aligned}$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (B.18),

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

and reduce,

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

where

$$\begin{aligned}
r_{pP}^{(111)} &= N_b^2 \sin \theta_0 (n_b^4 \sin^2 \theta_0 \chi^{zzz} + n_\ell^4 w_b^2 \chi^{zxx}) \\
&\quad - n_\ell^2 N_\ell^2 w_b W_b (2n_b^2 \sin \theta_0 \chi^{xxz} + n_\ell^2 w_b \chi^{xxx} \cos 3\phi).
\end{aligned} \tag{B.21}$$

### B.2.2 For the (110) surface

We take Eqs. (B.16) and (B.14), eliminate the components that do not contribute, and apply the symmetry relations as follows,

$$\begin{aligned}
\Upsilon_{pP}^{\text{MR},(110)} &= \Gamma_{pP}^{\text{MR}} \left[ R_p^{M+} \left( r_p^{M+} \right)^2 \sin^3 \theta_0 \chi^{zzz} \right. \\
&\quad + R_p^{M+} \left( r_p^{M-} \right)^2 w_\ell^2 \sin \theta_0 \sin^2 \phi \chi^{zyy} \\
&\quad + R_p^{M+} \left( r_p^{M-} \right)^2 w_\ell^2 \sin \theta_0 \cos^2 \phi \chi^{zxx} \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin^2 \phi \chi^{yyz} \\
&\quad \left. - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \cos^2 \phi \chi^{xxz} \right] \\
&= \Gamma_{pP}^{\text{MR}} \left[ R_p^{M+} \sin \theta_0 \left( \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} \right. \right. \\
&\quad + \left( r_p^{M-} \right)^2 w_\ell^2 \left( \frac{1}{2}(1 - \cos 2\phi) \chi^{zyy} + \frac{1}{2}(\cos 2\phi + 1) \chi^{zxx} \right) \left. \right) \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \left( \frac{1}{2}(1 - \cos 2\phi) \chi^{yyz} \right. \\
&\quad \left. \left. + \frac{1}{2}(\cos 2\phi + 1) \chi^{xxz} \right) \right] \\
&= \Gamma_{pP}^{\text{MR}} \left[ R_p^{M+} \sin \theta_0 \left( \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} \right. \right. \\
&\quad + \left( r_p^{M-} \right)^2 w_\ell^2 \left( \frac{\chi^{zyy} + \chi^{zxx}}{2} + \frac{\chi^{zyy} - \chi^{zxx}}{2} \cos 2\phi \right) \left. \right) \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \left( \frac{\chi^{yyz} + \chi^{xxz}}{2} + \frac{\chi^{yyz} - \chi^{xxz}}{2} \cos 2\phi \right) \left. \right] \\
&= \Gamma_{pP}^{\text{MR}} r_{pP}^{\text{MR},(110)},
\end{aligned}$$

where

$$\begin{aligned}
r_{pP}^{\text{MR},(110)} &= R_p^{M+} \sin \theta_0 \left( \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} \right. \\
&\quad + \left( r_p^{M-} \right)^2 w_\ell^2 \left( \frac{\chi^{zyy} + \chi^{zxx}}{2} + \frac{\chi^{zyy} - \chi^{zxx}}{2} \cos 2\phi \right) \left. \right) \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \left( \frac{\chi^{yyz} + \chi^{xxz}}{2} + \frac{\chi^{yyz} - \chi^{xxz}}{2} \cos 2\phi \right). \tag{B.22}
\end{aligned}$$

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

but starting with Eq. (B.18),

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

where

$$\begin{aligned}
r_{pP}^{(110)} &= N_b^2 \sin \theta_0 \left[ n_b^4 \sin^2 \theta_0 \chi^{zzz} + n_\ell^4 w_b^2 \left( \frac{\chi^{zyy} + \chi^{zxz}}{2} + \frac{\chi^{zyy} - \chi^{zxz}}{2} \cos 2\phi \right) \right] \\
&\quad - 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b \sin \theta_0 \left( \frac{\chi^{yyz} + \chi^{xxz}}{2} + \frac{\chi^{yyz} - \chi^{xxz}}{2} \cos 2\phi \right).
\end{aligned} \tag{B.23}$$

### B.2.3 For the (001) surface

We take Eqs. (B.16) and (B.14), eliminate the components that do not contribute, and apply the symmetry relations as follows,

$$\begin{aligned}
\Upsilon_{pP}^{\text{MR},(001)} &= \Gamma_{pP}^{\text{MR}} [ R_p^{M+} (r_p^{M+})^2 \sin^3 \theta_0 \chi^{zzz} \\
&\quad + R_p^{M+} (r_p^{M-})^2 w_\ell^2 \sin \theta_0 \sin^2 \phi \chi^{zxz} \\
&\quad + R_p^{M+} (r_p^{M-})^2 w_\ell^2 \sin \theta_0 \cos^2 \phi \chi^{zxz} \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \sin^2 \phi \chi^{xxz} \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \cos^2 \phi \chi^{xxz}] \\
&= \Gamma_{pP}^{\text{MR}} [ R_p^{M+} \sin \theta_0 \left( (r_p^{M+})^2 \sin^2 \theta_0 \chi^{zzz} + (r_p^{M-})^2 w_\ell^2 \chi^{zxz} \right) \\
&\quad - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \chi^{xxz}] \\
&= \Gamma_{pP}^{\text{MR}} r_{pP}^{\text{MR},(001)},
\end{aligned}$$

where

$$\begin{aligned} r_{pP}^{\text{MR},(001)} = & R_p^{M+} \sin \theta_0 \left( \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} + \left( r_p^{M-} \right)^2 w_\ell^2 \chi^{zxx} \right) \\ & - 2R_p^{M-} r_p^{M+} r_p^{M-} w_\ell W_\ell \sin \theta_0 \chi^{xxz}, \end{aligned} \quad (\text{B.24})$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (B.18),

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

where

$$\begin{aligned} r_{pP}^{(001)} = & N_b^2 \sin \theta_0 (n_b^4 \sin^2 \theta_0 \chi^{zzz} + n_\ell^4 w_b^2 \chi^{zxx}) \\ & - 2n_b^2 n_\ell^2 N_\ell^2 w_b W_b \sin \theta_0 \chi^{xxz}. \end{aligned} \quad (\text{B.25})$$

### B.3 $\mathcal{R}_{pS}$

Per Table B.1,  $\mathcal{R}_{pS}$  requires Eqs. (B.6) and (B.9). After some algebra, we obtain that

$$\begin{aligned} \Upsilon_{pS}^{\text{MR}} = & \Gamma_{pS}^{\text{MR}} [- \left( r_p^{M-} \right)^2 w_\ell^2 \sin \phi \cos^2 \phi \chi^{xxx} - 2 \left( r_p^{M-} \right)^2 w_\ell^2 \sin^2 \phi \cos \phi \chi^{xxy} \\ & - 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xxz} - \left( r_p^{M-} \right)^2 w_\ell^2 \sin^3 \phi \chi^{xyy} \\ & - 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin^2 \phi \chi^{xzy} - \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \sin \phi \chi^{xzz} \\ & + \left( r_p^{M-} \right)^2 w_\ell^2 \cos^3 \phi \chi^{yxx} + 2 \left( r_p^{M-} \right)^2 w_\ell^2 \sin \phi \cos^2 \phi \chi^{yxy} \\ & + 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \cos^2 \phi \chi^{yxz} + \left( r_p^{M-} \right)^2 w_\ell^2 \sin^2 \phi \cos \phi \chi^{yyy} \\ & + 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{yzy} + \left( r_p^{M+} \right)^2 \sin^2 \theta_0 \cos \phi \chi^{yzz}]. \end{aligned} \quad (\text{B.26})$$

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

$$\Gamma_{pS}^{\text{MR}} = T_s^{v\ell} R_s^{M+} \left( \frac{t_p^{v\ell}}{n_\ell} \right)^2 \quad (\text{B.27})$$

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

$$\begin{aligned} \Upsilon_{pS} = & \Gamma_{pS} [- n_\ell^4 w_b^2 \sin \phi \cos^2 \phi \chi^{xxx} - 2n_\ell^4 w_b^2 \sin^2 \phi \cos \phi \chi^{xxy} \\ & - 2n_\ell^2 n_b^2 w_b \sin \theta_0 \sin \phi \cos \phi \chi^{xxz} - n_\ell^4 w_b^2 \sin^3 \phi \chi^{xyy} \\ & - 2n_\ell^2 n_b^2 w_b \sin \theta_0 \sin^2 \phi \chi^{xzy} - n_b^4 \sin^2 \theta_0 \sin \phi \chi^{xzz} \\ & + n_\ell^4 w_b^2 \cos^3 \phi \chi^{yxx} + 2n_\ell^4 w_b^2 \sin \phi \cos^2 \phi \chi^{yxy} \\ & + 2n_\ell^2 n_b^2 w_b \sin \theta_0 \cos^2 \phi \chi^{yxz} + n_\ell^4 w_b^2 \sin^2 \phi \cos \phi \chi^{yyy} \\ & + 2n_\ell^2 n_b^2 w_b \sin \theta_0 \sin \phi \cos \phi \chi^{yzy} + n_b^4 \sin^2 \theta_0 \cos \phi \chi^{yzz}], \end{aligned} \quad (\text{B.28})$$

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

$$\Gamma_{pS} = T_s^{v\ell} T_s^{\ell b} \left( \frac{t_p^{v\ell} t_p^{\ell b}}{n_\ell^2 n_b} \right)^2. \quad (\text{B.29})$$

### B.3.1 For the (111) surface

We take Eqs. (B.26) and (B.13), eliminate the components that do not contribute, and apply the symmetry relations as follows,

$$\begin{aligned} \Upsilon_{pS}^{\text{MR},(111)} &= \Gamma_{pS}^{\text{MR}} [2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xxz} \\ &\quad - 2r_p^{M+} r_p^{M-} w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xxz} \\ &\quad - (r_p^{M-})^2 w_\ell^2 \sin \phi \cos^2 \phi \chi^{xxx} \\ &\quad - 2(r_p^{M-})^2 w_\ell^2 \sin \phi \cos^2 \phi \chi^{xxx} \\ &\quad + (r_p^{M-})^2 w_\ell^2 \sin^3 \phi \chi^{xxx}]. \end{aligned}$$

We reduce terms,

$$\begin{aligned} \Upsilon_{pS}^{\text{MR},(111)} &= \Gamma_{pS}^{\text{MR}} [ (r_p^{M-})^2 w_\ell^2 (\sin^3 \phi - 3 \sin \phi \cos^2 \phi) \chi^{xxx} ] \\ &= \Gamma_{pS}^{\text{MR}} [ - (r_p^{M-})^2 w_\ell^2 \chi^{xxx} \sin 3\phi ] \\ &= \Gamma_{pS}^{\text{MR}} r_{pS}^{\text{MR},(111)}, \end{aligned}$$

where

$$r_{pS}^{\text{MR},(111)} = - (r_p^{M-})^2 w_\ell^2 \chi^{xxx} \sin 3\phi. \quad (\text{B.30})$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (B.28),

$$\begin{aligned} \Upsilon_{pS} &= \Gamma_{pS} [n_\ell^4 w_b^2 (\sin^3 \phi - 3 \sin \phi \cos^2 \phi) \chi^{xxx}] \\ &= \Gamma_{pS} [ - n_\ell^4 w_b^2 \chi^{xxx} \sin 3\phi ] \\ &= \Gamma_{pS} r_{pS}^{(111)}, \end{aligned} \quad (\text{B.31})$$

where

$$r_{pS}^{(111)} = -n_\ell^4 w_b^2 \chi^{xxx} \sin 3\phi, \quad (\text{B.32})$$

and we use  $\Gamma_{pS}$  instead of  $\Gamma_{pS}^{\text{MR}}$ .

### B.3.2 For the (110) surface

We take Eqs. (B.26) and (B.14), eliminate the components that do not contribute, and apply the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{pS}^{\text{MR},(110)} &= \Gamma_{pS}^{\text{MR}} [2r_p^{M+}r_p^{M-}w_\ell \sin \theta_0 \sin \phi \cos \phi (\chi^{yyz} - \chi^{xxz})] \\ &= \Gamma_{pS}^{\text{MR}} [r_p^{M+}r_p^{M-}w_\ell \sin \theta_0 (\chi^{yyz} - \chi^{xxz}) \sin 2\phi] \\ &= \Gamma_{pS}^{\text{MR}} r_{pS}^{\text{MR},(110)}.\end{aligned}$$

where

$$r_{pS}^{\text{MR},(110)} = r_p^{M+}r_p^{M-}w_\ell \sin \theta_0 (\chi^{yyz} - \chi^{xxz}) \sin 2\phi. \quad (\text{B.33})$$

If we neglect the effects of the multiple reflections as mentioned above, we have

$$r_{pS}^{(110)} = n_\ell^2 n_b^2 w_b \sin \theta_0 (\chi^{yyz} - \chi^{xxz}) \sin 2\phi, \quad (\text{B.34})$$

and we use  $\Gamma_{pS}$  instead of  $\Gamma_{pS}^{\text{MR}}$ .

### B.3.3 For the (001) surface

We take Eqs. (B.26) and (B.14), eliminate the components that do not contribute, and apply the symmetry relations as follows,

$$\begin{aligned}\Upsilon_{pS}^{\text{MR},(001)} &= \Gamma_{pS}^{\text{MR}} [-2r_p^{M+}r_p^{M-}w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xxz} \\ &\quad + 2r_p^{M+}r_p^{M-}w_\ell \sin \theta_0 \sin \phi \cos \phi \chi^{xxz}] = 0.\end{aligned}$$

Neglecting the effects of multiple reflections will obviously yield the same result, thus

$$\Upsilon_{pS}^{\text{MR},(001)} = \Upsilon_{pS}^{(001)} = 0. \quad (\text{B.35})$$

## B.4 $\mathcal{R}_{sP}$

Per Table B.1,  $\mathcal{R}_{sP}$  requires Eqs. (B.5) and (B.10). After some algebra, we obtain that

$$\begin{aligned}\Upsilon_{sP}^{\text{MR}} &= \Gamma_{sP}^{\text{MR}} \left[ R_p^{M-} W_\ell (-\sin^2 \phi \cos \phi \chi^{xxx} + 2 \sin \phi \cos^2 \phi \chi^{xxy} - \cos^3 \phi \chi^{xyy}) \right. \\ &\quad + R_p^{M-} W_\ell (-\sin^3 \phi \chi^{yxx} + 2 \sin^2 \phi \cos \phi \chi^{yyx} - \sin \phi \cos^2 \phi \chi^{yyy}) \\ &\quad \left. + R_p^{M+} \sin \theta_0 (\sin^2 \phi \chi^{zxx} - 2 \sin \phi \cos \phi \chi^{zxy} + \cos^2 \phi \chi^{zyy}) \right].\end{aligned} \quad (\text{B.36})$$

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

$$\Gamma_{sP}^{\text{MR}} = \frac{T_p^{v\ell}}{N_\ell} \left( t_s^{v\ell} r_s^{M+} \right)^2 \quad (\text{B.37})$$

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

$$\begin{aligned}\Upsilon_{sP} = \Gamma_{sP} & \left[ N_\ell^2 W_b (-\sin^2 \phi \cos \phi \chi^{xxx} + 2 \sin \phi \cos^2 \phi \chi^{xxy} - \cos^3 \phi \chi^{xyy}) \right. \\ & + N_\ell^2 W_b (-\sin^3 \phi \chi^{yxx} + 2 \sin^2 \phi \cos \phi \chi^{yxy} - \sin \phi \cos^2 \phi \chi^{yy}) \\ & \left. + N_b^2 \sin \theta_0 (+\sin^2 \phi \chi^{zxx} - 2 \sin \phi \cos \phi \chi^{zxy} + \cos^2 \phi \chi^{zyy}) \right],\end{aligned}\quad (\text{B.38})$$

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

$$\Gamma_{sP} = \frac{T_p^{v\ell} T_p^{\ell b}}{N_\ell^2 N_b} \left( t_s^{v\ell} t_s^{\ell b} \right)^2. \quad (\text{B.39})$$

#### B.4.1 For the (111) surface

We take Eqs. (B.36) and (B.13), eliminate the components that do not contribute, and apply the symmetry relations as follows,

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

We reduce terms,

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

where

$$r_{sP}^{\text{MR},(111)} = R_p^{M+} \sin \theta_0 \chi^{zxx} + R_p^{M-} W_\ell \chi^{xxx} \cos 3\phi. \quad (\text{B.40})$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (B.38),

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

and reduce,

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

where

$$r_{sP}^{(111)} = N_b^2 \sin \theta_0 \chi^{zxx} + N_\ell^2 W_b \chi^{xxx} \cos 3\phi. \quad (\text{B.41})$$

### B.4.2 For the (110) surface

We take Eqs. (B.36) and (B.14), eliminate the components that do not contribute, and apply the symmetry relations as follows,

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

where

$$r_{sP}^{\text{MR},(110)} = R_p^{M+} \sin \theta_0 \left( \frac{\chi^{zxx} + \chi^{zyy}}{2} + \frac{\chi^{zyy} - \chi^{zxx}}{2} \cos 2\phi \right). \quad (\text{B.42})$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (B.38),

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

where

$$r_{sP}^{(110)} = N_b^2 \sin \theta_0 \left( \frac{\chi^{zxx} + \chi^{zyy}}{2} + \frac{\chi^{zyy} - \chi^{zxx}}{2} \cos 2\phi \right). \quad (\text{B.43})$$

### B.4.3 For the (001) surface

We take Eqs. (B.36) and (B.14), eliminate the components that do not contribute, and apply the symmetry relations as follows,

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

where

$$r_{sP}^{\text{MR},(001)} = R_p^{M+} \sin \theta_0 \chi^{zxx}. \quad (\text{B.44})$$

If we wish to neglect the effects of the multiple reflections, we follow the exact same procedure but starting with Eq. (B.38),

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

where

$$r_{sP}^{(001)} = N_b^2 \sin \theta_0 \chi^{zxx}. \quad (\text{B.45})$$

## B.5 $\mathcal{R}_{sS}$

Per Table B.1,  $\mathcal{R}_{sS}$  requires Eqs. (B.6) and (B.10). After some algebra, we obtain that

$$\begin{aligned} \Upsilon_{sS}^{\text{MR}} &= \Gamma_{sS}^{\text{MR}} [ -\sin^3 \phi \chi^{xxx} + 2 \sin^2 \phi \cos \phi \chi^{xxy} - \sin \phi \cos^2 \phi \chi^{xyy} \\ &\quad + \sin^2 \phi \cos \phi \chi^{yxx} - 2 \sin \phi \cos^2 \phi \chi^{yxy} + \cos^3 \phi \chi^{yyy} ]. \end{aligned} \quad (\text{B.46})$$

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

$$\Gamma_{sS}^{\text{MR}} = T_s^{v\ell} R_s^{M+} \left( t_s^{v\ell} r_s^{M+} \right)^2. \quad (\text{B.47})$$

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

$$\begin{aligned} \Upsilon_{sS} &= \Gamma_{sS} [ -\sin^3 \phi \chi^{xxx} + 2 \sin^2 \phi \cos \phi \chi^{xxy} - \sin \phi \cos^2 \phi \chi^{xyy} \\ &\quad + \sin^2 \phi \cos \phi \chi^{yxx} - 2 \sin \phi \cos^2 \phi \chi^{yxy} + \cos^3 \phi \chi^{yyy} ], \end{aligned} \quad (\text{B.48})$$

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

$$\Gamma_{sS} = T_s^{v\ell} T_s^{\ell b} \left( t_s^{v\ell} t_s^{\ell b} \right)^2. \quad (\text{B.49})$$

We note that both Eqs. (B.46) and (B.48) are identical save for the different  $\Gamma_{sS}$  terms. Therefore, we can safely derive the equations only once, and then use  $\Gamma_{sS}^{\text{MR}}$  when we wish to include multiple reflections, or  $\Gamma_{sS}$  when we do not.

### B.5.1 For the (111) surface

We take Eqs. (B.46) and (B.13), eliminate the components that do not contribute, and apply the symmetry relations as follows,

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

where

$$r_{sS}^{\text{MR},(111)} = \chi^{xxx} \sin 3\phi. \quad (\text{B.50})$$

As mentioned above,

$$r_{sS}^{(111)} = r_{sS}^{\text{MR},(111)}, \quad (\text{B.51})$$

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

### B.5.2 For the (110) surface

When considering Eqs. (B.46) and (B.14), we see that there are no nonzero components that contribute. Therefore,

$$\Upsilon_{pS}^{\text{MR},(110)} = \Upsilon_{pS}^{(110)} = 0. \quad (\text{B.52})$$

### B.5.3 For the (001) surface

When considering Eqs. (B.46) and (B.14), we see that there are no nonzero components that contribute. Therefore,

$$\Upsilon_{sS}^{\text{MR},(001)} = \Upsilon_{sS}^{(001)} = 0. \quad (\text{B.53})$$

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