phd thesis

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Chapter 1

Theory

1.1 Introduction

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

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

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

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

1.2 Non-linear Surface Susceptibility

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

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

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

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

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

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

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

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

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

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

for a centrosymmetric bulk.

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

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

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

$$\chi^{S}_{\mathrm{abc}} = d\chi_{\mathrm{abc}} \tag{1.7}$$

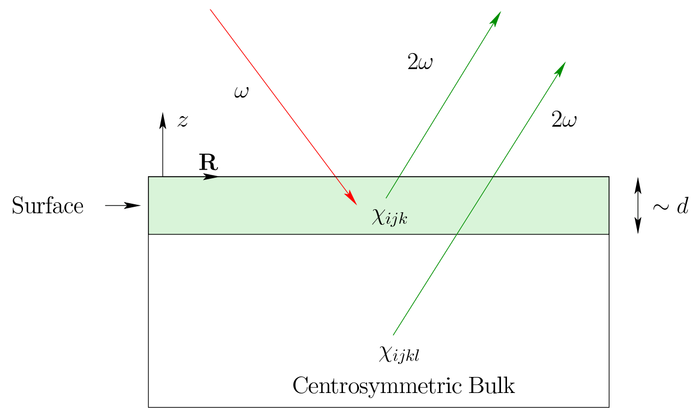

Figure 1.1: (Color Online) Sketch of the semi-infinite system with a centrosymmetric bulk. The surface region is of width $\sim d$. The incoming photon of frequency ω is represented by a downward red arrow, whereas both the surface and bulk created second harmonic photons of frequency 2ω are represented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

is the SH surface susceptibility. On the other hand,

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

gives the bulk polarization. We immediately recognize that the surface polarization is of dipolar order while the bulk polarization is of quadrupolar order. The surface, $\chi^S_{\rm abc}$, and bulk, $\chi_{\rm abcl}$, susceptibility tensor ranks are three and four, respectively. We will only concentrate on surface SHG in this article even though bulk generated SH is also a very important optical phenomenon. Also, we leave out of this article other interesting surface SH phenomena like, electric field induced second harmonic (EFISH), which would be represented by a surface susceptibility tensor of quadrupolar origin. In centrosymmetric systems for which the quadrupolar bulk response is much smaller than the dipolar surface response, SH is readily used as a very useful and powerful optical surface probe.[**?**]

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

1.3 Length Gauge

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

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

with

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

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

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

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

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

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

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

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

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

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

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

where

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

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

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

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}), \tag{1.18}$$

and

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

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

$$\hat{\mathbf{v}}^{\sigma} = \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{H}_0^{\sigma}], \tag{1.20}$$

and calculating its matrix elements

$$i\hbar\langle n\mathbf{k}|\mathbf{v}^{\sigma}|m\mathbf{k}\rangle = \langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0^{\sigma}]|m\mathbf{k}\rangle = \langle n\mathbf{k}|\hat{\mathbf{r}}\hat{H}_0^{\sigma} - \hat{H}_0^{\sigma}\hat{\mathbf{r}}|m\mathbf{k}\rangle = (\hbar\omega_m^{\sigma}(\mathbf{k}) - \hbar\omega_n^{\sigma}(\mathbf{k}))\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}\rangle, \tag{1.21}$$

thus defining $\omega_{nm}^{\sigma}(\mathbf{k}) = \omega_n^{\sigma}(\mathbf{k}) - \omega_m^{\sigma}(\mathbf{k})$ we get

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

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

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

with

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

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

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

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

where we have defined

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

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

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

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

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

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

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

and Eq. (1.22) gives

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

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

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

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

1.4 Time-dependent Perturbation Theory

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

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

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

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

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

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

where

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

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

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

that leads to

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

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

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

with

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

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

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

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

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

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

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

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

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

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

and

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

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

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

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

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

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

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

and from Eq. (1.23),

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

Then Eq. (1.45) becomes

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

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

$$\begin{aligned} R_e^{\mathrm{b}(0)}(\mathbf{k};t) &= \sum_\ell \Big(r^{\mathrm{b}}_{n\ell}(\mathbf{k})\rho^{(0)}_{\ell m}(\mathbf{k}) - \rho^{(0)}_{n\ell}(\mathbf{k}) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\Big) \\ &= \sum_\ell \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k})\delta_{\ell m} f_m(\hbar\omega^\sigma_m(\mathbf{k})) - \delta_{n\ell} f_n(\hbar\omega^\sigma_n(\mathbf{k})) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\right) \\ &= f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k}), \end{aligned} \tag{1.50}$$

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

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

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

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

with

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

and

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

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

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

and from Eq. (1.48)

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

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

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

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

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

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

1.5 Layered Current Density

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

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

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

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

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

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

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

where the operator for the electron's current is

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

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

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

where

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

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

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

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

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

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

to write

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

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

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

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

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

and using the following property

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

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

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

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

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

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

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

is all that is needed to change the velocity operator of the electron $\hat{\mathbf{v}}^\sigma$ to the new velocity operator $\boldsymbol{\mathcal{V}}^{\sigma,\ell}$ that implicitly takes into account the contribution of the region of the slab given by $\mathcal{C}^\ell(z)$. From Eq. (O.1),

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

We remark that the simple relationship between $\mathbf{v}^\sigma_{nm}(\mathbf{k})$ and $\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})$, given in Eq. (1.29), does not hold between $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k})$ and $\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$, i.e. $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k}) \neq (\omega^\sigma_{nm}/\omega_{nm})\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$ and $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nn}(\mathbf{k}) \neq \boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nn}(\mathbf{k})$, and thus, to calculate $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k})$ we must calculate the matrix elements of $\boldsymbol{\mathcal{V}}^{\mathcal{S},\ell}$ and $\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}$ (separately) according to the expressions of Appendix C. Aeroport Charles de Gaulle, Nov. 30, 2014, see Appendix I.15.

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

1.6 Microscopic surface susceptibility

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

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

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

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

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

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

and

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

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

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

and the following result shown in Appendix D,

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

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

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

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

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

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

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

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

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

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

and

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

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

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

where

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

and

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

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

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

Finally, we also need the following term (Eq. (H.10))

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

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

1.7 SHG yield in CGS

We follow the derivation established in Ref. [4].

We define the radiated SHG yied as

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

with the intensity as[1]

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

so,

$$R(\omega) = \frac{\frac{c}{2\pi}|E(2\omega)|^2}{(\frac{c}{2\pi})^2|E(\omega)|^4} = \frac{2\pi}{c}\frac{|E(2\omega)|^2}{|E(\omega)|^4}. \tag{1.91}$$

We start from the derivation in Ref. [6]. See Fig. 1.3. The electric field radiated by a polarized sheet is

$$E_{p\pm} = \frac{2\pi i\omega}{ck_z}\hat{\mathbf{p}}_\pm \cdot \boldsymbol{\mathcal{P}}, \tag{1.92}$$

$$E_s = \frac{2\pi i\omega}{ck_z}\hat{\mathbf{s}} \cdot \boldsymbol{\mathcal{P}}, \tag{1.93}$$

where,

$$k_z = \sqrt{\epsilon(\omega) - \sin^2\theta}, \tag{1.94}$$

and the nonlinear polarization produced by the incoming fields is,

$$\mathcal{P}_i = \chi_{ijk}E_j(\omega)E_k(\omega), \tag{1.95}$$

where repeated indices are to be summed over. The unit vectors for the polarization in s and p directions are

$$\hat{\mathbf{p}}_\pm = \frac{1}{\sqrt{\epsilon}}(\mp k_z\hat{\mathbf{x}} - \sin\theta\hat{\mathbf{z}}), \tag{1.96}$$

$$\hat{\mathbf{s}} = \hat{\mathbf{y}}. \tag{1.97}$$

We define the transmission, $\mathbf{T}$, and reflection, $\mathbf{R}$, tensors as,

$$\mathbf{T}_{\ell v} = \hat{\mathbf{s}}T_s^{\ell v}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\hat{\mathbf{P}}_{\ell+}, \tag{1.98}$$

and

$$\mathbf{R}_{\ell b} = \hat{\mathbf{s}}R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell+}R_p^{\ell b}\hat{\mathbf{P}}_{\ell-}, \tag{1.99}$$

where variables in capital letters are evaluated at the harmonic frequency 2ω. Notice that since $\hat{\mathbf{s}}$ is independent of ω, then $\hat{\mathbf{s}} = \hat{\mathbf{s}}$. The Fresnel factors, T_i, R_i, and $\tilde{T}_p$, for $i = s, p$ polarization, are evaluated at the appropriate interface ℓv or ℓb, and will be given below. The extra subscript in $\hat{\mathbf{P}}$ denotes the corresponding

[1]The original derivation, and Ref. [5] state the intensity has a factor of $c/8\pi$.

dielectric function to be used in its evaluation, i.e. $\epsilon_v = 1$ for vacuum (v), ϵ_ℓ for the layer (ℓ), and ϵ_b for the bulk (b). Therefore, the total radiated field at 2ω is

$$\begin{aligned}\mathbf{E}(2\omega) = E_s(2\omega)\,(\mathbf{T}_{\ell v} + \mathbf{T}_{\ell v}\cdot\mathbf{R}_{\ell b})\cdot\hat{\mathbf{s}}\\ + E_{p+}(2\omega)\mathbf{T}_{\ell v}\cdot\hat{\mathbf{P}}_{\ell +} + E_{p-}(2\omega)\mathbf{T}_{\ell v}\cdot\mathbf{R}_{\ell b}\cdot\hat{\mathbf{P}}_{\ell -}.\end{aligned} \tag{1.100}$$

First, we develop an intermediate result,

$$\begin{aligned}\mathbf{T}_{\ell v}\cdot\mathbf{R}_{\ell b} &= (\hat{\mathbf{s}}T_s^{\ell v}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\hat{\mathbf{P}}_{\ell +})\cdot(\hat{\mathbf{s}}R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell +}R_p^{\ell b}\hat{\mathbf{P}}_{\ell -})\\ &= \hat{\mathbf{s}}T_s^{\ell v}R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}R_p^{\ell b}\hat{\mathbf{P}}_{\ell -}\end{aligned}$$

We apply this result for the E_s term in Eq. (1.9),

$$\begin{aligned}(\mathbf{T}_{\ell v} + \mathbf{T}_{\ell v}\cdot\mathbf{R}_{\ell b})\cdot\hat{\mathbf{s}} =& \Big[\hat{\mathbf{s}}T_s^{\ell v}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\hat{\mathbf{P}}_{\ell +}\\ &+ \hat{\mathbf{s}}T_s^{\ell v}R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}R_p^{\ell b}\hat{\mathbf{P}}_{\ell -}\Big]\cdot\hat{\mathbf{s}}\\ =& \Big[\hat{\mathbf{s}}\tilde{T}_s^{\ell v}\big(1 + R_s^{\ell b})\hat{\mathbf{s}}\Big]\cdot\hat{\mathbf{s}}\\ =& \hat{\mathbf{s}}\tilde{T}_s^{\ell v}\big(1 + R_s^{\ell b}\big)\end{aligned} \tag{1.101}$$

For E_{p+},

$$\begin{aligned}\mathbf{T}_{\ell v}\cdot\hat{\mathbf{P}}_{\ell +} &= (\hat{\mathbf{s}}T_s^{\ell v}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\hat{\mathbf{P}}_{\ell +})\cdot\hat{\mathbf{P}}_{\ell +}\\ &= \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\end{aligned} \tag{1.102}$$

and lasty for For E_{p-},

$$\begin{aligned}\mathbf{T}_{\ell v}\cdot\mathbf{R}_{\ell b}\cdot\hat{\mathbf{P}}_{\ell -} &= (\hat{\mathbf{s}}T_s^{\ell v}R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}R_p^{\ell b}\hat{\mathbf{P}}_{\ell -})\cdot\hat{\mathbf{P}}_{\ell -}\\ &= \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}R_p^{\ell b}\end{aligned} \tag{1.103}$$

We replace Eqs. (1.101), (1.102), and (1.103) into Eq. (1.9),

$$\begin{aligned}\mathbf{E}(2\omega) = E_s(2\omega)\Big[\hat{\mathbf{s}}\tilde{T}_s^{\ell v}\big(1 + R_s^{\ell b}\big)\Big]\\ + E_{p+}(2\omega)\Big[\hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\Big] + E_{p-}(2\omega)\Big[\hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}R_p^{\ell b}\Big].\end{aligned} \tag{1.104}$$

From Eqs. (1.92) and (1.93), we get that

$$E_{p\pm}(2\omega) = \frac{4\pi i\omega}{cK_z}\hat{\mathbf{p}}_\pm\cdot\boldsymbol{\mathcal{P}}, \tag{1.105}$$

$$E_s(2\omega) = \frac{4\pi i\omega}{cK_z}\hat{\mathbf{s}}\cdot\boldsymbol{\mathcal{P}}, \tag{1.106}$$

Combining Eqs. (1.105) and (1.106) into Eq. (1.104)

$$\mathbf{E}(2\omega) = \frac{4\pi i\omega}{cK_z}\Big[\hat{\mathbf{s}}\tilde{T}_s^{\ell v}\big(1 + R_s^{\ell b})\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\hat{\mathbf{P}}_{\ell +} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}R_p^{\ell b}\hat{\mathbf{P}}_{\ell -}\Big]\cdot\boldsymbol{\mathcal{P}} \tag{1.107}$$

$$= \frac{4\pi i\omega}{cK_z}\Big[\hat{\mathbf{s}}\tilde{T}_s^{\ell v}\big(1 + R_s^{\ell b})\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\big(\hat{\mathbf{P}}_{\ell +} + R_p^{\ell b}\hat{\mathbf{P}}_{\ell -}\big)\Big]\cdot\boldsymbol{\mathcal{P}} \tag{1.108}$$

$$= \frac{4\pi i\omega}{cK_z}\mathbf{H}\cdot\boldsymbol{\mathcal{P}} \tag{1.109}$$

which matches Eq. (31) from Ref. [4]. We establish some simple relationships between T and R,

$$T_s^{\ell v} = \frac{K_{z\ell}}{\cos\theta} T_s^{v\ell}, \qquad \tilde{T}_p^{\ell v} = \frac{\sqrt{\epsilon_\ell(2\omega)} K_{z\ell}}{\cos\theta} T_p^{v\ell}, \tag{1.110}$$

$$1 - R_p^{\ell b} = \frac{\epsilon_\ell(2\omega) K_{zb}}{K_{z\ell}} T_p^{\ell b}, \qquad 1 + R_p^{\ell b} = \epsilon_b(2\omega) T_p^{\ell b}, \tag{1.111}$$

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

$$E(2\omega) = \frac{4\pi i\omega}{c} \mathbf{e}^{\,2\omega} \cdot \boldsymbol{\mathcal{P}}, \tag{1.112}$$

so

$$\mathbf{e}^{\,2\omega} = \frac{1}{K_{z\ell}} \hat{\mathbf{e}}^{out} \cdot \mathbf{H} \tag{1.113}$$

We rewrite $\mathbf{H}$ using Eqs. (1.110), (1.111), (1.96), and (1.97),

$$\mathbf{H} = \frac{K_{zl}}{\cos\theta} \Big[\hat{\mathbf{s}} T_s^{v\ell} T_s^{\ell b} \hat{\mathbf{y}} - \hat{\mathbf{P}}_{v+} T_p^{v\ell} T_p^{\ell b} \big(\epsilon_\ell(2\omega) K_{zb} \hat{\mathbf{x}} + \epsilon_b(2\omega) \sin\theta \hat{\mathbf{z}} \big) \Big], \tag{1.114}$$

and so,

$$\mathbf{e}^{\,2\omega} = \frac{1}{\cos\theta} \hat{\mathbf{e}}^{out} \cdot \Big[\hat{\mathbf{s}} T_s^{v\ell} T_s^{\ell b} \hat{\mathbf{y}} - \hat{\mathbf{P}}_{v+} T_p^{v\ell} T_p^{\ell b} \big(\epsilon_\ell(2\omega) K_{zb} \hat{\mathbf{x}} + \epsilon_b(2\omega) \sin\theta \hat{\mathbf{z}} \big) \Big] \tag{1.115}$$

We can now write our 2ω radiated fields as,

$$E_s(2\omega) = \frac{4\pi i\omega}{c\cos\theta} \Big[T_s^{v\ell} T_s^{\ell b} \hat{\mathbf{y}} \Big] \cdot \boldsymbol{\mathcal{P}} = \frac{4\pi i\omega}{c\cos\theta} T_s^{v\ell} T_s^{\ell b} \chi_{yij} E_i(\omega) E_j(\omega), \tag{1.116}$$

$$\begin{aligned} E_p(2\omega) &= -\frac{4\pi i\omega}{c\cos\theta} T_p^{v\ell} T_p^{\ell b} \Big[\epsilon_\ell(2\omega) K_{zb} \hat{\mathbf{x}} + \epsilon_b(2\omega) \sin\theta \hat{\mathbf{z}} \Big] \cdot \boldsymbol{\mathcal{P}} \\ &= -\frac{4\pi i\omega}{c\cos\theta} T_p^{v\ell} T_p^{\ell b} \Big[\epsilon_\ell(2\omega) K_{zb} \chi_{xij} + \epsilon_b(2\omega) \sin\theta \chi_{zij} \Big] E_i(\omega) E_j(\omega). \end{aligned} \tag{1.117}$$

As mentioned before $E_i(\omega)$ is the incident field given by the external field properly screened; then we have

$$\mathbf{E}_s(\omega) = E_o t_s^{v\ell} \left(1 + r_s^{\ell b}\right) \hat{\mathbf{y}}, \tag{1.118}$$

and

$$\mathbf{E}_p(\omega) = E_o \left[\tilde{t}_p^{v\ell} \left(1 - r_p^{\ell b}\right) \cos\theta_\ell \hat{\mathbf{x}} - \tilde{t}_p^{v\ell} \left(1 + r_p^{\ell b}\right) \sin\theta_\ell \hat{\mathbf{z}} \right], \tag{1.119}$$

where E_o is the incoming amplitude and θ_ℓ is the angle of refraction in the layer. Notice that the transmitted and reflected fields in the layer are taken into $\mathbf{E}_s$ and $\mathbf{E}_p$. From Eqs. (1.110-1.111) we get

$$\mathbf{E}_s(\omega) = E_o t_s^{v\ell} t_s^{\ell b} \hat{\mathbf{y}}, \tag{1.120}$$

and

$$\mathbf{E}_p(\omega) = E_o t_p^{v\ell} t_p^{\ell b} \left(\epsilon_\ell(\omega) k_{zb}\hat{\mathbf{x}} - \epsilon_b(\omega)\sin\theta\hat{\mathbf{z}}\right). \tag{1.121}$$

Substituting Eqs. (1.120) and (1.121) into Eqs. (1.116) and (1.117), then finally substituting those into Eq. (1.91), we get

$$R_{iF} = \frac{32\pi^3\omega^2}{(n_o e)^2 c^3 \cos^2\theta} \left| T_F^{v\ell} T_F^{\ell b} (t_i^{v\ell} t_i^{\ell b})^2 \, r_{iF} \right|^2, \tag{1.122}$$

where i (lower case) stands for initial polarization and F (upper case) stands for final polarization, with

$$r_{iP} = \left(\epsilon_\ell(2\omega) K_{zb}\chi_{xjk} + \epsilon_b(2\omega)\sin\theta\chi_{zjk}\right) E_j^i E_k^i, \tag{1.123}$$

and

$$r_{iS} = \chi_{yjk} E_j^i E_k^i, \tag{1.124}$$

where from Eqs. (1.120-1.121),

$$\mathbf{E}^s = \hat{\mathbf{y}} \tag{1.125a}$$

$$\mathbf{E}^p = \epsilon_\ell(\omega) k_{zb}\hat{\mathbf{x}} - \epsilon_b(\omega)\sin\theta\hat{\mathbf{z}}. \tag{1.125b}$$

The $n_o e$ factor in Eq. (1.122), with n_o the electronic density, renders $\boldsymbol{\chi}$ dimensionless. To complete the required formulas, we write down the Fresnel factors,

$$t_s^{v\ell} = \frac{2\cos\theta}{\cos\theta + k_{z\ell}}, \qquad t_p^{v\ell} = \frac{2\cos\theta}{\epsilon_\ell(\omega)\cos\theta + k_{z\ell}}, \tag{1.126}$$

$$t_s^{\ell b} = \frac{2k_{z\ell}}{k_{z\ell} + k_{zb}}, \qquad t_p^{\ell b} = \frac{2k_{z\ell}}{\epsilon_b(\omega) k_{z\ell} + \epsilon_s(\omega) k_{zb}}, \tag{1.127}$$

where the appropriate term $\sqrt{\epsilon(\omega)}$ from the usual definition of t_p has been taken out to give Eqs. (1.123) and (1.124).

1.8 Conclusions

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

1.9 Three layer model for SHG radiation

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

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

with the intensity

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

There are several ways to calculate R, one of which is the procedure followed by Cini [7]. This approach calculates the nonlinear susceptibility and at the same time the radiated fields. However, we present an alternative derivation based in the work of Mizrahi and Sipe [6], since the derivation of the three-layer-model is straightforward. Within our level of approximation this is the best model that we can use. In this scheme, we assume that the SH conversion takes place in a thin layer, just below the surface, that is characterized by a surface dielectric function $\epsilon_\ell(\omega)$. This layer is below vacuum and sits on top of the bulk characterized by $\epsilon_b(\omega)$ (see Fig. 1.4). The nonlinear polarization immersed in the thin layer, will radiate an electric field directly into vacuum and also into the bulk. This bulk directed field, will be reflected back into vacuum. Thus, the total field radiated into vacuum will be the sum of these two contributions (see Fig. 1.4). We decompose the field into s and p polarizations, then the electric field radiated by a polarization sheet,

$$\mathcal{P}_i(2\omega) = \chi_{ijk}E_j(\omega)E_k(\omega), \tag{1.128}$$

is given by [6],

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

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

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

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

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

In the above equations z is the direction perpendicular to the surface that points towards the vacuum, x is parallel to the surface, and θ is the angle of incidence, where the plane of incidence is chosen as the xz plane (see Fig. 1.4), thus $\hat{\mathbf{s}} = -\hat{\mathbf{y}}$. The function $k_i(\omega)$ is the projection of the wave vector perpendicular to the surface. As we see from Fig. 1.4, the SH field is refracted at the layer-vacuum interface (ℓv), and reflected from the layer-bulk (ℓb) interface, thus we can define the transmission, $\mathbf{T}$, and reflection, $\mathbf{R}$, tensors as,

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

and

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

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

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

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

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

where,

$$\mathbf{H}_\ell = \hat{\mathbf{s}}\,T_s^{\ell v}\left(1 + R_s^{\ell b}\right)\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}T_p^{\ell v}\left(\hat{\mathbf{P}}_{\ell+} + R_p^{\ell b}\hat{\mathbf{P}}_{\ell-}\right). \tag{1.129}$$

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

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

where using

$$\begin{aligned}1 + R_s^{\ell b} &= T_s^{\ell b}\\ 1 + R_p^{\ell b} &= \sqrt{\frac{\epsilon_b(2\omega)}{\epsilon_\ell(2\omega)}}T_p^{\ell b}\\ 1 - R_p^{\ell b} &= \sqrt{\frac{\epsilon_\ell(2\omega)}{\epsilon_b(2\omega)}}\frac{K_b}{K_\ell}T_p^{\ell b}\\ T_p^{\ell v} &= \frac{K_\ell}{K_v}T_p^{v\ell}\\ T_s^{\ell v} &= \frac{K_\ell}{K_v}T_s^{v\ell},\end{aligned} \tag{1.130}$$

we can write

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

where,

$$\begin{aligned}\mathbf{e}_\ell^{2\omega} &= \\ &\hat{\mathbf{e}}^{\rm out}\cdot\left[\hat{\mathbf{s}}T_s^{v\ell}T_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\frac{T_p^{v\ell}T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}\left(\epsilon_b(2\omega)\sin\theta_{\rm in}\hat{\mathbf{z}} - \epsilon_\ell(2\omega)K_b\hat{\mathbf{x}}\right)\right].\end{aligned} \tag{1.131}$$

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

$$\mathbf{e}_v^{2\omega} = \hat{\mathbf{e}}^{\rm out}\cdot\left[\hat{\mathbf{s}}T_s^{vb}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}}\left(\epsilon_b(2\omega)\sin\theta_{\rm in}\hat{\mathbf{z}} - K_b\hat{\mathbf{x}}\right)\right], \tag{1.132}$$

which agrees with Eq. (3.8) of Ref. [6].

In the three layer model the nonlinear polarization is located in layer ℓ, and then we evaluate the fundamental field required in Eq. (1.128) in this layer as well, then we write

$$\mathbf{E}_\ell(\omega) = E_0\left(\hat{\mathbf{s}}t_s^{v\ell}(1+r_s^{\ell b})\hat{\mathbf{s}} + \hat{\mathbf{p}}_{\ell-}t_p^{v\ell}\hat{\mathbf{p}}_{v-} + \hat{\mathbf{p}}_{\ell+}t_p^{v\ell}r_p^{\ell b}\hat{\mathbf{p}}_{v-}\right)\cdot\hat{\mathbf{e}}^{\rm in} = E_0\mathbf{e}_\ell^\omega, \tag{1.133}$$

and following the steps that lead to Eq. (1.131), we find that

$$\mathbf{e}_\ell^\omega = \left[\hat{\mathbf{s}}t_s^{v\ell}t_s^{\ell b}\hat{\mathbf{s}} + \frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\left(\epsilon_b(\omega)\sin\theta_{\rm in}\hat{\mathbf{z}} + \epsilon_\ell(\omega)k_b\hat{\mathbf{x}}\right)\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\rm in}. \tag{1.134}$$

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

$$\mathbf{e}_b^\omega = \left[\hat{\mathbf{s}}t_s^{vb}\hat{\mathbf{s}} + \frac{t_p^{vb}}{\sqrt{\epsilon_b(\omega)}}\left(\sin\theta_{\rm in}\hat{\mathbf{z}} + k_b\hat{\mathbf{x}}\right)\hat{\mathbf{p}}_{v-}\right]\cdot\hat{\mathbf{e}}^{\rm in}, \tag{1.135}$$

that is in agreement with Eq. (3.5) of Ref. [6].

With $\mathbf{e}^\omega$ we can write Eq. (1.128) as

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

and then from Eq. (1.9) we obtain that

$$\begin{aligned}
|E(2\omega)|^2 &= |E_0|^4 \frac{16\pi^2\omega^2}{c^2 K_v^2} \left|\mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega\right|^2 \\
\frac{c}{2\pi}|E(2\omega)|^2 &= \frac{32\pi^3\omega^2}{c^3 \cos^2\theta_{\text{in}}} \left|\mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega\right|^2 \left(\frac{c}{2\pi}|E_0|^2\right)^2, \\
I(2\omega) &= \frac{32\pi^3\omega^2}{c^3 \cos^2\theta_{\text{in}}} \left|\mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega\right|^2 I^2(\omega), \\
R(2\omega) &= \frac{32\pi^3\omega^2}{c^3 \cos^2\theta_{\text{in}}} \left|\mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_\ell^\omega \mathbf{e}_\ell^\omega\right|^2, \qquad (1.136)
\end{aligned}$$

as the SHG yield. At this point we mention that to recover the results of Ref. [6] which are equivalent of those of Ref. [8], we take $\mathbf{e}_\ell^{2\omega} \to \mathbf{e}_v^{2\omega}$, $\mathbf{e}_\ell^\omega \to \mathbf{e}_b^\omega$ and then

$$R(2\omega) = \frac{32\pi^3\omega^2}{c^3 \cos^2\theta_{\text{in}}} \left|\mathbf{e}_v^{2\omega} \cdot \boldsymbol{\chi} : \mathbf{e}_b^\omega \mathbf{e}_b^\omega\right|^2, \qquad (1.137)$$

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

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

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

1.10 $\mathcal{R}$ for different polarization cases

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

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

$$\hat{\boldsymbol{\kappa}} = \cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}}, \qquad (1.138)$$

and then

$$\hat{\mathbf{s}} = -\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}, \qquad (1.139)$$

1.10.1 $\mathcal{R}_{pP}$

To obtain $R_{pP}(2\omega)$ we use $\mathbf{e}^{\text{in}} = \hat{\mathbf{p}}_{v-}$ in Eq. (1.134), and $\mathbf{e}^{\text{out}} = \hat{\mathbf{P}}_{v+}$ in Eq. (1.131), to obtain that for a C_{3v} symmetry characteristic of a (111) surface,

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

where

$$
\begin{aligned}
r^{\ell}_{pP} &= \epsilon_b(2\omega)\sin\theta_{\rm in}\Big(\epsilon_b^2(\omega)\sin^2\theta_{\rm in}\chi_{zzz} + \epsilon_\ell^2(\omega)k_b^2(\omega)\chi_{zxx}\Big) \\
&\quad - \epsilon_\ell(2\omega)\epsilon_\ell(\omega)k_b(\omega)k_b(2\omega)\Big(2\epsilon_b(\omega)\sin\theta_{\rm in}\chi_{xxz} + \epsilon_\ell(\omega)k_b(\omega)\chi_{xxx}\cos(3\phi)\Big),
\end{aligned}
\tag{1.140}
$$

and

$$
\Gamma^{\ell}_{pP} = \frac{T_p^{\ell v}T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2. \tag{1.141}
$$

In order to reduce above result to that of Ref. [6] and [8], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_p^{\ell v} = 1$, $T_p^{\ell b} = T_p^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_p^{v\ell} = t_p^{vb}$, and $t_p^{\ell b} = 1$. With these choices,

$$
\begin{aligned}
r^{b}_{pP} &= \epsilon_b(2\omega)\sin\theta_{\rm in}\Big(\sin^2\theta_{\rm in}\chi_{zzz} + k_b^2(\omega)\chi_{zxx}\Big) \\
&\quad - k_b(\omega)k_b(2\omega)\Big(2\sin\theta_{\rm in}\chi_{xxz} + k_b(\omega)\chi_{xxx}\cos(3\phi)\Big),
\end{aligned}
$$

and

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

Taking all fields in the bulk

To evaluate the 2ω fields in the bulk, we take Eq. (1.129) considering that $\ell \to b$. We have already considered the 1ω fields in the bulk in Eq. (1.135). After some algebra, we get that

$$
\mathbf{e}_b^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_b^{\omega}\mathbf{e}_b^{\omega} = \Gamma^{b}_{pP}r^{b}_{pP}
$$

where

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

and

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

Taking all fields in the vacuum

To evaluate the 1ω fields in the vacuum, we take Eq. (1.133) considering that $\ell \to v$. We have already considered the 2ω fields in the vacuum in Eq. (1.132). After some algebra, we get that

$$
\mathbf{e}_v^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_v^{\omega}\mathbf{e}_v^{\omega} = \Gamma^{v}_{pP}r^{v}_{pP}
$$

where

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

and

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

1.10.2 $\mathcal{R}_{pS}$

To obtain $R_{pS}(2\omega)$ we use $\mathbf{e}^{\rm in} = \hat{\mathbf{p}}_{v-}$ in Eq. (1.134), and $\mathbf{e}^{\rm out} = \hat{\mathbf{S}}$ in Eq. (1.131). We also use the unit vectors defined in Eqs. (1.138) and (1.139). Substituting, we get

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

where

$$
r_{pS}^{\ell} = -\epsilon_\ell^2(\omega)k_b^2\sin 3\phi\chi_{xxx}, \tag{1.142}
$$

and

$$
\Gamma_{pS}^{\ell} = T_s^{v\ell}T_s^{\ell b}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2. \tag{1.143}
$$

In order to reduce above result to that of Ref. [6] and [8], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_s^{v\ell} = 1$, $T_s^{\ell b} = T_s^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_p^{v\ell} = t_p^{vb}$, and $t_p^{\ell b} = 1$. With these choices,

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

and

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

1.10.3 $\mathcal{R}_{sP}$

To obtain $R_{sP}(2\omega)$ we use $\mathbf{e}^{\rm in} = \hat{\mathbf{s}}$ in Eq. (1.134), and $\mathbf{e}^{\rm out} = \hat{\mathbf{P}}_{v+}$ in Eq. (1.131). We also use the unit vectors defined in Eqs. (1.138) and (1.139). Substituting, we get

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

where

$$
r_{sP}^{\ell} = \epsilon_b(2\omega)\sin\theta_{\rm in}\chi_{zxx} + \epsilon_\ell(2\omega)K_b\chi_{xxx}\cos 3\phi, \tag{1.144}
$$

and

$$
\Gamma_{sP}^{\ell} = \frac{T_p^{\ell v}T_p^{\ell b}\left(t_s^{v\ell}t_s^{\ell b}\right)^2}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}. \tag{1.145}
$$

In order to reduce above result to that of Ref. [6] and [8], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_p^{v\ell} = 1$, $T_p^{\ell b} = T_p^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_s^{v\ell} = t_s^{vb}$, and $t_s^{\ell b} = 1$. With these choices,

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

and

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

1.10.4 $\mathcal{R}_{sS}$

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

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

where

$$r_{sS}^\ell = \chi_{xxx}\sin 3\phi, \tag{1.146}$$

and

$$\Gamma_{sS}^\ell = T_s^{v\ell}T_s^{\ell b}\left(t_s^{v\ell}t_s^{\ell b}\right)^2. \tag{1.147}$$

In order to reduce above result to that of Ref. [6] and [8], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_s^{v\ell} = 1$, $T_s^{\ell b} = T_s^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_s^{v\ell} = t_s^{vb}$, and $t_s^{\ell b} = 1$. With these choices,

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

and

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

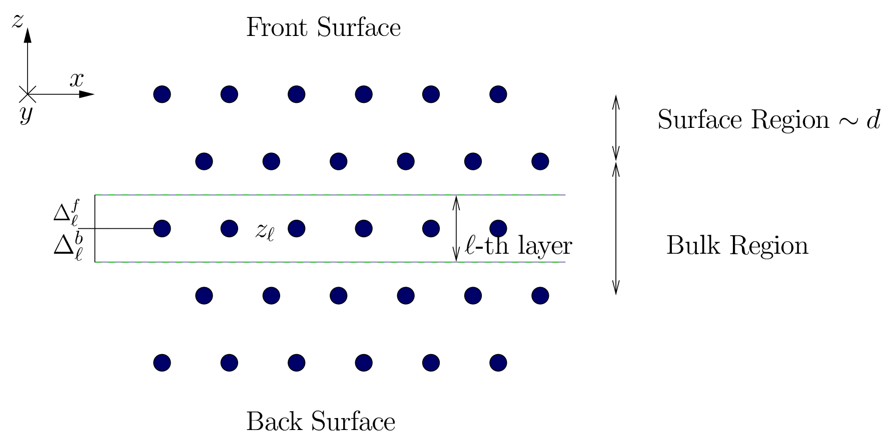

Figure 1.2: A sketch of a slab where the circles represent atoms.

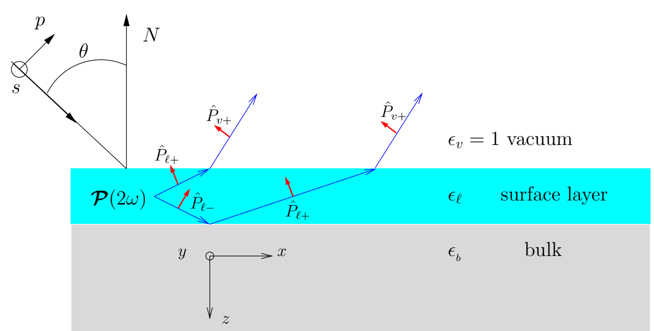

Figure 1.3: Sketch of the three layer model for SHG. Vacuum is on top with $\epsilon = 1$, the layer with non-linear polarization $\boldsymbol{\mathcal{P}}(2\omega)$ is characterized with $\epsilon_{\ell(}\omega)$ and the bulk with $\epsilon_b(\omega)$. In the dipolar approximation the bulk does not radiate SHG. The thin arrows are along the direction of propagation, and the unit vectors for p-polarization are denoted with thick arrows (capital letters denote SH components). The unit vector for s-polarization points along y (out of the page). N is normal to the surface, and θ is the angle of incidence for p or s input polarization.

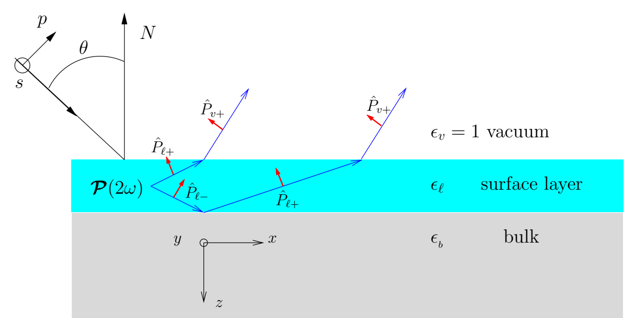

Figure 1.4: Sketch of the three layer model for SHG. Vacuum is on top with $\epsilon = 1$, the layer with nonlinear polarization $\mathbf{P}(2\omega)$ ischaracterized with $\epsilon_\ell(\omega)$ and the bulk with $\epsilon_b(\omega)$. In the dipolar approximation the bulk does not radiate SHG. The thin arrows are along the direction of propagation, and the unit vectors for p-polarization are denoted with thick arrows (capital letters denote SH components). The unit vector for s-polarization points along $-y$ (out of the page).

Appendix A

$\mathbf{r}_e$ 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

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

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

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

with Ω the volume of the unit cell.

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

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

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

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

on the other,

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \frac{\partial}{\partial \mathbf{k}}\int d\mathbf{r}\langle n\mathbf{k}|\mathbf{r}\rangle\langle \mathbf{r}|m\mathbf{k}'\rangle \\ &= \int d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r})\right)\psi_{m\mathbf{k}'}(\mathbf{r}),\end{aligned} \tag{A.5}$$

the derivative of the wavefunction is simply given by

$$\frac{\partial}{\partial \mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{\Omega}{8\pi^3}}\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)e^{-i\mathbf{k}\cdot\mathbf{r}} - i\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r}). \tag{A.6}$$

We take this back into Eq. (A.5), to obtain

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

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

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

to finally write,[**?**]

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\int_\Omega d\mathbf{r}\,\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)u_{m\mathbf{k}}(\mathbf{r}) \\ - i\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle.\end{aligned} \tag{A.9}$$

where Ω is the volume of the unit cell. From

$$\int_\Omega u_{m\mathbf{k}}u^*_{n\mathbf{k}}d\mathbf{r} = \delta_{nm}, \tag{A.10}$$

we easily find that

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

Therefore, we define

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i\int_\Omega d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r})\nabla_\mathbf{k}u_{m\mathbf{k}}(\mathbf{r}), \tag{A.12}$$

with $\partial/\partial\mathbf{k} = \nabla_\mathbf{k}$. 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

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

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

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_\mathbf{k}\delta(\mathbf{k}-\mathbf{k}')\right], \tag{A.14}$$

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}). \tag{A.15}$$

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,

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

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

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

Then,

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

with

$$
(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k})-i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k})-\boldsymbol{\xi}_{mm}(\mathbf{k})\right), \qquad \text{(A.19)}
$$

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 an arbitrary operator $\hat{\mathcal{O}}$. We use Eq. (1.31) and (A.18) in the next section.

Appendix B

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

From Eq. (1.26), we have that

$$
\begin{aligned}
\mathbf{v}^{\text{nl}}_{nm}(\mathbf{k}) = \langle n\mathbf{k}|\hat{\mathbf{v}}^{\text{nl}}|m\mathbf{k}'\rangle &= \frac{i}{\hbar}\langle n\mathbf{k}|[\hat{V}^{\text{nl}},\hat{\mathbf{r}}]|m\mathbf{k}'\rangle \\
&= \frac{i}{\hbar}\int d\mathbf{r}d\mathbf{r}'\langle n\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|[\hat{V}^{\text{nl}},\hat{\mathbf{r}}]|\mathbf{r}'\rangle\langle\mathbf{r}'|m\mathbf{k}'\rangle \\
&= \frac{i}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\langle\mathbf{r}|[\hat{V}^{\text{nl}},\hat{\mathbf{r}}]|\mathbf{r}'\rangle\psi_{m\mathbf{k}'}(\mathbf{r}'),
\end{aligned}
\tag{B.1}
$$

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

$$
\begin{aligned}
\langle\mathbf{r}|[\hat{V}^{\text{nl}},\hat{\mathbf{r}}]|\mathbf{r}'\rangle &= \langle\mathbf{r}|\hat{V}^{\text{nl}}\hat{\mathbf{r}}-\hat{\mathbf{r}}\hat{V}^{\text{nl}}|\mathbf{r}'\rangle = \langle\mathbf{r}|\hat{V}^{\text{nl}}\hat{\mathbf{r}}|\mathbf{r}'\rangle - \langle\mathbf{r}|\hat{\mathbf{r}}\hat{V}^{\text{nl}}|\mathbf{r}'\rangle \\
&= \langle\mathbf{r}|\hat{V}^{\text{nl}}\mathbf{r}'|\mathbf{r}'\rangle - \langle\mathbf{r}|\mathbf{r}\hat{V}^{\text{nl}}|\mathbf{r}'\rangle = \langle\mathbf{r}|\hat{V}^{\text{nl}}|\mathbf{r}'\rangle\big(\mathbf{r}'-\mathbf{r}\big) = V^{\text{nl}}(\mathbf{r},\mathbf{r}')\big(\mathbf{r}'-\mathbf{r}\big),
\end{aligned}
\tag{B.2}
$$

where we use $\hat{r}\langle\mathbf{r}| = r\langle\mathbf{r}|$, $\langle\mathbf{r}'|\hat{r} = \langle\mathbf{r}|r'$, and $V^{\text{nl}}(\mathbf{r},\mathbf{r}') = \langle\mathbf{r}|\hat{V}^{\text{nl}}|\mathbf{r}'\rangle$ (Eq. (1.12)). Also, we have the following identity which will be used shortly,

$$
\begin{aligned}
(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})\frac{1}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\text{nl}}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}' &= -i\frac{1}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}\left(\mathbf{r}V^{\text{nl}}(\mathbf{r},\mathbf{r}') - V^{\text{nl}}(\mathbf{r},\mathbf{r}')\mathbf{r}'\right)e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}' \\
(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})\langle\mathbf{K}|V^{\text{nl}}|\mathbf{K}'\rangle &= \frac{i}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\text{nl}}(\mathbf{r},\mathbf{r}')\big(\mathbf{r}'-\mathbf{r}\big)e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}',
\end{aligned}
\tag{B.3}
$$

where Ω is the volume of the unit cell, and we defined

$$
V^{\text{nl}}(\mathbf{K},\mathbf{K}') \equiv \langle\mathbf{K}|V^{\text{nl}}|\mathbf{K}'\rangle = \frac{1}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\text{nl}}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}',
\tag{B.4}
$$

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

$$\langle \mathbf{r}|n\mathbf{k}\rangle = \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G})e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{B.5}$$

with $\mathbf{K} = \mathbf{k} + \mathbf{G}$, we obtain from Eq. (B.1) and Eq. (B.3), that

$$\begin{aligned}
\mathbf{v}_{nm}^{\mathrm{nl}}(\mathbf{k}) &= \frac{i}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\sum_{\mathbf{G},\mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G})A_{m\mathbf{k}'}(\mathbf{G}')\frac{1}{\Omega}\int d\mathbf{r}d\mathbf{r}' e^{-i\mathbf{K}\cdot\mathbf{r}}\langle\mathbf{r}|[\hat{V}^{\mathrm{nl}},\hat{\mathbf{r}}]|\mathbf{r}'\rangle e^{i\mathbf{K}'\cdot\mathbf{r}'} \\
&= \frac{1}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\sum_{\mathbf{G},\mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G})A_{m\mathbf{k}'}(\mathbf{G}')\frac{i}{\Omega}\int d\mathbf{r}d\mathbf{r}' e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')\big(\mathbf{r}'-\mathbf{r}\big)e^{i\mathbf{K}'\cdot\mathbf{r}'} \\
&= \frac{1}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\sum_{\mathbf{G},\mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G})A_{m\mathbf{k}'}(\mathbf{G}')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V^{\mathrm{nl}}(\mathbf{K},\mathbf{K}').
\end{aligned} \tag{B.6}$$

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

$$\begin{aligned}
V_{\mathrm{KB}}^{\mathrm{nl}}(\mathbf{K},\mathbf{K}') &= \sum_s e^{i(\mathbf{K}-\mathbf{K}')\cdot\boldsymbol{\tau}_s}\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l F_{lm}^s(\mathbf{K})F_{lm}^{s*}(\mathbf{K}') \\
&= \sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l f_{lm}^s(\mathbf{K})f_{lm}^{s*}(\mathbf{K}'),
\end{aligned} \tag{B.7}$$

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

$$F_{lm}^s(\mathbf{K}) = \int d\mathbf{r}\, e^{-i\mathbf{K}\cdot\mathbf{r}}\delta V_l^S(\mathbf{r})\Phi_{lm}^{\mathrm{ps}}(\mathbf{r}). \tag{B.8}$$

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, $\Phi_{lm}^{\mathrm{ps}}(\mathbf{r})$ 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. [**?**]. From Eq. (B.7) we find

$$\begin{aligned}
(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V_{\mathrm{KB}}^{\mathrm{nl}}(\mathbf{K},\mathbf{K}') &= \sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})f_{lm}^s(\mathbf{K})f_{lm}^{s*}(\mathbf{K}') \\
&= \sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l\left(\left[\nabla_{\mathbf{K}}f_{lm}^s(\mathbf{K})\right]f_{lm}^{s*}(\mathbf{K}') + f_{lm}^s(\mathbf{K})\left[\nabla_{\mathbf{K}'}f_{lm}^{s*}(\mathbf{K}')\right]\right),
\end{aligned} \tag{B.9}$$

and using this in Eq. (B.6) leads to

$$
\begin{aligned}
\mathbf{v}^{\rm nl}_{nm}(\mathbf{k}) &= \frac{1}{\hbar}\sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l \sum_{\mathbf{G}\mathbf{G}'} A^*_{n,\vec{k}}(\mathbf{G})A_{n',\vec{k}}(\mathbf{G}') \\
&\times\left(\nabla_{\mathbf{K}} f^s_{lm}(\mathbf{K}) f^{s*}_{lm}(\mathbf{K}') + f^s_{lm}(\mathbf{K})\nabla_{\mathbf{K}'} f^{s*}_{lm}(\mathbf{K}')\right) \\
&= \frac{1}{\hbar}\sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l \left[\left(\sum_{\mathbf{G}} A^*_{n,\vec{k}}(\mathbf{G})\nabla_{\mathbf{K}} f^s_{lm}(\mathbf{K})\right)\left(\sum_{\mathbf{G}'} A_{n',\vec{k}}(\mathbf{G}') f^{s*}_{lm}(\mathbf{K}')\right)\right. \\
&+ \left.\left(\sum_{\mathbf{G}} A^*_{n,\vec{k}}(\mathbf{G}) f^s_{lm}(\mathbf{K})\right)\left(\sum_{\mathbf{G}'} A_{n',\vec{k}}(\mathbf{G}')\nabla_{\mathbf{K}'} f^{s*}_{lm}(\mathbf{K}')\right)\right],
\end{aligned}
\tag{B.10}
$$

where there are only single sums over $\mathbf{G}$. Above is implemented in the DP$^{\rm TM}$ code.[**?**]

Indeed, in DP$^{\rm TM}$ `calcolacommutatore.F90` above expansion coefficients are called
$E_l f^s_{lm}(\mathbf{K}) \rightarrow$ `fnlkslm` and $E_l\nabla_{\mathbf{K}} f^s_{lm}(\mathbf{K}) \rightarrow$ `fnldkslm`, where `fnlkslm` is an array indexed by $\mathbf{k}+\mathbf{G}$, and `fnldkslm` is vector array indexed by $\mathbf{k}+\mathbf{G}$.

Now we derive $\boldsymbol{\mathcal{V}}^{\rm nl,\ell}_{nm}(\mathbf{k})$. First we prove that

$$
\sum_{\mathbf{G}} |\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}| = 1. \tag{B.11}
$$

Proof:

$$
\langle n\mathbf{k}|1|n'\mathbf{k}\rangle = \delta_{nn'}, \tag{B.12}
$$

take

$$
\begin{aligned}
\sum_{\mathbf{G}}\langle n\mathbf{k}||\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}||n'\mathbf{k}\rangle &= \int d\mathbf{r}d\mathbf{r}'\sum_{\mathbf{G}}\langle n\mathbf{k}||\mathbf{r}\rangle\langle\mathbf{r}||\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}||\mathbf{r}'\rangle\langle\mathbf{r}'||n'\mathbf{k}\rangle \\
&= \int d\mathbf{r}d\mathbf{r}'\sum_{\mathbf{G}}\psi^*_{n\mathbf{k}}(\mathbf{r})\frac{1}{\sqrt{\Omega}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\frac{1}{\sqrt{\Omega}}e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}'}\psi_{m\mathbf{k}}(\mathbf{r}') \\
&= \int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}}(\mathbf{r}')\frac{1}{V}\sum_{\mathbf{G}}e^{i(\mathbf{k}+\mathbf{G})\cdot(\mathbf{r}-\mathbf{r}')} \\
&= \int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}}(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') = \int d\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}}(\mathbf{r}) = \delta_{nn'},
\end{aligned}
\tag{B.13}
$$

and thus Eq. (B.11) follows. `Q.E.D.` We used

$$
\langle\mathbf{r}|\mathbf{k}+\mathbf{G}\rangle = \frac{1}{\sqrt{\Omega}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \tag{B.14}
$$

From Eq. (1.71), we would like to calculate

$$
\boldsymbol{\mathcal{V}}^{\rm nl,\ell}_{nm}(\mathbf{k}) = \frac{1}{2}\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\rm nl} + \mathbf{v}^{\rm nl}C^\ell(z)|m\mathbf{k}\rangle. \tag{B.15}
$$

We work out the first term in the r.h.s,

$$
\begin{aligned}
\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\mathrm{nl}}|m\mathbf{k}\rangle &= \sum_{\mathbf{G}}\langle n\mathbf{k}|C^\ell(z)|\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}|\mathbf{v}^{\mathrm{nl}}|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\int d\mathbf{r}\int d\mathbf{r}'\langle n\mathbf{k}||\mathbf{r}\rangle\langle\mathbf{r}|C^\ell(z)|\mathbf{r}'\rangle\langle\mathbf{r}'||\mathbf{k}+\mathbf{G}\rangle \\
&\times\int d\mathbf{r}''\int d\mathbf{r}'''\langle\mathbf{k}+\mathbf{G}||\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{v}^{\mathrm{nl}}|\mathbf{r}'''\rangle\langle\mathbf{r}'''||m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\int d\mathbf{r}\int d\mathbf{r}'\langle n\mathbf{k}|\mathbf{r}\rangle C^\ell(z)\delta(\mathbf{r}-\mathbf{r}')\langle\mathbf{r}'|\mathbf{k}+\mathbf{G}\rangle \\
&\times\int d\mathbf{r}''\int d\mathbf{r}'''\langle\mathbf{k}+\mathbf{G}|\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{v}^{\mathrm{nl}}|\mathbf{r}'''\rangle\langle\mathbf{r}'''|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\int d\mathbf{r}\langle n\mathbf{k}|\mathbf{r}\rangle C^\ell(z)\langle\mathbf{r}|\mathbf{k}+\mathbf{G}\rangle \\
&\times\frac{i}{\hbar}\int d\mathbf{r}''\int d\mathbf{r}'''\langle\mathbf{k}+\mathbf{G}|\mathbf{r}''\rangle V^{\mathrm{nl}}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')\langle\mathbf{r}'''|m\mathbf{k}\rangle,
\end{aligned}
\tag{B.16}
$$

where we used Eq. (B.2) and (1.26). We use Eq. (B.5), (B.14) and (B.3) to obtain

$$
\begin{aligned}
\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\mathrm{nl}}|m\mathbf{k}\rangle &= \sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G}')\frac{1}{\Omega}\int d\mathbf{r}e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}}C^\ell(z)e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\
&\times\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')\frac{i}{\hbar\Omega}\int d\mathbf{r}''\int d\mathbf{r}'''e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}''}V^{\mathrm{nl}}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')e^{i(\mathbf{k}+\mathbf{G}'')\cdot\mathbf{r}'''} \\
&= \frac{1}{\hbar}\sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}f_\ell(\mathbf{G}_\perp-\mathbf{G}'_\perp)\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}''})V^{\mathrm{nl}}(\mathbf{K},\mathbf{K}''),
\end{aligned}
\tag{B.17}
$$

where

$$
\frac{1}{\Omega}\int d\mathbf{r}\,C^\ell(z)e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} = \delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}f_\ell(\mathbf{G}_\perp-\mathbf{G}'_\perp),
\tag{B.18}
$$

and

$$
f_\ell(g) = \frac{1}{L}\int_{z_\ell-\Delta^b_\ell}^{z_\ell+\Delta^f_\ell}e^{igz}dz,
\tag{B.19}
$$

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

$$
\mathcal{F}^\ell_{n\mathbf{k}}(\mathbf{G}) = \sum_{\mathbf{G}'}A_{n\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}f_\ell(\mathbf{G}'_\perp-\mathbf{G}_\perp),
\tag{B.20}
$$

and

$$
\mathcal{H}_{n\mathbf{k}}(\mathbf{G}) = \sum_{\mathbf{G}'}A_{n\mathbf{k}}(\mathbf{G}')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V^{\mathrm{nl}}(\mathbf{K},\mathbf{K}'),
\tag{B.21}
$$

thus we can compactly write,

$$\langle n\mathbf{k}|C^{\ell}(z)\mathbf{v}^{\text{nl}}|m\mathbf{k}\rangle = \frac{1}{\hbar}\sum_{\mathbf{G}}\mathcal{F}^{\ell *}_{n\mathbf{k}}(\mathbf{G})\mathcal{H}_{m\mathbf{k}}(\mathbf{G}). \tag{B.22}$$

Now, the second term of Eq. (B.15)

$$\begin{aligned}
\langle n\mathbf{k}|\mathbf{v}^{\text{nl}}C^{\ell}(z)|m\mathbf{k}\rangle &= \sum_{\mathbf{G}}\langle n\mathbf{k}|\mathbf{v}^{\text{nl}}|\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}|C^{\ell}(z)|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\int d\mathbf{r}''\int d\mathbf{r}'''\langle n\mathbf{k}||\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{v}^{\text{nl}}|\mathbf{r}'''\rangle\langle\mathbf{r}'''||\mathbf{k}+\mathbf{G}\rangle \\
&\times\int d\mathbf{r}\int d\mathbf{r}'\langle\mathbf{k}+\mathbf{G}||\mathbf{r}\rangle\langle\mathbf{r}|C^{\ell}(z)|\mathbf{r}'\rangle\langle\mathbf{r}'||m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\frac{i}{\hbar}\int d\mathbf{r}''\int d\mathbf{r}'''\langle n\mathbf{k}|\mathbf{r}''\rangle V^{\text{nl}}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')\langle\mathbf{r}'''|\mathbf{k}+\mathbf{G}\rangle \\
&\times\int d\mathbf{r}\langle\mathbf{k}+\mathbf{G}|\mathbf{r}\rangle C^{\ell}(z)\langle\mathbf{r}|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^{*}_{n\mathbf{k}}(\mathbf{G}')\frac{i}{\hbar\Omega}\int d\mathbf{r}''\int d\mathbf{r}'''e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}''}V^{\text{nl}}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}'''} \\
&\times\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')\frac{1}{\Omega}\int d\mathbf{r}e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}C^{\ell}(z)e^{i(\mathbf{k}+\mathbf{G}'')\cdot\mathbf{r}} \\
&= \frac{1}{\hbar}\sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^{*}_{n\mathbf{k}}(\mathbf{G}')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V^{\text{nl}}(\mathbf{K}',\mathbf{K}) \\
&\times\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')\delta_{\mathbf{G}_{\parallel}\mathbf{G}''_{\parallel}}f_{\ell}(\mathbf{G}''_{\perp}-\mathbf{G}_{\perp}) \\
&= \frac{1}{\hbar}\sum_{\mathbf{G}}\mathcal{H}^{*}_{n\mathbf{k}}(\mathbf{G})\mathcal{F}^{\ell}_{m\mathbf{k}}(\mathbf{G}).
\end{aligned} \tag{B.23}$$

Therefore Eq. (B.15) is compactly given by

$$\boldsymbol{\mathcal{V}}^{\text{nl},\ell}_{nm}(\mathbf{k}) = \frac{1}{2\hbar}\sum_{\mathbf{G}}\left(\mathcal{F}^{\ell *}_{n\mathbf{k}}(\mathbf{G})\mathcal{H}_{m\mathbf{k}}(\mathbf{G}) + \mathcal{H}^{*}_{n\mathbf{k}}(\mathbf{G})\mathcal{F}^{\ell}_{m\mathbf{k}}(\mathbf{G})\right). \tag{B.24}$$

For fully separable pseudopotentials in the Kleinman-Bylander (KB) form,[**?**, **?**, **?**] we can use Eq. (B.9) and evaluate above expression, that we have implemented in the DP$^{\mathrm{TM}}$ code.[**?**] Explicitly,

$$
\begin{aligned}
\boldsymbol{\mathcal{V}}^{\mathrm{nl},\ell}_{nm}(\mathbf{k}) = \frac{1}{2\hbar}\sum_s \sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l \\
\Bigg[\left(\sum_{\mathbf{G}''} \nabla_{\mathbf{G}''} f^s_{lm}(\mathbf{G}'') \sum_{\mathbf{G}} A^*_{n\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_{||}\mathbf{G}''_{||}} f_\ell(G_z - G''_z)\right)\left(\sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') f^{s*}_{lm}(\mathbf{K}')\right) \\
+\left(\sum_{\mathbf{G}''} f^s_{lm}(\mathbf{G}'') \sum_{\mathbf{G}} A^*_{n\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_{||}\mathbf{G}''_{||}} f_\ell(G_z - G''_z)\right)\left(\sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') \nabla_{\mathbf{K}'} f^{s*}_{lm}(\mathbf{K}')\right) \\
+\left(\sum_{\mathbf{G}} A^*_{n\mathbf{k}}(\mathbf{G}) \nabla_{\mathbf{G}} f^s_{lm}(\mathbf{G})\right)\left(\sum_{\mathbf{G}''} f^{s*}_{lm}(\mathbf{G}'') \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}'_{||}\mathbf{G}''_{||}} f_\ell(G''_z - G'_z)\right) \\
+\left(\sum_{\mathbf{G}} A^*_{n\mathbf{k}}(\mathbf{G}) f^s_{lm}(\mathbf{G})\right)\left(\sum_{\mathbf{G}''} \nabla_{\mathbf{G}''} f^{s*}_{lm}(\mathbf{G}'') \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}'_{||}\mathbf{G}''_{||}} f_\ell(G''_z - G'_z)\right)\Bigg].
\end{aligned}
\tag{B.25}
$$

For a full slab calculation, equivalent to a bulk calculation, $C^\ell(z) = 1$ and then $f_\ell(g) = \delta_{g0}$, and Eq. (B.25) reduces to Eq. (B.10).

Appendix C

$V_{nm}^{\sigma,\mathrm{a},\ell}$ and $\left(\mathcal{V}_{nm}^{\sigma,\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}}$

From Eq. (1.73)

$$\left(\mathcal{V}_{nm}^{\sigma,\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} = \left(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} + \left(\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} . \tag{C.1}$$

For the LDA term we have

$$\begin{aligned}
\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell} &= \frac{1}{2}\left(v^{\mathrm{LDA},\mathrm{a}}\mathcal{C}^{\ell} + \mathcal{C}^{\ell} v^{\mathrm{LDA},\mathrm{a}}\right)_{nm} \\
&= \frac{1}{2}\sum_q \left(v_{nq}^{\mathrm{LDA},\mathrm{a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell} v_{qm}^{\mathrm{LDA},\mathrm{a}}\right) \\
\left(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a}}\right)_{;k^{\mathrm{b}}} &= \frac{1}{2}\sum_q \left(v_{nq}^{\mathrm{LDA},\mathrm{a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell} v_{qm}^{\mathrm{LDA},\mathrm{a}}\right)_{;k^{\mathrm{b}}} \\
&= \frac{1}{2}\sum_q \left((v_{nq}^{\mathrm{LDA},\mathrm{a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + v_{nq}^{\mathrm{LDA},\mathrm{a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} + (\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}} v_{qm}^{\mathrm{LDA},\mathrm{a}} + \mathcal{C}_{nq}^{\ell}(v_{qm}^{\mathrm{LDA},\mathrm{a}})_{;k^{\mathrm{b}}}\right) ,
\end{aligned} \tag{C.2}$$

where we omitted $\mathbf{k}$ in all quantities. From Eq. (B.6) we know that $\mathbf{v}_{nm}^{\mathrm{nl}}(\mathbf{k})$ can be readily calculated, and from Appendix G, both v_{nm}^{a} and $\mathcal{C}_{nm}^{\ell}$ are also known quantities, and thus the $\mathbf{v}_{nm}^{\mathrm{LDA}}(\mathbf{k})$ are known, which in turns means that $\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}$ are also known. For the generalized derivative $(\mathbf{v}_{nm}^{\mathrm{LDA}}(\mathbf{k}))_{;\mathbf{k}}$ we use Eq. (1.31) to write

$$\begin{aligned}
(v_{nm}^{\mathrm{LDA},\mathrm{a}})_{;k^{\mathrm{b}}} &= im_e(\omega_{nm}^{\mathrm{LDA}} r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}} \\
&= im_e(\omega_{nm}^{\mathrm{LDA}})_{;k^{\mathrm{b}}} r_{nm}^{\mathrm{a}} + im_e\omega_{nm}^{\mathrm{LDA}}(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}} \\
&= im_e\Delta_{nm}^{b} r_{nm}^{\mathrm{a}} + im_e\omega_{nm}^{\mathrm{LDA}}(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}} \quad \text{for} \quad n \neq m,
\end{aligned} \tag{C.3}$$

where we used Eq (1.79) and $(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}}$ is given in Eq. (H.12).

Likewise,

$$\begin{aligned}
\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell} &= \frac{1}{2}\left(v^{\mathcal{S},\mathrm{a}}\mathcal{C}^{\ell} + \mathcal{C}^{\ell}v^{\mathcal{S},\mathrm{a}}\right)_{nm} \\
&= \frac{1}{2}\sum_{q}\left(v_{nq}^{\mathcal{S},\mathrm{a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell}v_{qm}^{\mathcal{S},\mathrm{a}}\right) \\
\left(\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a}}\right)_{;k^{\mathrm{b}}} &= \frac{1}{2}\sum_{q}\left(v_{nq}^{\mathcal{S},\mathrm{a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell}v_{qm}^{\mathcal{S},\mathrm{a}}\right)_{;k^{\mathrm{b}}} \\
&= \frac{1}{2}\sum_{q}\left((v_{nq}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + v_{nq}^{\mathcal{S},\mathrm{a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} + (\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}}v_{qm}^{\mathcal{S},\mathrm{a}} + \mathcal{C}_{nq}^{\ell}(v_{qm}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}}\right),
\end{aligned} \tag{C.4}$$

where $v_{nm}^{\mathcal{S},\mathrm{a}}(\mathbf{k})$ are given in Eq. (1.27) and $(v_{nm}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}}$ is given in Eq. A(6) of Ref. [9],

$$(v_{nm}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}} = i\Delta f_{mn}(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}}. \tag{C.5}$$

To evaluate $(\mathcal{C}_{nm}^{\ell})_{;k^{\mathrm{a}}}$, 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,

$$\langle n\mathbf{k}|\left[r^{\mathrm{a}},\mathcal{C}^{\ell}(z)\right]|m\mathbf{k}'\rangle = \langle n\mathbf{k}|\left[r_{e}^{\mathrm{a}},\mathcal{C}^{\ell}(z)\right]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|\left[r_{i}^{\mathrm{a}},\mathcal{C}^{\ell}(z)\right]|m\mathbf{k}'\rangle = 0. \tag{C.6}$$

The interband part reduces to,

$$\begin{aligned}
\left[r_{e}^{\mathrm{a}},\mathcal{C}^{\ell}(z)\right]_{nm} &= \sum_{q\mathbf{k}''}\left(\langle n\mathbf{k}|r_{e}^{\mathrm{a}}|q\mathbf{k}''\rangle\langle q\mathbf{k}''|\mathcal{C}^{\ell}(z)|m\mathbf{k}'\rangle - \langle n\mathbf{k}|\mathcal{C}^{\ell}(z)|q\mathbf{k}''\rangle\langle q\mathbf{k}''|r_{e}^{\mathrm{a}}|m\mathbf{k}'\rangle\right) \\
&= \sum_{q\mathbf{k}''}\delta(\mathbf{k}-\mathbf{k}'')\delta(\mathbf{k}'-\mathbf{k}'')\left((1-\delta_{qn})\xi_{nq}^{\mathrm{a}}\mathcal{C}_{qm}^{\ell} - (1-\delta_{qm})\mathcal{C}_{nq}^{\ell}\xi_{qm}^{\mathrm{a}}\right) \\
&= \delta(\mathbf{k}-\mathbf{k}')\left(\sum_{q}\left(\xi_{nq}^{\mathrm{a}}\mathcal{C}_{qm}^{\ell} - \mathcal{C}_{nq}^{\ell}\xi_{qm}^{\mathrm{a}}\right) + \mathcal{C}_{nm}^{\ell}(\xi_{mm}^{\mathrm{a}} - \xi_{nn}^{\mathrm{a}})\right),
\end{aligned} \tag{C.7}$$

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

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_{i},\mathcal{C}^{\ell}(z)]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{C}_{nm}^{\ell})_{;\mathbf{k}}, \tag{C.8}$$

then from Eq. (C.6)

$$\left((\mathcal{C}^\ell_{nm})_{;\mathbf{k}} - i\sum_q \left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm}\right) - i\mathcal{C}^\ell_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \right) i\delta(\mathbf{k}-\mathbf{k}') = 0$$

$$\begin{aligned}
\frac{1}{i}(\mathcal{C}^\ell_{nm})_{;\mathbf{k}} &= \sum_q \left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm}\right) + \mathcal{C}^\ell_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
&= \sum_{q\neq nm} \left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm}\right) + \left(\xi^{\mathrm{a}}_{nn}\mathcal{C}^\ell_{nm} - \mathcal{C}^\ell_{nn}\xi^{\mathrm{a}}_{nm}\right)_{q=n} + \left(\xi^{\mathrm{a}}_{nm}\mathcal{C}^\ell_{mm} - \mathcal{C}^\ell_{nm}\xi^{\mathrm{a}}_{mm}\right)_{q=m} \\
&+ \mathcal{C}^\ell_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
(\mathcal{C}^\ell_{nm})_{;\mathbf{k}} &= i\sum_{q\neq nm} \left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm}\right) + i\xi^{\mathrm{a}}_{nm}(\mathcal{C}^\ell_{mm} - \mathcal{C}^\ell_{nn}) \\
&= i\sum_{q\neq nm} \left(r^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}r^{\mathrm{a}}_{qm}\right) + ir^{\mathrm{a}}_{nm}(\mathcal{C}^\ell_{mm} - \mathcal{C}^\ell_{nn}) \\
&= i\left(\sum_{q\neq n} r^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \sum_{q\neq m}\mathcal{C}^\ell_{nq}r^{\mathrm{a}}_{qm}\right) + ir^{\mathrm{a}}_{nm}(\mathcal{C}^\ell_{mm} - \mathcal{C}^\ell_{nn}),
\end{aligned} \tag{C.9}$$

since in every ξ^{a}_{nm}, $n \neq m$, thus we replace it by r^{a}_{nm}. The matrix elements $\mathcal{C}^\ell_{nm}(\mathbf{k})$ are calculated in Appendix G.

For the general case of

$$\langle n\mathbf{k}| \left[\hat{r}^{\mathrm{a}}, \hat{\mathcal{G}}(\mathbf{r},\mathbf{p})\right] |m\mathbf{k}'\rangle = \mathcal{U}_{nm}(\mathbf{k}), \tag{C.10}$$

above result would lead to a more general expression,

$$(\mathcal{G}_{nm}(\mathbf{k}))_{;k^{\mathrm{a}}} = \mathcal{U}_{nm}(\mathbf{k}) + i\sum_{q\neq(nm)} \left(r^{\mathrm{a}}_{nq}(\mathbf{k})\mathcal{G}_{qm}(\mathbf{k}) - \mathcal{G}_{nq}(\mathbf{k})r^{\mathrm{a}}_{qm}(\mathbf{k})\right) + ir^{\mathrm{a}}_{nm}(\mathbf{k})(\mathcal{G}_{mm}(\mathbf{k}) - \mathcal{G}_{nn}(\mathbf{k})). \tag{C.11}$$

Appendix D

Generalized derivative $(\omega_n(\mathbf{k}))_{;\mathbf{k}}$

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

$$\langle n\mathbf{k}|\hat{H}_0^\sigma|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}')\hbar\omega_m^\sigma(\mathbf{k}), \tag{D.1}$$

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

$$\begin{aligned}(H_{0,nn}^\sigma)_{;\mathbf{k}} &= \nabla_{\mathbf{k}} H_{0,nn}^\sigma(\mathbf{k}) - iH_{0,nn}^\sigma(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{nn}(\mathbf{k})\right)\\ &= \hbar\nabla_{\mathbf{k}}\omega_m^\sigma(\mathbf{k}),\end{aligned} \tag{D.2}$$

where from Eq. (A.18),

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{H}_0]|m\mathbf{k}\rangle = i\delta_{nm}\hbar(\omega_m^\sigma(\mathbf{k}))_{;\mathbf{k}} = i\delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m^\sigma(\mathbf{k}), \tag{D.3}$$

then

$$(\omega_n^\sigma(\mathbf{k}))_{;\mathbf{k}} = \nabla_{\mathbf{k}}\omega_n^\sigma(\mathbf{k}). \tag{D.4}$$

From Eq. (1.20)

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0^\sigma]|m\mathbf{k}\rangle = i\hbar\mathbf{v}_{nm}^\sigma(\mathbf{k}), \tag{D.5}$$

therefore, substituting above into

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0^\sigma]|m\mathbf{k}\rangle = \langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{H}_0^\sigma]|m\mathbf{k}\rangle + \langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{H}_0^\sigma]|m\mathbf{k}\rangle, \tag{D.6}$$

we get

$$i\hbar\mathbf{v}_{nm}^\sigma(\mathbf{k}) = i\delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m^\sigma(\mathbf{k}) + \omega_{mn}^\sigma\mathbf{r}_{e,nm}(\mathbf{k}), \tag{D.7}$$

from where

$$
\begin{aligned}
\nabla_{\mathbf{k}}\omega_n^{\sigma}(\mathbf{k}) &= \mathbf{v}_{nn}^{\sigma}(\mathbf{k}) \\
\nabla_{\mathbf{k}}(\omega_n^{\mathrm{LDA}}(\mathbf{k}) + \frac{\Sigma}{\hbar}(1-f_n)) &= \nabla_{\mathbf{k}}\omega_n^{\mathrm{LDA}}(\mathbf{k}) \\
\nabla_{\mathbf{k}}\omega_n^{\mathrm{LDA}}(\mathbf{k}) &= \mathbf{v}_{nn}^{\sigma}(\mathbf{k}),
\end{aligned}
\tag{D.8}
$$

where we used Eq. (1.16), but from Eq. (1.27), $v_{nn}^{\mathcal{S}} = 0$, and then $\mathbf{v}_{nn}^{\sigma} = v_{nn}^{\mathrm{LDA}}$. Thus, from Eq. (D.4)

$$
(\omega_n^{\sigma}(\mathbf{k}))_{;k^{\mathrm{a}}} = (\omega_n^{\mathrm{LDA}}(\mathbf{k}))_{;k^{\mathrm{a}}} = v_{nn}^{\mathrm{LDA,a}}(\mathbf{k}),
\tag{D.9}
$$

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

Appendix E

Expressions for χ^S_{abc} in terms of $\mathcal{V}^{\sigma,\mathbf{a},\ell}_{mn}$

As can be seen from the prefactor of Eqs. (1.76) and (1.77), they diverge as $\tilde{\omega} \to 0$. To remove this apparent divergence of $\boldsymbol{\chi}^S$, we perform a partial fraction expansion in $\tilde{\omega}$.

E.1 Intraband Contributions

For the intraband term of Eq. (1.76) we obtain

$$\begin{aligned} I = C &\left[-\frac{1}{2(\omega^\sigma_{nm})^2} \frac{1}{\omega^\sigma_{nm} - \tilde{\omega}} + \frac{2}{(\omega^\sigma_{nm})^2} \frac{1}{\omega^\sigma_{nm} - 2\tilde{\omega}} + \frac{1}{2(\omega^\sigma_{nm})^2} \frac{1}{\tilde{\omega}} \right] \\ - D &\left[-\frac{3}{2(\omega^\sigma_{nm})^3} \frac{1}{\omega^\sigma_{nm} - \tilde{\omega}} + \frac{4}{(\omega^\sigma_{nm})^3} \frac{1}{\omega^\sigma_{nm} - 2\tilde{\omega}} + \frac{1}{2(\omega^\sigma_{nm})^3} \frac{1}{\tilde{\omega}} - \frac{1}{2(\omega^\sigma_{nm})^2} \frac{1}{(\omega^\sigma_{nm} - \tilde{\omega})^2} \right], \end{aligned} \tag{E.1}$$

where $C = f_{mn} \mathcal{V}^{\sigma,\mathrm{a}}_{mn} (r^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{c}}}$, and $D = f_{mn} \mathcal{V}^{\sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nm} \Delta^{\mathrm{c}}_{nm}$.

Time-reversal symmetry leads to the following relationships:

$$\begin{aligned} \mathbf{r}_{mn}(\mathbf{k})|_{-\mathbf{k}} &= \mathbf{r}_{nm}(\mathbf{k})|_{\mathbf{k}}, \\ (\mathbf{r}_{mn})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (-\mathbf{r}_{nm})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \\ \mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}(\mathbf{k})|_{-\mathbf{k}} &= -\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}(\mathbf{k})|_{\mathbf{k}}, \\ (\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \\ \omega^\sigma_{mn}(\mathbf{k})|_{-\mathbf{k}} &= \omega^\sigma_{mn}(\mathbf{k})|_{\mathbf{k}}, \\ \Delta^a_{nm}(\mathbf{k})|_{-\mathbf{k}} &= -\Delta^a_{nm}(\mathbf{k})|_{\mathbf{k}}. \end{aligned} \tag{E.2}$$

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 above relationships, we can show that the $1/\omega$ terms cancel each other out. Therefore, all the remaining non-zero terms in expressions (E.1) are simple ω and 2ω resonant denominators well behaved at zero frequency.

To apply time-reversal invariance, we notice that the energy denominators are invariant under $\mathbf{k} \to -\mathbf{k}$, and then we only look at the numerators, then

$$\begin{aligned} C \to f_{mn}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + f_{mn}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}} \\ = f_{mn}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \left(-\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)\left(-r^{\mathrm{LDA,b}}_{mn}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}}\right] \\ = f_{mn}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}} + \mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\left(r^{\mathrm{LDA,b}}_{mn}\right)_{;k^{\mathrm{c}}}\right] \\ = f_{mn}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}} + \left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right)^{*}\right] \\ = 2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right], \end{aligned} \tag{E.3}$$

and likewise,

$$\begin{aligned} D \to f_{mn}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + f_{mn}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\Delta^{\mathrm{c}}_{nm}|_{-\mathbf{k}} \\ = f_{mn}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + \left(-\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)r^{\mathrm{LDA,b}}_{mn}\left(-\Delta^{\mathrm{c}}_{nm}\right)|_{\mathbf{k}}\right] \\ = f_{mn}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm} + \mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm} \\ = f_{mn}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm} + \left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right)^{*}\right]\Delta^{\mathrm{c}}_{nm} \\ = 2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}. \end{aligned} \tag{E.4}$$

The last term in the second line of Eq. (E.1) is dealt with as follows.

$$\begin{aligned} \frac{D}{2(\omega^{\sigma}_{nm})^2}\frac{1}{(\omega^{\sigma}_{nm}-\tilde{\omega})^2} &= \frac{f_{mn}}{2}\frac{\mathcal{V}^{\sigma,\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\frac{\Delta^{\mathrm{c}}_{nm}}{(\omega^{\sigma}_{nm}-\tilde{\omega})^2} = -\frac{f_{mn}}{2}\frac{\mathcal{V}^{\sigma,\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\left(\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}}\right)_{;k^{\mathrm{c}}} \\ &= \frac{f_{mn}}{2}\left(\frac{\mathcal{V}^{\sigma,\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\right)_{;k^{\mathrm{c}}}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}}, \end{aligned} \tag{E.5}$$

where we used Eqs. (1.79) and for the last line, we performed an integration by parts over the Brillouin zone, where the contribution from the edges vanishes.[**?**] Now, we apply the chain rule, to get

$$\left(\frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\right)_{;k^{\mathrm{c}}} = \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}} + \frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}}{(\omega^{\sigma}_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}} - \frac{2\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^3}\left(\omega^{\sigma}_{nm}\right)_{;k^{\mathrm{c}}}, \tag{E.6}$$

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

$$\begin{aligned}
\frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}} &= \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{r^{\mathrm{LDA,b}}_{mn}}{(\omega^{\sigma}_{nm})^2}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} \\
&= \frac{1}{(\omega^{\sigma}_{nm})^2}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}} + \left(r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right)^*\right] \\
&= \frac{2}{(\omega^{\sigma}_{nm})^2}\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right],
\end{aligned} \tag{E.7}$$

the second term is reduced to

$$\begin{aligned}
\frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}}{(\omega^{\sigma}_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}}{(\omega^{\sigma}_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}} &= \frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}}{(\omega^{\sigma}_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}}{(\omega^{\sigma}_{nm})^2}\left(r^{\mathrm{LDA,b}}_{mn}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} \\
&= \frac{1}{(\omega^{\sigma}_{nm})^2}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}} + \left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right)^*\right] \\
&= \frac{2}{(\omega^{\sigma}_{nm})^2}\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right],
\end{aligned} \tag{E.8}$$

and by using (1.79), the third term is reduced to

$$\begin{aligned}
\frac{2\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^3}\left(\omega^{\sigma}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{2\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^3}\left(\omega^{\sigma}_{nm}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}} &= \frac{2\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^3}\Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + \frac{2\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^3}\Delta^{\mathrm{c}}_{nm}|_{-\mathbf{k}} \\
&= \frac{2\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}}{(\omega^{\sigma}_{nm})^3}\Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + \frac{2\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^3}\Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} \\
&= \frac{2}{(\omega^{\sigma}_{nm})^3}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn} + \left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right)^*\right]\Delta^{\mathrm{c}}_{nm} \\
&= \frac{4}{(\omega^{\sigma}_{nm})^3}\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm}.
\end{aligned} \tag{E.9}$$

Combining the results from (E.7), (E.8), and (E.9) into (E.6),

$$\begin{aligned}
&\frac{f_{mn}}{2}\left[\left(\frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \left(\frac{\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}}{(\omega^{\sigma}_{nm})^2}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}}\right]\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}} = \\
&\left(2\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right] + 2\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right] - \frac{4}{\omega^{\sigma}_{nm}}\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm}\right)\frac{f_{mn}}{2(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}}.
\end{aligned} \tag{E.10}$$

We substitute (J.13), (E.4), and (E.10) in (E.1),

$$I = \left[-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}} + \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-2\tilde{\omega}}\right]$$
$$+ \left[\frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{2(\omega^{\sigma}_{nm})^3}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^{\sigma}_{nm})^3}\frac{1}{\omega^{\sigma}_{nm}-2\tilde{\omega}}\right.$$
$$+ \frac{f_{mn}\left(2\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right] + 2\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right] - \frac{4}{\omega^{\sigma}_{nm}}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm}\right)}{2(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}}$$

If we simplify,

$$\begin{aligned}
I = &-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}} + \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-2\tilde{\omega}}\\
&+\frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{2(\omega^{\sigma}_{nm})^3}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^{\sigma}_{nm})^3}\frac{1}{\omega^{\sigma}_{nm}-2\tilde{\omega}}\\
&+\frac{2f_{mn}\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}}\\
&+\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega^{\sigma}_{nm})^2}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}}\\
&-\frac{4f_{mn}\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm}}{2(\omega^{\sigma}_{nm})^3}\frac{1}{\omega^{\sigma}_{nm}-\tilde{\omega}},
\end{aligned} \tag{E.11}$$

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

$$\begin{aligned}
I_{2\omega} &= -\frac{e^3}{\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^{\sigma}_{nm})^2} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^{\sigma}_{nm})^3}\right]\frac{1}{\omega^{\sigma}_{nm}-2\tilde{\omega}}\\
&= -\frac{e^3}{\hbar^2}\sum_{mn\mathbf{k}}\frac{4f_{mn}}{(\omega^{\sigma}_{nm})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{\omega^{\sigma}_{nm}}\right]\frac{1}{\omega^{\sigma}_{nm}-2\tilde{\omega}}.
\end{aligned} \tag{E.12}$$

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

$$\lim_{\eta\to 0}\frac{1}{x \pm i\eta} = P\frac{1}{x} \mp i\pi\delta(x), \tag{E.13}$$

and can finally rewrite (J.15) in the desired form,

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{a},\ell\mathrm{bc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^\sigma_{cv})^2}\left(\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left(r^{\mathrm{LDA,b}}_{cv}\right)_{;k^\mathrm{c}}\right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}r^{\mathrm{LDA,b}}_{cv}\right]\Delta^\mathrm{c}_{cv}}{\omega^\sigma_{cv}}\right)\delta(\omega^\sigma_{cv}-2\omega). \tag{E.14}$$

where we added a 1/2 from the sum over $\mathbf{k}\to-\mathbf{k}$. We do the same for the $\tilde\omega$ terms in (E.11) to obtain

$$\begin{aligned} I_\omega = -\frac{e^3}{2\hbar^2}\sum_{nm\mathbf{k}}\Bigg[&-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^\mathrm{c}}\right]}{(\omega^\sigma_{nm})^2} + \frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^\mathrm{c}_{nm}}{(\omega^\sigma_{nm})^3} \\ &+\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^\mathrm{c}}\right]}{(\omega^\sigma_{nm})^2} - \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right]\Delta^\mathrm{c}_{nm}}{(\omega^\sigma_{nm})^3} \\ &+\frac{2f_{mn}\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^\mathrm{c}}\right]}{(\omega^\sigma_{nm})^2}\Bigg]\frac{1}{\omega^\sigma_{nm}-\tilde\omega}. \end{aligned} \tag{E.15}$$

We reduce in the same way as (J.15),

$$I_\omega = -\frac{e^3}{2\hbar^2}\sum_{nm\mathbf{k}}\frac{f_{mn}}{(\omega^\sigma_{nm})^2}\left[2\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}\right)_{;k^\mathrm{c}}\right]+\frac{2\,\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^\mathrm{c}_{nm}}{\omega^\sigma_{nm}}\right]\frac{1}{\omega^\sigma_{nm}-\tilde\omega}, \tag{E.16}$$

and using (E.13) we obtain our final form,

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{a},\ell\mathrm{bc},\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{cv}\frac{1}{(\omega^\sigma_{cv})^2}\left(\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{cv}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\right)_{;k^\mathrm{c}}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}r^{\mathrm{LDA,b}}_{cv}\right]\Delta^\mathrm{c}_{cv}}{\omega^\sigma_{cv}}\right)\delta(\omega^\sigma_{cv}-\omega), \tag{E.17}$$

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

E.2 Interband Contributions

We follow an equivalent procedure for the interband contribution. From Eq. (1.77) we have

$$\begin{aligned} E = A&\left[-\frac{1}{2\omega^\sigma_{lm}(2\omega^\sigma_{lm}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{lm}-\tilde\omega} + \frac{2}{\omega^\sigma_{nm}(2\omega^\sigma_{lm}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{nm}-2\tilde\omega} + \frac{1}{2\omega^\sigma_{lm}\omega^\sigma_{nm}}\frac{1}{\tilde\omega}\right] \\ - B&\left[-\frac{1}{2\omega^\sigma_{nl}(2\omega^\sigma_{nl}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{nl}-\tilde\omega} + \frac{2}{\omega^\sigma_{nm}(2\omega^\sigma_{nl}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{nm}-2\tilde\omega} + \frac{1}{2\omega^\sigma_{nl}\omega^\sigma_{nm}}\frac{1}{\tilde\omega}\right], \end{aligned} \tag{E.18}$$

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

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

$$
\begin{aligned}
E = &\left[-\frac{A}{2\omega^\sigma_{lm}(2\omega^\sigma_{lm}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{lm}-\tilde{\omega}}+\frac{2A}{\omega^\sigma_{nm}(2\omega^\sigma_{lm}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{nm}-2\tilde{\omega}}\right] \\
&+\left[\frac{B}{2\omega^\sigma_{nl}(2\omega^\sigma_{nl}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{nl}-\tilde{\omega}}-\frac{2B}{\omega^\sigma_{nm}(2\omega^\sigma_{nl}-\omega^\sigma_{nm})}\frac{1}{\omega^\sigma_{nm}-2\tilde{\omega}}\right].
\end{aligned}
\tag{E.19}
$$

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

$$
\begin{aligned}
A \to f_{ml}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}|_{\mathbf{k}} + f_{ml}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}|_{-\mathbf{k}} \\
&= f_{ml}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}|_{\mathbf{k}}+\left(-\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)r^{\mathrm{c}}_{ln}r^{\mathrm{b}}_{ml}|_{\mathbf{k}}\right] \\
&= f_{ml}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}-\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{c}}_{ln}r^{\mathrm{b}}_{ml}\right] \\
&= f_{ml}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}-\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\right)^*\right] \\
&= -2f_{ml}\,\mathrm{Im}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\right],
\end{aligned}
$$

then B,

$$
\begin{aligned}
B \to f_{ln}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}|_{\mathbf{k}} + f_{ln}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}|_{-\mathbf{k}} \\
&= f_{ln}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}|_{\mathbf{k}}+\left(-\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)r^{\mathrm{b}}_{ln}r^{\mathrm{c}}_{ml}|_{\mathbf{k}}\right] \\
&= f_{ln}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}-\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{b}}_{ln}r^{\mathrm{c}}_{ml}\right] \\
&= f_{ln}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}-\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\right)^*\right] \\
&= -2f_{ln}\,\mathrm{Im}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\right].
\end{aligned}
$$

We then substitute in (E.19),

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

We manipulate indices and simplify,

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

and substitute in (1.77),

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

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

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

We use (E.13),

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

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

$$
\begin{aligned}
I = &\frac{\pi|e^3|}{2\hbar^2}\sum_{cv}\frac{1}{\omega^\sigma_{cv}}\left(\sum_{q\neq(v,c)}\left[\frac{\mathrm{Im}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{qc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vq}\}\right]}{2\omega^\sigma_{cv}-\omega^\sigma_{cq}} - \frac{\mathrm{Im}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vq}\{r^{\mathrm{c}}_{qc}r^{\mathrm{b}}_{cv}\}\right]}{2\omega^\sigma_{cv}-\omega^\sigma_{qv}}\right]\delta(\omega^\sigma_{cv}-\omega)\right. \\
&\left.-4\left[\sum_{v'\neq v}\frac{\mathrm{Im}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}\right]}{2\omega^\sigma_{cv'}-\omega^\sigma_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Im}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}\right]}{2\omega^\sigma_{c'v}-\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega)\right).
\end{aligned}
$$

Appendix F

Matrix elements of $\tau^{\mathrm{ab}}_{nm}(\mathbf{k})$

To calculate τ^{ab}_{nm}, first we need to calculate

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

for which we need the following triple commutator

$$\big[\hat{r}^{\mathrm{a}}, [\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^{\mathrm{b}}]\big] = \big[\hat{r}^{\mathrm{b}}, [\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^{\mathrm{a}}]\big], \tag{F.2}$$

where the r.h.s follows form the Jacobi identity, since $[\hat{r}^{\mathrm{a}}, \hat{r}^{\mathrm{b}}] = 0$. We expand the triple commutator as,

$$\begin{aligned}
\big[\hat{r}^{\mathrm{a}}, [\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^{\mathrm{b}}]\big] &= \big[\hat{r}^{\mathrm{a}}, \hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\hat{r}^{\mathrm{b}}\big] - \big[\hat{r}^{\mathrm{a}}, \hat{r}^{\mathrm{b}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\big] \\
&= \big[\hat{r}^{\mathrm{a}}, \hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\big]\hat{r}^{\mathrm{b}} - \hat{r}^{\mathrm{b}}\big[\hat{r}^{\mathrm{a}}, \hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\big] \\
&= \hat{r}^{\mathrm{a}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\hat{r}^{\mathrm{b}} - \hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\hat{r}^{\mathrm{a}}\hat{r}^{\mathrm{b}} - \hat{r}^{\mathrm{b}}\hat{r}^{\mathrm{a}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}') + \hat{r}^{\mathrm{b}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\hat{r}^{\mathrm{a}}.
\end{aligned} \tag{F.3}$$

Then,

$$\begin{aligned}
\frac{1}{\hbar^2}\langle n\mathbf{k}|\big[\hat{r}^{\mathrm{a}}, [\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^{\mathrm{b}}]\big]|m\mathbf{k}'\rangle &= \frac{1}{\hbar^2}\int d\mathbf{r}d\mathbf{r}'\langle n\mathbf{k}||\mathbf{r}\rangle\langle\mathbf{r}|\big[\hat{r}^{\mathrm{a}}, [\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^{\mathrm{b}}]\big]|\mathbf{r}'\rangle\langle\mathbf{r}'||m\mathbf{k}'\rangle\delta(\mathbf{k}-\mathbf{k}') \\
&= \frac{1}{\hbar^2}\int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\Big(r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')r'^{\mathrm{b}} - V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')r'^{\mathrm{a}}r'^{\mathrm{b}} \\
&- r^{\mathrm{b}}r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}') + r^{\mathrm{b}}V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')r'^{\mathrm{a}}\Big)\psi_{m\mathbf{k}}(\mathbf{r}')\delta(\mathbf{k}-\mathbf{k}') \\
&= \frac{1}{\hbar^2\Omega}\sum_{\mathbf{K},\mathbf{K}'}C^*_{n\mathbf{k}}(\mathbf{K})C_{m\mathbf{k}}(\mathbf{K}')\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}\Big(r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')r'^{\mathrm{b}} - V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')r'^{\mathrm{a}}r'^{\mathrm{b}} \\
&- r^{\mathrm{b}}r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}') + r^{\mathrm{b}}V^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')r'^{\mathrm{a}}\Big)e^{i\mathbf{K}'\cdot\mathbf{r}'}\delta(\mathbf{k}-\mathbf{k}').
\end{aligned} \tag{F.4}$$

We use the following identity

$$\begin{aligned}
&\Big(\frac{\partial^2}{\partial K^{\rm a}\partial K'^{\rm b}}+\frac{\partial^2}{\partial K'^{\rm a}\partial K'^{\rm b}}+\frac{\partial^2}{\partial K^{\rm a}\partial K^{\rm b}}+\frac{\partial^2}{\partial K^{\rm b}\partial K'^{\rm a}}\Big)\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\\
&=\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}\Big(r^{\rm a}V^{\rm nl}(\mathbf{r},\mathbf{r}')r'^{\rm b}-V^{\rm nl}(\mathbf{r},\mathbf{r}')r'^{\rm a}r'^{\rm b}-r^{\rm b}r^{\rm a}V^{\rm nl}(\mathbf{r},\mathbf{r}')+r^{\rm b}V^{\rm nl}(\mathbf{r},\mathbf{r}')r'^{\rm a}\Big)e^{i\mathbf{K}'\cdot\mathbf{r}'}\\
&=\Big(\frac{\partial^2}{\partial K^{\rm a}\partial K'^{\rm b}}+\frac{\partial^2}{\partial K'^{\rm a}\partial K'^{\rm b}}+\frac{\partial^2}{\partial K^{\rm a}\partial K^{\rm b}}+\frac{\partial^2}{\partial K^{\rm b}\partial K'^{\rm a}}\Big)\langle\mathbf{K}|V^{\rm nl}|\mathbf{K}'\rangle, \qquad (F.5)
\end{aligned}$$

to write

$$\mathcal{L}^{\rm ab}_{nm}(\mathbf{k})=\frac{1}{\hbar^2\Omega}\sum_{\mathbf{K},\mathbf{K}'}C^*_{n\mathbf{k}}(\mathbf{K})C_{m\mathbf{k}}(\mathbf{K}')\Big(\frac{\partial^2}{\partial K^{\rm a}\partial K'^{\rm b}}+\frac{\partial^2}{\partial K'^{\rm a}\partial K'^{\rm b}}+\frac{\partial^2}{\partial K^{\rm a}\partial K^{\rm b}}+\frac{\partial^2}{\partial K^{\rm b}\partial K'^{\rm a}}\Big)\langle\mathbf{K}|V^{\rm nl}|\mathbf{K}'\rangle$$
$$. \qquad (F.6)$$

The double derivatives with respect to $\mathbf{K}$ and $\mathbf{K}'$ can be worked out as it is done in Appendix B to obtain the matrix elements of $[\hat{V}^{\rm nl}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\rm b}]$,[?] and thus we could have the value of the matrix elements of the triple commutator.[?]

With above results we can proceed to evaluate the matrix elements $\tau_{nm}(\mathbf{k})$. From Eq. (H.1)

$$\begin{aligned}
\langle n\mathbf{k}|\tau^{\rm ab}|m\mathbf{k}'\rangle &= \langle n\mathbf{k}|\frac{i\hbar}{m_e}\delta_{ab}|m\mathbf{k}'\rangle+\langle n\mathbf{k}|\frac{1}{i\hbar}[r^{\rm a},v^{\rm nl,b}]|m\mathbf{k}'\rangle\\
\mathcal{L}^{\rm ab}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}') &= \delta(\mathbf{k}-\mathbf{k}')\Big(\frac{i\hbar}{m_e}\delta_{ab}\delta_{nm}+\mathcal{L}^{\rm ab}_{nm}(\mathbf{k})\Big)\\
\tau^{\rm ab}_{nm}(\mathbf{k})=\tau^{\rm ba}_{nm}(\mathbf{k}) &= \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm}+\mathcal{L}^{\rm ab}_{nm}(\mathbf{k}), \qquad (F.7)
\end{aligned}$$

which is an explicit expression that can be numerically calculated.

Appendix G

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

Expanding the wave function in plane waves we obtain

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \tag{G.1}$$

where $\{\mathbf{G}\}$ are the reciprocal basis vectors satisfying $e^{\mathbf{R}\cdot\mathbf{G}} = 1$, with $\{\mathbf{R}\}$ the translation vectors in real space, and $A_{n\mathbf{k}}(\mathbf{G})$ are the expansion coefficients. Using $m_e\mathbf{v} = -i\hbar\boldsymbol{\nabla}$ into Eqs. (1.72) and (1.70) we obtain,[3]

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

where

$$f_\ell(g) = \frac{1}{L}\int_{z_\ell-\Delta^b_\ell}^{z_\ell+\Delta^f_\ell} e^{igz} dz, \tag{G.3}$$

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

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

which we can express compactly as,

$$\mathcal{C}^{\ell}_{nm}(\mathbf{k}) = \sum_{\mathbf{G},\mathbf{G}'} A^*_{n\mathbf{k}}(\mathbf{G}')A_{m\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp). \tag{G.4}$$

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_ℓ at the center of an atom that belongs to layer ℓ, and thus above equations gives the ℓ-th atomic-layer contribution to the optical response.[3]

If $\mathcal{C}^\ell(z) = 1$ from Eqs. (G.2) and (G.4) we recover the well known result

$$\begin{aligned} v_{nm}(\mathbf{k}) &= \frac{\hbar}{m_e}\sum_{\mathbf{G}} A^*_{n\mathbf{k}}(\mathbf{G})A_{m\mathbf{k}}(\mathbf{G})(\mathbf{k}+\mathbf{G}) \\ \mathcal{C}^{\ell}_{nm} &= \delta_{nm}, \end{aligned} \tag{G.5}$$

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

We remark that $\boldsymbol{\mathcal{V}}^{\ell}_{nm}(\mathbf{k})$ of Eq. (G.2) does not contain the contribution coming from the scissors operator. As commented in the paragraph after Eq. (1.73) $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k}) \neq (\omega^\sigma_{nm}/\omega_{nm})\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$ and $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nn}(\mathbf{k}) \neq \boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nn}(\mathbf{k})$, relations that are correct whether or not the contribution of $\mathbf{v}^{\mathrm{nl}}$ is taken into account. Therefore, in order to take the scissors correction correctly, we must follow Appendix C.

G.1 Time–reversal relations

The following relations hold for time–reversal symmetry.

$$A^*_{n\mathbf{k}}(\mathbf{G}) = A_{n-\mathbf{k}}(\mathbf{G}),$$

$$\mathbf{P}_{n\ell}(-\mathbf{k}) = \hbar\sum_{\mathbf{G}} A^*_{n-\mathbf{k}}(\mathbf{G})A_{\ell-\mathbf{k}}(\mathbf{G})(-\mathbf{k}+\mathbf{G}),$$

$$(\mathbf{G}\to-\mathbf{G}) = -\hbar\sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G})A^*_{\ell\mathbf{k}}(\mathbf{G})(\mathbf{k}+\mathbf{G}) = -\mathbf{P}_{\ell n}(\mathbf{k}),$$

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

Appendix H

Generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$ for non-local potentials

We obtain the generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$ for the case of a non-local potential in the Hamiltonian. We start from (see Eq. (1.26))

$$[r^{\mathrm{a}}, v^{\mathrm{LDA,b}}] = [r^{\mathrm{a}}, v^{\mathrm{b}}] + [r^{\mathrm{a}}, v^{\mathrm{nl,b}}] = \frac{i\hbar}{m_e}\delta_{ab} + [r^{\mathrm{a}}, v^{\mathrm{nl,b}}] \equiv \tau^{\mathrm{ab}}, \tag{H.1}$$

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

$$\langle n\mathbf{k}|[r^{\mathrm{a}}, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle = \langle n\mathbf{k}|\tau^{\mathrm{ab}}|m\mathbf{k}'\rangle = \tau^{\mathrm{ab}}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'), \tag{H.2}$$

so

$$\langle n\mathbf{k}|[r^{\mathrm{a}}_i, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|[r^{\mathrm{a}}_e, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle = \tau^{\mathrm{ab}}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'), \tag{H.3}$$

where the matrix elements of $\tau^{\mathrm{ab}}_{nm}(\mathbf{k})$ are calculated in Appendix F. From Eq. (A.18) and (A.19)

$$\langle n\mathbf{k}|[r^{\mathrm{a}}_i, v^{\mathrm{b}}_{\mathrm{LDA}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} \tag{H.4}$$

$$(v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} = \nabla_{k^{\mathrm{a}}} v^{\mathrm{LDA,b}}_{nm}(\mathbf{k}) - i v^{\mathrm{LDA,b}}_{nm}(\mathbf{k})\left(\xi^{\mathrm{a}}_{nn}(\mathbf{k}) - \xi^{\mathrm{a}}_{mm}(\mathbf{k})\right), \tag{H.5}$$

and

$$\begin{aligned}
\langle n\mathbf{k}|[r_e^{\mathrm{a}}, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle &= \sum_{\ell\mathbf{k}''}\bigg(\langle n\mathbf{k}|r_e^{\mathrm{a}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|v^{\mathrm{LDA,b}}|m\mathbf{k}'\rangle \\
&- \langle n\mathbf{k}|v^{\mathrm{LDA,b}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|r_e^{\mathrm{a}}|m\mathbf{k}'\rangle\bigg) \\
&= \sum_{\ell\mathbf{k}''}\bigg((1-\delta_{n\ell})\delta(\mathbf{k}-\mathbf{k}'')\xi^{\mathrm{a}}_{n\ell}\delta(\mathbf{k}''-\mathbf{k}')v^{\mathrm{LDA,b}}_{\ell m} \\
&- \delta(\mathbf{k}-\mathbf{k}'')v^{\mathrm{LDA,b}}_{n\ell}(1-\delta_{\ell m})\delta(\mathbf{k}''-\mathbf{k}')\xi^{\mathrm{a}}_{\ell m}\bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\sum_{\ell}\bigg((1-\delta_{n\ell})\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} \\
&- (1-\delta_{\ell m})v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\bigg(\sum_{\ell}\bigg(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\bigg) \\
&+ v^{\mathrm{LDA,b}}_{nm}(\xi^{\mathrm{a}}_{mm}-\xi^{\mathrm{a}}_{nn})\bigg). \qquad \text{(H.6)}
\end{aligned}$$

Using Eqs. (H.4) and (H.6) into Eq. (H.3) gives

$$\begin{aligned}
i\delta(\mathbf{k}-\mathbf{k}')\bigg((v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} - i\sum_{\ell}\bigg(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\bigg) \\
- iv^{\mathrm{LDA,b}}_{nm}(\xi^{\mathrm{a}}_{mm}-\xi^{\mathrm{a}}_{nn})\bigg) = \tau^{\mathrm{ab}}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'), \qquad \text{(H.7)}
\end{aligned}$$

then

$$(v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} = -i\tau^{\mathrm{ab}}_{nm} + i\sum_{\ell}\bigg(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\bigg) + iv^{\mathrm{LDA,b}}_{nm}(\xi^{\mathrm{a}}_{mm}-\xi^{\mathrm{a}}_{nn}), \qquad \text{(H.8)}$$

and from Eq. (H.5),

$$\nabla_{k^{\mathrm{a}}}v^{\mathrm{LDA,b}}_{nm} = -i\tau^{\mathrm{ab}}_{nm} + i\sum_{\ell}\bigg(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\bigg). \qquad \text{(H.9)}$$

Now, there are two cases. We use Eq. (1.31).

Case $n = m$

$$\begin{aligned}\nabla_{k^{\rm a}} v_{nn}^{\rm LDA,b} &= -i\tau_{nn}^{\rm ab} + i\sum_{\ell}\Big(\xi_{n\ell}^{\rm a} v_{\ell n}^{\rm LDA,b} - v_{n\ell}^{\rm LDA,b}\xi_{\ell n}^{\rm a}\Big) \\ &= -i\tau_{nn}^{\rm ab} - \sum_{\ell\neq n}\Big(r_{n\ell}^{\rm a}\omega_{\ell n}^{\rm LDA} r_{\ell n}^{\rm b} - \omega_{n\ell}^{\rm LDA} r_{n\ell}^{\rm b} r_{\ell n}^{\rm a}\Big) \\ &= -i\tau_{nn}^{\rm ab} - \sum_{\ell\neq n}\omega_{\ell n}^{\rm LDA}\Big(r_{n\ell}^{\rm a} r_{\ell n}^{\rm b} - r_{n\ell}^{\rm b} r_{\ell n}^{\rm a}\Big), \end{aligned} \tag{H.10}$$

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 $\mathbf{v}^{\rm nl}$ in Eq. (H.1), we obtain $-i\tau_{nn}^{\rm ab} = \hbar/m_e\delta_{\rm ab}$ thus obtaining the familiar expression of $(m_n^{-1})_{ab}$.[**?**]

Case $n \neq m$

$$\begin{aligned}(v_{nm}^{\rm LDA,b})_{;k^{\rm a}} = &-i\tau_{nm}^{\rm ab} + i\sum_{\ell\neq m\neq n}\Big(\xi_{n\ell}^{\rm a} v_{\ell m}^{\rm LDA,b} - v_{n\ell}^{\rm LDA,b}\xi_{\ell m}^{\rm a}\Big) \\ &+ i\Big(\xi_{nm}^{\rm a} v_{mm}^{\rm LDA,b} - v_{nm}^{\rm LDA,b}\xi_{mm}^{\rm a}\Big) \\ &+ i\Big(\xi_{nn}^{\rm a} v_{nm}^{\rm LDA,b} - v_{nn}^{\rm LDA,b}\xi_{nm}^{\rm a}\Big) + iv_{nm}^{\rm LDA,b}(\xi_{mm}^{\rm a} - \xi_{nn}^{\rm a}) \\ = &-i\tau_{nm}^{\rm ab} - \sum_{\ell}\Big(\omega_{\ell m}^{\rm LDA} r_{n\ell}^{\rm a} r_{\ell m}^{\rm b} - \omega_{n\ell}^{\rm LDA} r_{n\ell}^{\rm b} r_{\ell m}^{\rm a}\Big) + i\xi_{nm}^{\rm a}(v_{mm}^{\rm LDA,b} - v_{nn}^{\rm LDA,b}) \\ = &-i\tau_{nm}^{\rm ab} - \sum_{\ell}\Big(\omega_{\ell m}^{\rm LDA} r_{n\ell}^{\rm a} r_{\ell m}^{\rm b} - \omega_{n\ell}^{\rm LDA} r_{n\ell}^{\rm b} r_{\ell m}^{\rm a}\Big) + ir_{nm}^{\rm a}\Delta_{mn}^{\rm b}, \end{aligned} \tag{H.11}$$

where we use $\Delta_{mn}^{\rm a}$ of Eq. (1.79). Now, for $n \neq m$, Eqs. (1.31), (D.9) and (H.11) and the chain rule, give

$$\begin{aligned}(r_{nm}^{\rm b})_{;k^{\rm a}} = &\left(\frac{v_{nm}^{\rm LDA,b}}{i\omega_{nm}^{\rm LDA}}\right)_{;k^{\rm a}} = \frac{1}{i\omega_{nm}^{\rm LDA}}\left(v_{nm}^{\rm LDA,b}\right)_{;k^{\rm a}} - \frac{v_{nm}^{\rm LDA,b}}{i(\omega_{nm}^{\rm LDA})^2}\left(\omega_{nm}^{\rm LDA}\right)_{;k^{\rm a}} \\ = &-i\tau_{nm}^{\rm ab} + \frac{i}{\omega_{nm}^{\rm LDA}}\sum_{\ell}\Big(\omega_{\ell m}^{\rm LDA} r_{n\ell}^{\rm a} r_{\ell m}^{\rm b} - \omega_{n\ell}^{\rm LDA} r_{n\ell}^{\rm b} r_{\ell m}^{\rm a}\Big) + \frac{r_{nm}^{\rm a}\Delta_{mn}^{\rm b}}{\omega_{nm}^{\rm LDA}} \\ &- \frac{r_{nm}^{\rm b}}{\omega_{nm}^{\rm LDA}}\left(\omega_{nm}^{\rm LDA}\right)_{;k^{\rm a}} \\ = &-i\tau_{nm}^{\rm ab} + \frac{i}{\omega_{nm}^{\rm LDA}}\sum_{\ell}\Big(\omega_{\ell m}^{\rm LDA} r_{n\ell}^{\rm a} r_{\ell m}^{\rm b} - \omega_{n\ell}^{\rm LDA} r_{n\ell}^{\rm b} r_{\ell m}^{\rm a}\Big) + \frac{r_{nm}^{\rm a}\Delta_{mn}^{\rm b}}{\omega_{nm}^{\rm LDA}} \\ &- \frac{r_{nm}^{\rm b}}{\omega_{nm}}\frac{v_{nn}^{\rm LDA,a} - v_{mm}^{\rm LDA,a}}{m_e} \\ = &-i\tau_{nm}^{\rm ab} + \frac{r_{nm}^{\rm a}\Delta_{mn}^{\rm b} + r_{nm}^{\rm b}\Delta_{mn}^{\rm a}}{\omega_{nm}^{\rm LDA}} + \frac{i}{\omega_{nm}^{\rm LDA}}\sum_{\ell}\Big(\omega_{\ell m}^{\rm LDA} r_{n\ell}^{\rm a} r_{\ell m}^{\rm b} - \omega_{n\ell}^{\rm LDA} r_{n\ell}^{\rm b} r_{\ell m}^{\rm a}\Big), \end{aligned} \tag{H.12}$$

where the $-i\tau^{\rm ab}_{nm}$ term, generalizes the usual expresion of $\mathbf{r}_{nm;\mathbf{k}}$ for local Hamiltonians,[**?**, 10, 9, **?**] to the case of a nonlocal potential in the Hamiltonian.

H.1 Layer Case

To obtain the generalized derivative expressions for the case of the layered matrix elements ar required by Eq. (1.71), we could start form Eq. (H.1) again, and replace $\hat{\mathbf{v}}^{\rm LDA}$ by $\boldsymbol{\mathcal{V}}^{\rm LDA}$, to obtain the equivalent of Eqs. (H.10) and (H.11), for which we need to calculate the new $\tau^{\rm ab}_{nm}$, that is given by

$$\begin{aligned}
\mathcal{T}^{\rm ab}_{nm} &= [r^{\rm a}, \mathcal{V}^{\rm LDA,b}]_{nm} = [r^{\rm a}, \mathcal{V}^{\rm b}]_{nm} + [r^{\rm a}, \mathcal{V}^{\rm nl,b}]_{nm} \\
&= \frac{1}{2}[r^{\rm a}, v^{\rm b}C^{\ell}(z) + C^{\ell}(z)v^{\rm b}]_{nm} + \frac{1}{2}[r^{\rm a}, v^{\rm nl,b}C^{\ell}(z) + C^{\ell}(z)v^{\rm nl,b}]_{nm} \\
&= \Big([r^{\rm a}, v^{\rm b}]C^{\ell}(z)\Big)_{nm} + \Big([r^{\rm a}, v^{\rm nl,b}]C^{\ell}(z)\Big)_{nm} \\
&= \sum_p [r^{\rm a}, v^{\rm b}]_{np}C^{\ell}_{pm} + \sum_p [r^{\rm a}, v^{\rm nl,b}]_{np}C^{\ell}_{pm} \\
&= \frac{i\hbar}{m_e}\delta_{\rm ab}C^{\ell}_{nm} + \sum_p [r^{\rm a}, v^{\rm nl,b}]_{np}C^{\ell}_{pm}.
\end{aligned} \tag{H.13}$$

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

$$(\mathcal{V}^{\rm LDA,a}_{nm})_{;k^{\rm b}} = \frac{\hbar}{m_e}\delta_{\rm ab}C^{\ell}_{nm} - i\sum_p [r^{\rm b}, v^{\rm nl,a}]_{np}C^{\ell}_{pm} + i\sum_{\ell}\left(r^{\rm b}_{n\ell}\mathcal{V}^{\rm LDA,a}_{\ell m} - \mathcal{V}^{\rm LDA,a}_{n\ell}r^{\rm b}_{\ell m}\right) + ir^{\rm b}_{nm}\tilde{\Delta}^{\rm a}_{mn}, \tag{H.14}$$

where

$$\tilde{\Delta}^{\rm a}_{mn} = \mathcal{V}^{\rm LDA,a}_{nn} - \mathcal{V}^{\rm LDA,a}_{mm}. \tag{H.15}$$

As mentioned before, the term $[r^{\rm b}, v^{\rm nl,a}]_{nm}$ calculated in Appendix F, is small compared to the other terms, thus we neglect it throwout this work.[**?**] The expression for C^{ℓ}_{nm} is calculated in Appendix G.

Appendix I

Coding

In this Appendix we reproduce all the quantities that should be coded.

Eqs. (I.1), (I.3), (I.2) and (I.4)

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

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

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

and

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

• Coding: $\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm} \to$ `calVsig`, $r^{\mathrm{a}}_{nm} \to$ `posMatElem`, $\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} \to$ `gdcalVsig`, $(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \to$ `derMatElem` $\Delta^{\mathrm{a}}_{nm} \to$ `Delta` and $\omega^\sigma_n \to$ `band(n)`

• proof:

To evaluate above expressions we need the following ($m_e = 1$):

$$\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}) = (1/m_e)\mathbf{p}_{nm}(\mathbf{k}) + \mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k}) = \mathbf{p}_{nm}(\mathbf{k}) + \mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k}), \tag{I.5}$$

that includes the local and nonlocal parts of the pseudopotential. They correspond to the following files:

• $\mathbf{p}_{nm}(\mathbf{k}) \to$ `me_pmn_*`

• $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k}) \to$ `me_vnlnm_*`

where the `nm` or `mn` order in the files is irrelevant, and ought to be fixed just for the *biuty* of it. Option `-n` in `all_responses.sh` does

1. > cp me_pmn_* me_pmn_*.o

2. adds me_pmn_* and me_vnlnm_* into me_pmn_*

3. calculates the response

4. > mv me_pmn_*.o me_pmn_*

so $\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})$, stored in vldaMatElem is available for the calculation of the response, and with it we calculate (Eqs. (1.29) and (1.30)),

$$\begin{aligned}
\mathbf{v}^{\sigma}_{nm}(\mathbf{k}) &= \left(1+\frac{\Sigma}{\omega_c(\mathbf{k})-\omega_v(\mathbf{k})}\right)\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}) \qquad n\notin D_m\\
\mathbf{v}^{\sigma}_{nn}(\mathbf{k}) &= \mathbf{v}^{\mathrm{LDA}}_{nn}(\mathbf{k})\\
\mathbf{r}_{nm}(\mathbf{k}) &= \frac{\mathbf{v}^{\sigma}_{nm}(\mathbf{k})}{i\omega^{\sigma}_{nm}(\mathbf{k})} = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n\notin D_m.
\end{aligned} \tag{I.6}$$

If option -n is not chosen, then the contribution of $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k})$ is neglected in the calculation of any response. Obviously, in this case the code only uses me_pmn_* without adding me_vnlnm_*

We need Eq. (C.1) and (C.2)

$$\begin{aligned}
\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm} &= \mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm} + \mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\\
\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} &= \left(\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} + \left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}}.
\end{aligned} \tag{I.7}$$

The first LDA term is

$$\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm} = \frac{1}{2}\sum_q \left(v^{\mathrm{LDA},\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} + \mathcal{C}^{\ell}_{nq}v^{\mathrm{LDA},\mathrm{a}}_{qm}\right). \tag{I.8}$$

If option -n is not chosen in all_responses.sh Eq. (I.8) is not calculated and
• $\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm} \to$ me_cpmn_*
If option -n is chosen Eq. (I.8) must be calculated as given in set_input_ascii.f90. We mention that $\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm}$ can be computed directly,[11] avoiding the sum over the full set of bands q, however we chose to compute Eq. (I.8), which is done in functions.f90 under the name calVlda. Then, we need Eq. (G.4)

$$\begin{aligned}
\mathcal{C}^{\ell}_{nm}(\mathbf{k}) &= \sum_{\mathbf{G},\mathbf{G}'} A^*_{n\mathbf{k}}(\mathbf{G}')A_{m\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp)\\
\mathcal{C}^{\ell}_{mn}(\mathbf{k}) &= \left(\mathcal{C}^{\ell}_{nm}(\mathbf{k})\right)^*,
\end{aligned} \tag{I.9}$$

which is coded in sub_pmn_ascii.f90 within the same subroutine of $\boldsymbol{\mathcal{V}}^{\ell}_{nm}$ calculated with Eq. (G.2). However, Sean out of the blue, call it me_cfmn_* in run_tiniba.sh, and Darwin won (what else? ID??), thus I call it cfMatElem in SRC_1setinput. ID would call it ccMatElem but long live CD!

The second LDA term is

$$\left(\mathcal{V}_{nm}^{\mathrm{LDA,a},\ell}\right)_{;k^{\mathrm{b}}} = \frac{1}{2}\sum_{q}\left((v_{nq}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + v_{nq}^{\mathrm{LDA,a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} + (\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}}v_{qm}^{\mathrm{LDA,a}} + \mathcal{C}_{nq}^{\ell}(v_{qm}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}}\right), \tag{I.10}$$

where
• for $n \neq m$
Eq. (C.3)

$$\begin{aligned}(v_{nm}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}} &= im_e\left(\Delta_{nm}^{b}r_{nm}^{\mathrm{a}} + \omega_{nm}^{\mathrm{LDA}}(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}}\right)\\ (v_{mn}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}} &= \left((v_{nm}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}}\right)^{*} \quad \text{for} \quad n \neq m,\end{aligned} \tag{I.11}$$

with Eq. (1.79)

$$\Delta_{nm}^{\mathrm{a}} = v_{nn}^{\mathrm{LDA,a}} - v_{mm}^{\mathrm{LDA,a}}, \tag{I.12}$$

and (H.12)

$$\begin{aligned}(r_{nm}^{\mathrm{b}})_{;k^{\mathrm{a}}} &= -i\mathcal{T}_{nm}^{\mathrm{ab}} + \frac{r_{nm}^{\mathrm{a}}\Delta_{mn}^{\mathrm{b}} + r_{nm}^{\mathrm{b}}\Delta_{mn}^{\mathrm{a}}}{\omega_{nm}^{\mathrm{LDA}}} + \frac{i}{\omega_{nm}^{\mathrm{LDA}}}\sum_{\ell}\left(\omega_{\ell m}^{\mathrm{LDA}}r_{n\ell}^{\mathrm{a}}r_{\ell m}^{\mathrm{b}} - \omega_{n\ell}^{\mathrm{LDA}}r_{n\ell}^{\mathrm{b}}r_{\ell m}^{\mathrm{a}}\right)\\ &\approx \frac{r_{nm}^{\mathrm{a}}\Delta_{mn}^{\mathrm{b}} + r_{nm}^{\mathrm{b}}\Delta_{mn}^{\mathrm{a}}}{\omega_{nm}^{\mathrm{LDA}}} + \frac{i}{\omega_{nm}^{\mathrm{LDA}}}\sum_{\ell}\left(\omega_{\ell m}^{\mathrm{LDA}}r_{n\ell}^{\mathrm{a}}r_{\ell m}^{\mathrm{b}} - \omega_{n\ell}^{\mathrm{LDA}}r_{n\ell}^{\mathrm{b}}r_{\ell m}^{\mathrm{a}}\right)\\ (r_{mn}^{\mathrm{b}})_{;k^{\mathrm{a}}} &= \left((r_{nm}^{\mathrm{b}})_{;k^{\mathrm{a}}}\right)^{*},\end{aligned} \tag{I.13}$$

where $\mathcal{T}_{nm}^{\mathrm{ab}} \approx 0$.
• for $n = m$
Since $\mathcal{T}_{nn}^{\mathrm{ab}} \approx (\hbar/m_e)\delta_{\mathrm{ab}}$, Eq. (1.90) gives

$$\begin{aligned}(v_{nn}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}} &= -i\mathcal{T}_{nn}^{\mathrm{ab}} - \sum_{\ell\neq n}\omega_{\ell n}^{\mathrm{LDA}}\left(r_{n\ell}^{\mathrm{a}}r_{\ell n}^{\mathrm{b}} + r_{n\ell}^{\mathrm{b}}r_{\ell n}^{\mathrm{a}}\right)\\ &\approx \frac{\hbar}{m_e}\delta_{\mathrm{ab}} - \sum_{\ell\neq n}\omega_{\ell n}^{\mathrm{LDA}}\left(r_{n\ell}^{\mathrm{a}}r_{\ell n}^{\mathrm{b}} + r_{n\ell}^{\mathrm{b}}r_{\ell n}^{\mathrm{a}}\right).\end{aligned} \tag{I.14}$$

For Eq. (I.10) we need (C.9)

$$\begin{aligned}(\mathcal{C}_{nm}^{\ell})_{;k^{\mathrm{a}}} &= i\sum_{q\neq nm}\left(r_{nq}^{\mathrm{a}}\mathcal{C}_{qm}^{\ell} - \mathcal{C}_{nq}^{\ell}r_{qm}^{\mathrm{a}}\right) + ir_{nm}^{\mathrm{a}}(\mathcal{C}_{mm}^{\ell} - \mathcal{C}_{nn}^{\ell})\\ (\mathcal{C}_{mn}^{\ell})_{;\mathbf{k}} &= \left((\mathcal{C}_{nm}^{\ell})_{;\mathbf{k}}\right)^{*}.\end{aligned} \tag{I.15}$$

For the scissor related term we have: Eq. (C.4) , (C.5) and (1.27)

$$\begin{aligned}\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell} &= \frac{1}{2}\sum_{q}\left(v_{nq}^{\mathcal{S},\mathrm{a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell}v_{qm}^{\mathcal{S},\mathrm{a}}\right)\\ \left(\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} &= \frac{1}{2}\sum_{q}\left((v_{nq}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + v_{nq}^{\mathcal{S},\mathrm{a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} + (\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}}v_{qm}^{\mathcal{S},\mathrm{a}} + \mathcal{C}_{nq}^{\ell}(v_{qm}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}}\right),\end{aligned} \tag{I.16}$$

with Eqs. (1.27) and (C.5)

$$v_{nm}^{\mathcal{S},\mathrm{a}} = i\Sigma f_{mn} r_{nm}^{\mathrm{a}}, \tag{I.17}$$

$$(v_{nm}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}} = i\Sigma f_{mn} (r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}}, \tag{I.18}$$

where $\hbar\Sigma$ is the scissors correction. Notice that $v_{nn}^{\mathcal{S},\mathrm{a}} = 0$ and $(v_{nn}^{\mathcal{S},\mathrm{a}})_{;k^{\mathrm{b}}} = 0$. Substuiting Eq. (I.17) into (I.16), we obtain

$$\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell} = \frac{i\Sigma}{2}\sum_q \left(f_{qn} r_{nq}^{\mathrm{a}} \mathcal{C}_{qm}^{\ell} + f_{mq}\mathcal{C}_{nq}^{\ell} r_{qm}^{\mathrm{a}}\right), \tag{I.19}$$

• Coding: `functions.f90` array `calVscissors` where f_n is coded in `set_input_ascii.f90` Notice that $q = n$ and $q = m$ give zero contribution from the f_{nm} factors, but we set in the code $r_{nn}^{\mathrm{a}} = 0$ so the program would not complain that such values of the array `posMatElem` do not exist, since actually, the diagonal elements do not exist. Explicitly (although, we don't code them),

$$\begin{aligned}
\mathcal{V}_{vc}^{S,a,\ell} &= -\frac{i\Sigma}{2}\left[\sum_{v'} r_{vv'}^{a} C_{v'c}^{\ell} + \sum_{c'} C_{vc'}^{\ell} r_{c'c}^{a}\right], \\
\mathcal{V}_{cv}^{S,a,\ell} &= \frac{i\Sigma}{2}\left[\sum_{v'} r_{cv'}^{a} C_{v'v}^{\ell} + \sum_{c'} C_{cc'}^{\ell} r_{c'v}^{a}\right], \\
\mathcal{V}_{cv}^{S,a,\ell} &= (\mathcal{V}_{vc}^{S,a,\ell})^*
\end{aligned} \tag{I.20}$$

and

$$\mathcal{V}_{cc}^{S,a,\ell} = -\Sigma\sum_v \mathrm{Im}\left[r_{cv}^{a} C_{vc}^{\ell}\right], \tag{I.21}$$

$$\mathcal{V}_{vv}^{S,a,\ell} = \Sigma\sum_c \mathrm{Im}\left[r_{vc}^{a} C_{cv}^{\ell}\right], \tag{I.22}$$

where the last two are real functions as they must, since they are velocities.

Substuiting Eqs. (I.17) and (I.18) into (I.16), we obtain

$$\begin{aligned}
\left(\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} &= \frac{i\Sigma}{2}\sum_q \left(f_{qn}\left[(r_{nq}^{\mathrm{a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + r_{nq}^{\mathrm{a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}}\right] + f_{mq}\left[(\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}} r_{qm}^{\mathrm{a}} + \mathcal{C}_{nq}^{\ell}(r_{qm}^{\mathrm{a}})_{;k^{\mathrm{b}}}\right]\right) \\
\left(\mathcal{V}_{mn}^{\mathcal{S},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} &= \left(\left(\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}}\right)^*,
\end{aligned} \tag{I.23}$$

• Coding:
$(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}} \to$ `derMatElem` $\mathcal{C}_{nm}^{\ell} \to$ `cfMatElem` $r_{nm}^{\mathrm{a}} \to$ `posMatElem` $(\mathcal{C}_{nm}^{\ell})_{;k^{\mathrm{b}}} \to$ `gdf`, and

$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} \rightarrow$ `gdcalVS`
Also

$$\left(\mathcal{V}^{\mathcal{S},\mathrm{a}\,\ell}_{cv}\right)_{;k^{\mathrm{b}}} = \frac{i\Sigma}{2}\left(\sum_{v'}\left((r^{\mathrm{a}}_{cv'})_{;k^{\mathrm{b}}}\mathcal{C}^{\ell}_{v'v} + r^{\mathrm{a}}_{cv'}(\mathcal{C}^{\ell}_{v'v})_{;k^{\mathrm{b}}}\right) + \sum_{c'}\left((\mathcal{C}^{\ell}_{cc'})_{;k^{\mathrm{b}}}r^{\mathrm{a}}_{c'v} + \mathcal{C}^{\ell}_{cc'}(r^{\mathrm{a}}_{c'v})_{;k^{\mathrm{b}}}\right)\right)$$

$$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{b}}} = \left(\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{cv}\right)_{;k^{\mathrm{b}}}\right)^{*}, \tag{I.24}$$

$$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{cc}\right)_{;k^{\mathrm{b}}} = -\Sigma\sum_{v}\mathrm{Im}\left[(r^{\mathrm{a}}_{cv})_{;k^{\mathrm{b}}}\mathcal{C}^{\ell}_{vc} + r^{\mathrm{a}}_{cv}(\mathcal{C}^{\ell}_{vc})_{;k^{\mathrm{b}}}\right], \tag{I.25}$$

and

$$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{vv}\right)_{;k^{\mathrm{b}}} = \Sigma\sum_{c}\mathrm{Im}\left[(r^{\mathrm{a}}_{vc})_{;k^{\mathrm{b}}}\mathcal{C}^{\ell}_{cv} + r^{\mathrm{a}}_{vc}(\mathcal{C}^{\ell}_{cv})_{;k^{\mathrm{b}}}\right]. \tag{I.26}$$

I.1 Coding for $\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}(\mathbf{k})$

Recall that $\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{mn} = (\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm})^{*}$ and $\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{mn} = (\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm})^{*}$

- If `-n` option is chosen in `all_responses.sh`
  - $\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm}$, comes from Eq. (I.8), coded in `functions.f90` as `calVlda`
- If `-n` option is NOT chosen in `all_responses.sh`
  - $\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm}$ is used from `me_cpmn_*` which is Eq. (G.2) and is coded in `sub_pmn_ascii.f90`

For either case

- $\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}$ is obtained from Eqs. (I.20), (I.21) or (I.22), depending on nm. This is coded in `functions.f90` and used in `set_input_ascii.f90`

Thus,
• $\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}(\mathbf{k}) = \mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm}(\mathbf{k}) + \mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}(\mathbf{k})$
is stored in `calMomMatElem` array, constructed in `set_input_ascii.f90`, and used in `SRC_2latm` for integrating the response function. A brave young soul, should change `calMomMatElem` to `calVelMatElem` in order to have a more appropriate name. But as good old DNA, we construct upon available ATGC; using the old structure, adding functionality and keeping all the usles non-codifying crap, thus making Darwin proud of us!

I.2 $\Delta^{\sigma,\mathrm{a},\ell}_{nm}(\mathbf{k})$

$\Delta^{\sigma,\mathrm{a},\ell}_{nm}(\mathbf{k})$ is given by

$$\Delta^{\sigma,\mathrm{a},\ell}_{nm}(\mathbf{k}) = \mathcal{V}^{\sigma,\mathrm{a},\ell}_{nn}(\mathbf{k}) - \mathcal{V}^{\sigma,\mathrm{a},\ell}_{mm}(\mathbf{k}) \tag{I.27}$$

$$\begin{aligned}\Delta_{nm}^{\sigma,\mathrm{a}}(\mathbf{k}) &= v_{nn}^{\sigma,\mathrm{a},\ell}(\mathbf{k}) - v_{mm}^{\sigma,\mathrm{a},\ell}(\mathbf{k}) \\ &= v_{nn}^{\mathrm{LDA},\mathrm{a},\ell}(\mathbf{k}) - v_{mm}^{\mathrm{LDA},\mathrm{a},\ell}(\mathbf{k}),\end{aligned} \tag{I.28}$$

since $\mathbf{v}_{nn}^{\mathcal{S}} = 0$.
• Coding: $\Delta_{nm}^{\sigma,\mathrm{a},\ell}(\mathbf{k}) \rightarrow$ `calDelta` and $\Delta_{nm}^{\sigma,\mathrm{a}}(\mathbf{k}) \rightarrow$ `Delta` both in `set_input_ascii.f90`

I.3 Coding for $(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}(\mathbf{k}))_{;k^{\mathrm{b}}}$

- Δ_{nm}^{a} available in array `Delta`, calculated in `set_input_ascii.f90`, and contains the contribution from $\mathbf{v}_{nm}^{\mathrm{nl}}(\mathbf{k})$ if the `-n` option is chosen in `all_responses.sh`

- $(r_{nm}^{\mathrm{a}}(\mathbf{k}))_{;k^{\mathrm{b}}}$ available in array `derMatElem`, calculated in `set_input_ascii.f90` and `functions.f90`, and contains the contribution from $\mathbf{v}_{nm}^{\mathrm{nl}}(\mathbf{k})$ if the `-n` option is chosen in `all_responses.sh`

- With above two we compute $(v_{nm}^{\mathrm{LDA},\mathrm{a}}(\mathbf{k}))_{;k^{\mathrm{b}}}$ in `set_input_ascii.f90` and store it in `gdVlda` for diagonal and off diagonal terms.

- $\left(\mathcal{C}_{nm}^{\ell}(\mathbf{k})\right)_{;k^{\mathrm{a}}}$ is coded in in `set_input_ascii.f90` and store it in `gdf` for diagonal and off diagonal terms. Darwin at work!

- $(v_{nq}^{\mathrm{LDA},\mathrm{a}})_{;k^{\mathrm{b}}} \rightarrow$ `gdVlda`, $\mathcal{C}_{qm}^{\ell} \rightarrow$ `cfMatElem`, $v_{nq}^{\mathrm{LDA},\mathrm{a}} \rightarrow$ `vldaMatElem`, $(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} \rightarrow$ `gdf`
$v_{nq}^{\mathrm{LDA},\mathrm{a}} \rightarrow$ `vldaMatElem`,

$$\begin{aligned}\left(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} &= \frac{1}{2}\sum_q \left((v_{nq}^{\mathrm{LDA},\mathrm{a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + v_{nq}^{\mathrm{LDA},\mathrm{a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} + (\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}} v_{qm}^{\mathrm{LDA},\mathrm{a}} + \mathcal{C}_{nq}^{\ell}(v_{qm}^{\mathrm{LDA},\mathrm{a}})_{;k^{\mathrm{b}}}\right) \\ \left(\mathcal{V}_{mn}^{\mathrm{LDA},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} &= \left(\left(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}}\right)^*,\end{aligned} \tag{I.29}$$

$\left(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} \rightarrow$ `gdcalVlda` and coded in `set_input_ascii.f90`

I.4 Summary

- $\mathcal{V}_{nm}^{\sigma,\mathrm{a},\ell}(\mathbf{k}) = \mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}(\mathbf{k}) + \mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}(\mathbf{k}) \rightarrow$ `calMomMatElem`

- $\left(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} \rightarrow$ `gdcalVlda`

- $\left(\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} \rightarrow$ `gdcalVS`

- $\left(\mathcal{V}_{nm}^{\sigma,\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} = \left(\mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} + \left(\mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}\right)_{;k^{\mathrm{b}}} \rightarrow$ `gdcalVsig`

I.5 Bulk expressions

For a bulk $\mathcal{C}^{\ell}_{nm}(\mathbf{k}) = \delta_{nm}$, then $(\mathcal{C}^{\ell}_{nm}(\mathbf{k}))_{;\mathbf{k}} = 0$, and Eq. (I.7) reduces to

$$\begin{aligned} v^{\sigma,\mathrm{a}}_{nm} &= v^{\mathrm{LDA,a}}_{nm} + v^{\mathcal{S},\mathrm{a}}_{nm} \\ \mathbf{v}^{\sigma}_{nm}(\mathbf{k}) &= \left(1 + \frac{\Sigma}{\omega_c(\mathbf{k}) - \omega_v(\mathbf{k})}\right) \mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}) \qquad n \notin D_m \\ \mathbf{v}^{\sigma}_{nn}(\mathbf{k}) &= \mathbf{v}^{\mathrm{LDA}}_{nn}(\mathbf{k}), \end{aligned} \tag{I.30}$$

where in `$TINIBA/latm` the values are coded in the array called `momMatElem`. If option `-n` is given while running `all_resposnses.sh`, then $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k})$ are included in `momMatElem`. Also,

$$\begin{aligned} (v^{\sigma,\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} &= \left(v^{\mathrm{LDA,a}}_{nm}\right)_{;k^{\mathrm{b}}} + \left(v^{\mathcal{S},\mathrm{a}}_{nm}\right)_{;k^{\mathrm{b}}} \\ &= \left(v^{\mathrm{LDA,a}}_{nm}\right)_{;k^{\mathrm{b}}} + i\Sigma f_{mn}(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \\ (v^{\sigma,\mathrm{a}}_{mn})_{;k^{\mathrm{b}}} &= \left((v^{\sigma,\mathrm{a}}_{nm})_{;k^{\mathrm{b}}}\right)^{*}, \end{aligned} \tag{I.31}$$

where with the r.h.s. expressions are given above.

- Coding: $\mathbf{v}^{\sigma}_{nm}(\mathbf{k}) \to$ `momMatElem`, $\left(v^{\mathrm{LDA,a}}_{nm}\right)_{;k^{\mathrm{b}}} \to$ `gdVlda`, $\left(r^{\mathrm{LDA,a}}_{nm}\right)_{;k^{\mathrm{b}}} \to$ `derMatElem`, and $(v^{\sigma,\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \to$ `gdVsig`

I.6 Layer or Bulk calculation

- Layer: The layer calculation is done by using Eqs. (J.21), (J.25), (J.23) and (J.27).
- Bulk: A bulk calculation can be performed by using the same Eqs. (J.21), (J.25), (J.23) and (J.27), and by simply replacing
  1. $\boldsymbol{\mathcal{V}}^{\sigma}_{nm}$ (`calMomMatElem`) $\to \mathbf{v}^{\sigma}_{nm}$ (`momMatElem`)
  2. $(\boldsymbol{\mathcal{V}}^{\sigma}_{nm})_{;\mathbf{k}}$ (`gdcalVsig`) $\to (\mathbf{v}^{\sigma}_{nm})_{;\mathbf{k}}$ (`gdVsig`)
- Therefore: For the code to run either possibility we use the same arrays as for the layered response, where, if bulk is chosen, it simply copies the bulk matrix elements into the layer arrays, i.e.
  - Layer: $\boldsymbol{\mathcal{V}}^{\sigma}_{nm}$ (`calMomMatElem`) and $(\boldsymbol{\mathcal{V}}^{\sigma}_{nm})_{;\mathbf{k}}$ (`gdcalVsig`)
  - Bulk: $\mathbf{v}^{\sigma}_{nm}$ (`momMatElem`→`calVsig`) and $(\mathbf{v}^{\sigma}_{nm})_{;\mathbf{k}}$ (`gdVsig`→`gdcalVsig`) This change is done in `set_input_ascii.f90` (look for `layer-to-bulk` tag)
  - ID: Notice that we have assigned `calMomMatElem`→ `calVsig` (keeping `calMomMatElem`), so it is easier to code the responses. Therefore, we have $\boldsymbol{\mathcal{V}}^{\sigma}_{nm} \to$ `calVsig` and $(\boldsymbol{\mathcal{V}}^{\sigma}_{nm})_{;\mathbf{k}} \to$ `gdcalVsig` either for bulk or layered response. If `calMomMatElem` is not used, we should get rid of it (ID at work).

I.7 $\mathcal{V}$ vs $\mathcal{R}$

Using $\mathrm{Re}[iz] = -\mathrm{Im}[z]$, $\mathrm{Im}[iz] = \mathrm{Re}[z]$, and

$$\mathcal{R}^{\mathrm{a}}_{nm} = \frac{\mathcal{P}^{\mathrm{a}}_{nm}}{im_e\omega_{nm}} = \frac{\mathcal{V}^{\mathrm{a}}_{nm}}{i\omega_{nm}} \qquad n \neq m, \tag{I.32}$$

we can show the equivalence between the two formulations, i.e.

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\left[\frac{\omega^S_{lc}\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{cl})} - \frac{\omega^S_{vl}\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{lv})}\right]\delta(\omega^S_{cv}-\omega), \tag{I.33}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\frac{1}{\omega^S_{cv}}\left[\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{cl})} - \frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{lv})}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{I.34}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{\omega^S_{cv}}\left[\mathrm{Im}[\{r^{\mathrm{b}}_{cv}\left(\mathcal{R}^{\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{c}}}\}] + \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-\omega), \tag{I.35}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{(\omega^S_{cv})^2}\left[\mathrm{Re}\left[\left\{r^{\mathrm{b}}_{cv}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{c}}}\right\}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\right\}\right]}{\omega^S_{cv}}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{I.36}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}4\left[\sum_{v'\neq v}\frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{2\omega^S_{cv'}-\omega^S_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{2\omega^S_{c'v}-\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{I.37}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\sum_{v'\neq v}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{2\omega^\sigma_{cv'}-\omega^\sigma_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{2\omega^\sigma_{c'v}-\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{I.38}$$

and

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\mathrm{Im}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\}] - \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{I.39}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^S_{cv})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\right\}\right] - \frac{2\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\right\}\right]}{\omega^S_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{I.40}$$

If we take $\mathcal{R}^{\mathrm{a},\ell}_{nm} \to r^{\mathrm{a}}_{nm}$, we would recover the expressions for a bulk response. We prefer to use the expressions in terms of $\mathcal{V}^\ell$, since they are more physically appealing, as the velocity is what gives the current of a given layer, from which the polarization is computed and the χ^ℓ extracted.

Remark: We mention that above expressions with $\mathcal{R}^{\mathrm{a},\ell}_{nm} \to r^{\mathrm{a}}_{nm}$, are coded in `integrands.f90`, instead of Eq. 40 and 41 of Cabellos et al.[9], which were derived by using Eq. 19 of Aversa and Sipe.[?] To obtain above equations, we started from Eq. 18 of Aversa and Sipe,[?] which has the advantage that applying the layer-by-layer formalism is very transparent and straightforward. This coding is what constitutes the *Length*-gauge implementation in TINIBA®, which is, within a very small numerical difference, equal to the *Velocity*-gauge implementation of Eq. 35 of Cabellos et al.[9], also in TINIBA®. THE SPIN FACTOR IS PUT IN `file_control.f90`. If there is no spin-orbit interaction the factor `spin_factor=2`. If there is spin-orbit interaction the factor `spin_factor=1`. The final result is multiplied by the `spin_factor` variable. So above expressions are not multiplied by the spin degeneracy, the code multiplies them.

I.8 Other responses

Warning: the layered responses MUST be looked at again, and modified according to the newly calculated $\boldsymbol{\mathcal{V}}^\sigma_{nm}$ and $(\boldsymbol{\mathcal{V}}^\sigma_{nm})_{;\mathbf{k}}$. Linear response, current and spin injection, should be revisited again!!

- Injection Current

  We need $\mathbf{v}^\sigma_{nn}(\mathbf{k})$ or $\boldsymbol{\mathcal{V}}^\sigma_{nn}(\mathbf{k})$, but $\mathbf{v}^{\mathcal{S}}_{nn}(\mathbf{k}) = 0$ and $\boldsymbol{\mathcal{V}}^{\mathcal{S}}_{nn}(\mathbf{k}) = 0$ (proven numerically, would be nice to try analytically), since the velocity of the electron in the conduction bands should not depend on the scissors rigid ($\mathbf{k}$-independent) correction thus

$$\begin{aligned} \boldsymbol{\mathcal{V}}^\sigma_{nn}(\mathbf{k}) &= \boldsymbol{\mathcal{V}}^{\mathrm{LDA}}_{nn}(\mathbf{k}) \\ \mathbf{v}^\sigma_{nn}(\mathbf{k}) &= \mathbf{v}^{\mathrm{LDA}}_{nn}(\mathbf{k}), \end{aligned} \tag{I.41}$$

  contained in `CalMomMatElem` and `momMatElem`, respectively. Both would have the contribution from $\mathbf{v}^{\mathrm{nl}}$ if the options `(-v,-n)` are used. If $\mathbf{v}^{\mathrm{nl}}$ is neglected, the option `-l` for a layer calculation would be much faster as we only need to calculate the diagonal elements of Eq. (G.2), but since the idea is to *always* include it, we are obliged to use Eq. (I.8), where $\mathcal{C}^\ell_{nm}(\mathbf{k})$ is needed, and thus we ought to use option `-c`. Since `CalMomMatElem` is calculated for off-diagonal elements only, we have added a `do` loop in `set_input_ascii.f90` to compute the diagonal part, Eq. (I.41), which is stored in `calVsig`. In accordance to I.12, we have checked that we obtain the same results by using Eq. (G.2) or Eq. (I.43), in a layered injection current calculation, which means that the results obtained thus far in our articles are correct, of course, neglecting $\mathbf{v}^{\mathrm{nl}}$.

  INCLUDE FIGURES.

I.9 Consistency check-up 1

To check that the layered expressions Eqs. (I.1), (I.3), (I.2) and (I.4), agree with a bulk calculation, we must take $\boldsymbol{\mathcal{V}}^{\sigma}_{nm} \rightarrow \mathbf{v}^{\sigma}_{nm}$ and $\boldsymbol{\mathcal{V}}^{\sigma}_{nm;\mathbf{k}} \rightarrow \mathbf{v}^{\sigma}_{nm;\mathbf{k}}$. To do this, proceed as follows

1. Run bulk GaAs using `rlayer.sh` and `chose_layers.sh` as if it were a surface, even though it make no sense.

2. In `$TINIBA/latm/SRC_1setinput/set_input_ascii.f90` look for
   `!########## MIMIC A BULK RESPONSE #######d`
   and follow instructions given there.

3. Compile `set_input_*` in `$TINIBA/latm/SRC_1setinput`

4. run `all_responses.sh` using
   `-w layer -r 44 ...`
   `-w total -r 21 ...`
   and
   `-w total -r 42 ...`
   thus obtaining a `layer` calculation using bulk matrix elements, a `total` calculation for the length and the velocity gauge, and plot the three χ's, they ouught to be identical, if not CRY!. Try out to reproduce Fig. I.1

I.10 Consistency check-up 2

In Fig. I.2 we show Im$[\chi_{xx}]$ for a surface, where the The full-slab result is twice the half-slab result, with or without $\mathbf{v}^{\mathrm{nl}}$, as it must be. Also, the scissors correction rigidly shifts the spectrum by $\hbar\Sigma$ as it should be.

I.11 Consistency check-up 3

Check-of-Checks: A (100) 2×1 surface has χ_{xxx} different from zero, whereas the ideally terminated (100) surface has $\chi_{xxx} = 0$. Clean Si(100) has the 2×1 surface as a possible reconstruction. Then, to calculate such a surface, one can use a slab such that its front surface is the reconstructed Si(100)2×1 surface and its back surface is H-terminated. Therefore, for the layer-by-layer scheme one should expect that

$$\chi^{\mathrm{half-slab}}_{xxx} \equiv \chi^{\mathrm{full-slab}}_{xxx}, \tag{I.42}$$

since the contribution from the back surface (H-terminated), would have zero contribution, since this tensor component of χ is symmetry forbidden. Fancy at Fig. I.3, and notice that $\chi^{\mathrm{nl}} < \chi$. i.e. the susceptibility with the inclusion of the non-local part of the pseudopotential is smaller than that without it.
King-of-Kings: Rejoice at Fig. I.4.

I.12 Consistency check-up 4

To check that the coding of $\mathcal{C}^{\ell}_{nm}(\mathbf{k})$ is correct, we can calculate $\mathcal{V}^{\mathrm{a},\ell}_{nm}(\mathbf{k})$ using Eq. (1.72) as follows

$$\begin{aligned}\mathcal{V}^{\mathrm{a},\ell}_{nm}(\mathbf{k}) &= \frac{1}{2m_e}\Big(\mathcal{C}^{\ell}(z)p^{\mathrm{a}} + p^{\mathrm{a}}\mathcal{C}^{\ell}(z)\Big)_{nm} \\ &= \frac{1}{2m_e}\sum_q \Big(\mathcal{C}^{\ell}_{nq}p^{\mathrm{a}}_{qm} + p^{\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm}\Big),\end{aligned} \tag{I.43}$$

which must give the same results as those computed through Eq. (G.2). Indeed, we have checked that this is the case. The `$TINIBA/util/consistency-of-cfmn.sh` is used to check this.

I.13 Consistency check-up 5

When the `-n` option is chosen, using `all_responses.sh` as coded above doesn't give consistent results, i.e. χ with $\mathbf{v}^{\mathrm{nl}}$ is not smaller than χ without $\mathbf{v}^{\mathrm{nl}}$. Thus, we follow the bellow approach instead.

We use Eq. (H.14)

$$(\mathcal{V}^{\mathrm{LDA,a}}_{nm})_{;k^{\mathrm{b}}} = \frac{\hbar}{m_e}\delta_{\mathrm{ab}}C^{\ell}_{nm} - i\sum_p [r^{\mathrm{b}}, v^{\mathrm{nl,a}}]_{np}C^{\ell}_{pm} + i\sum_{\ell}\left(r^{\mathrm{b}}_{n\ell}\mathcal{V}^{\mathrm{LDA,a}}_{\ell m} - \mathcal{V}^{\mathrm{LDA,a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right) + ir^{\mathrm{b}}_{nm}\tilde{\Delta}^{\mathrm{a}}_{mn}, \tag{I.44}$$

where

$$\tilde{\Delta}^{\mathrm{a}}_{mn} = \mathcal{V}^{\mathrm{LDA,a}}_{nn} - \mathcal{V}^{\mathrm{LDA,a}}_{mm}, \tag{I.45}$$

which is coded instead of Eq. (I.29). As mentioned before, the term $[r^{\mathrm{b}}, v^{\mathrm{nl,a}}]_{nm}$ calculated in Appendix F, is small compared to the other terms, thus we neglect it throwout this work.[?] The expression for C^{ℓ}_{nm} is calculated in Appendix G.

Likewise, with the help of Eq. (D.9) into Eq. (I.18), we obain

$$\begin{aligned}(v^{\mathcal{S},\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} &= i\Sigma f_{mn}(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} = i\Sigma f_{mn}\left(\frac{v^{\mathrm{LDA,a}}_{nm}}{i\omega^{\mathrm{LDA}}_{nm}}\right)_{;k^{\mathrm{b}}} \\ &= \Sigma\frac{f_{mn}}{\omega^{\mathrm{LDA}}_{nm}}\left[\left(v^{\mathrm{LDA},a}_{nm}\right)_{;k^{\mathrm{b}}} - \frac{v^{\mathrm{LDA},a}_{nm}}{\omega^{\mathrm{LDA}}_{nm}}\left(\omega^{\mathrm{LDA}}_{nm}\right)_{;k^{\mathrm{b}}}\right] \\ &= \Sigma\frac{f_{mn}}{\omega^{\mathrm{LDA}}_{nm}}\left[\left(v^{\mathrm{LDA},a}_{nm}\right)_{;k^{\mathrm{b}}} - \frac{\Delta^{b}_{nm}}{\omega^{\mathrm{LDA}}_{nm}}v^{\mathrm{LDA},a}_{nm}\right],\end{aligned} \tag{I.46}$$

which is generalized as follows

$$(\mathcal{V}^{\mathcal{S},\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} = \Sigma\frac{f_{mn}}{\omega^{\mathrm{LDA}}_{nm}}\left[\left(\mathcal{V}^{\mathrm{LDA},a}_{nm}\right)_{;k^{\mathrm{b}}} - \frac{\Delta^{b}_{nm}}{\omega^{\mathrm{LDA}}_{nm}}\mathcal{V}^{\mathrm{LDA},a}_{nm}\right], \tag{I.47}$$

although, I haven't found a way to prove this rigorously, it gives very similar results to those obtained by Eq. (I.23), which is coded. The following is also tempting,

$$
\begin{aligned}
v^{\mathcal{S},a}_{nm} &= \Sigma \frac{f_{mn}}{\omega^{\text{LDA}}_{nm}} v^{\text{LDA},a}_{nm} \\
\mathcal{V}^{\mathcal{S},a}_{nm} &= \Sigma \frac{f_{mn}}{\omega^{\text{LDA}}_{nm}} \mathcal{V}^{\text{LDA},a}_{nm} .
\end{aligned}
\tag{I.48}
$$

Again, I haven't found a way to prove this rigorously, but it gives very similar results to those obtained by Eq. (C.4), which is coded. In Fig. I.5 we show the comparison between the two alternatives, from where we see that they are basically equivalent.

I.14 Subroutines

The following subroutines/shells are involved in the coding, and are documented between
`#BMSd`
⋮
`#BMSu`
marks.

1. `$TINIBA/utils/all_responses.sh`

2. `$TINIBA/latm/SRC_1setinput/inparams.f90`
   Warning: compile both
   `$TINIBA/latm/SRC_1setinput/`
   and
   `$TINIBA/latm/SRC_2latm/`

3. `$TINIBA/latm/SRC_1setinput/set_input_ascii.f90`

I.15 Scissors renormalization for $\mathcal{V}_{nm}^{\Sigma}$

$$
\begin{aligned}
\langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle(E_m^{\Sigma}-E_n^{\Sigma}) &= \int d\mathbf{r}\,\psi_{n\mathbf{k}}^{*}(\mathbf{r})\mathcal{C}(z)\mathbf{r}(E_m^{\Sigma}-E_n^{\Sigma})\psi_{m\mathbf{k}}(\mathbf{r}) \\
&= \int d\mathbf{r}\,\psi_{n\mathbf{k}}^{*}(\mathbf{r})\mathcal{C}(z)[\mathbf{r},H^{\Sigma}]\psi_{m\mathbf{k}}(\mathbf{r}) \\
&= -i\int d\mathbf{r}\,\psi_{n\mathbf{k}}^{*}(\mathbf{r})\mathcal{C}(z)\mathbf{v}^{\Sigma}\psi_{m\mathbf{k}}(\mathbf{r}) \to \boldsymbol{\mathcal{V}}_{nm}^{\Sigma} \\
\langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle &\to \frac{\boldsymbol{\mathcal{V}}_{nm}^{\Sigma}}{\omega_{nm}^{\Sigma}} \\
\langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle(E_m^{\mathrm{LDA}}-E_n^{\mathrm{LDA}}) &= \int d\mathbf{r}\,\psi_{n\mathbf{k}}^{*}(\mathbf{r})\mathcal{C}(z)\mathbf{r}(E_m^{\mathrm{LDA}}-E_n^{\mathrm{LDA}})\psi_{m\mathbf{k}}(\mathbf{r}) \\
&= \int d\mathbf{r}\,\psi_{n\mathbf{k}}^{*}(\mathbf{r})\mathcal{C}(z)[\mathbf{r},H^{\mathrm{LDA}}]\psi_{m\mathbf{k}}(\mathbf{r}) \\
&= -i\int d\mathbf{r}\,\psi_{n\mathbf{k}}^{*}(\mathbf{r})\mathcal{C}(z)\mathbf{v}^{\mathrm{LDA}}\psi_{m\mathbf{k}}(\mathbf{r}) \to \boldsymbol{\mathcal{V}}_{nm}^{\mathrm{LDA}} \\
\langle n\mathbf{k}|\mathcal{C}(z)\mathbf{r}|m\mathbf{k}\rangle &\to \frac{\boldsymbol{\mathcal{V}}_{nm}^{\mathrm{LDA}}}{\omega_{nm}^{\mathrm{LDA}}} \\
\boldsymbol{\mathcal{V}}_{nm}^{\Sigma} &= \frac{\omega_{nm}^{\Sigma}}{\omega_{nm}^{\mathrm{LDA}}}\boldsymbol{\mathcal{V}}_{nm}^{\mathrm{LDA}} \quad \text{voila!!!.}
\end{aligned}
\tag{I.49}
$$

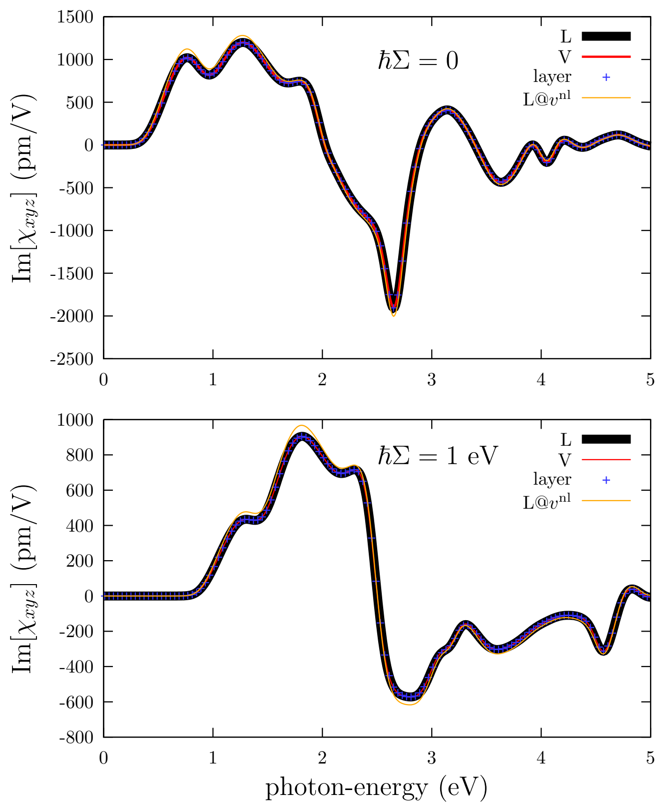

Figure I.1: Im[χ_{xyz}] for GaAs, 10 Ha and 47 **k**-points, using the layered formulation and mimicking a bulk. The correction due to $\mathbf{v}^{\mathrm{nl}}$, also agrees with the velocity and the layered approach (not shown in the figure for clarity).

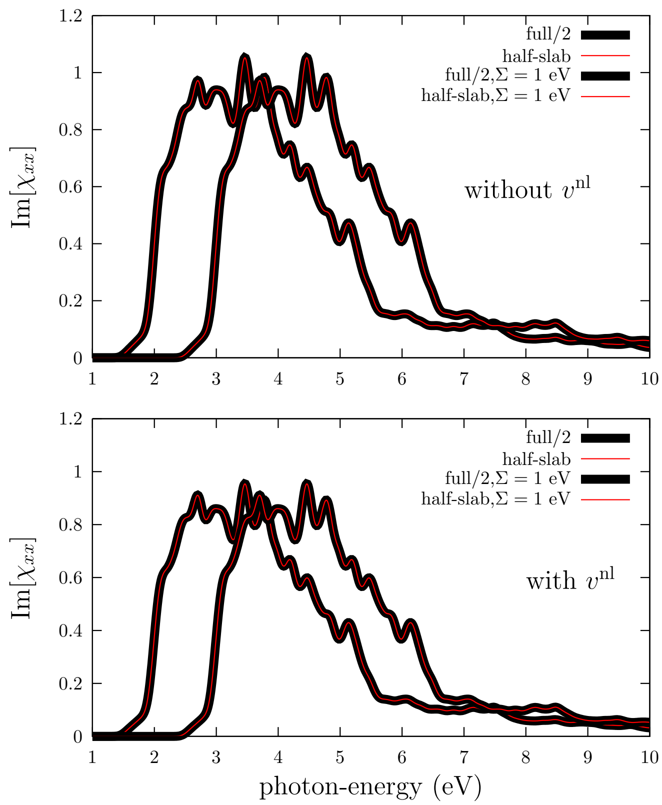

Figure I.2: Im[χ_{xx}] for a Si(111):As surface of 6-layers, 5 Ha and 14 **k**-points using the layered formulation. The full-slab result is twice the half-slab result, as it must be.

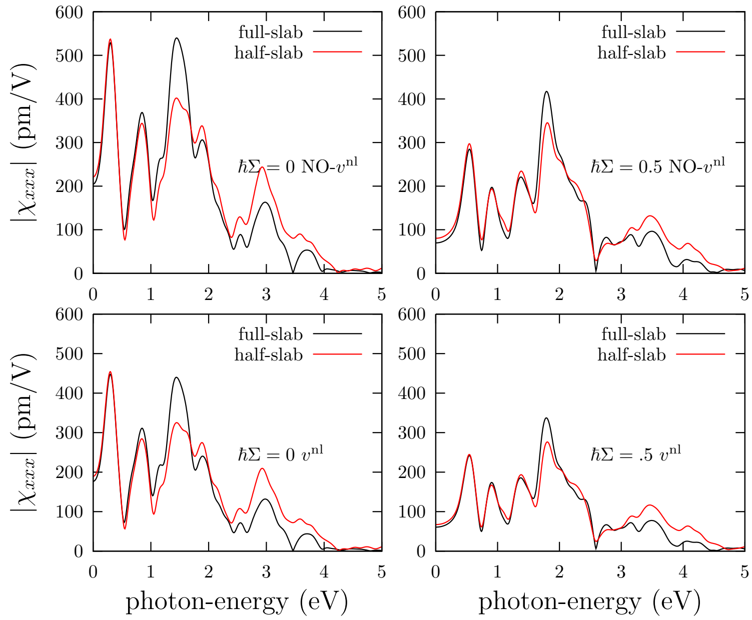

Figure I.3: $|\chi_{xxx}|$ for a Si(100)2 $\times$ 1 surface of 16 Si-layers and one H layer, 10 Ha, 132 bands, 244 **k**-points, and 1000 pwvs in DP$^{\rm TM}$, using the layered formulation. We see that $\chi_{xxx}^{\rm half-slab} \sim \chi_{xxx}^{\rm full-slab}$, validating the layer-by-layer approach.

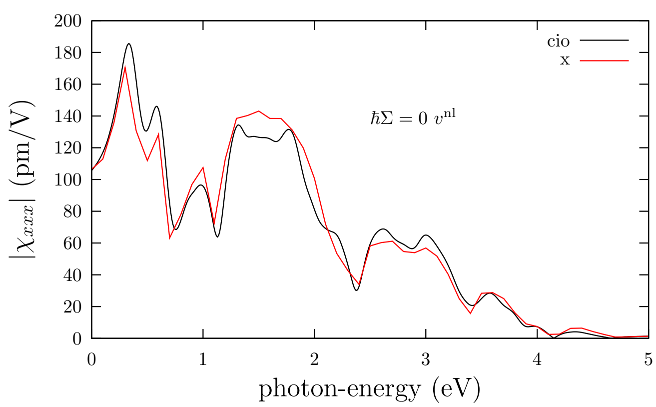

Figure I.4: $|\chi_{xxx}|$ for a Si(100)2 $\times$ 1 surface of 12 Si-layers and one H layer, 5 Ha, 100 bands and 244 **k**-points for the CIO-TINIBA$^{\circledR}$-coding and 256 **k**-point for the X-DP$^{\copyright}$-coding. Both broadened by 0.1 eV.

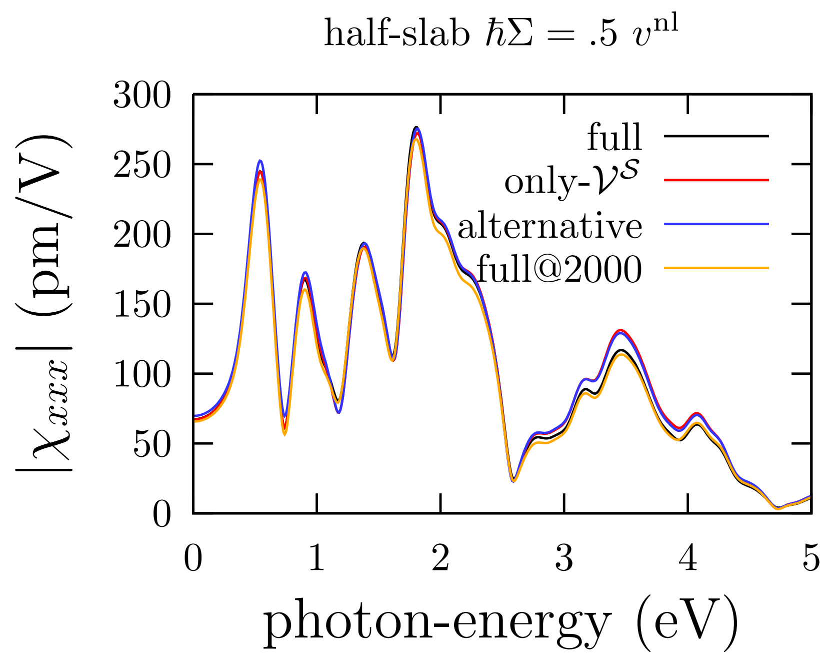

Figure I.5: $|\chi_{xxx}|$ for a Si(100)2×1 surface of 16 Si-layers and one H layer, 10 Ha, 132 bands, 244 **k**-points and and 1000 pwvs in DP$^{\mathrm{TM}}$, using the layered formulation. "Full" uses full coding of $\mathcal{V}^{\mathcal{S}}_{nm}$ and $\mathcal{V}^{\mathcal{S}}_{nm:\mathbf{k}}$ through Eq. (C.4); "only-$\mathcal{V}^{\mathcal{S}}$" uses $\mathcal{V}^{\mathcal{S}}_{nm}$ through Eq. (C.4) and $\mathcal{V}^{\mathcal{S}}_{nm:\mathbf{k}}$ through Eq. (I.47); "alternative" uses $\mathcal{V}^{\mathcal{S}}_{nm}$ through Eq. (I.48) and $\mathcal{V}^{\mathcal{S}}_{nm:\mathbf{k}}$ through Eq. (I.47). Also, we show the results for 2000 pwvs. Notice that all the curves are almost identical to each other.

Appendix J

Divergence Free Expressions for χ^{s}_{abc}

We add the $\mathbf{k}$ and $-\mathbf{k}$ terms of expressions (**??**) and (**??**) to obtain:

$$
\begin{aligned}
A\left[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}\right] &= -\frac{f_{ml}}{2}\left[\frac{\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\mathbf{k}}\right. \\
+\frac{\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{-\mathbf{k}}\Bigg] &= -\frac{f_{ml}}{2}\left[\frac{\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\mathbf{k}}\right. \\
-\frac{\mathcal{P}^{\mathrm{a}}_{nm}r^{\mathrm{c}}_{ln}r^{\mathrm{b}}_{ml}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\mathbf{k}}\Bigg] &= -\frac{f_{ml}}{2}\frac{1}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega} \\
&\times \qquad [\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{l
\end{aligned}
\tag{J.1}
$$

$$
= -\frac{f_{ml}}{2}\frac{1}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}\left[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}-(\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm})^{*}\right] = -\frac{f_{ml}}{2}\frac{2i\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}]}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega},
$$

where we used the Hermiticity of the momentum and position operators. Likewise we get that

$$
A\left[\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right] = f_{ml}\frac{4i\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}. \tag{J.2}
$$

Also,

$$
\begin{aligned}
&-f_{ln}\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right] \\
&= -2if_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}]\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right],
\end{aligned}
\tag{J.3}
$$

and therefore

$$
\begin{aligned}
E = {}& 2if_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}]\left[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}+\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right] \\
&- 2if_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}]\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right].
\end{aligned}
\tag{J.4}
$$

Using above results into Eq. (1.77) implies

$$
\begin{aligned}
\chi^{s,\ell}_{e,\mathrm{abc}} = {}& -\frac{2e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\Bigg[f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}]\Bigg[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}+\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega} \\
&- f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}]\Bigg[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\Bigg]\Bigg] \\
= {}& -\frac{2e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\Bigg[f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]\Bigg[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}+\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-} \\
&- f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]\Bigg[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\Bigg]\Bigg],
\end{aligned}
\tag{J.5}
$$

where $\{\}$ is the symmetrization of the Cartesian indices bc, i.e. $\{u^{\mathrm{b}}s^{\mathrm{c}}\} = (u^{\mathrm{b}}s^{\mathrm{c}}+u^{\mathrm{c}}s^{\mathrm{b}})/2$. Then, we see that $\chi^{s,\ell}_{e,\mathrm{abc}} = \chi^{s,\ell}_{e,acb}$. We further simplify the last equation as follows:

$$\begin{aligned}
\chi^{s,\ell}_{e,\text{abc}} &= -\frac{2e^3}{2m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[-\frac{f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}+\frac{2f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right.\\
&\left.+\left[\frac{f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}-\frac{2f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right]\\
&= -\frac{2e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}-\frac{2f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right.\\
&\left.+\left[\frac{f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}-\frac{f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\ell\leftrightarrow m}\right]\right]\\
&= -\frac{e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}-\frac{2f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right.\\
&\left.+\left[\frac{f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}-\frac{f_{lm}\text{Im}[\mathcal{P}^{\text{a}}_{ln}\{r^{\text{c}}_{nm}r^{\text{b}}_{ml}\}]}{2\omega_{ml}(2\omega_{ml}-\omega_{nl})}\frac{1}{\omega_{ml}-\omega}|_{n\leftrightarrow m}\right]\right]\\
&= -\frac{e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}-\frac{2f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right.\\
&\left.+\left[\frac{f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}-\frac{f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{lm}\{r^{\text{c}}_{mn}r^{\text{b}}_{nl}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{ml})}\frac{1}{\omega_{nl}-\omega}\right]\right]\\
&= -\frac{e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}-\frac{2f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right.\\
&\left.+f_{ln}\left[\frac{\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}-\frac{f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{lm}\{r^{\text{c}}_{mn}r^{\text{b}}_{nl}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{ml})}\right]\frac{1}{\omega_{nl}-\omega}\right], \qquad \text{(J.6)}
\end{aligned}$$

where the 2 in the denominator of the prefactor after the first equal sign comes from the $\mathbf{k}$ and $-\mathbf{k}$ addition, i.e. $\chi \to \sum_{\mathbf{k}>0}[\chi(\mathbf{k})+\chi(-\mathbf{k})]/2$. Taking $\omega\to\omega+i\eta$ and use $\lim_{\eta\to 0} 1/(x-i\eta) = P(1/x)+i\pi\delta(x)$, to get

$$\begin{aligned}
\text{Im}[\chi^{s,\ell}_{e,\text{abc}}] &= \frac{2\pi e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}-\frac{2f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\right]\delta(\omega_{nm}-2\omega)\right.\\
&\left.+f_{ln}\left[\frac{\text{Im}[\mathcal{P}^{\text{a}}_{lm}\{r^{\text{c}}_{mn}r^{\text{b}}_{nl}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{ml})}-\frac{\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\right]\delta(\omega_{nl}-\omega)\right]. \qquad \text{(J.7)}
\end{aligned}$$

We change $l\leftrightarrow m$ in the last term, to write

$$\begin{aligned}
\text{Im}[\chi^{s,\ell}_{e,\text{abc}}] &= \frac{\pi e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ln}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{b}}_{nl}r^{\text{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}-\frac{2f_{ml}\text{Im}[\mathcal{P}^{\text{a}}_{mn}\{r^{\text{c}}_{nl}r^{\text{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\right]\delta(\omega_{nm}-2\omega)\right.\\
&\left.+f_{mn}\left[\frac{\text{Im}[\mathcal{P}^{\text{a}}_{ml}\{r^{\text{c}}_{ln}r^{\text{b}}_{nm}\}]}{2\omega_{nm}(2\omega_{nm}-\omega_{lm})}-\frac{\text{Im}[\mathcal{P}^{\text{a}}_{ln}\{r^{\text{b}}_{nm}r^{\text{c}}_{ml}\}]}{2\omega_{nm}(2\omega_{nm}-\omega_{nl})}\right]\delta(\omega_{nm}-\omega)\right]. \qquad \text{(J.8)}
\end{aligned}$$

From the delta functions it follows that $n = c$ and $m = v$, then $f_{ln} = 1$ with $l = v'$, $f_{ml} = 1$ with $l = c'$, and $f_{mn} = 1$ with $l = c'$ or v', and

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc}}] = \frac{\pi e^3}{m_e \hbar^2} \sum_{vc\mathbf{k}} \Bigg[\Bigg[\sum_{v' \neq v} \frac{2\mathrm{Im}[\mathcal{P}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'} r^{\mathrm{c}}_{v'v}\}]}{\omega_{cv}(2\omega_{cv'} - \omega_{cv})} - \sum_{c' \neq c} \frac{2\mathrm{Im}[\mathcal{P}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'} r^{\mathrm{b}}_{c'v}\}]}{\omega_{cv}(2\omega_{c'v} - \omega_{cv})} \Bigg] \delta(\omega_{cv} - 2\omega) + \sum_{l \neq (v,c)} \Bigg[\frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc} r^{\mathrm{b}}_{cv}\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{lv})} - \frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv} r^{\mathrm{c}}_{vl}\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{cl})} \Bigg] \delta(\omega_{cv} - \omega) \Bigg], \tag{J.9}$$

where we put the layer ℓ dependence in $\mathcal{P}$. Using Eq. (O.13), we can obtain the following result

$$\begin{aligned} 2i\mathrm{Im}[\mathcal{P}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\}] &= \mathcal{P}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\} - (\mathcal{P}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\})^* \\ &= i m_e \omega_{nm} \mathcal{R}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\} - (i m_e \omega_{nm} \mathcal{R}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\})^* \\ &= i m_e \omega_{nm} \left(\mathcal{R}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\} + (\mathcal{R}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\})^* \right) \\ &= 2 i m_e \omega_{nm} \mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{nm}\{r^{\mathrm{b}}_{ml} r^{\mathrm{c}}_{ln}\}], \end{aligned} \tag{J.10}$$

then, using $\omega_{vc} = -\omega_{vc}$ we obtain

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc}}] = \frac{\pi e^3}{\hbar^2} \sum_{vc\mathbf{k}} \Bigg[\Bigg[- \sum_{v' \neq v} \frac{2\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'} r^{\mathrm{c}}_{v'v}\}]}{2\omega_{cv'} - \omega_{cv}} + \sum_{c' \neq c} \frac{2\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'} r^{\mathrm{b}}_{c'v}\}]}{2\omega_{c'v} - \omega_{cv}} \Bigg] \delta(\omega_{cv} - 2\omega) + \sum_{l \neq (v,c)} \Bigg[\frac{\omega_{vl}\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc} r^{\mathrm{b}}_{cv}\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{lv})} - \frac{\omega_{lc}\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv} r^{\mathrm{c}}_{vl}\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{cl})} \Bigg] \delta(\omega_{cv} - \omega) \Bigg]. \tag{J.11}$$

Finally, following Ref. [?, ?] we simply change $\omega_{nm} \to \omega^S_{nm}$ to obtain the scissored expresion of

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc}}] = \frac{\pi e^3}{2\hbar^2} \sum_{vc\mathbf{k}} \Bigg[4 \Bigg[- \sum_{v' \neq v} \frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'} r^{\mathrm{c}}_{v'v}\}]}{2\omega^S_{cv'} - \omega^S_{cv}} + \sum_{c' \neq c} \frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'} r^{\mathrm{b}}_{c'v}\}]}{2\omega^S_{c'v} - \omega^S_{cv}} \Bigg] \delta(\omega^S_{cv} - 2\omega) + \sum_{l \neq (v,c)} \Bigg[\frac{\omega^S_{vl}\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc} r^{\mathrm{b}}_{cv}\}]}{\omega^S_{cv}(2\omega^S_{cv} - \omega^S_{lv})} - \frac{\omega^S_{lc}\mathrm{Re}[\mathcal{R}^{\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv} r^{\mathrm{c}}_{vl}\}]}{\omega^S_{cv}(2\omega^S_{cv} - \omega^S_{cl})} \Bigg] \delta(\omega^S_{cv} - \omega) \Bigg], \tag{J.12}$$

where we have "pulled" a factor of 1/2, so the prefactor is the same as that of the velocity gauge formalism.[?] For the I term of Eq. (??), we notice that the energy denominators are invariant under $\mathbf{k} \to -\mathbf{k}$, and then we only look at the numerators, then

$$
\begin{aligned}
C \to f_{mn}\mathcal{P}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}}|_{\mathbf{k}} + f_{mn}\mathcal{P}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}}|_{-\mathbf{k}} &= f_{mn}\left[\mathcal{P}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}}|_{\mathbf{k}} + (-\mathcal{P}^{\rm a}_{nm})(-(r^{\rm b}_{mn})_{;k^{\rm c}})|_{\mathbf{k}}\right] \\
&= f_{mn}\left[\mathcal{P}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}} + \mathcal{P}^{\rm a}_{nm}(r^{\rm b}_{mn})_{;k^{\rm c}}\right] \\
&= f_{mn}\left[\mathcal{P}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}} + (\mathcal{P}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}})^*\right] \\
&= m_e f_{mn}\omega_{mn}\left[i\mathcal{R}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}} + (i\mathcal{R}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}})^*\right] \\
&= i m_e f_{mn}\omega_{mn}\left[\mathcal{R}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}} - (\mathcal{R}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}})^*\right] \\
&= -2m_e f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}}],
\end{aligned}
\tag{J.13}
$$

with similar results for $D = -2f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}]\Delta^{\rm c}_{nm}$. Now, from Eq. (E.6), we obtain that the first term reduces to

$$
\begin{aligned}
\frac{r^{\rm b}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\rm a}_{mn}\right)_{;k^{\rm c}}|_{\mathbf{k}} + \frac{r^{\rm b}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\rm a}_{mn}\right)_{;k^{\rm c}}|_{-\mathbf{k}} &= \frac{r^{\rm b}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\rm a}_{mn}\right)_{;k^{\rm c}}|_{\mathbf{k}} - \frac{r^{\rm b}_{mn}}{\omega_{nm}}\left(\mathcal{R}^{\rm a}_{nm}\right)_{;k^{\rm c}}|_{\mathbf{k}} \\
&= \frac{1}{\omega_{nm}}\left[r^{\rm b}_{nm}\left(\mathcal{R}^{\rm a}_{mn}\right)_{;k^{\rm c}} - \left(r^{\rm b}_{nm}\left(\mathcal{R}^{\rm a}_{mn}\right)_{;k^{\rm c}}\right)^*\right] \\
&= \frac{2i}{\omega_{nm}}\mathrm{Im}[r^{\rm b}_{nm}\left(\mathcal{R}^{\rm a}_{mn}\right)_{;k^{\rm c}}],
\end{aligned}
\tag{J.14}
$$

with similar results for the other two terms. First, we collect the 2ω terms form Eq. (**??**) that contribute to Eq. (1.76)

$$
\begin{aligned}
I_{2\omega} &= -\frac{e^3}{2\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{-4f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}}]}{\omega^2_{nm}} - \frac{-8f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}]\Delta^{\rm c}_{nm}}{\omega^3_{nm}}\right]\frac{1}{\omega_{nm}-2\omega} \\
&= \frac{e^3}{2\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{4f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}}]}{\omega^2_{nm}} - \frac{8f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}]\Delta^{\rm c}_{nm}}{\omega^3_{nm}}\right]\frac{1}{\omega_{nm}-2\omega} \\
&= \frac{e^3}{2\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{-4f_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}}]}{\omega_{nm}} + \frac{8f_{mn}\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}]\Delta^{\rm c}_{nm}}{\omega^2_{nm}}\right]\frac{1}{\omega_{nm}-2\omega},
\end{aligned}
\tag{J.15}
$$

where the 2 in the denominator of the prefactor comes from the $\mathbf{k}$ and $-\mathbf{k}$ addition, as previously noted. Taking $\eta \to 0$ we get that

$$
\begin{aligned}
\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},2\omega}] &= \frac{\pi|e|^3}{2\hbar^2}\sum_{mn\mathbf{k}}\frac{4f_{mn}}{\omega_{nm}}\left[\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}}] - \frac{2\mathrm{Im}[\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}]\Delta^{\rm c}_{nm}}{\omega_{nm}}\right]\delta(\omega_{nm}-2\omega) \\
&= \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\mathrm{Im}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{\left(r^{\rm b}_{cv}\right)_{;k^{\rm c}}\}] - \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\rm b}_{cv}]\Delta^{\rm c}_{cv}\}}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega),
\end{aligned}
\tag{J.16}
$$

where from the delta term we must have $n = c$ and $m = v$. The expression is symmetric in the last two indices and is properly scissor shifted as well.

The ω terms are

$$
\begin{aligned}
I_\omega &= -\frac{e^3}{m_e 2\hbar^2}\sum_{nm\mathbf{k}}\left[\left[-\frac{C}{2\omega_{nm}^2}+\frac{3D}{2\omega_{nm}^3}\right]\frac{1}{\omega_{nm}-\omega}+\frac{D}{2\omega_{nm}^2}\frac{1}{(\omega_{nm}-\omega)^2}\right] \\
&= -\frac{e^3}{m_e 2\hbar^2}\sum_{nm\mathbf{k}}\left[\left[-\frac{-2m_e f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{2\omega_{nm}^2}+\frac{3(-2m_e f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm})}{2\omega_{nm}^3}\right]\frac{1}{\omega_{nm}-\omega}\right. \\
&+\left.\frac{-im_e f_{mn}}{2}\left(\frac{\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}}\right)_{;k^{\mathrm{c}}}\frac{1}{\omega_{nm}-\omega}\right] \\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}} f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}-\frac{i}{2}\left(\frac{\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}}\right)_{;k^{\mathrm{c}}}\right]\frac{1}{\omega_{nm}-\omega} \\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}} f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}-\frac{i}{2}\left[\frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}\right.\right. \\
&+\left.\left.\frac{\mathcal{R}^{\mathrm{a}}_{mn}}{\omega_{nm}}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}-\frac{\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}^2}\left(\omega_{nm}\right)_{;k^{\mathrm{c}}}\right]\right]\frac{1}{\omega_{nm}-\omega} \\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}} f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}-\frac{i}{2}\left[\frac{2i}{\omega_{nm}}\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right.\right. \\
&+\left.\left.\frac{2i}{\omega_{nm}}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]-\frac{2i}{\omega_{nm}^2}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}\right]\right]\frac{1}{\omega_{nm}-\omega} \\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}} f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}+\frac{1}{\omega_{nm}}\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right. \\
&+\left.\frac{1}{\omega_{nm}}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]-\frac{1}{\omega_{nm}^2}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}\right]\frac{1}{\omega_{nm}-\omega},
\end{aligned}
\tag{J.17}
$$

or

$$
\begin{aligned}
I_\omega &= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}\frac{f_{mn}}{\omega_{nm}}\left[-\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}}+\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right. \\
&+\left.\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]-\frac{1}{\omega_{nm}}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}\right]\frac{1}{\omega_{nm}-\omega} \\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}\frac{f_{mn}}{\omega_{nm}}\left[\frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}}+\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right]\frac{1}{\omega_{nm}-\omega}.
\end{aligned}
\tag{J.18}
$$

Taking $\eta\to 0$ we get that

$$
\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{\omega^S_{cv}}\left[\mathrm{Im}[\{r^{\mathrm{b}}_{cv}\left(\mathcal{R}^{\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{c}}}\}]+\frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv}]\Delta^{\mathrm{c}}_{cv}\}}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-\omega),
\tag{J.19}
$$

where from the delta term we must have $n = c$ and $m = v$. The expression is symmetric in the last two indices and is properly scissor shifted as well.

Eq. (J.12), (J.16) and (J.19) are the main results of this appendix, from which we have that $\chi^{s,\ell}_{\rm abc} = \chi^{s,\ell}_{e,\rm abc} + \chi^{s,\ell}_{i,\rm abc}$ where $\chi^{s,\ell}_{i,\rm abc} = \chi^{s,\ell}_{i,{\rm abc},\omega} + \chi^{s,\ell}_{i,{\rm abc},2\omega}$. In the continuous limit of $\mathbf{k}$ $(1/\Omega)\sum_{\mathbf{k}} \to \int d^3\mathbf{k}/(8\pi^3)$ and the real part is obtained with a Kramers-Kronig transformation. We have checked that these results are equivalent to Eqs. 40 and 41 of Cabellos et. al., Ref. [?], for a bulk system for which we simply take $\mathcal{R}^{\rm a,\ell}_{nm} \to r^{\rm a}_{nm}$.

In summary we have

$$\mathrm{Im}[\chi^{s,\ell}_{e,{\rm abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\left[\frac{\omega^S_{lc}\mathrm{Re}[\mathcal{R}^{\rm a,\ell}_{lc}\{r^{\rm b}_{cv}r^{\rm c}_{vl}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{cl})} - \frac{\omega^S_{vl}\mathrm{Re}[\mathcal{R}^{\rm a,\ell}_{vl}\{r^{\rm c}_{lc}r^{\rm b}_{cv}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{lv})}\right]\delta(\omega^S_{cv}-\omega), \tag{J.20}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,{\rm abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\frac{1}{\omega^S_{cv}}\left[\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\rm a,\ell}_{lc}\{r^{\rm b}_{cv}r^{\rm c}_{vl}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{cl})} - \frac{\mathrm{Im}[\mathcal{V}^{\sigma,\rm a,\ell}_{vl}\{r^{\rm c}_{lc}r^{\rm b}_{cv}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{lv})}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{J.21}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,{\rm abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{\omega^S_{cv}}\left[\mathrm{Im}[\{r^{\rm b}_{cv}\left(\mathcal{R}^{\rm a,\ell}_{vc}\right)_{;k^{\rm c}}\}] + \frac{2\mathrm{Im}[\mathcal{R}^{\rm a,\ell}_{vc}\{r^{\rm b}_{cv}\Delta^{\rm c}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-\omega), \tag{J.22}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,{\rm abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{(\omega^S_{cv})^2}\left[\mathrm{Re}\left[\left\{r^{\rm b}_{cv}\left(\mathcal{V}^{\sigma,\rm a,\ell}_{vc}\right)_{;k^{\rm c}}\right\}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\sigma,\rm a,\ell}_{vc}\left\{r^{\rm b}_{cv}\Delta^{\rm c}_{cv}\right\}\right]}{\omega^S_{cv}}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{J.23}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,{\rm abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}4\left[\sum_{v'\neq v}\frac{\mathrm{Re}[\mathcal{R}^{\rm a,\ell}_{vc}\{r^{\rm b}_{cv'}r^{\rm c}_{v'v}\}]}{2\omega^S_{cv'}-\omega^S_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Re}[\mathcal{R}^{\rm a,\ell}_{vc}\{r^{\rm c}_{cc'}r^{\rm b}_{c'v}\}]}{2\omega^S_{c'v}-\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{J.24}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,{\rm abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\sum_{v'\neq v}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\rm a,\ell}_{vc}\{r^{\rm b}_{cv'}r^{\rm c}_{v'v}\}]}{2\omega^\sigma_{cv'}-\omega^\sigma_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\rm a,\ell}_{vc}\{r^{\rm c}_{cc'}r^{\rm b}_{c'v}\}]}{2\omega^\sigma_{c'v}-\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{J.25}$$

and

$$\mathrm{Im}[\chi^{s,\ell}_{i,{\rm abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\mathrm{Im}[\mathcal{R}^{\rm a,\ell}_{vc}\{\left(r^{\rm b}_{cv}\right)_{;k^{\rm c}}\}] - \frac{2\mathrm{Im}[\mathcal{R}^{\rm a,\ell}_{vc}\{r^{\rm b}_{cv}\Delta^{\rm c}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{J.26}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,{\rm abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^S_{cv})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\sigma,\rm a,\ell}_{vc}\left\{\left(r^{\rm b}_{cv}\right)_{;k^{\rm c}}\right\}\right] - \frac{2\mathrm{Re}\left[\mathcal{V}^{\sigma,\rm a,\ell}_{vc}\left\{r^{\rm b}_{cv}\Delta^{\rm c}_{cv}\right\}\right]}{\omega^S_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{J.27}$$

where $e^3 = -|e|^3$, and we used $\mathrm{Re}[iz] = -\mathrm{Im}[z]$ and $\mathrm{Im}[iz] = \mathrm{Re}[z]$.

Appendix K

Some results of Dirac's notation

We derive a series of results that follow from Dirac's notation and that are useful in the various derivations.

Let's start with the Fourier transform of the wave function written in the Schrödinger representation, i.e.

$$\psi(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{p}\psi(\mathbf{p})e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{K.1}$$

and inversely

$$\psi(\mathbf{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{r}\psi(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{K.2}$$

Now,

$$\langle\mathbf{r}|\psi\rangle = \psi(\mathbf{r}) = \int d\mathbf{p}\langle\mathbf{r}|\mathbf{p}\rangle\langle\mathbf{p}|\psi\rangle = \int d\mathbf{p}\langle\mathbf{r}|\mathbf{p}\rangle\psi(\mathbf{p}), \tag{K.3}$$

that when compared with Eq. (K.1) allow us to identify,

$$\langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{K.4}$$

By the same token,

$$\langle\mathbf{p}|\psi\rangle = \psi(\mathbf{p}) = \int d\mathbf{r}\langle\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle = \int d\mathbf{r}\langle\mathbf{p}|\mathbf{r}\rangle\psi(\mathbf{r}), \tag{K.5}$$

that when compared with Eq. (K.2) allow us to identify,

$$\langle\mathbf{p}|\mathbf{r}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{K.6}$$

where

$$\langle\mathbf{r}|\mathbf{p}\rangle = (\langle\mathbf{p}|\mathbf{r}\rangle)^*, \tag{K.7}$$

is succinctly verified.

We calculate the matrix elements of $\mathbf{p}$ in the $\mathbf{r}$ representation,

$$\begin{aligned}\langle \mathbf{r}|\hat{p}_x|\mathbf{r}'\rangle &= \int d\mathbf{p}\langle \mathbf{r}|\hat{p}_x|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{r}'\rangle \\ &= \int d\mathbf{p} p_x \langle \mathbf{r}|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{r}'\rangle \\ &= \frac{1}{(2\pi\hbar)^3}\int d\mathbf{p} p_x e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar} \\ &= \frac{1}{(2\pi\hbar)^3}\int dp_x p_x e^{ip_x(x-x')/\hbar}\int dp_y e^{ip_y(y-y')/\hbar}\int dp_z e^{ip_z(z-z')/\hbar} \\ &= \frac{1}{2\pi\hbar}\int dp_x p_x e^{ip_x(x-x')/\hbar}\delta(y-y')\delta(z-z'),\end{aligned} \tag{K.8}$$

where we used the fact that

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle, \tag{K.9}$$

and that

$$\delta(q-q') = \frac{1}{2\pi\hbar}\int dp e^{ip(q-q')/\hbar}. \tag{K.10}$$

Now,

$$\frac{1}{2\pi\hbar}\int dp_x p_x e^{ip_x(x-x')/\hbar} = -i\hbar\frac{\partial}{\partial x}\int \frac{dp_x}{2\pi\hbar}e^{ip_x(x-x')/\hbar} = -i\hbar\frac{\partial}{\partial x}\delta(x-x'), \tag{K.11}$$

from where we finally get

$$\langle \mathbf{r}|\hat{p}_x|\mathbf{r}'\rangle = (-i\hbar\frac{\partial}{\partial x}\delta(x-x'))\delta(y-y')\delta(z-z'), \tag{K.12}$$

with similar results for $\hat{p}_y$ and $\hat{p}_z$. Now we can calculate

$$\begin{aligned}\langle \mathbf{r}|\hat{p}_x|\psi\rangle &= \int d\mathbf{r}'\langle \mathbf{r}|\hat{p}_x|\mathbf{r}'\rangle\langle \mathbf{r}'|\psi\rangle \\ &= \int dx'(-i\hbar\frac{\partial}{\partial x}\delta(x-x'))\int dy'\delta(y-y')\int dz'\delta(z-z')\psi(x',y',z') \\ &= -i\hbar\int dx'(\frac{\partial}{\partial x}\delta(x-x'))\psi(x',y,z) = -i\hbar\frac{\partial}{\partial x}\int dx'\delta(x-x')\psi(x',y,z) \\ &= -i\hbar\frac{\partial}{\partial x}\psi(x,y,z),\end{aligned} \tag{K.13}$$

which confirms that in the $\mathbf{r}$ representation, the $\hat{\mathbf{p}}$ operator is replaced with the differential operator $-i\hbar\boldsymbol{\nabla}$.

Appendix L

Basic relationships

We present some basic results needed in the derivation of the main results. The normalization of the states $\psi_{n\mathbf{q}}(\mathbf{r})$ are chosen such that

$$\psi_{m\mathbf{q}}(\mathbf{r}) = \left(\frac{\Omega}{8\pi^3}\right)^{\frac{1}{2}} u_{m\mathbf{q}}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{L.1}$$

and

$$\int_\Omega d^3r\, u^*_{n\mathbf{k}}(\mathbf{r}) u_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm}\delta_{\mathbf{k},\mathbf{q}}, \tag{L.2}$$

where Ω is the volume is the unit cell and $\delta_{a,b}$ is the Kronecker delta that gives one if $a = b$ and zero otherwise. For box normalization, where we have N unit cells in some volume $V = N\Omega$, this gives

$$\int_V d^3r\, \psi^*_{n\mathbf{k}}(\mathbf{r}) \psi_{m\mathbf{q}}(\mathbf{r}) = \frac{V}{8\pi^3}\delta_{nm}\delta_{\mathbf{k},\mathbf{q}}, \tag{L.3}$$

which lets us have in the limit of $N \to \infty$

$$\int d^3r\, \psi^*_{n\mathbf{k}}(\mathbf{r}) \psi_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm}\delta(\mathbf{k}-\mathbf{q}), \tag{L.4}$$

for which the Kornecker-δ is replaced by

$$\delta_{\mathbf{k},\mathbf{q}} \to \frac{8\pi^3}{V}\delta(\mathbf{k}-\mathbf{q}), \tag{L.5}$$

and we recall that $\delta(x) = \delta(-x)$. Now, for any periodic function $f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R})$ we have

$$
\begin{aligned}
\int d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) &= \sum_j^{\text{unit cells}} \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{r}+\mathbf{R}_j)} f(\mathbf{r}+\mathbf{R}_j), \\
&= \sum_j^{\text{unit cells}} \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{r}+\mathbf{R}_j)} f(\mathbf{r}), \\
&= \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) \sum_j^{\text{unit cells}} e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{R}_j}, \\
&= \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) N \sum_{\mathbf{K}} \delta_{\mathbf{K},\mathbf{q}-\mathbf{k}}, \\
&= N \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) \delta_{\mathbf{0},\mathbf{q}-\mathbf{k}}, \\
&= N\delta_{\mathbf{q},\mathbf{k}} \int_\Omega d^3r\, f(\mathbf{r}), \\
&= \frac{8\pi^3}{\Omega} \delta(\mathbf{q}-\mathbf{k}) \int_\Omega d^3r\, f(\mathbf{r}),
\end{aligned}
\tag{L.6}
$$

where we have assumed that $\mathbf{k}$ and $\mathbf{q}$ are restricted to the first Brillouin zone, and thus the reciprocal lattice vector $\mathbf{K} = 0$.

Appendix M

Generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$

We obtain the generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$. We start with the basic result

$$[r^{\mathrm{a}}, p^{\mathrm{b}}] = i\hbar\delta_{ab}, \tag{M.1}$$

then

$$\langle n\mathbf{k}|[r^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{M.2}$$

so

$$\langle n\mathbf{k}|[r_i^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|[r_e^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'). \tag{M.3}$$

From Eq. (A.18) and (A.19)

$$\langle n\mathbf{k}|[r_i^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} \tag{M.4}$$

$$(p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} = \nabla_{k^{\mathrm{a}}} p^{\mathrm{b}}_{nm}(\mathbf{k}) - ip^{\mathrm{b}}_{nm}(\mathbf{k})\left(\xi^{\mathrm{a}}_{nn}(\mathbf{k}) - \xi^{\mathrm{a}}_{mm}(\mathbf{k})\right), \tag{M.5}$$

and

$$\begin{aligned}
\langle n\mathbf{k}|[r_e^{\rm a}, p^{\rm b}]|m\mathbf{k}'\rangle &= \sum_{\ell\mathbf{k}''}\Big(\langle n\mathbf{k}|r_e^{\rm a}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|p^{\rm b}|m\mathbf{k}'\rangle \\
&- \langle n\mathbf{k}|p^{\rm b}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|r_e^{\rm a}|m\mathbf{k}'\rangle\Big) \\
&= \sum_{\ell\mathbf{k}''}\Big((1-\delta_{n\ell})\delta(\mathbf{k}-\mathbf{k}'')\xi_{n\ell}^{\rm a}\delta(\mathbf{k}''-\mathbf{k}')p_{\ell m}^{\rm b} \\
&- \delta(\mathbf{k}-\mathbf{k}'')p_{n\ell}^{\rm b}(1-\delta_{\ell m})\delta(\mathbf{k}''-\mathbf{k}')\xi_{\ell m}^{\rm a}\Big) \\
&= \delta(\mathbf{k}-\mathbf{k}')\sum_{\ell}\Big((1-\delta_{n\ell})\xi_{n\ell}^{\rm a}p_{\ell m}^{\rm b} \\
&- (1-\delta_{\ell m})p_{n\ell}^{\rm b}\xi_{\ell m}^{\rm a}\Big) \\
&= \delta(\mathbf{k}-\mathbf{k}')\bigg(\sum_{\ell}\Big(\xi_{n\ell}^{\rm a}p_{\ell m}^{\rm b} - p_{n\ell}^{\rm b}\xi_{\ell m}^{\rm a}\Big) \\
&+ p_{nm}^{\rm b}(\xi_{mm}^{\rm a} - \xi_{nn}^{\rm a})\bigg). \qquad \text{(M.6)}
\end{aligned}$$

Using Eqs. (M.4) and (M.6) into Eq. (M.3) gives

$$\begin{aligned}
i\delta(\mathbf{k}-\mathbf{k}')\bigg((p_{nm}^{\rm b})_{;k^{\rm a}} - i\sum_{\ell}\Big(\xi_{n\ell}^{\rm a}p_{\ell m}^{\rm b} - p_{n\ell}^{\rm b}\xi_{\ell m}^{\rm a}\Big) \\
- ip_{nm}^{\rm b}(\xi_{mm}^{\rm a} - \xi_{nn}^{\rm a})\bigg) = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \qquad \text{(M.7)}
\end{aligned}$$

then

$$\begin{aligned}
(p_{nm}^{\rm b})_{;k^{\rm a}} = \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell}\Big(\xi_{n\ell}^{\rm a}p_{\ell m}^{\rm b} - p_{n\ell}^{\rm b}\xi_{\ell m}^{\rm a}\Big) \\
+ ip_{nm}^{\rm b}(\xi_{mm}^{\rm a} - \xi_{nn}^{\rm a}), \qquad \text{(M.8)}
\end{aligned}$$

and from Eq. (M.5),

$$\nabla_{k^{\rm a}}p_{nm}^{\rm b} = \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell}\Big(\xi_{n\ell}^{\rm a}p_{\ell m}^{\rm b} - p_{n\ell}^{\rm b}\xi_{\ell m}^{\rm a}\Big). \qquad \text{(M.9)}$$

Now, there are two cases. We use Eqs. (**??**) and (1.31).
Case $n = m$

$$\frac{1}{\hbar}\nabla_{k^{\rm a}}p_{nn}^{\rm b} = \delta_{ab} - \frac{m_e}{\hbar}\sum_{\ell}\omega_{\ell n}\Big(r_{n\ell}^{\rm a}r_{\ell n}^{\rm b} + r_{n\ell}^{\rm b}r_{\ell n}^{\rm a}\Big), \qquad \text{(M.10)}$$

that gives the familiar expansion for the inverse effective mass tensor $(m_n^{-1})_{ab}$.[**?**]

Case $n \neq m$

$$
\begin{aligned}
(p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} &= \hbar\delta_{ab}\delta_{nm} + i \sum_{\ell\neq m\neq n} \Big(\xi^{\mathrm{a}}_{n\ell} p^{\mathrm{b}}_{\ell m} - p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m} \Big) \\
&+ i\Big(\xi^{\mathrm{a}}_{nm} p^{\mathrm{b}}_{mm} - p^{\mathrm{b}}_{nm}\xi^{\mathrm{a}}_{mm} \Big) \\
&+ i\Big(\xi^{\mathrm{a}}_{nn} p^{\mathrm{b}}_{nm} - p^{\mathrm{b}}_{nn}\xi^{\mathrm{a}}_{nm} \Big) + ip^{\mathrm{b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
&= -m_e \sum_{\ell} \Big(\omega_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m} \Big) + i\xi^{\mathrm{a}}_{nm}(p^{\mathrm{b}}_{mm} - p^{\mathrm{b}}_{nn}) \\
&= -m_e \sum_{\ell} \Big(\omega_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m} \Big) + im_e r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn},
\end{aligned}
\tag{M.11}
$$

where

$$
\Delta^{\mathrm{b}}_{mn} = \frac{p^{\mathrm{b}}_{mm} - p^{\mathrm{b}}_{nn}}{m_e}. \tag{M.12}
$$

Now, for $n \neq m$, Eqs. (1.31), (D.9) and (M.11) and the chain rule, give

$$
\begin{aligned}
(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} &= \left(\frac{p^{\mathrm{b}}_{nm}}{im_e\omega_{nm}} \right)_{;k^{\mathrm{a}}} = \frac{1}{im_e\omega_{nm}} \left(p^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{a}}} - \frac{p^{\mathrm{b}}_{nm}}{im_e\omega^2_{nm}} \left(\omega_{nm}\right)_{;k^{\mathrm{a}}} \\
&= \frac{i}{\omega_{nm}} \sum_{\ell} \Big(\omega_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m} \Big) + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn}}{\omega_{nm}} \\
&- \frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}} \left(\omega_{nm}\right)_{;k^{\mathrm{a}}} \\
&= \frac{i}{\omega_{nm}} \sum_{\ell} \Big(\omega_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m} \Big) + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn}}{\omega_{nm}} \\
&- \frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}} \frac{p^{\mathrm{a}}_{nn} - p^{\mathrm{a}}_{mm}}{m_e} \\
&= \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn} + r^{\mathrm{b}}_{nm}\Delta^{\mathrm{a}}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{\ell} \Big(\omega_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m} \Big)
\end{aligned}
\tag{M.13}
$$

Appendix N

$\left(\mathcal{R}^{\mathrm{a}}_{nm}\right)_{;k^{\mathrm{b}}}$

NOT NEEDED, and perhaps is even wrong!!

We rewrite Eq. (M.11) and (1.31) as

$$(p^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} = ir^{\mathrm{b}}_{nm}(p^{\mathrm{a}}_{mm} - p^{\mathrm{a}}_{nn}) + i\sum_{\ell\neq m,n}\left(p^{\mathrm{a}}_{\ell m}r^{\mathrm{b}}_{n\ell} - p^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right), \tag{N.1}$$

which is valid for any operator $\hat{\mathbf{p}}$, thus $p^{\mathrm{a}} \to \mathcal{P}^{\mathrm{a}}$, then

$$\begin{aligned}(\mathcal{P}^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} &= ir^{\mathrm{b}}_{nm}(\mathcal{P}^{\mathrm{a}}_{mm} - \mathcal{P}^{\mathrm{a}}_{nn}) + i\sum_{\ell\neq m,n}\left(\mathcal{P}^{\mathrm{a}}_{\ell m}r^{\mathrm{b}}_{n\ell} - \mathcal{P}^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right)\\ &= im_e r^{\mathrm{b}}_{nm}\Delta^{\mathrm{a},\ell}_{mn} + i\sum_{\ell\neq m,n}\left(\mathcal{P}^{\mathrm{a}}_{\ell m}r^{\mathrm{b}}_{n\ell} - \mathcal{P}^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right),\end{aligned} \tag{N.2}$$

where

$$\Delta^{\mathrm{a},\ell} = \frac{\mathcal{P}^{\mathrm{a}}_{mm} - \mathcal{P}^{\mathrm{a}}_{nn}}{m_e}, \tag{N.3}$$

where we omitted the ℓ-layer label from $\mathcal{P}$. Eq. (1.31) trivially gives

$$\mathcal{R}^{\mathrm{a}}_{nm} = \frac{\mathcal{P}^{\mathrm{a}}_{nm}}{im_e\omega_{nm}} \qquad n \neq m, \tag{N.4}$$

then, using Eq. (N.2)

$$
\begin{aligned}
(\mathcal{R}^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} &= \left(\frac{\mathcal{P}^{\mathrm{a}}_{nm}}{im_e\omega_{nm}}\right)_{;k^{\mathrm{b}}} = \frac{1}{im_e\omega_{nm}}\left(\mathcal{P}^{\mathrm{a}}_{nm}\right)_{;k^{\mathrm{b}}} - \frac{\mathcal{P}^{\mathrm{a}}_{nm}}{im_e\omega^2_{nm}}\left(\omega_{nm}\right)_{;k^{\mathrm{b}}} \\
&= \frac{r^{\mathrm{b}}_{nm}\Delta^{\mathrm{LDA},\mathrm{a},\ell}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_{\ell}\left(\omega_{\ell m}r^{\mathrm{b}}_{n\ell}\mathcal{R}^{\mathrm{a}}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right) \\
&- \frac{\mathcal{R}^{\mathrm{a}}_{nm}}{\omega_{nm}}\left(\omega_{nm}\right)_{;k^{\mathrm{b}}} \\
&= \frac{r^{\mathrm{b}}_{nm}\Delta^{\mathrm{LDA},\mathrm{a},\ell}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_{\ell}\left(\omega_{\ell m}r^{\mathrm{b}}_{n\ell}\mathcal{R}^{\mathrm{a}}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right) \\
&- \frac{\mathcal{R}^{\mathrm{a}}_{nm}}{\omega_{nm}}\frac{p^{\mathrm{b}}_{nn} - p^{\mathrm{b}}_{mm}}{m_e} \\
&= \frac{r^{\mathrm{b}}_{nm}\Delta^{\mathrm{LDA},\mathrm{a},\ell}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_{\ell}\left(\omega_{\ell m}r^{\mathrm{b}}_{n\ell}\mathcal{R}^{\mathrm{a}}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right) \\
&+ \frac{\mathcal{R}^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn}}{\omega_{nm}} \\
&= \frac{r^{\mathrm{b}}_{nm}\Delta^{\mathrm{LDA},\mathrm{a},\ell}_{mn} + \mathcal{R}^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_{\ell}\left(\omega_{\ell m}r^{\mathrm{b}}_{n\ell}\mathcal{R}^{\mathrm{a}}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m}\right)
\end{aligned}
\tag{N.5}
$$

Appendix O

Odds and Ends

We proceed to give an explicit expression for $\mathcal{V}^{a,\ell}_{mn}(\mathbf{k})$, for which we should work with the velocity operator, that is given by

$$i\hbar\hat{\mathbf{v}} = [\hat{\mathbf{r}}, \hat{H}_0]$$
$$= [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}(\mathbf{r}) + \hat{v}(\mathbf{r}, \hat{\mathbf{p}})] \approx [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m}] = i\hbar\frac{\hat{\mathbf{p}}}{m}, \tag{O.1}$$

where the possible contribution of the non-local pseudopotential $\hat{v}(\mathbf{r}, \hat{\mathbf{p}})$ is neglected. Now, from above equation,

$$m\hat{\mathbf{v}} \approx \hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}, \tag{O.2}$$

is the explicit functional form of the velocity or momentum operator. From Eq. (1.63), we need

$$\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle = \int d^3r' \langle\mathbf{r}|\hat{\mathbf{v}}|\mathbf{r}'\rangle\langle\mathbf{r}'|n\mathbf{k}\rangle \approx \frac{1}{m}\hat{\mathbf{p}}\psi_{n\mathbf{k}}(\mathbf{r}), \tag{O.3}$$

where we used

$$\langle\mathbf{r}|\hat{v^x}|\mathbf{r}'\rangle \approx \frac{1}{m}\langle\mathbf{r}|\hat{p^x}|\mathbf{r}'\rangle = \delta(y-y')\delta(z-z')\left(-i\hbar\frac{\partial}{\partial x}\delta(x-x')\right), \tag{O.4}$$

with similar results for the y and z Cartesian directions. Now, from Eqs. (1.65) and (1.63) we obtain

$$\boldsymbol{\mathcal{V}}^{\ell}_{mn}(\mathbf{k}) = \frac{1}{2}\int \mathrm{d}^3r\, \mathcal{F}_\ell(z)\Big[\langle m\mathbf{k}|\mathbf{v}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{v}|n\mathbf{k}\rangle\Big], \tag{O.5}$$

and using Eq. (O.3), we can write, for any function $\mathcal{F}_\ell(z)$ used to identify the response from a region of the slab, that

$$\boldsymbol{\mathcal{V}}_{mn}(\mathbf{k}) \approx \frac{1}{2m}\int d^3r\mathcal{F}_\ell(z)\Big[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}^*\psi^*_{m\mathbf{k}}(\mathbf{r}) + \psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}\psi_{n\mathbf{k}}(\mathbf{r})\Big], \tag{O.6}$$

$$= \frac{1}{m}\int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{\mathcal{F}_\ell(z)\mathbf{p}+\mathbf{p}\mathcal{F}_\ell(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r}), \tag{O.7}$$

$$= \frac{1}{m}\int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\boldsymbol{\mathcal{P}}}\psi_{n\mathbf{k}}(\mathbf{r}) \equiv \frac{1}{m}\boldsymbol{\mathcal{P}}_{mn}(\mathbf{k}). \tag{O.8}$$

Here an integration by parts is performed on the first term of the right hand side of Eq. (O.6); since the $\langle\mathbf{r}|n\mathbf{k}\rangle = e^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r})$ are periodic over the unit cell, the surface term vanishes.

****

We would obtain, instead of Eq. (1.76) and (1.77)

$$\chi^{s,\ell}_{i,\mathrm{abc}} = -\frac{e^3}{m_e\Omega\hbar^2\omega_3}\sum_{mn\mathbf{k}}\frac{m_e\mathcal{V}^{\mathrm{a},\ell}_{mn}}{\omega_{nm}-\omega_3}\left(\frac{f_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}-\omega_\beta}\right)_{;k^{\mathrm{c}}}, \tag{O.9}$$

and

$$\chi^{s,\ell}_{e,\mathrm{abc}} = \frac{ie^3}{m_e\Omega\hbar^2\omega_3}\sum_{\ell mn\mathbf{k}}\frac{m_e\mathcal{V}^{\mathrm{a},\ell}_{mn}}{\omega_{nm}-\omega_3}\left(\frac{r^{\mathrm{c}}_{n\ell}r^{\mathrm{b}}_{\ell m}f_{m\ell}}{\omega_{\ell m}-\omega_\beta} - \frac{r^{\mathrm{b}}_{n\ell}r^{\mathrm{c}}_{\ell m}f_{\ell n}}{\omega_{n\ell}-\omega_\beta}\right), \tag{O.10}$$

where

$$m_e\mathcal{V}^{\mathrm{a},\ell}_{mn}(\mathbf{k}) = \mathcal{P}^{\mathrm{a},\ell}_{mn}(\mathbf{k}) + m_e\mathcal{V}^{S,\mathrm{a},\ell}_{mn}(\mathbf{k}), \tag{O.11}$$

where the non-local contribution of H_0 is neglected, and from Eq. (O.7)

$$\mathcal{P}^{\mathrm{a},\ell}_{mn} = \int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{\mathcal{F}_\ell(z)p^{\mathrm{a}}+p^{\mathrm{a}}\mathcal{F}_\ell(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r}). \tag{O.12}$$

****

From the following well known result, $im_e\omega_{nm}\mathbf{r}_{nm} = \mathbf{p}_{nm}$ $(n\neq m)$, we can write

$$\mathcal{R}^{\mathrm{a}}_{nm} = \frac{\mathcal{P}^{\mathrm{a}}_{nm}}{im_e\omega_{nm}} \quad (n\neq m), \tag{O.13}$$

O.1 Full derivations for $\mathcal{R}$ for different polarization cases

O.1.1 $\mathcal{R}_{pP}$

Taking all fields in the bulk

To consider the 2ω fields in the bulk, we start with Eq. (1.129) but substitute $\ell \to b$, thus

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

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

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

and we define

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

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

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

The 1ω fields will still be evaluated inside the bulk, so we have Eq. (1.135)

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

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

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

and

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

So lastly, we have that

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

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

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

and reducing,

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

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

where,

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

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

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

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

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

Taking all fields in the vacuum

To consider the 1ω fields in the vacuum, we start with Eq. (1.133) but substitute $\ell \to v$, thus

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

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

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

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

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

and

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

We also require the 2ω fields evaluated in the vacuum, which is Eq. (1.132),

$$\mathbf{e}_v^{2\omega} = \hat{\mathbf{e}}^{\text{out}} \cdot \left[\hat{\mathbf{s}} T_s^{vb} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} \frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega) \sin\theta_{\text{in}} \hat{\mathbf{z}} - K_b \hat{\boldsymbol{\kappa}} \right) \right], \tag{O.14}$$

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

$$\mathbf{e}_v^{2\omega} = \frac{T_p^{vb}}{\sqrt{\epsilon_b(2\omega)}} \left(\epsilon_b(2\omega) \sin\theta_{\text{in}} \hat{\mathbf{z}} - K_b \cos\phi \hat{\mathbf{x}} - K_b \sin\phi \hat{\mathbf{y}} \right). \tag{O.15}$$

So lastly, we have that

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

and after eliminating components,

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

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

where

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

O.1.2 $\mathcal{R}_{pS}$

To obtain $R_{pS}(2\omega)$ we use $\mathbf{e}^{\rm in} = \hat{\mathbf{p}}_{v-}$ in Eq. (1.134), and $\mathbf{e}^{\rm out} = \hat{\mathbf{S}}$ in Eq. (1.131). We also use the unit vectors defined in Eqs. (1.138) and (1.139). Substituting, we get

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

for 2ω, and for the fundamental fields,

$$\begin{aligned}
\hat{\mathbf{e}}^{\omega}_{\ell}\hat{\mathbf{e}}^{\omega}_{\ell} &= \left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2 \left(\epsilon_b(\omega)\sin\theta_{\rm in}\hat{\mathbf{z}} + \epsilon_\ell(\omega)k_b\cos\phi\hat{\mathbf{x}} + \epsilon_\ell(\omega)k_b\sin\phi\hat{\mathbf{y}}\right)^2 . \\
&= \left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2 \big(\epsilon_b^2(\omega)\sin^2\theta_{\rm in}\hat{\mathbf{z}}\hat{\mathbf{z}} + 2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b\sin\theta_{\rm in}\cos\phi\hat{\mathbf{z}}\hat{\mathbf{x}} \\
&\qquad + \epsilon_\ell^2(\omega)k_b^2\cos^2\phi\hat{\mathbf{x}}\hat{\mathbf{x}} + 2\epsilon_\ell^2(\omega)k_b^2\cos\phi\sin\phi\hat{\mathbf{x}}\hat{\mathbf{y}} \\
&\qquad + \epsilon_\ell^2(\omega)k_b^2\sin^2\phi\hat{\mathbf{y}}\hat{\mathbf{y}} + 2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b\sin\theta_{\rm in}\sin\phi\hat{\mathbf{y}}\hat{\mathbf{z}}\big).
\end{aligned}$$

Therefore,

$$\begin{aligned}
&\hat{\mathbf{e}}^{2\omega}_{\ell}\cdot\boldsymbol{\chi}:\hat{\mathbf{e}}^{\omega}_{\ell}\hat{\mathbf{e}}^{\omega}_{\ell} = \\
&T_s^{v\ell}T_s^{\ell b}\left(\frac{t_p^{v\ell}t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2 \big[-\epsilon_b^2(\omega)\sin^2\theta_{\rm in}\sin\phi\chi_{xzz} \\
&\qquad -2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b\sin\theta_{\rm in}\cos\phi\sin\phi\chi_{xxz} \\
&\qquad -\epsilon_\ell^2(\omega)k_b^2\cos^2\phi\sin\phi\chi_{xxx} \\
&\qquad -2\epsilon_\ell^2(\omega)k_b^2\cos\phi\sin^2\phi\chi_{xxy} \\
&\qquad -\epsilon_\ell^2(\omega)k_b^2\sin^3\phi\chi_{xyy} \\
&\qquad -2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b\sin\theta_{\rm in}\sin^2\phi\chi_{xyz} \\
&\qquad +\epsilon_b^2(\omega)\sin^2\theta_{\rm in}\cos\phi\chi_{yzz} \\
&\qquad +2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b\sin\theta_{\rm in}\cos^2\phi\chi_{yxz} \\
&\qquad +\epsilon_\ell^2(\omega)k_b^2\cos^3\phi\chi_{yxx} \\
&\qquad +2\epsilon_\ell^2(\omega)k_b^2\cos^2\phi\sin\phi\chi_{yxy} \\
&\qquad +\epsilon_\ell^2(\omega)k_b^2\cos\phi\sin^2\phi\chi_{yyy} \\
&\qquad +2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b\sin\theta_{\rm in}\cos\phi\sin\phi\chi_{yyz}\big],
\end{aligned}$$

and taking into account that $\chi_{xzz} = \chi_{xxy} = \chi_{xyz} = \chi_{yzz} = \chi_{yxz} = \chi_{yxx} = \chi_{yyy} = 0$, we have

$$
\begin{aligned}
= \Gamma^{\ell}_{pS}\big[&+\epsilon^2_\ell(\omega)k_b^2 \sin^3\phi\chi_{xxx} \\
&-2\epsilon^2_\ell(\omega)k_b^2 \cos^2\phi \sin\phi\chi_{xxx} \\
&-\epsilon^2_\ell(\omega)k_b^2 \cos^2\phi \sin\phi\chi_{xxx} \\
&+2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b \sin\theta_{\text{in}} \cos\phi\sin\phi\chi_{xxz} \\
&-2\epsilon_b(\omega)\epsilon_\ell(\omega)k_b \sin\theta_{\text{in}} \cos\phi\sin\phi\chi_{xxz}\big]
\end{aligned}
$$

$$
= \Gamma^{\ell}_{pS}\big[\epsilon^2_\ell(\omega)k_b^2(\sin^3\phi - 3\cos^2\phi\sin\phi)\chi_{xxx}\big]
$$

$$
= \Gamma^{\ell}_{pS}\big[- \epsilon^2_\ell(\omega)k_b^2 \sin 3\phi\chi_{xxx}\big].
$$

We summarize as follows,

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

where

$$
r^{\ell}_{pS} = -\epsilon^2_\ell(\omega)k_b^2 \sin 3\phi\chi_{xxx},
$$

and

$$
\Gamma^{\ell}_{pS} = T^{v\ell}_s T^{\ell b}_s \left(\frac{t^{v\ell}_p t^{\ell b}_p}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}}\right)^2
$$

In order to reduce above result to that of Ref. [6] and [8], we take the 2-ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T^{v\ell}_s = 1$, $T^{\ell b}_s = T^{vb}_s$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t^{v\ell}_p = t^{vb}_p$, and $t^{\ell b}_p = 1$. With these choices,

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

and

$$
\Gamma^{b}_{pS} = T^{vb}_s \left(\frac{t^{vb}_p}{\sqrt{\epsilon_b(\omega)}}\right)^2.
$$

O.1.3 $\mathcal{R}_{sP}$

To obtain $R_{sP}(2\omega)$ we use $\mathbf{e}^{\text{in}} = \hat{\mathbf{s}}$ in Eq. (1.134), and $\mathbf{e}^{\text{out}} = \hat{\mathbf{P}}_{v+}$ in Eq. (1.131). We also use the unit vectors defined in Eqs. (1.138) and (1.139). Substituting, we get

$$
\hat{\mathbf{e}}^{2\omega}_\ell = \frac{T^{v\ell}_p T^{\ell b}_p}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}\left[\epsilon_b(2\omega)\sin\theta_{\text{in}}\hat{\mathbf{z}} - \epsilon_\ell(2\omega)K_b\cos\phi\hat{\mathbf{x}} - \epsilon_\ell(2\omega)K_b\sin\phi\hat{\mathbf{y}}\right],
$$

for 2ω, and for the fundamental fields,

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

Therefore,

$$\begin{aligned}
\hat{\mathbf{e}}^{2\omega}_{\ell}\cdot\boldsymbol{\chi} :&\hat{\mathbf{e}}^{\omega}_{\ell}\hat{\mathbf{e}}^{\omega}_{\ell} = \\
&\frac{T^{v\ell}_{p}T^{\ell b}_{p}\left(t^{v\ell}_{s}t^{\ell b}_{s}\right)^{2}}{\epsilon_{\ell}(2\omega)\sqrt{\epsilon_{b}(2\omega)}}\big[\epsilon_{b}(2\omega)\sin\theta_{\text{in}}\sin^{2}\phi\chi_{zxx} + \epsilon_{b}(2\omega)\sin\theta_{\text{in}}\cos^{2}\phi\chi_{zyy} \\
&- 2\epsilon_{b}(2\omega)\sin\theta_{\text{in}}\sin\phi\cos\phi\chi_{zxy} - \epsilon_{\ell}(2\omega)K_{b}\cos\phi\sin^{2}\phi\chi_{xxx} \\
&- \epsilon_{\ell}(2\omega)K_{b}\cos\phi\cos^{2}\phi\chi_{xyy} + 2\epsilon_{\ell}(2\omega)K_{b}\cos\phi\sin\phi\cos\phi\chi_{xxy} \\
&- \epsilon_{\ell}(2\omega)K_{b}\sin\phi\sin^{2}\phi\chi_{yxx} - \epsilon_{\ell}(2\omega)K_{b}\sin\phi\cos^{2}\phi\chi_{yyy} \\
&+ 2\epsilon_{\ell}(2\omega)K_{b}\sin\phi\sin\phi\cos\phi\chi_{yxy}\big],
\end{aligned}$$

and taking into account that $\chi_{zxy} = \chi_{xxy} = \chi_{yxx} = \chi_{yyy} = 0$, we have

$$\begin{aligned}
&= \Gamma^{\ell}_{sP}\big[\epsilon_{b}(2\omega)\sin\theta_{\text{in}}\sin^{2}\phi\chi_{zxx} + \epsilon_{b}(2\omega)\sin\theta_{\text{in}}\cos^{2}\phi\chi_{zxx} \\
&\qquad - \epsilon_{\ell}(2\omega)K_{b}\cos\phi\sin^{2}\phi\chi_{xxx} + \epsilon_{\ell}(2\omega)K_{b}\cos^{3}\phi\chi_{xxx} \\
&\qquad - 2\epsilon_{\ell}(2\omega)K_{b}\sin^{2}\phi\cos\phi\chi_{xxx}\big] \\
\\
&= \Gamma^{\ell}_{sP}\big[\epsilon_{b}(2\omega)\sin\theta_{\text{in}}(\sin^{2}\phi + \cos^{2}\phi)\chi_{zxx} \\
&\qquad - \epsilon_{\ell}(2\omega)K_{b}(\cos\phi\sin^{2}\phi - \cos^{3}\phi + 2\sin^{2}\phi\cos\phi)\chi_{xxx}\big] \\
\\
&= \Gamma^{\ell}_{sP}\big[\epsilon_{b}(2\omega)\sin\theta_{\text{in}}\chi_{zxx} + \epsilon_{\ell}(2\omega)K_{b}(\cos^{3}\phi - 3\sin^{2}\phi\cos\phi)\chi_{xxx}\big] \\
\\
&= \Gamma^{\ell}_{sP}\big[\epsilon_{b}(2\omega)\sin\theta_{\text{in}}\chi_{zxx} + \epsilon_{\ell}(2\omega)K_{b}\cos 3\phi\chi_{xxx}\big].
\end{aligned}$$

We summarize as follows,

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

where

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

and

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

In order to reduce above result to that of Ref. [6] and [8], we take the 2-ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_{\ell}(2\omega) = 1$, $T^{v\ell}_{p} = 1$, $T^{\ell b}_{p} = T^{vb}_{p}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_{\ell}(\omega) = \epsilon_{b}(\omega)$, $t^{v\ell}_{s} = t^{vb}_{s}$, and $t^{\ell b}_{s} = 1$. With these choices,

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

and

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

O.1.4 $\mathcal{R}_{sS}$

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

$$\begin{aligned}
\hat{\mathbf{e}}^{2\omega}_\ell &= T_s^{v\ell} T_s^{\ell b} \left[-\sin\phi \hat{\mathbf{x}} + \cos\phi \hat{\mathbf{y}} \right], \\
\hat{\mathbf{e}}^{\omega}_\ell \hat{\mathbf{e}}^{\omega}_\ell &= \left(t_s^{v\ell} t_s^{\ell b} \right)^2 \left(\sin^2\phi \hat{\mathbf{x}}\hat{\mathbf{x}} + \cos^2\phi \hat{\mathbf{y}}\hat{\mathbf{y}} - 2\sin\phi\cos\phi \hat{\mathbf{x}}\hat{\mathbf{y}} \right).
\end{aligned}$$

Therefore,

$$\begin{aligned}
\hat{\mathbf{e}}^{2\omega}_\ell \cdot \boldsymbol{\chi} : \hat{\mathbf{e}}^{\omega}_\ell \hat{\mathbf{e}}^{\omega}_\ell &= T_s^{v\ell} T_s^{\ell b} \left(t_s^{v\ell} t_s^{\ell b} \right)^2 \big[-\sin^3\phi \chi_{xxx} - \sin\phi\cos^2\phi \chi_{xyy} + 2\sin^2\phi\cos\phi \chi_{xxy} \\
&\qquad + \sin^2\phi\cos\phi \chi_{yxx} + \cos^3\phi \chi_{yyy} - 2\sin\phi\cos^2\phi \chi_{yxy} \big] \\
&= T_s^{v\ell} T_s^{\ell b} \left(t_s^{v\ell} t_s^{\ell b} \right)^2 \big[-\sin^3\phi \chi_{xxx} + 3\sin\phi\cos^2\phi \chi_{xxx} \big] \\
&= T_s^{v\ell} T_s^{\ell b} \left(t_s^{v\ell} t_s^{\ell b} \right)^2 \;\chi_{xxx} \sin 3\phi
\end{aligned}$$

Summarizing,

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

where

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

and

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

In order to reduce above result to that of Ref. [6] and [8], we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_s^{v\ell} = 1$, $T_s^{\ell b} = T_s^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_s^{v\ell} = t_s^{vb}$, and $t_s^{\ell b} = 1$. With these choices,

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

and

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

O.2 The two layer model for SHG radiation from Sipe, Moss, and van Driel

In this treatment we follow the work of Ref. [8]. They define the following for all polarizations;

$$\begin{aligned} f_s &= \frac{\kappa}{n\tilde{\omega}} = \frac{\kappa}{\sqrt{\epsilon(\omega)}\tilde{\omega}}, \\ f_c &= \frac{w}{n\tilde{\omega}} = \frac{w}{\sqrt{\epsilon(\omega)}\tilde{\omega}}, \\ f_s^2 &+ f_c^2 = 1, \end{aligned} \tag{O.16}$$

where

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

$$w_0 = \sqrt{\tilde{\omega} - \kappa^2} = \tilde{\omega}\cos\theta, \tag{O.17}$$

$$w = \sqrt{\tilde{\omega}\epsilon(\omega) - \kappa^2} = \tilde{\omega}k_z(\omega). \tag{O.18}$$

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

$$\begin{aligned} \delta_{11} &= \chi^{xxx} = -\chi^{xyy} = -\chi^{yyx}, \\ \delta_{15} &= \chi^{xxz} = \chi^{yyz}, \\ \delta_{31} &= \chi^{zxx} = \chi^{zyy}, \\ \delta_{33} &= \chi^{zzz}. \end{aligned} \tag{O.19}$$

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

$$\begin{aligned} A_p &= \frac{4\pi\tilde{\Omega}\sqrt{\epsilon(2\omega)}}{W_0\epsilon(2\omega) + W}, \\ A_s &= \frac{4\pi\tilde{\Omega}}{W_0 + W}. \end{aligned} \tag{O.20}$$

O.2.1 $\mathcal{R}_{pP}$

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

$$\frac{E^{(2\omega)}(\|,\|)}{E_p^2 A_p} = a_{\|,\|} + c^{(3)}_{\|,\|}\cos 3\phi. \tag{O.21}$$

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

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

We substitute these in Eq. (O.21),

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

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

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

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

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

factor after substituting the appropriate terms from Eq. (O.16),

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

We substitute Eq. (O.20) to complete the expression,

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

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

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

and we can finally complete the expression,

$$
\begin{aligned}
\mathcal{R}_{pP} &= \frac{2\pi}{c}\left|\frac{4i\pi\tilde{\omega}}{\cos\theta}\frac{1}{\epsilon(\omega)}\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}r_{pP}\right|^2 \\
&= \frac{32\pi^3\tilde{\omega}^2}{c\cos^2\theta}\left|t_p(\omega)T_p(2\omega)r_{pP}\right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|t_p(\omega)T_p(2\omega)r_{pP}\right|^2,
\end{aligned} \tag{O.22}
$$

where

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

O.2.2 $\mathcal{R}_{pS}$

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

$$
\frac{E^{(2\omega)}(\|,\perp)}{E_p^2 A_s} = b^{(3)}_{\|,\perp}\sin 3\phi, \tag{O.23}
$$

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

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

Substituting this coeffecient and Eq. (O.20) into Eq. (O.23),

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

As before, we must calculate

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

to obtain the final expression,

$$\begin{aligned}\mathcal{R}_{pS} &= \frac{2\pi}{c}\left|\frac{4i\pi\omega}{c\cos\theta}\frac{1}{\epsilon(\omega)}\frac{2\cos\theta}{\cos\theta+k_z(2\omega)}k_z^2(\omega)\chi^{xxx}\sin 3\phi\right|^2\\ &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|\frac{1}{\epsilon(\omega)}\frac{2\cos\theta}{\cos\theta+k_z(2\omega)}k_z^2(\omega)\chi^{xxx}\sin 3\phi\right|^2\\ &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|t_p(\omega)T_s(2\omega)k_z^2(\omega)r_{pS}\right|^2,\end{aligned} \tag{O.24}$$

where

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

O.2.3 $\mathcal{R}_{sP}$

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

$$\frac{E^{(2\omega)}(\perp,\|)}{E_s^2A_p} = a_{\perp,\|} + c^{(3)}_{\perp,\|}\cos 3\phi, \tag{O.25}$$

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

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

Substituting this coeffecient and Eq. (O.20) into Eq. (O.25),

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

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

$$\begin{aligned}
\mathcal{R}_{sP} &= \frac{2\pi}{c}\left|\frac{E^{(2\omega)}(\perp,\|)}{E_s^2}\right|^2 \\
&= \frac{2\pi}{c}\left|\frac{4i\pi\omega}{c\cos\theta}\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi)\right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|\frac{2\cos\theta}{\epsilon(2\omega)\cos\theta + k_z(2\omega)}(\sin\theta\epsilon(2\omega)\chi^{zxx} + k_z(2\omega)\chi^{xxx}\cos 3\phi)\right|^2 \\
&= \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|t_s(\omega)T_p(2\omega)r_{sP}\right|^2, \qquad \text{(O.26)}
\end{aligned}$$

where

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

O.2.4 Summary

We unify the final expressions for the SHG yield, Eqs. (O.22), (O.24), and (O.26), as

$$\mathcal{R}_i F = \frac{32\pi^3\omega^2}{c^3\cos^2\theta}\left|t_i(\omega)T_F(2\omega)r_{iF}\right|^2. \qquad \text{(O.27)}$$

The necessary factors are summarized in Table O.1.

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

Table O.1: The necessary factors for Eq. (O.27) for each polarization case.

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