Optimized Software for Theoretical Optical Calculations

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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The amount of it, be sure, is merely a scream, but sometimes a scream is better than a thesis.

Ralph Waldo Emerson

Abstract

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Dedication

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INTRODUCTION

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1.1 Motivation

The principal motivation for this work is the analysis of different nanoparticles following two concepts:

First, the use of second-order nonlinear optical effects that are very effective for surface analysis.

Second, the use of a special technique for optical spectroscopy – the two beam, cross-polarized second harmonic/sum-frequency generation (XP2SHG/ SFG) technique.

Metallic nanoparticles are currently a "hot topic" in the scientific world because the scope of their potential applications is very large, from biological applications [1], imaging and detection [2, 3, 4], and more [5, 6]. Silicon nanoparticles, although more common, are not far behind – their use in new solar cell technologies [7] and biological markers [8] are also cutting edge research.

None of the techniques described in this thesis are particularly new, but they have been used with great success in a variety of different materials. Although some literature exists on metallic nanoparticles characterized by these techniques, there is a relatively small amount of research on the subject. The optical methods included here are both non-destructive and potentially surface specific. Combining these with interesting nanostructures may prove to be a promising path for future developments in the nanosciences.

The focus of this thesis will be the study of second-order nonlinear effects in nanosystems. Nanoparticles have huge surface to volume ratios because they are so small; they contain few atoms and the bulk is tiny compared to the outside surface. The second-order nonlinearities, second harmonic generation (SHG) and sum-frequency generation (SFG), are both suitable for spectroscopic analysis of nanoparticles. These can be greatly enhanced using the two beam, cross-polarized SHG/SFG (XP2SHG/SFG) technique [9]. The purpose of this work is to study the properties of these nanostructures using the aforementioned methods.

1.2 Nonlinear Optics in a Nutshell

Linear optics has long dominated the study of light. Much like Newton's mechanics, it describes an incomplete picture of the interaction between light and the matter that forms our world. This is not to say the picture is incorrect; the interactions described work for our everyday situations. We call them "linear" because matter interacts in a directly proportional way with the electric field of the incoming light. The linear response of most materials is more appreciable than the other responses, making them difficult to observe – we call these "nonlinear effects." We will elaborate further on this point in chapter **??**.

We can approximate most potentials within the atom using a harmonic oscillator model. These potentials represent the effect electrons feel when confined. They restrict the way electrons can move and determine many of the important material properties. These can tell us whether a material would make a good semiconductor for an optical device or for a computer microprocessor, or would make a very conductive metal, amongst many other things.

An example of a harmonic oscillator is a spring with a mass on one end. The other end is fixed and unmovable. If the mass is moved a little ways away from the equilibrium point and released, the mass will begin to oscillate for some time until it eventually stops once again at equilibrium (as it is dampened by gravity or friction). However, if you pull the spring too far it can deform from all the extra force. The spring follows a linear response according to the well established SHO equations when the displacement is small. Larger displacements are unaccounted for in this model – now we are talking about *nonlinear* behavior.

So the electrons behave in a similar manner if we model our electronic potentials as SHOs. This model works well for low intensities of incoming light, when the electron is displaced only a little from the "bottom" of the potential well. This provides the linear response between light and matter and is the reason why linear interactions dominate our everyday life. Although the light is very intense, the radiation that does reach us is spread out over half our world. Even when focused down to a very bright point it lacks the ability to deliver energy in an organized and efficient way. So our everyday light can only give electrons a little bit of energy and they move accordingly. Even the sun cannot provide the necessary conditions to allow electrons to move significantly from the bottom of a potential well.

We had the sun and different light bulbs, and used them often for experiments. I just explained why these sources can't help us past the linear regime. So people were stuck with this problem for a long time until a new light source, the LASER, was invented. LASER is an acronym for *Light Amplification by Stimulated Emission of Radiation*. One of the main characteristics of a laser is that it emits an energetic, unidirectional, coherent beam of light that can be focused to a very small spot further concentrating the energy.

This discovery revolutionized optical science. The laser was precisely what was needed to produce high energy densities that could move the electrons away from the bottom of the potential well. Experimentalists starting shooting lasers into all kinds of materials – and just like the spring and mass, the model stopped describing the experiment and all sorts of strange things started happening.

In this way we discovered nonlinear optics. These strange effects were difficult to explain at first. A new model had to be devised and tested against the experiments. Fortunately, it was not very long before one was created and found to work; not only did it explain everything observed until then, but it also predicted many things that had not yet been discovered [10, 11, 12]. I will elaborate on the math of this new model in chapter.

SHG, a special case of SFG, was one of the first observed, and predominant optical nonlinearities that can appear from many substances. While all materials are technically nonlinear, the response of most are not appreciable for low intensities of incoming light, and are destroyed before we can see the effects. Some metals and semiconductors are excellent nonlinear materials, as are many different crystals. SHG is usually the first nonlinear effect to appear and can be the easiest to produce. As we will explain in section , it is often attributed to surface emission which makes it an excellent tool for studying and characterizing surfaces and interfaces.

1.3 Outline

This thesis is divided into 5 chapters including this introduction. Chapter details the mathematics, formalism, and theory that make up our description of nonlinear optics. Chapter describes the materials to be characterized and the experimental setup used to study them. Chapter consists of the experimental data and analysis, with comparisons to existing literature. Finally, chapter is dedicated to the final observations and remarks. The complete bibliography is located at the end of the document for easy reference.

1.4 A Review of Nonlinear Optics

1.4.1 Historical Overview

The discovery of the optical maser by Townes [13] and the construction of the laser by Maiman in the late 1950s and early 1960s ushered a new age of optical discoveries. The ability to produce optical beams with these devices automatically lead to very highly focused energies distributed over very small areas. These concentrated energies allowed scientists to finally move into the optical nonlinear regime for many different materials.

The optical maser allowed for the first recorded observation of optical SHG by Franken et al. in 1961 [14]. They produced a second beam of light at twice the frequency of the original by exciting a piece of crystalline quartz. This frequency doubling effect was dubbed SHG and was observed to be much less intense than the exciting beam.

There is a humorous anecdote about this experiment. Apparently, the editor of Physical Review Letters thought that the second harmonic dot on the photographic plate was a speck of dust, which he edited out. The image found in the article has an arrow pointing at the empty spot where it should be. However, this did not detract from the importance of the find.

Other developments followed promptly. In 1962, Bloembergen et al. [15, 16] developed the mathematical framework to explain nonlinear optical phenomena.

That same year, Terhune et al. [17] observed SHG in calcite. These discoveries were amongst others [18] that lead to further research into the geometrical dependence of nonlinear effects, and helped verify that the majority of the SHG signal produced in a centrosymmetric material comes from surface contribution, where inversion symmetry is broken.

In the late 1960s, Bloembergen [19] and others [20] studied SHG in a variety of centrosymmetric materials and semiconductors. The advent of pulsed lasers during the 1970s [21] allowed for even greater intensities to be obtained. Dye lasers came to prominence during these years, offering very large bandwidths and relatively short picosecond pulses. However, these lasers were very difficult to maintain and the dyes used were typically very toxic and presented serious health risks.

Interest began to form around using SHG to study surfaces and interfaces, since it had been proven [22] to be exclusive to the surface area of a centrosymmetric material in the dipole approximation. Shen et al. published [23] that there is also a quadrupole bulk contribution for this kind of material, and in 1989 [24] published a review article summarizing most of the trends in surface spectroscopy using SHG. Theoretical work also played an important role in the 1990s, with new theoretical models by Sipe [25] and others [26, 27, 28, 29]. Downer et al. [30] and Lüpke [31] both produced very thorough and referenced texts on SHG surface spectroscopy of semiconductors in the late 1990s and early 2000s. This period of time provided the foundations for surface optics today.

At around the same time, the first Ti:sapphire lasers were being produced and analyzed [32]. These early ultrafast lasers were capable of producing femtosecond pulses via mode-locked oscillators. Since the active medium is in solid state form, they present none of the risks of using dyes. These lasers were considerably more compact than dye lasers since they no longer needed external dye control systems. These lasers became commercial in the early 1990s.

Chirped pulse amplification (CPA) was invented in 1985 by Mourou and Strickland [33]. This technique allowed Ti:sapphire lasers to achieve much higher peak energy without compromising the ultrashort pulse duration. During the 1990s, CPA became the prominent method for increasing energy output in Ti:sapphire lasers. At this point, Ti:sapphire lasers using the CPA technique were both compact, efficient, and cost effective. These factors would only improve over the following decade as the Ti:sapphire laser became the standard for high energy, ultrashort pulse applications.

1.4.2 Defintion of Nonlinear Optics

As explained briefly in section 1.2, linear optics predominate in our everyday lives. The intensity of the light sources that surround us is typically not sufficient to modify the optical properties of a material. The discovery of the laser gave us access to higher intensity of polarized, directional, and coherent light. Beyond this, the ultrafast pulsed laser provides energy distributed into a much shorter time-frame which increases the peak irradiance delivered. These advances have greatly reduced the cost and effort needed to study nonlinear phenomena.

Light is nothing more than electromagnetic radiation, and is therefore composed of electromagnetic fields. This means that the study of how matter interacts with light is merely the study of how the light fields interact with the structure of matter. This can be readily appreciated for crystals and materials with very organized structures – in fact, the best nonlinear materials are almost always crystalline in nature.

1.4.2.1 Nonlinear Polarization and Susceptibility

So what happens when very intense light coincides on a given material? Let us talk about the dipole moment per unit volume, or polarization $\mathbf{P}(t)$. This polarization describes the effect light has on a material and vice versa; it represents the optical response of a material.Taking Maxwell's equations with the usual considerations of zero charge density ($\rho = 0$) and no free currents ($\mathbf{J} = 0$), we have

$$\nabla \cdot \mathbf{D} = 0, \tag{1.1}$$

$$\nabla \cdot \mu_0 \mathbf{H} = 0, \tag{1.2}$$

$$\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t}, \tag{1.3}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}. \tag{1.4}$$

We take into account the nonlinearity of the material by relating the $\mathbf{D}$ and $\mathbf{E}$ fields with the total (linear and nonlinear) polarization $\mathbf{P}$,

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}. \tag{1.5}$$

Proceeding in the usual manner for deriving the wave equation, we obtain

$$\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E} = -\frac{1}{\epsilon_0 c^2}\frac{\partial^2 \mathbf{P}}{\partial t^2}, \tag{1.6}$$

which can be considerably simplified thanks to the identity

$$\nabla \times \nabla \times \mathbf{E} = \nabla\left(\nabla \cdot \mathbf{E}\right) - \nabla^2 \mathbf{E}. \tag{1.7}$$

The $\nabla(\nabla\cdot\mathbf{E})$ term is usually negligible (for instance, if $\mathbf{E}$ is of the form of a transverse, infinite plane wave), so we can finally express the inhomogenous wave equation as

$$\nabla^2\mathbf{E} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E} = \frac{1}{\epsilon_0 c^2}\frac{\partial^2\mathbf{P}}{\partial t^2}. \tag{1.8}$$

In this form, it is clear that the polarization acts as a source for this differential equation and we can recall our oscillator example from section 1.2. The polarization can be expressed by a power series of the form

$$P(t) = \epsilon_0\left[\chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \ldots\right] \tag{1.9}$$

$$\equiv P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \ldots, \tag{1.10}$$

where $\chi^{(n)}$ is the n$^{\text{th}}$-order susceptibility of the material. We can define the susceptibility as a constant of proportionallity that describes the degree of polarizability a material has in terms of the strength of an incoming optical electric field. The first term

$$P(t) = \epsilon_0\chi^{(1)}E(t), \tag{1.11}$$

is the linear term that describes most everyday interactions between light and matter. When taking into account that the incoming fields are vectorial in nature, the linear susceptibility $\chi^{(1)}$ becomes a second-rank tensor. $\chi^{(2)}$, the second-order nonlinear optical susceptibility is a third-rank tensor [10].

The nonlinear susceptibilities are very small in nature. If $\chi^{(1)}$ is unity, $\chi^{(2)}$ is on the order of $\approx 10^{-12}$ m/V. This explains why such high intensity fields are needed to produce nonlinear interactions – each term in equation (1.9) depends on a higher power of the incoming field but has a much smaller value for the corresponding susceptibility.

A more general definition of the nonlinear polarization can be found when treating the input field as a superposition of plane waves. We assume that the electric field vector is of the form

$$\mathbf{E}(\mathbf{r}, t) = \sum_n \mathbf{E}_n(\mathbf{r}, t), \tag{1.12}$$

where

$$\mathbf{E}_n(\mathbf{r}, t) = \mathbf{E}_n(\mathbf{r})e^{-i\omega_n t} + \text{c.c.}. \tag{1.13}$$

If we look at the form of equation (1.10), we can express the nonlinear polarization in its full form as

$$\mathbf{P}(\mathbf{r}, t) = \sum_n \mathbf{P}(\omega_n)e^{-i\omega_n t}. \tag{1.14}$$

Since we are only interested in second-order effects we can define the corresponding nonlinear polarization in terms of the second order susceptibility as

$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(nm)} \chi^{(2)}_{ijk}(\omega_n + \omega_m; \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m), \tag{1.15}$$

where the indices ijk refer to the Cartesian components of the fields, and (nm) notes that n and m can be varied while the sum $\omega_n + \omega_m$ remains fixed.

We can study the generalized case when we have two incoming fields with frequencies ω_1 and ω_2. We can represent this in the following form

$$E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + \text{c.c.} \tag{1.16}$$

Assuming the form of equation (1.9)

$$P^{(2)} = \epsilon_0 \chi^{(2)} E(t)^2, \tag{1.17}$$

and substituting expression (1.16) we get

$$\begin{aligned} P^{(2)}(t) = \epsilon_0 \chi^{(2)} \Big[& E_1^2 e^{-i2\omega_1 t} + E_2^2 e^{-i2\omega_2 t} \\ & + 2E_1 E_2 e^{-i(\omega_1+\omega_2)t} + 2E_1 E_2^* e^{-i(\omega_1-\omega_2)t} + \text{c.c.} \Big] \\ & + 2\epsilon_0 \chi^{(2)} \left[E_1 E_1^* + E_2 E_2^* \right]. \end{aligned} \tag{1.18}$$

We separate this expression into its components and the nonlinear effect that each represents in the following manner (abbreviations defined in table 1.1),

$$\begin{aligned} P(2\omega_1) &= \epsilon_0 \chi^{(2)} E_1^2 e^{-i2\omega_1 t} + \text{c.c.} \quad \text{(SHG)}, \\ P(2\omega_2) &= \epsilon_0 \chi^{(2)} E_2^2 e^{-i2\omega_2 t} + \text{c.c.} \quad \text{(SHG)}, \\ P(\omega_1 + \omega_2) &= 2\epsilon_0 \chi^{(2)} E_1 E_2 e^{-i(\omega_1+\omega_2)t} + \text{c.c.} \quad \text{(SFG)}, \\ P(\omega_1 - \omega_2) &= 2\epsilon_0 \chi^{(2)} E_1 E_2^* e^{-i(\omega_1-\omega_2)t} + \text{c.c.} \quad \text{(DFG)}, \\ P(0) &= 2\epsilon_0 \chi^{(2)} \left(E_1 E_1^* + E_2 E_2^* \right) + \text{c.c.} \quad \text{(OR)}. \end{aligned} \tag{1.19}$$

Janner [34] has a wonderfully formatted table in her dissertation that summarizes the first few optical processes, which I reproduce here as follows.

From this point forward we will only be concerned with second-order effects.

1.4.2.2 Symmetry Considerations for Centrosymmetric Materials

As mentioned previously, $\chi^{(2)}$ is a third-rank tensor with 27 elements. The amount of non-zero elements varies with the symmetry properties of the medium. Knowing these properties can help us reduce the amount of unknown elements to calculate.

$\chi^{(n)}(-\omega;\omega_1,\ldots,\omega_n)$	Process	Order
$-\omega \;;\; \omega$	Linear absorption / emission and refractive index	1
$0 \;;\; \omega,-\omega$	Optical rectification (OR)	2
$-\omega \;;\; 0,\omega$	Pockels effect	2
$-2\omega \;;\; \omega,\omega$	Second-harmonic generation (SHG)	2
$-(\omega_1+\omega_2) \;;\; \omega_1,\omega_2$	Sum-frequency generation (SFG)	2
$-(\omega_1-\omega_2) \;;\; \omega_1,\omega_2$	Difference-frequency generation (DFG) / Parametric amplifcation and oscillation	2
$-\omega \;;\; 0,0,\omega$	d.c. Kerr effect	3
$-2\omega \;;\; 0,\omega,\omega$	Electric Field induced SHG (EFISH)	3
$-3\omega \;;\; \omega,\omega,\omega$	Third-harmonic generation (THG)	3
$-\omega \;;\; \omega,-\omega,\omega$	Degenerate four-wave mixing (DFWM)	3
$-\omega \;;\; -\omega_2,\omega_2,\omega_1$	Two-photon absorption (TPA) / ionization / emission	3

Table 1.1: Optical processes described by $\chi^{(n)}(-\omega;\omega_1,\ldots,\omega_n)$

I will mention only one that proves to be of extreme importance for surface optics. A centrosymmetric material, or a material with an inversion center, is a material that for every point at coordinates (x, y, z), there is an identical point located at $(-x,-y,-z)$. For instance, many crystals are centrosymmetric. If we assume that we are in the bulk of a centrosymmetric material, we can write the nonlinear polarization as

$$P(t) = \epsilon_0\chi^{(2)}E^2(t). \tag{1.20}$$

If the medium is centrosymmetric, a sign change must affect both the electric field and the polarization. So,

$$-P(t) = \epsilon_0\chi^{(2)}\left[-E(t)\right]^2, \tag{1.21}$$

$$= \epsilon_0\chi^{(2)}E^2(t). \tag{1.22}$$

However, substituting (1.22) into (1.20) we get $P(t) = -P(t)$. We can finally deduce that

$$\chi^{(2)} = 0. \tag{1.23}$$

Therefore, all second-order processes are forbidden in the bulk of centrosymmetric materials in the dipole approximation. We will talk about the other important approximation in section 1.4.3. This property is broken at the surface since that region no longer presents an inversion center. This very special property is what enables second-order nonlinearities to be so effective for surface and interface measurements. Likewise, any other mechanism that breaks the symmetry, such as an electric field or mechanical stress will also allow a second-order signal to be produced. See Bloembergen's [35] excellent review about second-order effects for surface spectroscopy for further reading.

1.4.3 Bulk Quadrupolar and Other Contributions

Everything that I have stated up to this point assumes what we call the *dipole approximation* that arises from assuming that the polarization can take the form of a multipole expansion. The dipole approximation simply assumes that the dipolar contribution is significantly greater than all the others. This is not necessarily the case in many materials. In particular, we find that there can be a non-negligible electric quadrupole contribution from the bulk of centrosymmetric materials. Bloembergen et al. [19] elaborate on this as early as the 1960s. This adds a severe complication to the use of second-order nonlinearities as surface probes since signal is actually produced from both surface and bulk. Sipe et al. [36] go into some detail about this problem, stating that it is very difficult to separate the surface and bulk contributions as the various nonlinear coefficients cannot be measured separately. Guyot-Sionnest and Shen [23] go one step further and state that the contributions are impossible to separate. They suggest that the best way to distinguish one from the other is by taking measurements before and after altering the surface and observing the overall changes to the produced signal. About a decade later, Shen et al. [37] state that bulk contributions not only come from the electric quadrupole, but also from the magnetic dipole, although the latter is typically much less intense than either of the former. They express the bulk polarization as a multipole series as follows,

$$\mathbf{P}^B(\omega) = \mathbf{P}_D(\omega) - \nabla \cdot \mathbf{Q}(\omega) - \left(\frac{c}{i\omega}\right) \nabla \times \mathbf{M}(\omega) + \ldots, \tag{1.24}$$

where $\mathbf{P}_D(\omega)$ is the dipolar polarization, $\mathbf{Q}(\omega)$ is the electric quadrupole polarization, and $\mathbf{M}(\omega)$ is the magnetic dipole polarization. Indeed, if only the dipolar contribution is forbidden for centrosymmetric materials then there will be a contribution from the other two in addition to the dipolar contribution at the surface. The group does however go on to explain that there are a few experimental ways to help distinguish between surface and bulk contributions.

If $\mathbf{Q}(\omega)$ is assumed to take some form similar to

$$\mathbf{Q}(\omega) \approx \chi_q^{(2)}(\omega_1 + \omega_2)\mathbf{E}(\omega_1)\nabla\mathbf{E}(\omega_w), \tag{1.25}$$

then $\chi_q^{(2)}$ is a fourth-rank tensor with 81 independent elements. Clearly this adds some considerable complication to our problem and makes selecting the appropriate symmetry that much more important.

In summary, bulk electric quadrupole and magnetic dipole contributions to second-order surface effects may not be negligible and need to be taken into account. We will see later in sections 1.5 and 1.6 that these considerations are important for studying nanoparticles when using the XP2SHG/SFG technique.

1.4.4 SFG and SHG

We call the third process in expression (1.19) Sum-frequency generation (SFG). It is a second-order process that involves two photons, of frequencies ω_1 and ω_2 that combine to form one photon of frequency $\omega_3 = \omega_1 + \omega_2$. This is represented mathematically in the previous expression

$$P(\omega_1 + \omega_2) = 2\epsilon_0 \chi^{(2)} E_1 E_2 e^{-i(\omega_1+\omega_2)t} + \text{c.c.}, \tag{1.26}$$

where the term is explicitly stated in the exponential.

A special case of sum-frequency generation is when both incoming frequencies are the same, i.e. $\omega_1 = \omega_2$. The resulting frequency is then exactly double that of the input frequency.

As mentioned previously, second-order nonlinear processes are prohibited in the bulk of centrosymmetric materials (in the dipole approximation). Since it has a very strong surface contribution (where the inversion symmetry is broken), it can be used as a very precise diagnostic tool for surface and interface regions.

The use of these second-order nonlinearites for surface studies had gained momentum in the 1990s. McGilp wrote a review about using SHG and SFG as surface and interface probes in 1996 [38]. He adds experimental confirmation to his theories in 1999 [39] in an extremely thorough review about using SHG on the surface of almost any material you can think of. Aktsipetrov et al. [40] followed a different approach by establishing what they call electric field induced second-harmonic generation, or EFISH. In this paper he elaborates how the sensitivity of SHG to surfaces can be enhanced by applying an electric field across the interface.

The theoretical side of things was further developed in a paper by Maytorena et al. [29] discussing the formalities of SFG from surfaces by finding the exact expressions for the susceptibility based on modeling conductors and dielectrics. These models include fluid based, classical dynamics in addition to the wave equation treatment. A couple of interesting review papers by Downer et al. [30] and Scheidt et al. [41] exist, where they report results of SHG spectroscopies from a variety of different surfaces and interfaces including nanocrystals. These works are all predecessors for the later works we will discuss in section 1.5.

1.4.4.1 Phase-Matching

What happens when the generated nonlinear wave propagates through a medium is that it becomes out of phase with the induced polarization after some distance. When this happens, the induced polarization will create new light out of phase with the light it created earlier and the two contributions will cancel out. This can be avoided if both frequencies of light (the fundamental and the produced second-order field) travel at the same phase velocity through the medium. Each wave with a different frequency will have a different wave-vector ($\mathbf{k}$) and wavenumber (k). Optimally, we would like a material such that

$$\Delta k = k_1 + k_2 - k_3 = 0, \tag{1.27}$$

where $k_1 = k_2$ for SHG. Equation (1.27) exemplifies a *phase-matched* process. In practice, dispersion does not let this happen since the index of refraction of a material is almost never the same for different frequencies. There are certain materials that overcome this limitation (such as birefringent materials) that possess two indices of refraction.

Introducing equation (1.27) into the wave equation and solving, we can obtain the intensity profile [10] as

$$I(L) = \beta\, |P|^2\, L^2 \mathrm{sinc}^2\left(\frac{\Delta k L}{2}\right), \tag{1.28}$$

where L is the length of the material, Δk is the phase mismatch, and β are constants. The sinc function has a maximum at zero, so it is important to reduce the phase mismatch as much as possible. The inclusion of L also indicates a relation to the material thickness. These considerations are important when selecting a nonlinear material such as a crystal – most are sold in varying thicknesses that are optimized to work with certain frequencies.

In practice, phase-matching is usually improved through crystal orientation, selecting the right crystal thickness, and careful selection of the type of crystal being used.

1.4.5 Optical Parametric Amplifiers

We talked about how we can obtain different frequencies of light through wave mixing in section 1.4.4. In practice however, it is considerably more difficult to implement a system in which we can easily create frequency addition or difference. It is no small task even with a fixed input wavelength. Most ultrafast lasers are tunable to some degree by adjusting internal components. We'll need something much more sophisticated if we want a variety of frequency choices.

An optical parametric amplifier (OPA) is a device that allows the user to obtain a wide bandwidth of wavelengths to work with, via the nonlinear processes of difference frequency generation (DFG) and optical parametric generation (OPG). Additionally, many commercial OPAs allow the user to tune the output by means of a motorized, computer-controlled interface. Some OPAs work on the basis of sum and difference frequency generation, using crystals to add and subtract the different frequencies in order to obtain the desired one.

OPG is a by-product of DFG. DFG occurs when a high frequency (ω_1) photon is absorbed by an atom that jumps to a virtual level after being excited. It then decays producing two photons of lower frequency (ω_2 and ω_3). The creation of the ω_2 photon is what we call OPG. If we instigate this process in the presence of an ω_2 field, the same frequency (ω_2) gets amplified at expense of the original ω_1 photon. The ω_3 frequency is called the idler and can be used in the same way as ω_2 if desired. This effect is called optical parametric amplification. Therefore, we can create an OPA by creating a new frequency via OPG, and amplifying it using a crystal or other nonlinear media through optical parametric amplification.

In practice most OPAs work like this: a high frequency, high power pump beam amplifies a lower frequency, lower power signal beam in a nonlinear crystal which is our desired ω_2. This pump beam is usually the laser fundamental. This fixed pump beam transfers energy to produce the signal beam that is selectable via phase matching. This signal beam then feeds a second crystal to produce optical parametric amplification. We might be inclined to think that this is a form of stimulated emission similar to what happens in a laser (sans cavity). In stimulated emission, an electron drops from a higher level to a lower level due to the outside perturbing influence of an incident photon. It radiates with the exact same characteristics as the incoming field. OPA involves a transfer of energy from one photon to another (in our example, ω_2 and ω_1) to amplify ω_2 while annihilating ω_1.

1.4.6 Noncollinear Optical Parametric Amplifiers

A noncollinear optical parametric amplifier (NOPA) replaces the ω_2 signal with a white light super continuum. Tuning a NOPA is achieved by changing the angle between the seed and the pump beam, by changing the orientation of the crystal, or by using a delay stage to temporally overlap the fundamental with the desired frequency from the continuum.

In practice, the white light seed is typically generated from a sapphire window. The pump is normally the frequency doubled fundamental at 400 nm [42, 43]. The NOPA has a larger bandwidth than a regular OPA, and the resulting pulsewidth is dependent only on the bandwidth of the seed and not on the pulsewidth of the laser. For this reason, the NOPA has improved stability and spatial qualities. The added flexibility of the NOPA allows for different geometries to be implemented [44]. Gale [45] and Wilhelm et al. [46] wrote some of the earliest papers refering to this type of OPA. Lee [47] explains some of the formalism behind the operation of a NOPA.

1.5 Second-Order Nonlinear Response of Nanoparticles

The theory up to this point explains how second-order nonlinearities interact with matter and how they have been used for studying planar surfaces. I mentioned in chapter **??** how nanoparticles have very large surface to volume ratios. The study of nanosystems with conventional optics has further motivated scientists to begin using second-order nonlinear phenomena to obtain more information from their samples.

I will briefly review some of the current models for describing the optical response for nanoparticles. These models consist of parametrizing the nonlinear response and then calculating the second-order emissions from the idealized nanosystem.

Dadap et al. [48] developed some early work in 1999, and later expanded on that in 2004 [49]. They modeled SHG for a centrosymmetric nanosphere and concluded that SHG is produced via nonlocal excitation of the electric dipole moment and local excitation of the electric quadrupole moment. In other words, the electric-dipole can have excitation from either the electric quadrupole or the magnetic dipole, in addition to excitation provided by the incoming field. These results where verified experimentally by Shan et al. [50] in an article from 2006, by taking angle- and polarization-resolved measurements of dye-coated polystyrene spheres. Brudny et al. [51] created a similar model that focuses on analytical expressions for the dipolar and quadrupolar second-order susceptibilities for a small dielectric sphere, and the nonlinear response for a Si sphere above a substrate.

A more relevant treatment was published by Mochán et al. for an array of nanoparticles [52] that builds on their previous article [51]. This approach assumes spherical nanoparticles and should work well with the samples described in this work (see figures **??** and **??**). I'll briefly review the method as follows.

1.5.1 Theoretical Model

Let us assume a nanosphere centered at the origin. It has a linear response characterized in the usual way by its dielectric function $\epsilon(\omega)$. We assume the applied field, $\mathbf{E}^{\mathrm{ex}}(\mathbf{r})$ is inhomogeneous and varies on a much larger scale than R, the radius of the nanoparticle. The dipole moment $\mathbf{p}^{(2)}$ is in some way related to $\mathbf{E}^{\mathrm{ex}}(0)$ and $\nabla\mathbf{E}^{\mathrm{ex}}(0)$, and is nonlocal as dictated by the symmetry of the sphere. We can express this relation as

$$\mathbf{p}^{(2)} = \gamma^{\rho}\mathbf{E}^{\text{ex}}(0)\nabla\cdot\mathbf{E}^{\text{ex}}(0) + \gamma^{e}\mathbf{E}^{\text{ex}}(0)\cdot\nabla\mathbf{E}^{\text{ex}}(0) + \gamma^{m}\mathbf{E}^{\text{ex}}(0)\times\left[\nabla\times\mathbf{E}^{\text{ex}}(0)\right], \quad (1.29)$$

where γ^{ρ}, γ^{e}, and γ^{m} are nonlinear response parameters. It is clearly nonlocal as it contains the field derivative. Likewise, [51] shows that the quadrupole moment, $\mathbf{Q}^{(2)}$, should be local, and symmetric of the form

$$\mathbf{Q}^{(2)} = \gamma^{q}\left(\mathbf{E}^{\text{ex}}(0)\mathbf{E}^{\text{ex}}(0) - \frac{1}{3}\left[\mathbf{E}^{\text{ex}}(0)\right]^{2}\mathbf{1}\right), \quad (1.30)$$

where γ^{q} is the parametric response parameter. Note that it is local and does not depend on the field derivative. As there is no external charge inside the sphere, $\gamma^{\rho} = 0$. A lengthy derivation is necessary to obtain the remaining response parameters and I will not include it here. From those parameters we obtain the values of $\mathbf{p}^{(2)}$ and $\mathbf{Q}^{(2)}$, with

$$Q^{(2)} = \gamma^{q}\left[\mathbf{E}^{\text{ex}}(0)\right]^{2}. \quad (1.31)$$

Substituting these into the expression for the macroscopic nonlinear polarization for the entire array of spheres

$$\mathbf{P}^{nl} = n_s\mathbf{p}^{(2)} - \frac{1}{6}\nabla\cdot n_s\mathbf{Q}^{(2)} - \frac{1}{6}\nabla n_s Q^{(2)}, \quad (1.32)$$

where n_s is the nanocrystal volume density; we can then obtain

$$\mathbf{P}^{nl} = \Gamma\nabla E^{2} + \Delta'\left(\mathbf{E}\cdot\nabla\mathbf{E}\right). \quad (1.33)$$

The first term can be neglected because it is longitudinal and does not radiate. With $\Delta' \equiv n_s\left(\gamma^{e} - \gamma^{m} - \gamma^{q}/6\right)$, we can finally write the expression for the polarization as

$$\mathbf{P}^{(2)} = \Delta'\left(\mathbf{E}\cdot\nabla\mathbf{E}\right), \quad (1.34)$$

where $\mathbf{E}$ represents the incoming laser field. The relevance of this expression will become apparent in section 1.6, when we discuss the XP2SHG/SFG technique.

1.5.2 Other Works

Two relatively recent articles have studied different nonlinear effects on a variety of nanoscale gold shapes (primarily split-ring resonators) [53, 54]. The group hypothesizes that the samples show improved SHG due to local and nonlocal fields; in this case, magnetic resonances.

Zeng et al. [55] developed a model based on classical electrodynamics to predict SHG in metallic nanostructures. Solving Maxwell's equations yields an expression for the SHG signal intensity and is surprisingly close to experimental values. However, the derivation is considerably easier due to the approximations.

For further reading, Link and El-Sayed [56] offer a very extensive review of many other optical properties of nanoparticles.

1.5.3 Summary

In this section we saw how the theory indicates that the second-order response of nanoparticles depends both on the strength of the incoming field, but also on its characteristics. We also introduced the dependence on $(\mathbf{E} \cdot \nabla) \mathbf{E}$ of the nonlinear second-order polarization. With this information in hand we can determine the best technique to optimize our nonlinear signal.

Formally, we learned that the second-order nonlinearities are produced in nanoparticles thanks to local interface electric dipole contributions, plus quadrupolar contributions from the interior of the nanoparticles.

1.6 Theory for the XP2SHG/SFG Technique

In 2003, Cattaneo and Kauranen [57] published about a promising new technique involving two beams coinciding on a thin film. They proposed that the use of the second beam reduces the number of nonlinear coefficients to be determined if the polarization of the two beams is properly described beforehand. The method was simple enough – they expressed the parallel and perpendicular fields separately as a sum of expansion coefficients that are in themselves linear combinations of susceptibility components. Changing the polarization of the control and probe beam would determine different coefficients. Adding the linear optical properties of the film and modeling with Green's-function led to the desired $\chi^{(2)}$ coefficients.

Following in 2005, Figliozzi et al. [9] note the importance of the aforementioned $(\mathbf{E} \cdot \nabla \mathbf{E})$ term and relate it to the enhanced quadrupolar contribution; they go on to experimentally verify that dependence. They also discover that the two beam arrangement greatly enhances the entire SHG signal, both from the microscopic contributions of the particles as well as the bulk quadrupolar contribution from the substrate. This brings up the issue of how to discriminate between the two contributions to the SHG signal, which they manage to do by contrasting the difference in signal at different polarizations between the particles and the unimplanted glass.

In 2009 Wang et al. with some of the same people from references [53] and [54] elaborate a study on a gold thin film using a two-beam configuration [58]. They follow a similar model to that described in [9], but their goal is separating the surface and bulk components of the SH field. This is done by finding material parameters due to the magnetic dipole and electric quadrupole by varying the polarization of the incoming beams. They succeed in finding which components of $\chi^{(2)}$ belong to surface only, bulk only, or both.

A very recent and thorough article [43] by Wei et al. presents experimental evidence that supports the use of two-beam SHG with nanoparticles. They go into detail about the linear characterization of the Si nanocrystals used, which includes photoluminescence spectra, spectroscopic ellipsometry, and Raman microspectroscopy. By moving the sample across the overlapping beam region (the Z-scan technique) they were able to effectively determine which signal was produced by nanoparticles and which by bulk contributions from the substrate. They conclude with a very complete characterization of the Si nanocrystals after comparing the obtained data with that of the other conventional spectroscopies. Coincidentally, the setup described in this article is the exact one used in the experimental portion of this work, and is detailed in chapter **??**.

A 2008 article [59] by Wirth et al. provides excellent review of the exact technique used in this work. It is also noteworthy in that it is the first article to refer to this technique as XP2SHG. Following on the work that we discussed in section 1.5.1, they establish that the polarization of the samples can be separated into two expressions,

$$\mathbf{P}_{nc}^{(2)} \equiv n_b \left(\gamma^e - \gamma^m - \frac{\gamma^q}{6} \right) (\mathbf{E} \cdot \nabla) \, \mathbf{E}, \tag{1.35}$$

$$\mathbf{P}_{g}^{(2)} \equiv (\delta - \beta - 2\gamma) (\mathbf{E} \cdot \nabla) \, \mathbf{E}, \tag{1.36}$$

where equation (1.35) is identical to (1.34). The article confirms that the XP2SHG technique enhances both the nanocrystal and glass signals, and goes on to say that the detected SHG signal is a product of the interference of both. This would account for shape of the plotted data from the results of the Z-scan presented in [59], in [43], and in chapter **??** of this thesis.

The fields can be described by the amplitudes of the SH field from the nanocrystals $|\Gamma_{nc}|$, the glass Γ_g, and the phase Φ between them such that

$$\mathbf{P}_{nc}^{(2)} \equiv |\Gamma_{nc}| e^{i\Phi} \, (\mathbf{E} \cdot \nabla) \, \mathbf{E}, \tag{1.37}$$

$$\mathbf{P}_{g}^{(2)} \equiv \Gamma_g \, (\mathbf{E} \cdot \nabla) \, \mathbf{E}. \tag{1.38}$$

Three independent Z-scan measurements are needed to enable isolation of the nanocrystal signal and obtain the three unknowns $|\Gamma_{nc}|$, Γ_g, and Φ: a glass scan, a scan with the nanocrystals at the entrance position, and with the nanocrystals at the exit position. They establish an empirical model based on the wave equations for each measurement, thus determining the intensity profile expressions in terms of the unknowns. All that is left is running the scans and plugging in the data to determine them and fully isolate the different contributions.

Studies like those included in [43] and [59] are precisely in line with the work presented in this thesis.

1.6.1 Signal enhancement with XP2SHG/SFG

It was confirmed [9, 60] by Sun and Figliozzi et al. that the dipolar SHG single beam count rate scales as

$$N_{SHG} \sim f_{\text{rep}} I^2 A\tau = \frac{f_{\text{rep}}\mathcal{E}^2}{\tau A}, \tag{1.39}$$

where A is the beam spot size ($A = \pi w_0^2$), τ is the pulse duration, $\mathcal{E}$ is the pulse energy, and f_{rep} is the repetition rate of the pulses. In correlation with the $(\mathbf{E}\cdot\nabla)\,\mathbf{E}$ dependence, that same group determined that the derivative creates an additional term for a Gaussian beam. This term comes from the quadrupolar contribution and introduces an extra factor of A, such that

$$N_{SHG} \sim \frac{f_{\text{rep}}\mathcal{E}^2}{\tau A^2}. \tag{1.40}$$

If we use two incoming plane wave fields, we obtain from (1.35) (ignoring constants)

$$\mathbf{P}_{nc}^{(2)} \approx \left[(\mathbf{E}_1\cdot\nabla)\mathbf{E}_2 + (\mathbf{E}_2\cdot\nabla)\mathbf{E}_1\right] e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}}. \tag{1.41}$$

We define the incoming fields as

$$\mathbf{E}_i(\mathbf{r}) = \hat{\epsilon}_i \mathcal{E} e^{i\mathbf{k}_i\cdot\mathbf{r}}, \tag{1.42}$$

where $\hat{\epsilon}_i$ is the polarization. For *cross-polarized* beams, $\hat{\epsilon}_1 \perp \hat{\epsilon}_2$; if $\hat{\epsilon}_1 = \hat{y}$, then

$$\mathbf{P}_{nc}^{(2)} \approx \frac{1}{\lambda}\mathcal{E}_1\mathcal{E}_2 \sin\alpha\,\hat{y}, \tag{1.43}$$

where $\frac{1}{\lambda} = k$. Now the signal intensity scales as

$$N_{SHG} \sim \frac{f_{\text{rep}}\mathcal{E}_1\mathcal{E}_2 \sin^2\alpha}{\lambda^2 \tau A^2}, \tag{1.44}$$

where α is the angle between the beams. The $\frac{1}{\lambda}^2$ factor increases the intensity of the signal very significantly, while the $\sin^2\alpha$ term allows us to optimize the beam angle.

1.6.2 Summary

We used this section to discuss the fine points behind the XP2SHG/SFG technique. It offers three benefits over single beam second-order spectroscopy:

1. The SHG/SFG signal intensities are much higher than for single beam SHG/SFG.
2. The enhanced SHG/SFG signal allows for more elements of the nonlinear susceptibility $\chi^{(2)}$, and therefore of the second order polarization to be determined.
3. Dipole contribution from the surface can be discriminated from electric quadrupole and magnetic dipole contributions from bulk for planar materials.
4. Hybrid (dipole and quadrupole) contribution from the nanoparticles can be discriminated from electric quadrupole and magnetic dipole contributions from the substrate bulk.

1.7 some old shit

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.[61, 62]

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. [61, 63, 64, 65, 66, 67, 68, 69, 70]

In a previous article[71] 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.[72] 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.

CHAPTER 2

CHI2

Contents

2.1 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

$$\begin{aligned} P_{\mathrm{a}}(2\omega) &= \chi_{\mathrm{abc}}(-2\omega;\omega,\omega)E_{\mathrm{b}}(\omega)E_{\mathrm{c}}(\omega) \\ &\quad + \chi_{\mathrm{abcl}}(-2\omega;\omega,\omega)E_{\mathrm{b}}(\omega)\nabla_{\mathrm{c}}E_{\mathrm{l}}(\omega) + \cdots, \end{aligned} \tag{2.1}$$

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

$$P_{\mathrm{a}}(\mathbf{r}) = \chi_{\mathrm{abc}}E_{\mathrm{b}}(\mathbf{r})E_{\mathrm{c}}(\mathbf{r}) + \chi_{\mathrm{abcl}}E_{\mathrm{b}}(\mathbf{r})\frac{\partial}{\partial \mathbf{r}_{\mathrm{c}}}E_{\mathrm{l}}(\mathbf{r}) + \cdots, \tag{2.2}$$

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

$$\begin{aligned} P_{\mathrm{a}}(-\mathbf{r}) &= \chi_{\mathrm{abc}}E_{\mathrm{b}}(-\mathbf{r})E_{\mathrm{c}}(-\mathbf{r}) \\ &\quad + \chi_{\mathrm{abcl}}E_{\mathrm{b}}(-\mathbf{r})\frac{\partial}{\partial(-\mathbf{r}_{\mathrm{c}})}E_{\mathrm{l}}(-\mathbf{r}) + \cdots, \end{aligned} \tag{2.3}$$

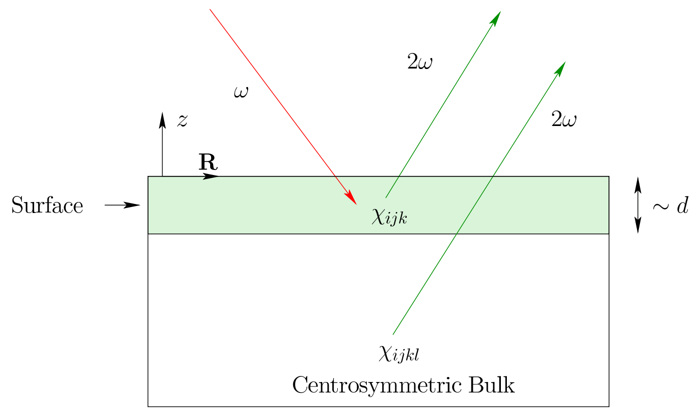

Figure 2.1: (Color Online) Sketch of the semi-infinite system with a centrosymmetric bulk. The surface region is of width $\sim d$. The incoming photon of frequency ω is represented by a downward red arrow, whereas both the surface and bulk created second harmonic photons of frequency 2ω are represented 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.

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. (2.3) reduces to

$$\begin{aligned} -P_{\rm a}(\mathbf{r}) &= \chi_{\rm abc}(-E_{\rm b}(\mathbf{r}))(-E_{\rm c}(\mathbf{r})) - \chi_{\rm abcl}(-E_{\rm b}(\mathbf{r}))(-\frac{\partial}{\partial \mathbf{r}_{\rm c}})(-E_{\rm l}(\mathbf{r})) + \cdots, \\ P_{\rm a}(\mathbf{r}) &= -\chi_{\rm abc}E_{\rm b}(\mathbf{r})E_{\rm c}(\mathbf{r}) + \chi_{\rm abcl}E_{\rm b}(\mathbf{r})\frac{\partial}{\partial \mathbf{r}_{\rm c}}E_{\rm l}(\mathbf{r}) + \cdots, \end{aligned} \tag{2.4}$$

that when compared with Eq. (2.2) leads to the conclusion that

$$\chi_{\rm abc} = 0 \tag{2.5}$$

for a centrosymmetric bulk.

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

$$\int dz P_{\rm a}(\mathbf{R}, z) \approx dP_{\rm a} \equiv P^S_{\rm a} \equiv \chi^S_{\rm abc}E_{\rm b}E_{\rm c}, \tag{2.6}$$

where d is the surface region from which the dipolar signal of $\mathbf{P}$ is different from zero (see Fig. 2.1), and $\mathbf{P}^S \equiv d\mathbf{P}$ is the surface SH polarization. Then, from Eq. (2.1) we obtain that

$$\chi^S_{\rm abc} = d\chi_{\rm abc} \tag{2.7}$$

is the SH surface susceptibility. On the other hand,

$$P^b_{\rm a}(\mathbf{r}) = \chi_{\rm abcl} E_{\rm b}(\mathbf{r}) \nabla_{\rm c} E_{\rm l}(\mathbf{r}), \tag{2.8}$$

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.[61]

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

2.2 Length Gauge

We follow the article by Aversa and Sipe[73] to calculate the optical properties of a given system within the longitudinal gauge. More recent derivations can also be found in Refs. [74, 75]. Assuming the long-wavelength approximation which implies a position independent electric field, $\mathbf{E}(t)$, the Hamiltonian in the length gauge approximation is given by

$$\hat{H} = \hat{H}^\sigma_0 - e\hat{\mathbf{r}} \cdot \mathbf{E}, \tag{2.9}$$

with

$$\hat{H}^\sigma_0 = \hat{H}^{\rm LDA}_0 + \mathcal{S}(\mathbf{r}, \mathbf{p}), \tag{2.10}$$

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

$$\begin{aligned} \hat{H}^{\rm LDA}_0 &= \frac{\hat{p}^2}{2m_e} + \hat{V}^{\rm ps} \\ \hat{V}^{\rm ps} &= \hat{V}^l(\hat{\mathbf{r}}) + \hat{V}^{\rm nl}, \end{aligned} \tag{2.11}$$

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

$$V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}') \equiv \langle \mathbf{r}|\hat{V}^{\mathrm{nl}}|\mathbf{r}'\rangle \neq 0 \quad \text{for} \quad \mathbf{r} \neq \mathbf{r}', \tag{2.12}$$

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

$$\left(\frac{-\hbar^2}{2m_e}\nabla^2 + \hat{V}^l(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}'\,\hat{V}^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}') = E_i\psi_{n\mathbf{k}}(\mathbf{r}), \tag{2.13}$$

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

$$\mathcal{S}(\mathbf{r},\mathbf{p}) = \hbar\Sigma\sum_n \int d^3k'(1 - f_n(\mathbf{k}))|n\mathbf{k}'\rangle\langle n\mathbf{k}'|, \tag{2.14}$$

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

$$\begin{aligned} H_0^{\mathrm{LDA}}|n\mathbf{k}\rangle &= \hbar\omega_n^{\mathrm{LDA}}(\mathbf{k})|n\mathbf{k}\rangle \\ H_0^{\sigma}|n\mathbf{k}\rangle &= \hbar\omega_n^{\sigma}(\mathbf{k})|n\mathbf{k}\rangle, \end{aligned} \tag{2.15}$$

where

$$\hbar\omega_n^{\sigma}(\mathbf{k}) = \hbar\omega_n^{\mathrm{LDA}}(\mathbf{k}) + \hbar\Sigma(1 - f_n), \tag{2.16}$$

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[76, 77, 73]

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\xi_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right], \tag{2.17}$$

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\xi_{nm}(\mathbf{k}), \tag{2.18}$$

and

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i\frac{(2\pi)^3}{\Omega}\int_\Omega d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r})\nabla_\mathbf{k} u_{m\mathbf{k}}(\mathbf{r}). \tag{2.19}$$

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

$$\hat{\mathbf{v}}^\sigma = \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{H}^\sigma_0], \tag{2.20}$$

and calculating its matrix elements

$$i\hbar\langle n\mathbf{k}|\mathbf{v}^\sigma|m\mathbf{k}\rangle = \langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}^\sigma_0]|m\mathbf{k}\rangle = \langle n\mathbf{k}|\hat{\mathbf{r}}\hat{H}^\sigma_0 - \hat{H}^\sigma_0\hat{\mathbf{r}}|m\mathbf{k}\rangle = (\hbar\omega^\sigma_m(\mathbf{k}) - \hbar\omega^\sigma_n(\mathbf{k}))\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}\rangle, \tag{2.21}$$

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

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^\sigma_{nm}(\mathbf{k})}{i\omega^\sigma_{nm}(\mathbf{k})} \qquad n \notin D_m, \tag{2.22}$$

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[73]

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\mathcal{O}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{2.23}$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_\mathbf{k}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})\right), \tag{2.24}$$

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

As can be seen from Eq. (2.10) and (2.11), 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.[78] We proceed as follows; from Eqs. (2.20), (2.10) and (2.11) we find

$$\begin{aligned}\hat{\mathbf{v}}^\sigma &= \frac{\hat{\mathbf{p}}}{m_e} + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')] + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{\mathcal{S}}(\mathbf{r},\mathbf{p})]\\ &\equiv \hat{\mathbf{v}} + \hat{\mathbf{v}}^{\mathrm{nl}} + \hat{\mathbf{v}}^{\mathcal{S}} = \hat{\mathbf{v}}^{\mathrm{LDA}} + \hat{\mathbf{v}}^{\mathcal{S}},\end{aligned} \tag{2.25}$$

where we have defined

$$\begin{aligned}\hat{\mathbf{v}} &= \frac{\hat{\mathbf{p}}}{m_e}\\ \hat{\mathbf{v}}^{\mathrm{nl}} &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\mathrm{nl}}]\\ \hat{\mathbf{v}}^{\mathcal{S}} &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{S}(\mathbf{r},\mathbf{p})]\\ \hat{\mathbf{v}}^{\mathrm{LDA}} &= \hat{\mathbf{v}} + \hat{\mathbf{v}}^{\mathrm{nl}}\end{aligned} \tag{2.26}$$

with $\hat{\mathbf{p}} = -i\hbar\nabla$ the momentum operator. Using Eq. (2.14), we obtain that the matrix elements of $\hat{\mathbf{v}}^{\mathcal{S}}$ are given by

$$\mathbf{v}^{\mathcal{S}}_{nm} = i\Sigma f_{mn}\mathbf{r}_{nm}, \tag{2.27}$$

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

$$\begin{aligned}
\mathbf{v}^{\sigma}_{nm} &= \mathbf{v}^{\mathrm{LDA}}_{nm} + i\Sigma f_{mn}\mathbf{r}_{nm} \\
&= \mathbf{v}^{\mathrm{LDA}}_{nm} + i\Sigma f_{mn}\frac{\mathbf{v}^{\sigma}_{nm}(\mathbf{k})}{i\omega^{\sigma}_{nm}(\mathbf{k})} \\
\mathbf{v}^{\sigma}_{nm}\frac{\omega^{\sigma}_{nm} - \Sigma f_{mn}}{\omega^{\sigma}_{nm}} &= \mathbf{v}^{\mathrm{LDA}}_{nm} \\
\mathbf{v}^{\sigma}_{nm}\frac{\omega^{\mathrm{LDA}}_{nm}}{\omega^{\sigma}_{nm}} &= \mathbf{v}^{\mathrm{LDA}}_{nm} \\
\frac{\mathbf{v}^{\sigma}_{nm}}{\omega^{\sigma}_{nm}} &= \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}}{\omega^{\mathrm{LDA}}_{nm}},
\end{aligned} \tag{2.28}$$

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

$$\begin{aligned}
\mathbf{v}^{\sigma}_{nm}(\mathbf{k}) &= \frac{\omega^{\sigma}_{nm}}{\omega^{\mathrm{LDA}}_{nm}}\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}) = \left(1 + \frac{\Sigma}{\omega_c(\mathbf{k}) - \omega_v(\mathbf{k})}\right)\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}) \qquad n \notin D_m \\
\mathbf{v}^{\sigma}_{nn}(\mathbf{k}) &= \mathbf{v}^{\mathrm{LDA}}_{nn}(\mathbf{k}),
\end{aligned} \tag{2.29}$$

and Eq. (2.22) gives

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\sigma}_{nm}(\mathbf{k})}{i\omega^{\sigma}_{nm}(\mathbf{k})} = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n \notin D_m. \tag{2.30}$$

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

$$\mathbf{r}_{e,nm} \to \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n \notin D_m, \tag{2.31}$$

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.[79, 80, 81] In Appendix B we outline how this can be accomplished.

2.3 Time-dependent Perturbation Theory

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

$$\mathcal{O} = \mathrm{Tr}(\hat{\mathcal{O}}\hat{\rho}) = \mathrm{Tr}(\hat{\rho}\hat{\mathcal{O}}), \tag{2.32}$$

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

$$i\hbar\frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}], \tag{2.33}$$

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

$$\hat{\mathcal{O}}_I = \hat{U}\hat{\mathcal{O}}\hat{U}^\dagger, \tag{2.34}$$

where

$$\hat{U} = e^{i\hat{H}_0 t/\hbar}, \tag{2.35}$$

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. (2.33) into

$$i\hbar\frac{d\hat{\rho}_I(t)}{dt} = [-e\hat{\mathbf{r}}_I(t)\cdot\mathbf{E}(t), \hat{\rho}_I(t)], \tag{2.36}$$

that leads to

$$\hat{\rho}_I(t) = \hat{\rho}_I(t=-\infty) + \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I(t')]. \tag{2.37}$$

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

$$\mathbf{E}(t) = \mathbf{E}e^{-i\omega t}e^{\eta t} = \mathbf{E}e^{-i\tilde{\omega}t}, \tag{2.38}$$

with

$$\tilde{\omega} = \omega + i\eta, \tag{2.39}$$

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

$$\langle n\mathbf{k}|\hat{\rho}_0|m\mathbf{k}'\rangle = f_n(\hbar\omega_n^\sigma(\mathbf{k}))\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{2.40}$$

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

We solve Eq. (2.37) using the standard iterative solution, for which we write

$$\hat{\rho}_I = \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots, \tag{2.41}$$

where $\hat{\rho}_I^{(N)}$ is the density operator to order N in $\mathbf{E}(t)$. Then, Eq. (2.37) reads

$$\hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots = \hat{\rho}_0 + \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots], \tag{2.42}$$

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

$$\hat{\rho}_I^{(0)} \equiv \hat{\rho}_0, \tag{2.43}$$

and

$$\hat{\rho}_I^{(N)}(t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I^{(N-1)}(t')]. \tag{2.44}$$

It is simple to show that matrix elements of Eq. (2.44) satisfy $\langle n\mathbf{k}|\rho_I^{(N+1)}(t)|m\mathbf{k}'\rangle = \rho_{I,nm}^{(N+1)}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')$, with

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt'\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t'), \hat{\rho}_I^{(N)}(t')]|m\mathbf{k}\rangle\cdot\mathbf{E}(t'). \tag{2.45}$$

We now work out the commutator of Eq. (2.45). Then,

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t), \hat{\rho}_I^{(N)}(t)]|m\mathbf{k}\rangle &= \langle n\mathbf{k}|[\hat{U}\hat{\mathbf{r}}\hat{U}^\dagger, \hat{U}\hat{\rho}^{(N)}(t)\hat{U}^\dagger]|m\mathbf{k}\rangle \\ &= \langle n\mathbf{k}|\hat{U}[\hat{\mathbf{r}}, \hat{\rho}^{(N)}(t)]\hat{U}^\dagger|m\mathbf{k}\rangle \\ &= e^{i\omega_{nm\mathbf{k}}^\sigma t}\Big(\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)] + [\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle\Big).\end{aligned} \tag{2.46}$$

We calculate the interband term first, so using Eq. (2.31) we obtain

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle &= \sum_\ell\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_e|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\rho}^{(N)}(t)|m\mathbf{k}\rangle \\ &\quad -\langle n\mathbf{k}|\hat{\rho}^{(N)}(t)|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle\Big) \\ &= \sum_{\ell\neq n,m}\Big(\mathbf{r}_{n\ell}(\mathbf{k})\rho_{\ell m}^{(N)}(\mathbf{k};t) - \rho_{n\ell}^{(N)}(\mathbf{k};t)\mathbf{r}_{\ell m}(\mathbf{k})\Big) \\ &\equiv \mathbf{R}_e^{(N)}(\mathbf{k};t),\end{aligned} \tag{2.47}$$

and from Eq. (2.23),

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\rho_{nm}^{(N)}(t))_{;\mathbf{k}} \equiv \delta(\mathbf{k}-\mathbf{k}')\mathbf{R}_i^{(N)}(\mathbf{k};t). \tag{2.48}$$

Then Eq. (2.45) becomes

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}^{\sigma}-\tilde{\omega})t'}\left[R_e^{\mathrm{b}(N)}(\mathbf{k};t') + R_i^{\mathrm{b}(N)}(\mathbf{k};t')\right]E^{\mathrm{b}}, \tag{2.49}$$

where the roman superindices a, b, c denote Cartesian components that are summed over if repeated. Starting from the linear response and proceeding from Eq. (2.40) and (2.47),

$$\begin{aligned} R_e^{\mathrm{b}(0)}(\mathbf{k};t) &= \sum_{\ell}\left(r_{n\ell}^{\mathrm{b}}(\mathbf{k})\rho_{\ell m}^{(0)}(\mathbf{k}) - \rho_{n\ell}^{(0)}(\mathbf{k})r_{\ell m}^{\mathrm{b}}(\mathbf{k})\right) \\ &= \sum_{\ell}\left(r_{n\ell}^{\mathrm{b}}(\mathbf{k})\delta_{\ell m}f_m(\hbar\omega_m^{\sigma}(\mathbf{k})) - \delta_{n\ell}f_n(\hbar\omega_n^{\sigma}(\mathbf{k}))r_{\ell m}^{\mathrm{b}}(\mathbf{k})\right) \\ &= f_{mn\mathbf{k}}r_{nm}^{\mathrm{b}}(\mathbf{k}), \end{aligned} \tag{2.50}$$

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. (2.48) and Eq. (2.24) that

$$R_i^{\mathrm{b}(0)}(\mathbf{k}) = i(\rho_{nm}^{(0)})_{;k^{\mathrm{b}}} = i\delta_{nm}(f_{n\mathbf{k}})_{;k^{\mathrm{b}}} = i\delta_{nm}\nabla_{k^{\mathrm{b}}}f_{n\mathbf{k}}. \tag{2.51}$$

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,

$$\begin{aligned} \rho_{I,nm}^{(1)}(\mathbf{k};t) &= \frac{ie}{\hbar}f_{mn\mathbf{k}}r_{nm}^{\mathrm{b}}(\mathbf{k})E^{\mathrm{b}}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}^{\sigma}-\tilde{\omega})t'} \\ &= \frac{e}{\hbar}f_{mn\mathbf{k}}r_{nm}^{\mathrm{b}}(\mathbf{k})E^{\mathrm{b}}\frac{e^{i(\omega_{nm\mathbf{k}}^{\sigma}-\tilde{\omega})t}}{\omega_{nm\mathbf{k}}^{\sigma}-\tilde{\omega}} \\ &= e^{i\omega_{nm\mathbf{k}}^{\sigma}t}B_{mn}^{\mathrm{b}}(\mathbf{k})E^{\mathrm{b}}(t) \\ &= e^{i\omega_{nm\mathbf{k}}^{\sigma}t}\rho_{nm}^{(1)}(\mathbf{k};t), \end{aligned} \tag{2.52}$$

with

$$B_{nm}^{\mathrm{b}}(\mathbf{k},\omega) = \frac{e}{\hbar}\frac{f_{mn\mathbf{k}}r_{nm}^{\mathrm{b}}(\mathbf{k})}{\omega_{nm\mathbf{k}}^{\sigma}-\tilde{\omega}}, \tag{2.53}$$

and

$$\rho_{nm}^{(1)}(\mathbf{k};t) = B_{mn}^{\mathrm{b}}(\mathbf{k},\omega)E^{\mathrm{b}}(\omega)e^{-i\tilde{\omega}t}. \tag{2.54}$$

Now, we calculate the second-order response. Then, from Eq. (2.47)

$$\begin{aligned} R_e^{\mathrm{b}(1)}(\mathbf{k};t) &= \sum_{\ell}\left(r_{n\ell}^{\mathrm{b}}(\mathbf{k})\rho_{\ell m}^{(1)}(\mathbf{k};t) - \rho_{n\ell}^{(1)}(\mathbf{k};t)r_{\ell m}^{\mathrm{b}}(\mathbf{k})\right) \\ &= \sum_{\ell}\left(r_{n\ell}^{\mathrm{b}}(\mathbf{k})B_{\ell m}^{\mathrm{c}}(\mathbf{k},\omega) - B_{n\ell}^{\mathrm{c}}(\mathbf{k},\omega)r_{\ell m}^{\mathrm{b}}(\mathbf{k})\right)E^{\mathrm{c}}(t), \end{aligned} \tag{2.55}$$

and from Eq. (2.48)

$$R_i^{\mathrm{b}(1)}(\mathbf{k};t) = i(\rho_{nm}^{(1)}(t))_{;k^{\mathrm{b}}} = iE^{\mathrm{c}}(t)(B_{nm}^{\mathrm{c}}(\mathbf{k},\omega))_{;k^{\mathrm{b}}}. \tag{2.56}$$

Using Eqs. (2.55) and (2.56) in Eq. (2.49), we obtain

$$\begin{aligned}
\rho_{I,nm}^{(2)}(\mathbf{k};t) &= \frac{ie}{\hbar}\Bigg[\sum_{\ell}\Big(r_{n\ell}^{\mathrm{b}}(\mathbf{k})B_{\ell m}^{\mathrm{c}}(\mathbf{k},\omega) - B_{n\ell}^{\mathrm{c}}(\mathbf{k},\omega)r_{\ell m}^{\mathrm{b}}(\mathbf{k})\Big) \\
&\quad + i(B_{nm}^{\mathrm{c}}(\mathbf{k},\omega))_{;k^{\mathrm{b}}}\Bigg]E_{\omega}^{\mathrm{b}}E_{\omega}^{\mathrm{c}}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}^{\sigma}-2\tilde{\omega})t'} \\
&= \frac{e}{\hbar}\Bigg[\sum_{\ell}\Big(r_{n\ell}^{\mathrm{b}}(\mathbf{k})B_{\ell m}^{\mathrm{c}}(\mathbf{k},\omega) - B_{n\ell}^{\mathrm{c}}(\mathbf{k},\omega)r_{\ell m}^{\mathrm{b}}(\mathbf{k})\Big) \\
&\quad + i(B_{nm}^{\mathrm{c}}(\mathbf{k},\omega))_{;k^{\mathrm{b}}}\Bigg]E_{\omega}^{\mathrm{b}}E_{\omega}^{\mathrm{c}}\frac{e^{i(\omega_{nm\mathbf{k}}^{\sigma}-2\tilde{\omega})t}}{\omega_{nm\mathbf{k}}^{\sigma}-2\tilde{\omega}} \\
&= e^{i\omega_{nm\mathbf{k}}^{\sigma}t}\rho_{nm}^{(2)}(\mathbf{k};t).
\end{aligned} \tag{2.57}$$

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

$$\begin{aligned}
\rho_{nm}^{(2)}(\mathbf{k};2\omega) &= \frac{e}{i\hbar}\frac{1}{\omega_{nm\mathbf{k}}^{\sigma}-2\tilde{\omega}}\Bigg[-(B_{nm}^{\mathrm{c}}(\mathbf{k},\omega)_{;k^{\mathrm{b}}} \\
&\quad + i\sum_{\ell}\Big(r_{n\ell}^{\mathrm{b}}B_{\ell m}^{\mathrm{c}}(\mathbf{k},\omega) - B_{n\ell}^{\mathrm{c}}(\mathbf{k},\omega)r_{\ell m}^{\mathrm{b}}\Big)\Bigg]E^{\mathrm{b}}(\omega)E^{\mathrm{c}}(\omega)
\end{aligned} \tag{2.58}$$

where $B_{\ell m}^{\mathrm{a}}(\mathbf{k},\omega)$ are given by Eq. (2.53). 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.

2.4 Layered Current Density

In this section, we derive the expressions for the microscopic current density of a given layer in the unit cell of the system. The approach we use to study the surface of a semi-infinite semiconductor crystal is as follows. Instead of using a semi-infinite system, we replace it by a slab (see Fig. 2.2). The slab consists of a front and back surface, and in between these two surfaces is the bulk of the system. In general the surface of a crystal reconstructs or relaxes as the atoms move to find equilibrium positions. This is due to the fact that the otherwise balanced forces are disrupted when the surface atoms do not find their partner atoms that are now absent at the surface of the slab.

To take the reconstruction or relaxation into account, we take "surface" to mean the true surface of the first layer of atoms, and some of the atomic sub-layers adjacent to it. Since the front and the back surfaces of the slab are usually identical the total slab is centrosymmetric. This implies that $\chi^{\text{slab}}_{\text{abc}} = 0$, 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 $\chi^{\text{slab}}_{\text{abc}} \neq 0$, we still need a procedure to extract the front surface χ^{f}_{abc} and the back surface χ^{b}_{abc} from the non-linear susceptibility $\chi^{\text{slab}}_{\text{abc}} = \chi^{f}_{\text{abc}} - \chi^{b}_{\text{abc}}$ 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.[82] 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,

$$\mathcal{C}^{\ell}(z) = \Theta(z - z_{\ell} + \Delta^{\text{b}}_{\ell})\Theta(z_{\ell} - z + \Delta^{f}_{\ell}), \tag{2.59}$$

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. 2.2).

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

$$\mathbf{j}(\mathbf{r}, t) = \text{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)), \tag{2.60}$$

where the operator for the electron's current is

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{e}{2}\left(\hat{\mathbf{v}}^{\sigma}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^{\sigma}\right), \tag{2.61}$$

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

$$\begin{aligned}
\text{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t) &= \text{Tr}(\hat{\rho}(t)\hat{\mathbf{j}}(\mathbf{r})) = \frac{e}{2}\left(\text{Tr}(\hat{\rho}\hat{\mathbf{v}}^{\sigma}\hat{\mu}) + \text{Tr}(\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^{\sigma})\right)\\
&= \frac{e}{2}\sum_{n\mathbf{k}}\left(\langle n\mathbf{k}|\hat{\rho}\hat{\mathbf{v}}^{\sigma}\hat{\mu}|n\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^{\sigma}|n\mathbf{k}\rangle\right)\\
&= \frac{e}{2}\sum_{nm\mathbf{k}}\langle n\mathbf{k}|\hat{\rho}|m\mathbf{k}\rangle\left(\langle m\mathbf{k}|\hat{\mathbf{v}}^{\sigma}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^{\sigma}|n\mathbf{k}\rangle\right)\\
\mathbf{j}(\mathbf{r}, t) &= \sum_{nm\mathbf{k}}\rho_{nm}(\mathbf{k}; t)\mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}),
\end{aligned} \tag{2.62}$$

where

$$\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}) = \frac{e}{2}\left(\langle m\mathbf{k}|\hat{\mathbf{v}}^\sigma|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^\sigma|n\mathbf{k}\rangle\right), \tag{2.63}$$

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

$$\frac{1}{\Omega}\int d^3r\,\mathcal{C}^\ell(z)\,\mathbf{j}(\mathbf{r},t) \equiv \mathbf{J}^\ell(t), \tag{2.64}$$

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

$$e\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{mn}(\mathbf{k}) \equiv \int d^3r\,\mathcal{C}^\ell(z)\,\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}), \tag{2.65}$$

to write

$$J^{(N,\ell)}_a(t) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{\sigma,a,\ell}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};t), \tag{2.66}$$

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. (2.53) and (2.58) respectively. The Fourier component of microscopic current of Eq. (2.66) is given by

$$J^{(N,\ell)}_{\mathrm{a}}(\omega_3) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{\sigma,\mathrm{a},\ell}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};\omega_3). \tag{2.67}$$

We proceed to give an explicit expression of $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{mn}(\mathbf{k})$. From Eqs. (2.65) and (2.63) we obtain

$$\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{mn}(\mathbf{k}) = \frac{1}{2}\int \mathrm{d}^3r\,\mathcal{C}^\ell(z)\Big[\langle m\mathbf{k}|\mathbf{v}^\sigma|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{v}^\sigma|n\mathbf{k}\rangle\Big], \tag{2.68}$$

and using the following property

$$\langle\mathbf{r}|\hat{\mathbf{v}}^\sigma(\mathbf{r},\mathbf{r}')|n\mathbf{k}\rangle = \int d^3r''\langle\mathbf{r}|\hat{\mathbf{v}}^\sigma(\mathbf{r},\mathbf{r}')|\mathbf{r}''\rangle\langle\mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^\sigma(\mathbf{r},\mathbf{r}'')\int d^3r''\langle\mathbf{r}|\mathbf{r}''\rangle\langle\mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^\sigma(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}), \tag{2.69}$$

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

$$\begin{aligned}\mathcal{V}^{\sigma,\ell}_{mn}(\mathbf{k}) &= \frac{1}{2}\int d^3r\, \mathcal{C}^\ell(z)\Big[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^{\sigma*}\psi^*_{m\mathbf{k}}(\mathbf{r}) + \psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^\sigma\psi_{n\mathbf{k}}(\mathbf{r})\Big]\\ &= \int d^3r\,\psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{\mathcal{C}^\ell(z)\mathbf{v}^\sigma + \mathbf{v}^\sigma\mathcal{C}^\ell(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r})\\ &= \int d^3r\,\psi^*_{m\mathbf{k}}(\mathbf{r})\mathcal{V}^{\sigma,\ell}\psi_{n\mathbf{k}}(\mathbf{r}).\end{aligned} \tag{2.70}$$

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

$$\mathcal{V}^{\sigma,\ell} = \frac{\mathcal{C}^\ell(z)\mathbf{v}^\sigma + \mathbf{v}^\sigma\mathcal{C}^\ell(z)}{2}, \tag{2.71}$$

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

$$\hat{\mathbf{v}}^\sigma \rightarrow \hat{\mathcal{V}}^{\sigma,\ell} = \left[\frac{\mathcal{C}^\ell(z)\hat{\mathbf{v}}^\sigma + \hat{\mathbf{v}}^\sigma\mathcal{C}^\ell(z)}{2}\right], \tag{2.72}$$

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

$$\begin{aligned}\mathcal{V}^{\sigma,\ell} &= \mathcal{V}^{\mathrm{LDA},\ell} + \mathcal{V}^{\mathcal{S},\ell}\\ \mathcal{V}^{\mathrm{LDA},\ell} &= \mathcal{V}^{\ell} + \mathcal{V}^{\mathrm{nl},\ell} = \frac{1}{m_e}\mathcal{P}^\ell + \mathcal{V}^{\mathrm{nl},\ell}.\end{aligned} \tag{2.73}$$

We remark that the simple relationship between $\mathbf{v}^\sigma_{nm}(\mathbf{k})$ and $\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})$, given in Eq. (2.29), does not hold between $\mathcal{V}^{\sigma,\ell}_{nm}(\mathbf{k})$ and $\mathcal{V}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$, i.e. $\mathcal{V}^{\sigma,\ell}_{nm}(\mathbf{k}) \neq (\omega^\sigma_{nm}/\omega_{nm})\mathcal{V}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$ and $\mathcal{V}^{\sigma,\ell}_{nn}(\mathbf{k}) \neq \mathcal{V}^{\mathrm{LDA},\ell}_{nn}(\mathbf{k})$, and thus, to calculate $\mathcal{V}^{\sigma,\ell}_{nm}(\mathbf{k})$ we must calculate the matrix elements of $\mathcal{V}^{\mathcal{S},\ell}$ and $\mathcal{V}^{\mathrm{LDA},\ell}$ (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. (2.71) for $\mathcal{V}^\ell = \mathcal{P}^\ell/m_e$ was proposed in Ref. [82] and later used in Refs. [67], [63], [83], and [84] also in the context of SHG. The layer-by-layer analysis of Refs. [85] and [86] used Eq. (2.59), 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. [87] for the linear response, and here in this article, for the second harmonic optical response of semiconductors.

2.5 Microscopic surface susceptibility

In this section we obtain the expressions for the surface susceptibility tensor $\chi^{S}_{\rm abc}$. We start with the basic relation $\mathbf{J} = d\mathbf{P}/dt$ with $\mathbf{J}$ the current calculated in Sec. 2.4. From Eq. (2.67) we obtain

$$J^{(2,\ell)}_{\rm a}(2\omega) = -i2\tilde{\omega}P_{\rm a}(2\omega) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}(\mathbf{k})\rho^{(2)}_{nm}(\mathbf{k};2\omega), \tag{2.74}$$

and using Eqs. (2.58) and (2.7) leads to

$$\begin{aligned}\chi^{S,\ell}_{\rm abc} &= \frac{ie}{AE^{\rm b}_1E^{\rm c}_2 2\tilde{\omega}}\sum_{mn\mathbf{k}}\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}(\mathbf{k})\rho^{(2)}_{nm}(\mathbf{k};2\tilde{\omega})\\ &= \frac{e^2}{A\hbar 2\tilde{\omega}}\sum_{mn\mathbf{k}}\frac{\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}(\mathbf{k})}{\omega^{\sigma}_{nm\mathbf{k}}-2\tilde{\omega}}\Bigg[-\left(B^{\rm c}_{nm}(\mathbf{k},\omega)\right)_{;k^{\rm b}}\\ &+ i\sum_{\ell}\left(r^{\rm b}_{n\ell}B^{\rm c}_{\ell m}(\mathbf{k},\omega) - B^{\rm c}_{n\ell}(\mathbf{k},\omega)r^{\rm b}_{\ell m}\right)\Bigg],\end{aligned} \tag{2.75}$$

which gives the surface-like susceptibility of ℓ-th layer, where $\boldsymbol{\mathcal{V}}^{\sigma}$ is given in Eq. (2.73), where $A = \Omega/d$ is the surface area of the unit cell that characterizes the surface of the system. Using Eq. (2.53) we split this equation into two contributions from the first and second terms on the right hand side,

$$\chi^{S,\ell}_{i,{\rm abc}} = -\frac{e^3}{A\hbar^2 2\tilde{\omega}}\sum_{mn\mathbf{k}}\frac{\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}}{\omega^{\sigma}_{nm}-2\tilde{\omega}}\left(\frac{f_{mn}r^{\rm b}_{nm}}{\omega^{\sigma}_{nm}-\tilde{\omega}}\right)_{;k^{\rm c}}, \tag{2.76}$$

and

$$\chi^{S,\ell}_{e,{\rm abc}} = \frac{ie^3}{A\hbar^2 2\tilde{\omega}}\sum_{\ell mn\mathbf{k}}\frac{\mathcal{V}^{\sigma,{\rm a},\ell}_{mn}}{\omega^{\sigma}_{nm}-2\tilde{\omega}}\left(\frac{r^{\rm c}_{n\ell}r^{\rm b}_{\ell m}f_{m\ell}}{\omega^{\sigma}_{\ell m}-\tilde{\omega}} - \frac{r^{\rm b}_{n\ell}r^{\rm c}_{\ell m}f_{\ell n}}{\omega^{\sigma}_{n\ell}-\tilde{\omega}}\right), \tag{2.77}$$

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. (2.76) we use the chain rule

$$\left(\frac{f_{mn}r^{\rm b}_{nm}}{\omega^{\sigma}_{nm}-\tilde{\omega}}\right)_{;k^{\rm c}} = \frac{f_{mn}}{\omega^{\sigma}_{nm}-\tilde{\omega}}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}} - \frac{f_{mn}r^{\rm b}_{nm}\Delta^{\rm c}_{nm}}{(\omega^{\sigma}_{nm}-\tilde{\omega})^2}, \tag{2.78}$$

and the following result shown in Appendix D,

$$(\omega^{\sigma}_{nm})_{;k^{\rm a}} = \left(\omega^{\rm LDA}_{nm}\right)_{;k^{\rm a}} = v^{\rm LDA,a}_{nn} - v^{\rm LDA,a}_{mm} \equiv \Delta^{\rm a}_{nm}. \tag{2.79}$$

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

$$\boldsymbol{\chi}^{S} \equiv \sum_{\ell=1}^{N}\boldsymbol{\chi}^{S,\ell}, \tag{2.80}$$

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. 2.1), such that

$$\chi^{S,\ell=N} = 0, \tag{2.81}$$

in accordance to Eq. (2.5) 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. (2.81) to be satisfied and to give converged results for χ^S. We can use Eq. (2.80) for either the front or the back surface.

We can see from the prefactors of Eqs. (2.76) and (2.77) that they diverge as $\tilde{\omega} \to 0$. To remove this apparent divergence of $\chi^{S,\ell}$, 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 χ^S,

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\frac{1}{\omega^\sigma_{cv}}\left[\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{lc}\{r^\mathrm{b}_{cv}r^\mathrm{c}_{vl}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{cl})} - \frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vl}\{r^\mathrm{c}_{lc}r^\mathrm{b}_{cv}\}]}{(2\omega^\sigma_{cv}-\omega^\sigma_{lv})}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{2.82}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{(\omega^\sigma_{cv})^2}\left[\mathrm{Re}\left[\left\{r^\mathrm{b}_{cv}\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\right)_{;k^\mathrm{c}}\right\}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{r^\mathrm{b}_{cv}\Delta^\mathrm{c}_{cv}\right\}\right]}{\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-\omega), \tag{2.83}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^\sigma_{cv}}\left[\sum_{v'\neq v}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^\mathrm{b}_{cv'}r^\mathrm{c}_{v'v}\}]}{2\omega^\sigma_{cv'}-\omega^\sigma_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Im}[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\{r^\mathrm{c}_{cc'}r^\mathrm{b}_{c'v}\}]}{2\omega^\sigma_{c'v}-\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{2.84}$$

and

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^\sigma_{cv})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{\left(r^\mathrm{b}_{cv}\right)_{;k^\mathrm{c}}\right\}\right] - \frac{2\mathrm{Re}\left[\mathcal{V}^{\sigma,\mathrm{a},\ell}_{vc}\left\{r^\mathrm{b}_{cv}\Delta^\mathrm{c}_{cv}\right\}\right]}{\omega^\sigma_{cv}}\right]\delta(\omega^\sigma_{cv}-2\omega), \tag{2.85}$$

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,[88] 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,[89] 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

$$(r^\mathrm{b}_{nm})_{;k^\mathrm{a}} = -i\mathcal{T}^{\mathrm{ab}}_{nm} + \frac{r^\mathrm{a}_{nm}\Delta^\mathrm{b}_{mn} + r^\mathrm{b}_{nm}\Delta^\mathrm{a}_{mn}}{\omega^{\mathrm{LDA}}_{nm}} + \frac{i}{\omega^{\mathrm{LDA}}_{nm}}\sum_\ell\left(\omega^{\mathrm{LDA}}_{\ell m}r^\mathrm{a}_{n\ell}r^\mathrm{b}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell}r^\mathrm{b}_{n\ell}r^\mathrm{a}_{\ell m}\right), \tag{2.86}$$

where

$$\mathcal{T}^{\rm ab}_{nm} = [r^{\rm a}, v^{\rm LDA,b}] = \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm} + \mathcal{L}^{\rm ab}_{nm}, \tag{2.87}$$

and

$$\mathcal{L}^{\rm ab}_{nm} = \frac{1}{i\hbar}[r^{\rm a}, v^{\rm nl,b}]_{nm}, \tag{2.88}$$

is the contribution to the generalized derivative of $\mathbf{r}_{nm}$ coming from the nonlocal part of the pseudopotential. In Appendix F we calculate $\mathcal{L}^{\rm ab}_{nm}$, that is a term with very small numerical value but with a computational time at least an order of magnitude larger than for all the other terms involved in the expressions for $\chi^{s,\ell}_{\rm abc}$.[90] Therefore, we neglect it throughout this article and take

$$\mathcal{T}^{\rm ab}_{nm} \approx \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm}. \tag{2.89}$$

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

$$\begin{aligned}(v^{\rm LDA,a}_{nn})_{;k^{\rm b}} = \nabla_{k^{\rm a}} v^{\rm LDA,b}_{nn}(\mathbf{k}) &= -i\mathcal{T}^{\rm ab}_{nn} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\left(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n} + r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\right) \\ &\approx \frac{\hbar}{m_e}\delta_{\rm ab} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\left(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n} + r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\right),\end{aligned} \tag{2.90}$$

among other quantities for $\mathcal{V}^{\sigma,{\rm a},\ell}_{nm;\mathbf{k}}$, where we also use Eq. (2.89). Above is the standard effective-mas sum rule. [91]

2.6 Conclusions

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

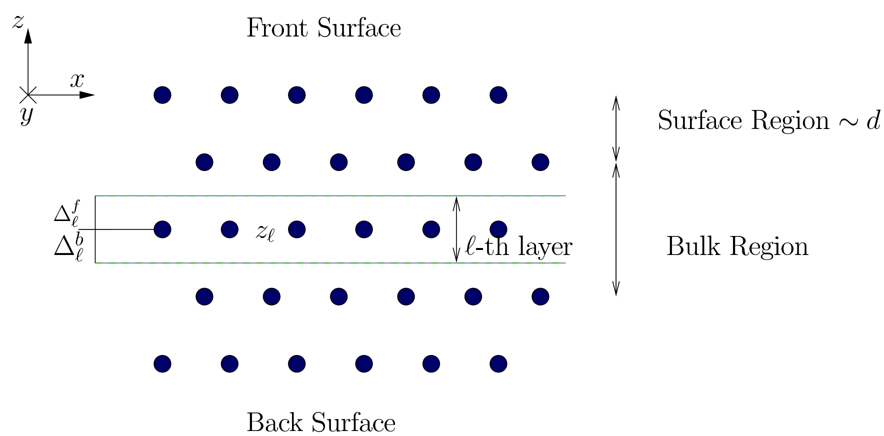

Figure 2.2: A sketch of a slab where the circles represent atoms.

Chapter 3

SHG Yield

Contents

3.1 Three layer model for SHG radiation

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

$$\mathcal{R}(\omega) = \frac{I(2\omega)}{I^2(\omega)}, \tag{3.1}$$

with the intensity in the MKS system is given by[92]

$$I(\omega) = 2n(\omega)\epsilon_0 c|E(\omega)|^2, \tag{3.2}$$

where $n(\omega) = \sqrt{\epsilon(\omega)}$ is the index of refraction with $\epsilon(\omega)$ the dielectric function, ϵ_0 is the vacuum permittivity, and c the speed of light in vacuum.

There are several ways to calculate R, one of which is the procedure followed by Cini [93]. 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 [94], since the derivation of the three-layer-model is straightforward. In this scheme, we represent the surface by three regions or layers. The first layer is the vacuum region (denoted by v) with a dielectric function $\epsilon_v(\omega) = 1$ from where the fundamental electric field $\mathbf{E}_v(\omega)$ impinges on the material. The second layer is a thin layer (denoted by ℓ) of thickness d characterized by a dielectric function $\epsilon_\ell(\omega)$. Is in this layer where the second harmonic generation takes place. The third layer is the bulk region denoted by b and characterized by $\epsilon_b(\omega)$. Both the vacuum layer and the bulk layer are semiinfinite (see Fig. 3.1).

To model the electromagnetic response of the three-layer model we follow Ref. [94], and assume a polarization sheet of the form

$$\mathbf{P}(\mathbf{r}, t) = \boldsymbol{\mathcal{P}} e^{i\boldsymbol{\kappa}\cdot\mathbf{R}} e^{-i\omega t} \delta(z - z_\beta) + \text{c.c.}, \tag{3.3}$$

where $\mathbf{R} = (x, y)$, $\boldsymbol{\kappa}$ is the component of the wave vector $\boldsymbol{\nu}_\beta$ paralel to the surface, and z_β is the position of the sheet within medium β (see Fig. 3.1). In Ref. [95] it has been shown that the solution of the Maxwell equations for the radiated fields $E_{\beta,p\pm}$ and $E_{\beta,s}$ with $\mathbf{P}(\mathbf{r}, t)$as a source can be written, at points $z \neq 0$, as

$$(E_{\beta,p\pm}, E_{\beta,s}) = (\frac{\gamma i \tilde{\omega}^2}{\tilde{w}_\beta} \hat{\mathbf{p}}_{\beta\pm} \cdot \boldsymbol{\mathcal{P}}, \frac{\gamma i \tilde{\omega}^2}{\tilde{w}_\beta} \hat{\mathbf{s}} \cdot \boldsymbol{\mathcal{P}}), \tag{3.4}$$

where $\gamma = 2\pi$ in cgs units and $\gamma = 1/2\epsilon_0$ in MKS units. Also, $\hat{\mathbf{s}}$ and $\hat{\mathbf{p}}_{\beta\pm}$ are the unitary vectors for the s and p polarization of the radiated field, respectively, and the $\pm$ refers to upward $(+)$ or downward $(-)$ direction of propagation within medium β, as shown in Fig. 3.1, and $\tilde{\omega} = \omega/c$. Also, $\tilde{w}_\beta(\omega) = \tilde{\omega} w_\beta$, where

$$w_\beta(\omega) = \left(\epsilon_\beta(\omega) - \sin^2\theta_0\right)^{1/2}, \tag{3.5}$$

where θ_0 is the angle of incidence of $\mathbf{E}_v(\omega)$, and

$$\hat{\mathbf{p}}_{\beta\pm}(\omega) = \frac{\kappa(\omega)\hat{\mathbf{z}} \mp \tilde{w}_\beta(\omega)\hat{\boldsymbol{\kappa}}}{\tilde{\omega} n_\beta(\omega)} = \frac{\sin\theta_0 \hat{\mathbf{z}} \mp w_\beta(\omega)\hat{\boldsymbol{\kappa}}}{n_\beta(\omega)}, \tag{3.6}$$

where $\kappa(\omega) = |\boldsymbol{\kappa}| = \tilde{\omega}\sin\theta_0$, $n_\beta(\omega) = \sqrt{\epsilon_\beta(\omega)}$ is the index of refraction of medium β, and z is the direction perpendicular to the surface that points towards the vacuum. We chose the plane of incidence along the $\boldsymbol{\kappa} z$ plane, then

$$\hat{\boldsymbol{\kappa}} = \cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}}, \tag{3.7}$$

and

$$\hat{\mathbf{s}} = -\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}, \tag{3.8}$$

where ϕ the angle with respect to the x axis.

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

$$\mathcal{P}_i(2\omega) = \begin{cases} \chi_{ijk}(2\omega)E_j(\omega)E_k(\omega) & \text{(cgs units)} \\ \epsilon_0 \chi_{ijk}(2\omega)E_j(\omega)E_k(\omega) & \text{(MKS units)} \end{cases}, \tag{3.9}$$

where the tensor $\boldsymbol{\chi}(2\omega)$ is the surface nonlinear dipolar susceptibility and the Cartesian indices i, j, k are summed if repeated. Also, $\chi_{ijk}(2\omega) = \chi_{ikj}(2\omega)$ is the intrinsic permutation symmetry due to the fact that SHG is degenerate in $E_j(\omega)$ and $E_k(\omega)$. As it was done in Ref. [94], in presenting the results Eq. (3.4)-(3.8) we have taken the polarization sheet (Eq. (3.3)) to be oscillating at some frequency ω. However, in the following we find it convenient to use ω exclusively to denote the fundamental frequency and $\boldsymbol{\kappa}$ to denote the component of the incident wave vector parallel to the surface. Then the nonlinear generated polarization is oscillating at $\Omega = 2\omega$ and will be characterized by a wave vector parallel to the surface $\mathbf{K} = 2\boldsymbol{\kappa}$. We can carry over Eqs. (3.3)-(3.8) simply by replacing the lowercase symbols $(\omega, \tilde{\omega}, \boldsymbol{\kappa}, n_\beta, \tilde{w}_\beta, w_\beta, \hat{\mathbf{p}}_{\beta\pm}, \hat{\mathbf{s}})$ with uppercase symbols $(\Omega, \tilde{\Omega}, \mathbf{K}, N_\beta, \tilde{W}_\beta, W_\beta, \hat{\mathbf{P}}_{\beta\pm}, \hat{\mathbf{S}})$, all evaluated at 2ω and we always have $\hat{\mathbf{S}} = \hat{\mathbf{s}}$.

To describe the propagation of the SH field, we see from Fig. 3.1, that it is refracted at the layer-vacuum interface (ℓv), and multiply reflected from the layer-bulk (ℓb) and layer-vacuum (ℓv) interfaces, thus we can define,

$$\mathbf{T}^{\ell v} = \hat{\mathbf{s}} T_s^{\ell v} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+} T_p^{\ell v} \hat{\mathbf{P}}_{\ell+}, \tag{3.10}$$

as the tensor for transmission from ℓv interface,

$$\mathbf{R}^{\ell b} = \hat{\mathbf{s}} R_s^{\ell b} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell+} R_p^{\ell b} \hat{\mathbf{P}}_{\ell-}, \tag{3.11}$$

as the tensor of reflection from the ℓb interface, and

$$\mathbf{R}^{\ell v} = \hat{\mathbf{s}} R_s^{\ell v} \hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell-} R_p^{\ell v} \hat{\mathbf{P}}_{\ell+}, \tag{3.12}$$

as that of the ℓv interface. The Fresnel factors in uppercase letters, $T_{s,p}^{ij}$ and $R_{s,p}^{ij}$, are evaluated at 2ω from the following well known formulas

$$\begin{aligned} t_s^{ij}(\omega) &= \frac{2k_i(\omega)}{k_i(\omega) + k_j(\omega)}, & t_p^{ij}(\omega) &= \frac{2k_i(\omega)\sqrt{\epsilon_i(\omega)\epsilon_j(\omega)}}{k_i(\omega)\epsilon_j(\omega) + k_j(\omega)\epsilon_i(\omega)}, \\ r_s^{ij}(\omega) &= \frac{k_i(\omega) - k_j(\omega)}{k_i(\omega) + k_j(\omega)}, & r_p^{ij}(\omega) &= \frac{k_i(\omega)\epsilon_j(\omega) - k_j\epsilon_i(\omega)}{k_i(\omega)\epsilon_j(\omega) + k_j(\omega)\epsilon_i(\omega)}. \end{aligned} \tag{3.13}$$

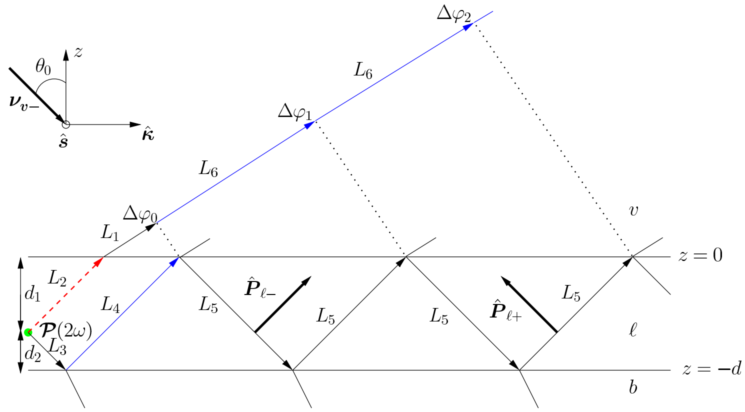

Figure 3.1: Sketch of the three layer model for SHG. Vacuum (v) is on top with $\epsilon_v = 1$; the layer ℓ, of thickness $d = d_1 + d_2$, is characterized with $\epsilon_\ell(\omega)$, and it is where the SH polarization sheet $\boldsymbol{\mathcal{P}}(2\omega)$ is located at $z_\ell = d_1$; The bulk b is described with $\epsilon_b(\omega)$. The arrows point along the direction of propagation, and the p-polarization unit vector, $\hat{\mathbf{P}}_{\ell-(+)}$, along the downward (upward) direction is denoted with a thick arrow. The s-polarization unit vector $\hat{\mathbf{s}}$, points out of the page. The fundamental field $\mathbf{E}(\omega)$ is incident from the vacuum side along the $z\hat{\boldsymbol{\kappa}}$-plane, with θ_0 its angle of incidence and $\boldsymbol{\nu}_{v-}$ its wave vector. $\Delta\varphi_i$ denote the phase difference of the multiply reflected beams with respect to the first vacuum transmitted beam (dashed-red arrow), where the dotted lines are perpendicular to this beam (see the text for details).

From these expressions one can show that,

$$
\begin{aligned}
1 + r_s^{\ell b} &= t_s^{\ell b} \\
1 + r_p^{\ell b} &= \frac{n_b}{n_\ell} t_p^{\ell b} \\
1 - r_p^{\ell b} &= \frac{n_\ell}{n_b}\frac{w_b}{w_\ell} t_p^{\ell b} \\
t_p^{\ell v} &= \frac{w_\ell}{w_v} t_p^{v\ell} \\
t_s^{\ell v} &= \frac{w_\ell}{w_v} t_s^{v\ell}.
\end{aligned}
\tag{3.14}
$$

3.1.1 Multiple SH reflections

The SH field $\mathbf{E}(2\omega)$ radiated by the SH polarization $\boldsymbol{\mathcal{P}}(2\omega)$ will radiate directly into vacuum and also into the bulk, where it will be reflected back at the thin-layer-bulk interface into the thin layer again and this beam will be multiple-transmitted and reflected as shown in Fig. 3.1. As the two beams propagate a phase difference will develop between them, according to

$$\begin{aligned}\Delta\varphi_m &= \tilde{\Omega}\Big(\big(L_3 + L_4 + 2mL_5\big)N_\ell - \big(L_2 N_\ell + (L_1 + mL_6)N_v\big)\Big)\\ &= \delta_0 + m\delta \quad m = 0, 1, 2, \ldots,\end{aligned} \tag{3.15}$$

where

$$\delta_0 = 8\pi\left(\frac{d_2}{\lambda_0}\right)\sqrt{n_\ell^2(2\omega) - \sin^2\theta_0}, \tag{3.16}$$

$$\delta = 8\pi\left(\frac{d}{\lambda_0}\right)\sqrt{n_\ell^2(2\omega) - \sin^2\theta_0}, \tag{3.17}$$

where λ_0 is the wavelength of the fundamental field in vacuum, d the thickness of layer ℓ and d_2 the distance of $\boldsymbol{\mathcal{P}}(2\omega)$ from the ℓb interface (see Fig. 3.1). We see that δ_0 is the phase difference of the first and second transmitted beams, and $m\delta$ that of the first and third ($m = 1$), fourth ($m = 2$), etc. beams (see Fig. 3.1).

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

$$\begin{aligned}\mathbf{E}(2\omega) &= E_{p+}(2\omega)\mathbf{T}^{\ell v}\cdot\hat{\mathbf{P}}_{\ell+} + E_{p-}(2\omega)\mathbf{T}^{\ell v}\cdot\mathbf{R}^{\ell b}\cdot\hat{\mathbf{P}}_{\ell-}e^{i\Delta\varphi_0} + E_{p-}(2\omega)\mathbf{T}^{\ell v}\cdot\mathbf{R}^{\ell b}\cdot\mathbf{R}^{\ell v}\cdot\mathbf{R}^{\ell b}\cdot\hat{\mathbf{P}}_{\ell-}e^{i\Delta\varphi_1}\\ &\quad + E_{p-}(2\omega)\mathbf{T}^{\ell v}\cdot\mathbf{R}^{\ell b}\cdot\mathbf{R}^{\ell v}\cdot\mathbf{R}^{\ell b}\cdot\mathbf{R}^{\ell v}\cdot\mathbf{R}^{\ell b}\cdot\hat{\mathbf{P}}_{\ell-}e^{i\Delta\varphi_2} + \cdots\\ &= E_{p+}(2\omega)\mathbf{T}^{\ell v}\cdot\hat{\mathbf{P}}_{\ell+} + E_{p-}(2\omega)\mathbf{T}^{\ell v}\cdot\sum_{m=0}^{\infty}\left(\mathbf{R}^{\ell b}\cdot\mathbf{R}^{\ell v}e^{i\delta}\right)^m\cdot\mathbf{R}^{\ell b}\cdot\hat{\mathbf{P}}_{\ell-}e^{i\delta_0}.\end{aligned} \tag{3.18}$$

From Eqs. (3.10)-(3.12) is easy to show that

$$\mathbf{T}^{\ell v}\cdot\left(\mathbf{R}^{\ell b}\cdot\mathbf{R}^{\ell v}\right)^n\cdot\mathbf{R}^{\ell b} = \hat{\mathbf{s}}T_s^{\ell v}\left(R_s^{\ell b}R_s^{\ell v}\right)^n R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}T_p^{\ell v}\left(R_p^{\ell b}R_p^{\ell v}\right)^n R_p^{\ell b}\hat{\mathbf{P}}_{\ell-}, \tag{3.19}$$

then,

$$\mathbf{E}(2\omega) = \hat{\mathbf{P}}_{\ell+}T_p^{\ell v}\left(E_{p+}(2\omega) + \frac{R_p^{\ell b}e^{i\delta_0}}{1 + R_p^{v\ell}R_p^{\ell b}e^{i\delta}}E_{p-}(2\omega)\right), \tag{3.20}$$

where we used $R_{s,p}^{ij} = -R_{s,p}^{ji}$. Using Eq. (3.4), we can readily write

$$\mathbf{E}(2\omega) = \frac{\gamma i\tilde{\Omega}}{W_\ell}\mathbf{H}_\ell\cdot\boldsymbol{\mathcal{P}}(2\omega), \tag{3.21}$$

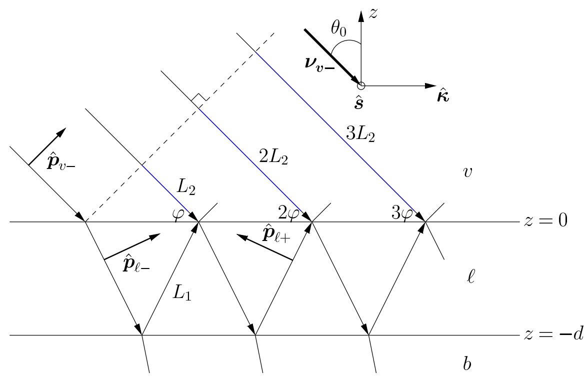

Figure 3.2: (color on line) Sketch for the multiple reflected fundamental field $\mathbf{E}(\omega)$, which impinges from the vacuum side along the $z\hat{\boldsymbol{\kappa}}$-plane, with θ_0 and $\boldsymbol{\nu}_{\nu-}$ its angle of incidence and wave vector, respectively. The arrows point along the direction of propagation. The p-polarization unit vectors, $\hat{\mathbf{p}}_{\beta\pm}$, along the downward (-) or upward (+) direction are denoted with thick arrows, where $\beta = \nu$ or ℓ. The s-polarization unit vector $\hat{\mathbf{s}}$ points out of the page, and $(1, 2, 3, \ldots)\phi$ denotes the phase difference for the multiply reflected beams with respect to the incident field, where the dotted line is perpendicular to this beam (see the text for details).

where

$$\mathbf{H}_\ell = \hat{\mathbf{s}}\, T_s^{\ell\nu}\left(1 + R_s^M\right)\hat{\mathbf{s}} + \hat{\mathbf{P}}_{\nu+} T_p^{\ell\nu}\left(\hat{\mathbf{P}}_{\ell+} + R_p^M \hat{\mathbf{P}}_{\ell-}\right). \tag{3.22}$$

and

$$R_l^M \equiv \frac{R_l^{\ell b} e^{i\delta_0}}{1 + R_l^{\nu\ell} R_l^{\ell b} e^{i\delta}} \qquad l = s, p, \tag{3.23}$$

is defined as the multiple (M) reflection coefficient. To make touch with the work of Ref. [94] where $\boldsymbol{\mathcal{P}}(2\omega)$ is located on top of the vacuum-surface interface and only the vacuum radiated beam and the first (and only) reflected beam need to be considered, we take $\ell = \nu$ and $d_2 = 0$, then $T^{\ell\nu} = 1$, $R^{\nu\ell} = 0$ and $\delta_0 = 0$, with which $R_l^M = R_l^{\nu b}$. Thus, Eq. (3.22) coincides with Eq. (3.8) of Ref. [94].

3.1.2 Multiple reflections for the linear field

Similar to the SH field, here we consider the multiple reflections of the fundamental field $\mathbf{E}(\omega)$ inside the thin ℓ layer. In Fig. 3.2 we show the situation where $\mathbf{E}(\omega)$ impinges from the vacuum side with an angle of incidence θ_0. As the first transmitted beam is multiply reflected from the ℓb and the $\ell\nu$ interfaces, it accumulates a phase difference of $n\phi$, with $n = 1, 2, 3, \ldots$, given by

$$\begin{aligned}\phi &= \frac{\omega}{c}(2L_1 n_\ell - L_2 n_v)\\ &= 4\pi\left(\frac{d}{\lambda_0}\right)\sqrt{n_\ell^2 - \sin^2\theta_0},\end{aligned}\tag{3.24}$$

where $n_v = 1$. Besides the equivalent of Eqs. (3.11) and (3.12), for ω, we also need

$$\mathbf{t}^{v\ell} = \hat{\mathbf{s}}t_s^{v\ell}\hat{\mathbf{s}} + \hat{\mathbf{p}}_{\ell-}t_p^{v\ell}\hat{\mathbf{p}}_{v-},\tag{3.25}$$

to write

$$\begin{aligned}\mathbf{E}(\omega) &= E_0\Big[\mathbf{t}^{v\ell} + \mathbf{r}^{\ell b}\cdot\mathbf{t}^{v\ell}e^{i\phi} + \mathbf{r}^{\ell b}\cdot\mathbf{r}^{\ell v}\cdot\mathbf{r}^{\ell b}\cdot\mathbf{t}^{v\ell}e^{i2\phi} + \mathbf{r}^{\ell b}\cdot\mathbf{r}^{\ell v}\cdot\mathbf{r}^{\ell b}\cdot\mathbf{r}^{\ell v}\cdot\mathbf{r}^{\ell b}\cdot\mathbf{t}^{v\ell}e^{i3\phi} + \cdots\Big]\cdot\mathbf{e}^{\mathrm{in}}\\ &= E_0\Big[1 + \Big(1 + \mathbf{r}^{\ell b}\cdot\mathbf{r}^{\ell v}e^{i\phi} + (\mathbf{r}^{\ell b}\cdot\mathbf{r}^{\ell v})^2 e^{i2\phi} + \cdots\Big)\cdot\mathbf{r}^{\ell b}e^{i\phi}\Big]\cdot\mathbf{t}^{v\ell}\cdot\mathbf{e}^{\mathrm{in}}\\ &= E_0\Big[\hat{\mathbf{s}}t_s^{v\ell}(1 + r_s^M)\hat{\mathbf{s}} + t_p^{v\ell}\left(\hat{\mathbf{p}}_{\ell-} + \hat{\mathbf{p}}_{\ell+}r_p^M\right)\hat{\mathbf{p}}_{v-}\Big]\cdot\mathbf{e}^{\mathrm{in}}\end{aligned}\tag{3.26}$$

where

$$r_l^M = \frac{r_l^{\ell b}e^{i\phi}}{1 + r_l^{v\ell}r_l^{\ell b}e^{i\phi}} \quad l = s, p.\tag{3.27}$$

We define $\mathbf{E}^l(\omega) \equiv E_0\mathbf{e}_\ell^{\omega,l}$ ($l = s, p$), where using Eq. (3.6), we obtain that

$$\mathbf{e}_\ell^{\omega,p} = \frac{t_p^{v\ell}}{n_\ell}\left(r_p^{M+}\sin\theta_0\hat{\mathbf{z}} + r_p^{M-}w_\ell\hat{\boldsymbol{\kappa}}\right),\tag{3.28}$$

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

$$\mathbf{e}_\ell^{\omega,s} = t_s^{v\ell}r_s^{M+}\hat{\mathbf{s}},\tag{3.29}$$

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

$$r_l^{M\pm} = 1 \pm r^M \quad l = s, p.\tag{3.30}$$

3.1.3 SHG Yield

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

$$\begin{aligned}\hat{\mathbf{P}}_{\ell+} + R_p^M\hat{\mathbf{P}}_{\ell-} &= \frac{\sin\theta_0\hat{\mathbf{z}} - W_\ell\hat{\boldsymbol{\kappa}}}{N_\ell} + R_p^M\frac{\sin\theta_0\hat{\mathbf{z}} + W_\ell\hat{\boldsymbol{\kappa}}}{N_\ell}\\ &= \frac{1}{N_\ell}\left(\sin\theta_0 R_{p+}^M\hat{\mathbf{z}} - K_\ell R_{p-}^M\hat{\boldsymbol{\kappa}}\right),\end{aligned}\tag{3.31}$$

where

$$R_l^{M\pm} \equiv 1 \pm R_l^M \quad l = s, p. \tag{3.32}$$

Using Eq. (3.14) we write Eq. (3.21) as

$$E(2\omega) = \frac{2\gamma i\omega}{cW_\ell}\hat{\mathbf{e}}^{\text{out}} \cdot \mathbf{H}_\ell \cdot \boldsymbol{\mathcal{P}}(2\omega) = \frac{2\gamma i\omega}{cW_\nu}\mathbf{e}_\ell^{2\omega} \cdot \boldsymbol{\mathcal{P}}(2\omega). \tag{3.33}$$

$$\mathbf{e}_\ell^{2\omega} = \hat{\mathbf{e}}^{\text{out}} \cdot \left[\hat{\mathbf{s}}T_s^{\nu\ell}R_s^{M+}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{\nu+}\frac{T_p^{\nu\ell}}{N_\ell}\left(\sin\theta_0 R_p^{M+}\hat{\mathbf{z}} - W_\ell R_p^{M-}\hat{\boldsymbol{\kappa}}\right)\right]. \tag{3.34}$$

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 $\ell = \nu$ ($T_{s,p}^{\ell\nu} = 1$), to get

$$\mathbf{e}_\nu^{2\omega} = \hat{\mathbf{e}}^{\text{out}} \cdot \left[\hat{\mathbf{s}}T_s^{\nu b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{\nu+}\frac{T_p^{\nu b}}{\sqrt{\epsilon_b(2\omega)}}\left(\epsilon_b(2\omega)\sin\theta_0\hat{\mathbf{z}} - W_b\hat{\boldsymbol{\kappa}}\right)\right], \tag{3.35}$$

which agrees with Eq. (3.10) of Ref. [94].

In the three layer model the SH polarization $\boldsymbol{\mathcal{P}}(2\omega)$ is located in layer ℓ, where we evaluate the fundamental field required in Eq. (3.9). We write

$$\mathbf{E}_\ell(\omega) = E_0\left(\hat{\mathbf{s}}t_s^{\nu\ell}(1 + r_s^{\ell b})\hat{\mathbf{s}} + \hat{\mathbf{p}}_{\ell-}t_p^{\nu\ell}\hat{\mathbf{p}}_{\nu-} + \hat{\mathbf{p}}_{\ell+}t_p^{\nu\ell}r_p^{\ell b}\hat{\mathbf{p}}_{\nu-}\right) \cdot \hat{\mathbf{e}}^{\text{in}} = E_0\mathbf{e}_\ell^\omega, \tag{3.36}$$

where $\mathbf{e}^{\text{in}}$ is the s ($\hat{\mathbf{s}}$) or p ($\hat{\mathbf{p}}_{\nu-}$) incoming polarization of the fundamental electric field. Above field is composed of the transmitted field and its first reflection from the ℓb interface for s and p polarizations. The fundamental field, once inside the layer ℓ will be multiply reflected at the $\ell\nu$ and ℓb interfaces, however each reflection will diminish the intensity of the fundamental field, and as the SHG yield goes with the square of this field, the contribution of the subsequent reflections, other than the one considered in Eq. (3.36), could be safely neglected. From Eq. (3.14) we find that

$$\mathbf{e}_\ell^\omega = \left[\hat{\mathbf{s}}t_s^{\nu\ell}t_s^{\ell b}\hat{\mathbf{s}} + \frac{t_p^{\nu\ell}t_p^{\ell b}}{n_\ell^2 n_b}\left(n_b^2\sin\theta_0\hat{\mathbf{z}} + n_\ell^2 w_b\hat{\boldsymbol{\kappa}}\right)\hat{\mathbf{p}}_{\nu-}\right] \cdot \hat{\mathbf{e}}^{\text{in}}. \tag{3.37}$$

Again, to touch base with Ref. [94], if we would like to evaluate the fields in the bulk, instead of the layer ℓ, we simply take $n_\ell = n_b$, ($t_{s,p}^{\ell b} = 1$), to obtain

$$\mathbf{e}_b^\omega = \left[\hat{\mathbf{s}}t_s^{\nu b}\hat{\mathbf{s}} + \frac{t_p^{\nu b}}{n_b}\left(\sin\theta_0\hat{\mathbf{z}} + w_b\hat{\boldsymbol{\kappa}}\right)\hat{\mathbf{p}}_{\nu-}\right] \cdot \hat{\mathbf{e}}^{\text{in}}, \tag{3.38}$$

that is in agreement with Eq. (3.5) of Ref. [94]. Then, we can write Eq. (3.9) as

$$\boldsymbol{\mathcal{P}}(2\omega)=\begin{cases} E_0^2\,\boldsymbol{\chi}:\mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega & \text{(cgs units)}\\ \epsilon_0 E_0^2\,\boldsymbol{\chi}:\mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega & \text{(MKS units)}\end{cases}, \tag{3.39}$$

where E_0 is the intensity of the fundamental electric field. Finally, with above equation we write Eq. (3.33) as

$$E(2\omega)=\frac{2\eta i\omega}{cW_\nu}\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega, \tag{3.40}$$

where $\eta=2\pi$ for cgs units and $\eta=1/2$ for MKS units. To ease on the notation, we define

$$\Upsilon_{\mathrm{iO}}\equiv\mathbf{e}_\ell^{2\omega}\cdot\boldsymbol{\chi}:\mathbf{e}_\ell^\omega\mathbf{e}_\ell^\omega, \tag{3.41}$$

where i stands for the incoming polarization of the fundamental electric field given by $\hat{\mathbf{e}}^{\mathrm{in}}$ in Eq. (3.37), and O for the outgoing polarization of the SH electric field given by $\hat{\mathbf{e}}^{\mathrm{out}}$ in Eq. (3.34).

From Eqs. (3.1) and (3.2) we obtain that in the cgs units ($\eta=2\pi$)

$$\begin{aligned}
|E(2\omega)|^2 &= |E_0|^4\frac{16\pi^2\omega^2}{c^2W_\nu^2}|\Upsilon_{\mathrm{iO}}|^2\\
\frac{c}{2\pi}|\sqrt{N_\nu}E(2\omega)|^2 &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta_0}\left|\frac{\sqrt{N_\nu}}{n_\ell^2}\Upsilon_{\mathrm{iO}}\right|^2\left(\frac{c}{2\pi}|\sqrt{n_\ell}E_0|^2\right)^2,\\
I(2\omega) &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta_0}\left|\frac{\sqrt{N_\nu}}{n_\ell^2}\Upsilon_{\mathrm{iO}}\right|^2 I^2(\omega),\\
\mathcal{R}_{\mathrm{iO}}(2\omega) &= \frac{32\pi^3\omega^2}{c^3\cos^2\theta_0}\left|\frac{1}{n_\ell}\Upsilon_{\mathrm{iO}}\right|^2,
\end{aligned} \tag{3.42}$$

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

$$\begin{aligned}
|E(2\omega)|^2 &= |E_0|^4\frac{\omega^2}{c^2W_\nu^2}|\Upsilon_{\mathrm{iO}}|^2\\
2\epsilon_0 c|\sqrt{N_\nu}E(2\omega)|^2 &= \frac{2\epsilon_0\omega^2}{c\cos^2\theta_0}\left|\frac{\sqrt{N_\nu}}{n_\ell^2}\Upsilon_{\mathrm{iO}}\right|^2\frac{1}{4\epsilon_0^2c^2}\left(2\epsilon_0 c|\sqrt{n_\ell}E_0|^2\right)^2,\\
I(2\omega) &= \frac{\omega^2}{2\epsilon_0c^3\cos^2\theta_0}\left|\frac{\sqrt{N_\nu}}{n_\ell^2}\Upsilon_{\mathrm{iO}}\right|^2 I^2(\omega),\\
\mathcal{R}_{\mathrm{iO}}(2\omega) &= \frac{\omega^2}{2\epsilon_0c^3\cos^2\theta_0}\left|\frac{1}{n_\ell}\Upsilon_{\mathrm{iO}}\right|^2,
\end{aligned} \tag{3.43}$$

$$\mathcal{R}_{\rm iO}(2\omega)\left\{\begin{array}{ll}\frac{32\pi^3\omega^2}{c^3\cos^2\theta_0}\left|\frac{1}{n_\ell}\Upsilon_{\rm iO}\right|^2 & \text{(cgs units)}\\ \frac{\omega^2}{2\epsilon_0 c^3\cos^2\theta_0}\left|\frac{1}{n_\ell}\Upsilon_{\rm iO}\right|^2 & \text{(MKS units)}\end{array}\right., \tag{3.44}$$

as the SHG yield, where $N_\nu = 1$ and $W_\nu = \cos\theta_0$. In the MKS unit system $\boldsymbol{\chi}$ is given in m^2/V, since it is a surface second order nonlinear susceptibility, and $\mathcal{R}_{\rm iO}$ is given in m^2/W.

`tal vez esto al apendice` At this point we mention that to recover the results of Ref. [94] which are equivalent of those of Ref. [96], we take $\mathbf{e}^{2\omega}_\ell \to \mathbf{e}^{2\omega}_\nu$, $\mathbf{e}^{\omega}_\ell \to \mathbf{e}^{\omega}_b$, and then

$$\mathcal{R}(2\omega) = \frac{32\pi^3\omega^2}{c^3\cos^2\theta_0}\left|\mathbf{e}^{2\omega}_\nu\cdot\boldsymbol{\chi}:\mathbf{e}^{\omega}_b\mathbf{e}^{\omega}_b\right|^2, \tag{3.45}$$

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 $\epsilon_b(\omega)$.

3.2 One SH Reflection

Therefore, the total radiated field at 2ω is

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

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

$$\mathbf{E}(2\omega) = \frac{2\pi i\tilde{\Omega}}{K_\ell}\mathbf{H}_\ell\cdot\boldsymbol{\mathcal{P}}(2\omega), \tag{3.46}$$

where,

$$\mathbf{H}_\ell = \hat{\mathbf{s}}\,T^{\ell v}_s\left(1 + R^{\ell b}_s\right)\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}T^{\ell v}_p\left(\hat{\mathbf{P}}_{\ell+} + R^{\ell b}_p\hat{\mathbf{P}}_{\ell-}\right). \tag{3.47}$$

3.3 $\mathcal{R}$ for different polarization cases

3.3.1 $\mathcal{R}_{pP}$

We develop five different scenarios for $\mathcal{R}_{pP}$ that explore different cases for where the polarization and fundamental fields are located. In all these scenarios, we use $\hat{\mathbf{e}}^{\rm in} = \hat{\mathbf{p}}_{v-}$ in Eq. (3.37), and $\hat{\mathbf{e}}^{\rm out} = \hat{\mathbf{P}}_{v+}$ in Eq. (**??**).

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

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

where

$$\begin{aligned} r_{pP}^\ell &= \epsilon_b(2\omega) \sin\theta_{\text{in}} \Big(\epsilon_b^2(\omega) \sin^2\theta_{\text{in}} \chi_{zzz} + \epsilon_\ell^2(\omega) k_b^2 \chi_{zxx} \Big) \\ &\quad - \epsilon_\ell(2\omega)\epsilon_\ell(\omega) k_b K_b \Big(2\epsilon_b(\omega) \sin\theta_{\text{in}} \chi_{xxz} + \epsilon_\ell(\omega) k_b \chi_{xxx} \cos(3\phi) \Big), \end{aligned} \tag{3.48}$$

and

$$\Gamma_{pP}^\ell = \frac{T_p^{\ell v} T_p^{\ell b}}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}} \left(\frac{t_p^{v\ell} t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}} \right)^2. \tag{3.49}$$

3.3.2 $\mathcal{R}_{pS}$

To obtain $R_{pS}(2\omega)$ we use $\hat{\mathbf{e}}^{\text{in}} = \hat{\mathbf{p}}_{v-}$ in Eq. (3.37), and $\hat{\mathbf{e}}^{\text{out}} = \hat{\mathbf{S}}$ in Eq. (**??**). We also use the unit vectors defined in Eqs. (P.1) and (P.2). Substituting, we get

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

where

$$r_{pS}^\ell = -\epsilon_\ell^2(\omega) k_b^2 \sin 3\phi \chi_{xxx}, \tag{3.50}$$

and

$$\Gamma_{pS}^\ell = T_s^{v\ell} T_s^{\ell b} \left(\frac{t_p^{v\ell} t_p^{\ell b}}{\epsilon_\ell(\omega)\sqrt{\epsilon_b(\omega)}} \right)^2. \tag{3.51}$$

In order to reduce above result to that of Ref. [94] and [96], 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

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

3.3.3 $\mathcal{R}_{sP}$

To obtain $R_{sP}(2\omega)$ we use $\hat{\mathbf{e}}^{\text{in}} = \hat{\mathbf{s}}$ in Eq. (3.37), and $\hat{\mathbf{e}}^{\text{out}} = \hat{\mathbf{P}}_{\nu+}$ in Eq. (**??**). We also use the unit vectors defined in Eqs. (P.1) and (P.2). Substituting, we get

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

where

$$r_{sP}^{\ell} = \epsilon_b(2\omega) \sin\theta_{\text{in}} \chi_{zxx} + \epsilon_\ell(2\omega) K_b \chi_{xxx} \cos 3\phi, \tag{3.52}$$

and

$$\Gamma_{sP}^{\ell} = \frac{T_p^{\ell\nu} T_p^{\ell b} \left(t_s^{\nu\ell} t_s^{\ell b}\right)^2}{\epsilon_\ell(2\omega)\sqrt{\epsilon_b(2\omega)}}. \tag{3.53}$$

In order to reduce above result to that of Ref. [94] and [96], we take the 2ω radiations factors for vacuum by taking $\ell = \nu$, thus $\epsilon_\ell(2\omega) = 1$, $T_p^{\nu\ell} = 1$, $T_p^{\ell b} = T_p^{\nu b}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_s^{\nu\ell} = t_s^{\nu b}$, and $t_s^{\ell b} = 1$. With these choices,

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

and

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

3.3.4 $\mathcal{R}_{sS}$

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

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

where

$$r_{sS}^{\ell} = \chi_{xxx} \sin 3\phi, \tag{3.54}$$

and

$$\Gamma_{sS}^{\ell} = T_s^{\nu\ell} T_s^{\ell b} \left(t_s^{\nu\ell} t_s^{\ell b}\right)^2. \tag{3.55}$$

In order to reduce above result to that of Ref. [94] and [96], we take the 2ω radiations factors for vacuum by taking $\ell = \nu$, thus $\epsilon_\ell(2\omega) = 1$, $T_s^{\nu\ell} = 1$, $T_s^{\ell b} = T_s^{\nu b}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_s^{\nu\ell} = t_s^{\nu b}$, and $t_s^{\ell b} = 1$. With these choices,

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

and

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

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

Table 3.1: The expressions needed to calculate the SHG yield for the (111) surface, for each polarization case.

3.3.5 Summary

We present the final expressions for each polarization case in Table 3.1.

Part II

Appendices

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,[77]

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

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,

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

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

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

Then,

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

with

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

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. (2.31) and (A.18) in the next section.

Appendix B

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

From Eq. (2.26), we have that

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

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,

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

where we use $\hat{r}\langle\mathbf{r}| = r\langle\mathbf{r}|$, $\langle\mathbf{r}'|\hat{r} = \langle\mathbf{r}|r'$, and $V^{\rm nl}(\mathbf{r},\mathbf{r}') = \langle\mathbf{r}|\hat{V}^{\rm nl}|\mathbf{r}'\rangle$ (Eq. (2.12)). Also, we have the following identity which will be used shortly,

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

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

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

where $V^{\rm nl}(\mathbf{K}',\mathbf{K}) = V^{\rm nl*}(\mathbf{K},\mathbf{K}')$, since $V^{\rm nl}(\mathbf{r}',\mathbf{r}) = V^{\rm nl*}(\mathbf{r},\mathbf{r}')$ due to the fact that $\hat{V}^{\rm nl}$ 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

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

For fully separable pseudopotentials in the Kleinman-Bylander (KB) form,[79, **?**, 81] the matrix elements $\langle \mathbf{K} | V^{\mathrm{nl}} | \mathbf{K}' \rangle = V^{\mathrm{nl}}(\mathbf{K},\mathbf{K}')$ can be readily calculated. [79] Indeed, the Fourier representation assumes the form,[81, 97, 98]

$$\begin{aligned}
V^{\mathrm{nl}}_{\mathrm{KB}}(\mathbf{K},\mathbf{K}') &= \sum_s e^{i(\mathbf{K}-\mathbf{K}')\cdot\boldsymbol{\tau}_s} \sum_{l=0}^{l_s} \sum_{m=-l}^{l} E_l F^s_{lm}(\mathbf{K}) F^{s*}_{lm}(\mathbf{K}') \\
&= \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^{l} E_l f^s_{lm}(\mathbf{K}) f^{s*}_{lm}(\mathbf{K}'), \qquad \text{(B.7)}
\end{aligned}$$

with $f^s_{lm}(\mathbf{K}) = e^{i\mathbf{K}\cdot\boldsymbol{\tau}_s} F^s_{lm}(\mathbf{K})$, and

$$F^s_{lm}(\mathbf{K}) = \int d\mathbf{r}\, e^{-i\mathbf{K}\cdot\mathbf{r}} \delta V^S_l(\mathbf{r}) \Phi^{\mathrm{ps}}_{lm}(\mathbf{r}). \qquad \text{(B.8)}$$

Here $\delta V^S_l(\mathbf{r})$ is the non-local contribution of the ionic pseudopotential centered at the atomic position $\boldsymbol{\tau}_s$ located in the unit cell, $\Phi^{\mathrm{ps}}_{lm}(\mathbf{r})$ 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. [98]. From Eq. (B.7) we find

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

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

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

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

Indeed, in DP `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. (2.71), we would like to calculate

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

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 (2.26). 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

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

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,

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

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

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

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

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

For fully separable pseudopotentials in the Kleinman-Bylander (KB) form,[79, **?**, 81] we can use Eq. (B.9) and evaluate above expression, that we have implemented in the DP code.[**?**] Explicitly,

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

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

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

From Eq. (2.73)

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

For the LDA term we have

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

where we omitted $\mathbf{k}$ in all quantities. From Eq. (B.6) we know that $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k})$ can be readily calculated, and from Appendix G, both v^{a}_{nm} and $\mathcal{C}^{\ell}_{nm}$ are also known quantities, and thus the $\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})$ are known, which in turns means that $\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm}$ are also known. For the generalized derivative $(\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}))_{;\mathbf{k}}$ we use Eq. (2.31) to write

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

where we used Eq (2.79) and $(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}}$ is given in Eq. (H.12).

Likewise,

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

where $v^{\mathcal{S},\mathrm{a}}_{nm}(\mathbf{k})$ are given in Eq. (2.27) and $(v^{\mathcal{S},\mathrm{a}}_{nm})_{;k^{\mathrm{b}}}$ is given in Eq. A(6) of Ref. [99],

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

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

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

The interband part reduces to,

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

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

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

then from Eq. (C.6)

$$
\begin{aligned}
\left((\mathcal{C}^{\ell}_{nm})_{;\mathbf{k}} - i\sum_{q}\left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} - \mathcal{C}^{\ell}_{nq}\xi^{\mathrm{a}}_{qm}\right) - i\mathcal{C}^{\ell}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn})\right) i\delta(\mathbf{k}-\mathbf{k}') &= 0 \\
\frac{1}{i}(\mathcal{C}^{\ell}_{nm})_{;\mathbf{k}} &= \sum_{q}\left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} - \mathcal{C}^{\ell}_{nq}\xi^{\mathrm{a}}_{qm}\right) + \mathcal{C}^{\ell}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
&= \sum_{q\neq nm}\left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} - \mathcal{C}^{\ell}_{nq}\xi^{\mathrm{a}}_{qm}\right) + \left(\xi^{\mathrm{a}}_{nn}\mathcal{C}^{\ell}_{nm} - \mathcal{C}^{\ell}_{nn}\xi^{\mathrm{a}}_{nm}\right)_{q=n} + \left(\xi^{\mathrm{a}}_{nm}\mathcal{C}^{\ell}_{mm} - \mathcal{C}^{\ell}_{nm}\xi^{\mathrm{a}}_{mm}\right)_{q=m} \\
&+ \mathcal{C}^{\ell}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
(\mathcal{C}^{\ell}_{nm})_{;\mathbf{k}} &= i\sum_{q\neq nm}\left(\xi^{\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} - \mathcal{C}^{\ell}_{nq}\xi^{\mathrm{a}}_{qm}\right) + i\xi^{\mathrm{a}}_{nm}(\mathcal{C}^{\ell}_{mm} - \mathcal{C}^{\ell}_{nn}) \\
&= i\sum_{q\neq nm}\left(r^{\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} - \mathcal{C}^{\ell}_{nq}r^{\mathrm{a}}_{qm}\right) + ir^{\mathrm{a}}_{nm}(\mathcal{C}^{\ell}_{mm} - \mathcal{C}^{\ell}_{nn}) \\
&= i\left(\sum_{q\neq n} r^{\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} - \sum_{q\neq m}\mathcal{C}^{\ell}_{nq}r^{\mathrm{a}}_{qm}\right) + ir^{\mathrm{a}}_{nm}(\mathcal{C}^{\ell}_{mm} - \mathcal{C}^{\ell}_{nn}),
\end{aligned}
\tag{C.9}
$$

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 $n = m$

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

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. (2.20)

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

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

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

from where

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

where we used Eq. (2.16), but from Eq. (2.27), $v_{nn}^{\mathcal{S}} = 0$, 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 $\mathcal{V}^{\sigma,\text{A},\ell}_{mn}$

As can be seen from the prefactor of Eqs. (2.76) and (2.77), they diverge as $\tilde{\omega} \to 0$. To remove this apparent divergence of χ^S, we perform a partial fraction expansion in $\tilde{\omega}$.

E.1 Intraband Contributions

For the intraband term of Eq. (2.76) 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 $C = f_{mn}\mathcal{V}^{\sigma,\text{a}}_{mn}(r^{\text{LDA},\text{b}}_{nm})_{;k^{\text{c}}}$, and $D = f_{mn}\mathcal{V}^{\sigma,\text{a}}_{mn}r^{\text{b}}_{nm}\Delta^{\text{c}}_{nm}$.

Time-reversal symmetry leads to the following relationships:

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

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. (2.79) 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

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

the second term is reduced to

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

and by using (2.79), the third term is reduced to

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

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

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

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

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

If we simplify,

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

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

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

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. (2.77) 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),

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

We manipulate indices and simplify,

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

and substitute in (2.77),

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

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

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

We use (E.13),

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

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

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

Appendix F

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

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

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

for which we need the following triple commutator

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

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,

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

Then,

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

We use the following identity

$$\left(\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K'^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{b}}\partial K'^{\mathrm{a}}}\right)\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}$$
$$=\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}\Big(r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{b}}-V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}r'^{\mathrm{b}}-r^{\mathrm{b}}r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')+r^{\mathrm{b}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}\Big)e^{i\mathbf{K}'\cdot\mathbf{r}'}$$
$$=\left(\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K'^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{b}}\partial K'^{\mathrm{a}}}\right)\langle\mathbf{K}|V^{\mathrm{nl}}|\mathbf{K}'\rangle, \tag{F.5}$$

to write

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

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 $[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\mathrm{b}}]$,[100] and thus we could have the value of the matrix elements of the triple commutator.[90]

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

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

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 $m_e\mathbf{v} = -i\hbar\nabla$ into Eqs. (2.72) and (2.70) we obtain,[87]

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

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.[87]

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. (2.73) $\boldsymbol{\mathcal{V}}^{\sigma,\ell}_{nm}(\mathbf{k}) \neq (\omega^\sigma_{nm}/\omega_{nm})\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}_{nm}(\mathbf{k})$ 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.

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

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

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. (2.26))

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

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

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

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

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

then

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

and from Eq. (H.5),

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

Now, there are two cases. We use Eq. (2.31).

Case $n = m$

$$
\begin{aligned}
\nabla_{k^{\mathrm{a}}} v^{\mathrm{LDA,b}}_{nn} &= -i\tau^{\mathrm{ab}}_{nn} + i\sum_{\ell}\left(\xi^{\mathrm{a}}_{n\ell} v^{\mathrm{LDA,b}}_{\ell n} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell n}\right) \\
&= -i\tau^{\mathrm{ab}}_{nn} - \sum_{\ell\neq n}\left(r^{\mathrm{a}}_{n\ell}\omega^{\mathrm{LDA}}_{\ell n} r^{\mathrm{b}}_{\ell n} - \omega^{\mathrm{LDA}}_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell n}\right) \\
&= -i\tau^{\mathrm{ab}}_{nn} - \sum_{\ell\neq n}\omega^{\mathrm{LDA}}_{\ell n}\left(r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell n} - r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell n}\right),
\end{aligned} \tag{H.10}
$$

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

Case $n \neq m$

$$
\begin{aligned}
(v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} &= -i\tau^{\mathrm{ab}}_{nm} + i\sum_{\ell\neq m\neq n}\left(\xi^{\mathrm{a}}_{n\ell} v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\right) \\
&\quad + i\left(\xi^{\mathrm{a}}_{nm} v^{\mathrm{LDA,b}}_{mm} - v^{\mathrm{LDA,b}}_{nm}\xi^{\mathrm{a}}_{mm}\right) \\
&\quad + i\left(\xi^{\mathrm{a}}_{nn} v^{\mathrm{LDA,b}}_{nm} - v^{\mathrm{LDA,b}}_{nn}\xi^{\mathrm{a}}_{nm}\right) + iv^{\mathrm{LDA,b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
&= -i\tau^{\mathrm{ab}}_{nm} - \sum_{\ell}\left(\omega^{\mathrm{LDA}}_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m}\right) + i\xi^{\mathrm{a}}_{nm}(v^{\mathrm{LDA,b}}_{mm} - v^{\mathrm{LDA,b}}_{nn}) \\
&= -i\tau^{\mathrm{ab}}_{nm} - \sum_{\ell}\left(\omega^{\mathrm{LDA}}_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m}\right) + ir^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn},
\end{aligned} \tag{H.11}
$$

where we use Δ^{a}_{mn} of Eq. (2.79). Now, for $n \neq m$, Eqs. (2.31), (D.9) and (H.11) and the chain rule, give

$$
\begin{aligned}
(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} &= \left(\frac{v^{\mathrm{LDA,b}}_{nm}}{i\omega^{\mathrm{LDA}}_{nm}}\right)_{;k^{\mathrm{a}}} = \frac{1}{i\omega^{\mathrm{LDA}}_{nm}}\left(v^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{a}}} - \frac{v^{\mathrm{LDA,b}}_{nm}}{i(\omega^{\mathrm{LDA}}_{nm})^2}\left(\omega^{\mathrm{LDA}}_{nm}\right)_{;k^{\mathrm{a}}} \\
&= -i\tau^{\mathrm{ab}}_{nm} + \frac{i}{\omega^{\mathrm{LDA}}_{nm}}\sum_{\ell}\left(\omega^{\mathrm{LDA}}_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m}\right) + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn}}{\omega^{\mathrm{LDA}}_{nm}} \\
&\quad - \frac{r^{\mathrm{b}}_{nm}}{\omega^{\mathrm{LDA}}_{nm}}\left(\omega^{\mathrm{LDA}}_{nm}\right)_{;k^{\mathrm{a}}} \\
&= -i\tau^{\mathrm{ab}}_{nm} + \frac{i}{\omega^{\mathrm{LDA}}_{nm}}\sum_{\ell}\left(\omega^{\mathrm{LDA}}_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m}\right) + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn}}{\omega^{\mathrm{LDA}}_{nm}} \\
&\quad - \frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}}\frac{v^{\mathrm{LDA,a}}_{nn} - v^{\mathrm{LDA,a}}_{mm}}{m_e} \\
&= -i\tau^{\mathrm{ab}}_{nm} + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn} + r^{\mathrm{b}}_{nm}\Delta^{\mathrm{a}}_{mn}}{\omega^{\mathrm{LDA}}_{nm}} + \frac{i}{\omega^{\mathrm{LDA}}_{nm}}\sum_{\ell}\left(\omega^{\mathrm{LDA}}_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m}\right),
\end{aligned}
\tag{H.12}
$$

where the $-i\tau^{\mathrm{ab}}_{nm}$ term, generalizes the usual expresion of $\mathbf{r}_{nm;\mathbf{k}}$ for local Hamiltonians,[73, 101, 99, 89] 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. (2.71), we could start form Eq. (H.1) again, and replace $\hat{\mathbf{v}}^{\mathrm{LDA}}$ by $\boldsymbol{\mathcal{V}}^{\mathrm{LDA}}$, to obtain the equivalent of Eqs. (H.10) and (H.11), for which we need to calculate the new τ^{ab}_{nm}, that is given by

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

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 $\mathcal{T}^{\mathrm{ab}}_{nm} \to \tau^{\mathrm{ab}}_{nm}$. Thus, the layered expression for $\mathcal{V}_{nm}^{\mathrm{LDA},a}$ becomes

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

where

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

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.[90] The expression for C_{nm}^{ℓ} 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 $\mathbf{v}^{\text{LDA}}_{nm}(\mathbf{k})$, stored in `vldaMatElem` is available for the calculation of the response, and with it we calculate (Eqs. (2.29) and (2.30)),

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

If option `-n` is not chosen, then the contribution of $\mathbf{v}^{\text{nl}}_{nm}(\mathbf{k})$ 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)

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

The first LDA term is

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

If option `-n` is not chosen in `all_responses.sh` Eq. (I.8) is not calculated and
• $\mathcal{V}^{\text{LDA},\text{a},\ell}_{nm} \to$ `me_cpmn_*`
If option `-n` is chosen Eq. (I.8) must be calculated as given in `set_input_ascii.f90`. We mention that $\mathcal{V}^{\text{LDA},\text{a},\ell}_{nm}$ can be computed directly,[102] 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

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

where
• for $n \neq m$
Eq. (C.3)

$$\begin{aligned}(v^{\mathrm{LDA,a}}_{nm})_{;k^{\mathrm{b}}} &= i m_e\left(\Delta^{b}_{nm} r^{\mathrm{a}}_{nm} + \omega^{\mathrm{LDA}}_{nm}(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}}\right)\\ (v^{\mathrm{LDA,a}}_{mn})_{;k^{\mathrm{b}}} &= \left((v^{\mathrm{LDA,a}}_{nm})_{;k^{\mathrm{b}}}\right)^{*} \quad \text{for} \quad n \neq m,\end{aligned} \tag{I.11}$$

with Eq. (2.79)

$$\Delta^{\mathrm{a}}_{nm} = v^{\mathrm{LDA,a}}_{nn} - v^{\mathrm{LDA,a}}_{mm}, \tag{I.12}$$

and (H.12)

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

where $\mathcal{T}^{\mathrm{ab}}_{nm} \approx 0$.
• for $n = m$
Since $\mathcal{T}^{\mathrm{ab}}_{nn} \approx (\hbar/m_e)\delta_{\mathrm{ab}}$, Eq. (2.90) gives

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

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

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

For the scissor related term we have: Eq. (C.4) , (C.5) and (2.27)

$$\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm} = \frac{1}{2}\sum_q \left(v^{\mathcal{S},\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} + \mathcal{C}^{\ell}_{nq}v^{\mathcal{S},\mathrm{a}}_{qm}\right)$$
$$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} = \frac{1}{2}\sum_q \left((v^{\mathcal{S},\mathrm{a}}_{nq})_{;k^{\mathrm{b}}}\mathcal{C}^{\ell}_{qm} + v^{\mathcal{S},\mathrm{a}}_{nq}(\mathcal{C}^{\ell}_{qm})_{;k^{\mathrm{b}}} + (\mathcal{C}^{\ell}_{nq})_{;k^{\mathrm{b}}}v^{\mathcal{S},\mathrm{a}}_{qm} + \mathcal{C}^{\ell}_{nq}(v^{\mathcal{S},\mathrm{a}}_{qm})_{;k^{\mathrm{b}}}\right), \tag{I.16}$$

with Eqs. (2.27) and (C.5)

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

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

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

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

• 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 $r^{\mathrm{a}}_{nn} = 0$ 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),

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

and

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

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

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

$$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} = \frac{i\Sigma}{2}\sum_q \Big(f_{qn}\Big[(r^{\mathrm{a}}_{nq})_{;k^{\mathrm{b}}}\mathcal{C}^{\ell}_{qm} + r^{\mathrm{a}}_{nq}(\mathcal{C}^{\ell}_{qm})_{;k^{\mathrm{b}}}\Big] + f_{mq}\Big[(\mathcal{C}^{\ell}_{nq})_{;k^{\mathrm{b}}}r^{\mathrm{a}}_{qm} + \mathcal{C}^{\ell}_{nq}(r^{\mathrm{a}}_{qm})_{;k^{\mathrm{b}}}\Big]\Big)$$

$$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{b}}} = \left(\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}}\right)^{*}, \tag{I.23}$$

• Coding:
$(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \to$ `derMatElem` $\mathcal{C}^{\ell}_{nm} \to$ `cfMatElem` $r^{\mathrm{a}}_{nm} \to$ `posMatElem` $(\mathcal{C}^{\ell}_{nm})_{;k^{\mathrm{b}}} \to$ `gdf`,
and
$\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} \to$ `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,
• $\mathcal{V}_{nm}^{\sigma,\mathrm{a},\ell}(\mathbf{k}) = \mathcal{V}_{nm}^{\mathrm{LDA},\mathrm{a},\ell}(\mathbf{k}) + \mathcal{V}_{nm}^{\mathcal{S},\mathrm{a},\ell}(\mathbf{k})$
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 $\Delta_{nm}^{\sigma,\mathrm{a},\ell}(\mathbf{k})$

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

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

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

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`,

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

$$\left(\mathcal{V}^{\mathrm{LDA,a},\ell}_{mn}\right)_{;k^{\mathrm{b}}} = \left(\left(\mathcal{V}^{\mathrm{LDA,a},\ell}_{nm}\right)_{;k^{\mathrm{b}}}\right)^{*}, \tag{I.29}$$

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

I.4 Summary

- $\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}(\mathbf{k}) = \mathcal{V}^{\mathrm{LDA,a},\ell}_{nm}(\mathbf{k}) + \mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}(\mathbf{k}) \to$ `calMomMatElem`
- $\left(\mathcal{V}^{\mathrm{LDA,a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} \to$ `gdcalVlda`
- $\left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} \to$ `gdcalVS`
- $\left(\mathcal{V}^{\sigma,\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} = \left(\mathcal{V}^{\mathrm{LDA,a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} + \left(\mathcal{V}^{\mathcal{S},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} \to$ `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`) → $\mathbf{v}^{\sigma}_{nm}$ (`momMatElem`)
  2. $(\boldsymbol{\mathcal{V}}^{\sigma}_{nm})_{;\mathbf{k}}$ (`gdcalVsig`) → $(\mathbf{v}^{\sigma}_{nm})_{;\mathbf{k}}$ (`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
    $\boldsymbol{\mathcal{V}}^{\sigma}_{nm}$ → `calVsig` and $(\boldsymbol{\mathcal{V}}^{\sigma}_{nm})_{;\mathbf{k}}$ → `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.

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

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

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

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

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

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

and

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

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

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.[99], which were derived by using Eq. 19 of Aversa and Sipe.[73] To obtain above equations, we started from Eq. 18 of Aversa and Sipe,[73] 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.[99], 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 $\boldsymbol{\mathcal{V}}^{\sigma}_{nm} \to \mathbf{v}^{\sigma}_{nm}$ and $\boldsymbol{\mathcal{V}}^{\sigma}_{nm;\mathbf{k}} \to \mathbf{v}^{\sigma}_{nm;\mathbf{k}}$. 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

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

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. (2.72) 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.[90] 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

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

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,

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

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 $\mathcal{V}^{\Sigma}_{nm}$

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

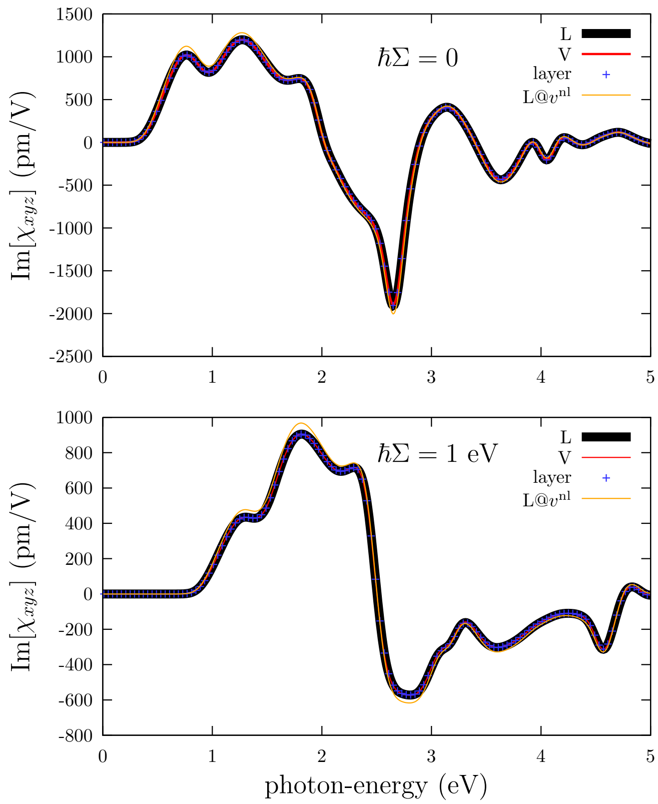

Figure I.1: Im[χ_{xyz}] for GaAs, 10 Ha and 47 **k**-points, using the layered formulation and mimicking a bulk. The correction due to $\mathbf{v}^{\mathrm{nl}}$, also agrees with the velocity and the layered approach (not shown in the figure for clarity).

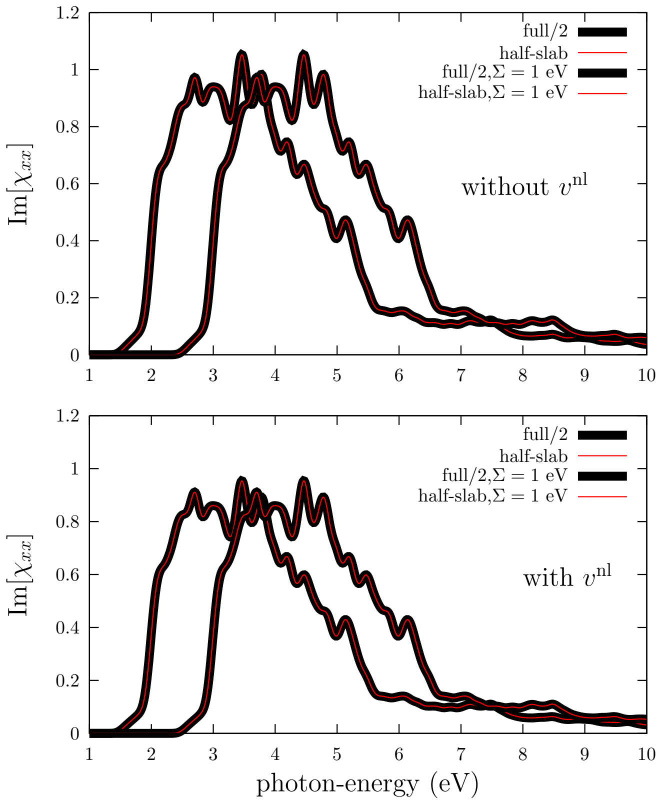

Figure I.2: Im[χ_{xx}] for a Si(111):As surface of 6-layers, 5 Ha and 14 **k**-points using the layered formulation. The full-slab result is twice the half-slab result, as it must be.

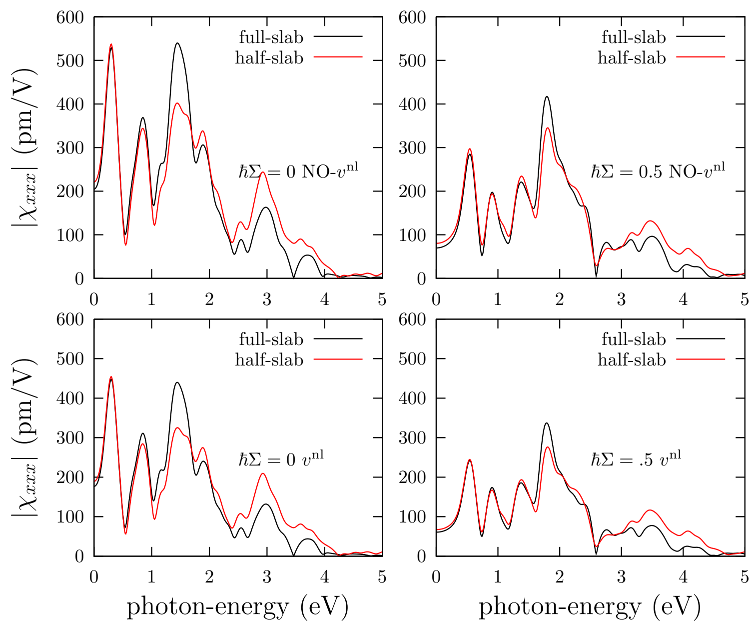

Figure I.3: $|\chi_{xxx}|$ for a Si(100)2 × 1 surface of 16 Si-layers and one H layer, 10 Ha, 132 bands, 244 **k**-points, and 1000 pwvs in DPŮ, using the layered formulation. We see that $\chi^{\text{half}-\text{slab}}_{xxx} \sim \chi^{\text{full}-\text{slab}}_{xxx}$, validating the layer-by-layer approach.

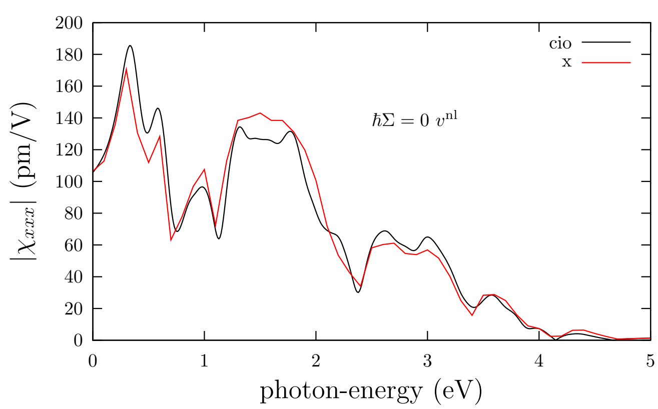

Figure I.4: $|\chi_{xxx}|$ for a Si(100)2 × 1 surface of 12 Si-layers and one H layer, 5 Ha, 100 bands and 244 **k**-points for the CIO-TINIBA®-coding and 256 **k**-point for the X-DP©-coding. Both broadened by 0.1 eV.

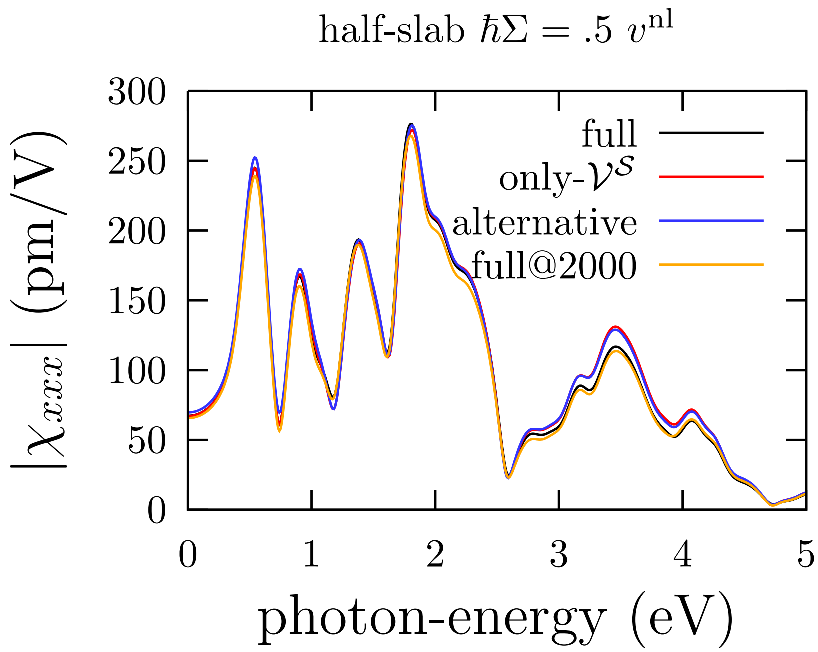

Figure I.5: $|\chi_{xxx}|$ for a Si(100)2×1 surface of 16 Si-layers and one H layer, 10 Ha, 132 bands, 244 **k**-points and and 1000 pwvs in DPŮ, using the layered formulation. "Full" uses full coding of $\mathcal{V}^{\mathcal{S}}_{nm}$ and $\mathcal{V}^{\mathcal{S}}_{nm:\mathbf{k}}$ through Eq. (C.4); "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 **k** and −**k** terms of expressions (**??**) and (**??**) to obtain:

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

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

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. (2.77) implies

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

with similar results for the other two terms. First, we collect the 2ω terms form Eq. (??) that contribute to Eq. (2.76)

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

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

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

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^2_{nm}} + \frac{3D}{2\omega^3_{nm}}\right]\frac{1}{\omega_{nm}-\omega} + \frac{D}{2\omega^2_{nm}}\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^2_{nm}} + \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^3_{nm}}\right]\frac{1}{\omega_{nm}-\omega}\right.\\
&\quad\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^2_{nm}} - \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^2_{nm}} - \frac{i}{2}\left[\frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}\right.\right.\\
&\quad\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^2_{nm}}\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^2_{nm}} - \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.\\
&\quad\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^2_{nm}}\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^2_{nm}} + \frac{1}{\omega_{nm}}\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right.\\
&\quad\left. + \frac{1}{\omega_{nm}}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}] - \frac{1}{\omega^2_{nm}}\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

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

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 $\chi^{s,\ell}_{\mathrm{abc}} = \chi^{s,\ell}_{e,\mathrm{abc}} + \chi^{s,\ell}_{i,\mathrm{abc}}$ where $\chi^{s,\ell}_{i,\mathrm{abc}} = \chi^{s,\ell}_{i,\mathrm{abc},\omega} + \chi^{s,\ell}_{i,\mathrm{abc},2\omega}$. 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 $\mathcal{R}^{\mathrm{a},\ell}_{nm} \to r^{\mathrm{a}}_{nm}$.

In summary we have

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

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

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

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

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

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

and

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

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

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 $-i\hbar\nabla$.

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

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

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)

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

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

and

$$\begin{aligned}
\langle n\mathbf{k}|[r_e^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle &= \sum_{\ell\mathbf{k}''}\Bigg(\langle n\mathbf{k}|r_e^{\mathrm{a}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|p^{\mathrm{b}}|m\mathbf{k}'\rangle \\
&- \langle n\mathbf{k}|p^{\mathrm{b}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|r_e^{\mathrm{a}}|m\mathbf{k}'\rangle\Bigg) \\
&= \sum_{\ell\mathbf{k}''}\Bigg((1-\delta_{n\ell})\delta(\mathbf{k}-\mathbf{k}'')\xi^{\mathrm{a}}_{n\ell}\delta(\mathbf{k}''-\mathbf{k}')p^{\mathrm{b}}_{\ell m} \\
&- \delta(\mathbf{k}-\mathbf{k}'')p^{\mathrm{b}}_{n\ell}(1-\delta_{\ell m})\delta(\mathbf{k}''-\mathbf{k}')\xi^{\mathrm{a}}_{\ell m}\Bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\sum_{\ell}\Bigg((1-\delta_{n\ell})\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} \\
&- (1-\delta_{\ell m})p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\Bigg(\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} - p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big) \\
&+ p^{\mathrm{b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn})\Bigg).
\end{aligned} \tag{M.6}$$

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

$$\begin{aligned}
i\delta(\mathbf{k}-\mathbf{k}')\Bigg((p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} - i\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} - p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big) \\
- ip^{\mathrm{b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn})\Bigg) = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'),
\end{aligned} \tag{M.7}$$

then

$$\begin{aligned}
(p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} &= \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} - p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big) \\
&+ ip^{\mathrm{b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}),
\end{aligned} \tag{M.8}$$

and from Eq. (M.5),

$$\nabla_{k^{\mathrm{a}}}p^{\mathrm{b}}_{nm} = \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} - p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big). \tag{M.9}$$

Now, there are two cases. We use Eqs. (**??**) and (2.31).

Case $n = m$

$$\frac{1}{\hbar}\nabla_{k^{\mathrm{a}}} p^{\mathrm{b}}_{nn} = \delta_{ab} - \frac{m_e}{\hbar}\sum_{\ell}\omega_{\ell n}\left(r^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell n} + r^{\mathrm{b}}_{n\ell}r^{\mathrm{a}}_{\ell n}\right), \tag{M.10}$$

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

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

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. (2.31), (D.9) and (M.11) and the chain rule, give

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

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 (2.31) as

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

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

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

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. (2.31) trivially gives

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

then, using Eq. (N.2)

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

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

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

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

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

is the explicit functional form of the velocity or momentum operator. From Eq. (2.63), 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. (2.65) and (2.63) 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

$$\begin{aligned} \boldsymbol{\mathcal{V}}_{mn}(\mathbf{k}) &\approx \frac{1}{2m}\int d^3r\mathcal{F}_\ell(z)\Big[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}^*\psi^*_{m\mathbf{k}}(\mathbf{r}) + \psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}\psi_{n\mathbf{k}}(\mathbf{r})\Big], && \text{(O.6)} \\ &= \frac{1}{m}\int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{\mathcal{F}_\ell(z)\mathbf{p} + \mathbf{p}\mathcal{F}_\ell(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r}), && \text{(O.7)} \\ &= \frac{1}{m}\int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\boldsymbol{\mathcal{P}}}\psi_{n\mathbf{k}}(\mathbf{r}) \equiv \frac{1}{m}\boldsymbol{\mathcal{P}}_{mn}(\mathbf{k}). && \text{(O.8)} \end{aligned}$$

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

****

We would obtain, instead of Eq. (2.76) and (2.77)

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

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

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

Appendix P

Derived expressions for the SHG yield

P.1 Some useful expressions

We are interested in finding

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

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

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

and

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

where ϕ the angle with respect to the x axis.

P.1.1 2ω terms

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

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

and neglecting the multiple reflections reduces this expression to

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

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

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

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

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

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

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

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

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

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

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

P.1.2 1ω terms

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

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

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

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

so

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\chi_{xxz}, \chi_{yyz}, \chi_{zxx}, \chi_{zyy}, \chi_{zzz}. \tag{P.14}$$

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

$$\begin{aligned} &\chi_{xxz} = \chi_{yyz}, \\ &\chi_{zxx} = \chi_{zyy}, \\ &\chi_{zzz}. \end{aligned} \tag{P.15}$$

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

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

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

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

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

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

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

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

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

P.2.1 For the (111) surface

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

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

We reduce terms,

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

where

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

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

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

and reduce,

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

where

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

P.2.2 For the (110) surface

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

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

where

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

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

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

where

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

P.2.3 For the (001) surface

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

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

where

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

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

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

where

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

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

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

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

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

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

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

$$\begin{aligned}\Upsilon_{pS} = \Gamma_{pS}\Big[&- n_\ell^4 w_b^2 \sin\phi\cos^2\phi\chi_{xxx} - 2n_\ell^4 w_b^2 \sin^2\phi\cos\phi\chi_{xxy} \\ &- 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{xxz} - n_\ell^4 w_b^2 \sin^3\phi\chi_{xyy} \\ &- 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin^2\phi\chi_{xyz} - n_b^4 \sin^2\theta_0 \sin\phi\chi_{xzz} \\ &+ n_\ell^4 w_b^2 \cos^3\phi\chi_{yxx} + 2n_\ell^4 w_b^2 \sin\phi\cos^2\phi\chi_{yxy} \\ &+ 2n_\ell^2 n_b^2 w_b \sin\theta_0 \cos^2\phi\chi_{yxz} + n_\ell^4 w_b^2 \sin^2\phi\cos\phi\chi_{yyy} \\ &+ 2n_\ell^2 n_b^2 w_b \sin\theta_0 \sin\phi\cos\phi\chi_{yyz} + n_b^4 \sin^2\theta_0 \cos\phi\chi_{yzz}\Big],\end{aligned} \tag{P.28}$$

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

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

P.3.1 For the (111) surface

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

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

We reduce terms,

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

where

$$r_{pS}^{\mathrm{MR},(111)} = -\left(r_p^{M-}\right)^2 w_\ell^2 \chi_{xxx}\sin 3\phi. \tag{P.30}$$

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

$$\begin{aligned}
\Upsilon_{pS} &= \Gamma_{pS}\big[n_\ell^4 w_b^2 (\sin^3\phi - 3\sin\phi\cos^2\phi)\chi_{xxx}\big] \\
&= \Gamma_{pS}\big[-n_\ell^4 w_b^2 \chi_{xxx}\sin 3\phi\big] \qquad\qquad (\mathrm{P.31}) \\
&= \Gamma_{pS}\, r_{pS}^{(111)},
\end{aligned}$$

where

$$r_{pS}^{(111)} = -n_\ell^4 w_b^2 \chi_{xxx}\sin 3\phi, \tag{P.32}$$

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

P.3.2 For the (110) surface

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

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

where

$$
r_{pS}^{\mathrm{MR},(110)} = r_p^{M+}r_p^{M-}w_\ell \sin\theta_0(\chi_{yyz}-\chi_{xxz})\sin 2\phi. \tag{P.33}
$$

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

$$
r_{pS}^{(110)} = n_\ell^2 n_b^2 w_b \sin\theta_0(\chi_{yyz}-\chi_{xxz})\sin 2\phi, \tag{P.34}
$$

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

P.3.3 For the (001) surface

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

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

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

$$
\Upsilon_{pS}^{\mathrm{MR},(001)} = \Upsilon_{pS}^{(001)} = 0. \tag{P.35}
$$

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

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

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

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

$$\Gamma^{\mathrm{MR}}_{sP} = \frac{T_p^{v\ell}}{N_\ell}\left(t_s^{v\ell} r_s^{M+}\right)^2 \tag{P.37}$$

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

$$\begin{aligned}\Upsilon_{sP} = \Gamma_{sP}\Big[& N_\ell^2 W_b\big(-\sin^2\phi\cos\phi\chi_{xxx} + 2\sin\phi\cos^2\phi\chi_{xxy} - \cos^3\phi\chi_{xyy}\big)\\ & + N_\ell^2 W_b\big(-\sin^3\phi\chi_{yxx} + 2\sin^2\phi\cos\phi\chi_{yxy} - \sin\phi\cos^2\phi\chi_{yyy}\big)\\ & + N_b^2\sin\theta_0\big(+\sin^2\phi\chi_{zxx} - 2\sin\phi\cos\phi\chi_{zxy} + \cos^2\phi\chi_{zyy}\big)\Big],\end{aligned} \tag{P.38}$$

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

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

P.4.1 For the (111) surface

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

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

We reduce terms,

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

where

$$r_{sP}^{\mathrm{MR},(111)} = R_p^{M+} \sin\theta_0 \chi_{zxx} + R_p^{M-} W_\ell \chi_{xxx} \cos 3\phi. \tag{P.40}$$

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

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

and reduce,

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

where

$$r_{sP}^{(111)} = N_b^2 \sin\theta_0 \chi_{zxx} + N_\ell^2 W_b \chi_{xxx} \cos 3\phi. \tag{P.41}$$

P.4.2 For the (110) surface

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

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

where

$$r_{sP}^{\mathrm{MR},(110)} = R_p^{M+}\sin\theta_0\left(\frac{\chi_{zxx}+\chi_{zyy}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right). \tag{P.42}$$

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

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

where

$$r_{sP}^{(110)} = N_b^2\sin\theta_0\left(\frac{\chi_{zxx}+\chi_{zyy}}{2} + \frac{\chi_{zyy}-\chi_{zxx}}{2}\cos 2\phi\right). \tag{P.43}$$

P.4.3 For the (001) surface

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

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

where

$$r_{sP}^{\mathrm{MR},(001)} = R_p^{M+}\sin\theta_0\chi_{zxx}. \tag{P.44}$$

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

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

where

$$r_{sP}^{(001)} = N_b^2 \sin\theta_0 \chi_{zxx}. \tag{P.45}$$

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

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

$$\begin{aligned}\Upsilon_{sS}^{\mathrm{MR}} = \Gamma_{sS}^{\mathrm{MR}}\Big[&- \sin^3\phi\chi_{xxx} + 2\sin^2\phi\cos\phi\chi_{xxy} - \sin\phi\cos^2\phi\chi_{xyy} \\ &+ \sin^2\phi\cos\phi\chi_{yxx} - 2\sin\phi\cos^2\phi\chi_{yxy} + \cos^3\phi\chi_{yyy}\Big].\end{aligned} \tag{P.46}$$

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

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

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

$$\begin{aligned}\Upsilon_{sS} = \Gamma_{sS}\Big[&- \sin^3\phi\chi_{xxx} + 2\sin^2\phi\cos\phi\chi_{xxy} - \sin\phi\cos^2\phi\chi_{xyy} \\ &+ \sin^2\phi\cos\phi\chi_{yxx} - 2\sin\phi\cos^2\phi\chi_{yxy} + \cos^3\phi\chi_{yyy}\Big],\end{aligned} \tag{P.48}$$

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

$$\Gamma_{sS} = T_s^{v\ell} T_s^{\ell b} \left(t_s^{v\ell} t_s^{\ell b}\right)^2. \tag{P.49}$$

We note that both Eqs. (P.46) and (P.48) are identical save for the different Γ_{sS} terms. Therefore, we can safely derive the equations only once, and then use $\Gamma_{sS}^{\mathrm{MR}}$ when we wish to include multiple reflections, or Γ_{sS} when we do not.

P.5.1 For the (111) surface

We take Eqs. (P.46) and (P.13), eliminate the components that do not contribute, and apply the the symmetry relations as follows,

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

where

$$r_{sS}^{\text{MR},(111)} = \chi_{xxx}\sin 3\phi. \tag{P.50}$$

As mentioned above,

$$r_{sS}^{(111)} = r_{sS}^{\text{MR},(111)}, \tag{P.51}$$

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

P.5.2 For the (110) surface

When considering Eqs. (P.46) and (P.14), we see that there are no nonzero components that contribute. Therefore,

$$\Upsilon_{pS}^{\text{MR},(110)} = \Upsilon_{pS}^{(110)} = 0. \tag{P.52}$$

P.5.3 For the (001) surface

When considering Eqs. (P.46) and (P.14), we see that there are no nonzero components that contribute. Therefore,

$$\Upsilon_{sS}^{\text{MR},(001)} = \Upsilon_{sS}^{(001)} = 0. \tag{P.53}$$

Appendix Q

Some limiting cases of interest

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

Q.1 The two layer model

In order to reduce above result to that of Ref. [94] and [96], we now consider that $\mathcal{P}(2\omega)$ is evaluated in the vacuum region, while the fundamental fields are evaluated in the bulk region. To do this, we take the 2ω radiations factors for vacuum by taking $\ell = v$, thus $\epsilon_\ell(2\omega) = 1$, $T_p^{\ell v} = 1$, $T_p^{\ell b} = T_p^{vb}$, and the fundamental field inside medium b by taking $\ell = b$, thus $\epsilon_\ell(\omega) = \epsilon_b(\omega)$, $t_p^{v\ell} = t_p^{vb}$, and $t_p^{\ell b} = 1$. With these choices

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

where,

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

and

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

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

To consider the 2ω fields in the bulk, we start with Eq. (3.47) but substitute $\ell \to b$, thus

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

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

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

and we define

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

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

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

The 1ω fields will still be evaluated inside the bulk, so we have Eq. (3.38)

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

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

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

and

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

So lastly, we have that

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

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

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

and reducing,

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

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

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

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

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

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

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

To consider the 1ω fields in the vacuum, we start with Eq. (3.36) 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

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

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

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

and

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

We also require the 2ω fields evaluated in the vacuum, which is Eq. (3.35),

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

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

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

So lastly, we have that

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

and after eliminating components,

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

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

where

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

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

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

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

and Eq. (3.38),

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

Thus,

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

We eliminate and replace components,

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

so lastly

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

where

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

Appendix R

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

In this treatment we follow the work of Ref. [96]. They define the following for all polarizations;

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

where

$$
\begin{aligned}
\kappa &= \tilde{\omega} \sin\theta, \\
w_0 &= \sqrt{\tilde{\omega} - \kappa^2} = \tilde{\omega}\cos\theta, \qquad \text{(R.2)} \\
w &= \sqrt{\tilde{\omega}\epsilon(\omega) - \kappa^2} = \tilde{\omega} k_z(\omega). \qquad \text{(R.3)}
\end{aligned}
$$

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,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

and we can finally complete the expression,

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

where

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

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

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

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

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

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

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

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

As before, we must calculate

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

to obtain the final expression,

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

where

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

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

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

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

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

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

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

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

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

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

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

where

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

R.4 Summary

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

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

The necessary factors are summarized in Table R.1.

Bibliography

[1] B. Baroli, M.G. Ennas, F. Loffredo, M. Isola, R. Pinna, and M.A. López-Quintela. Penetration of metallic nanoparticles in human full-thickness skin. *Journal of Investigative Dermatology*, 127(7):1701–1712, 2007.

[2] K. Lindfors, T. Kalkbrenner, P. Stoller, and V. Sandoghdar. Detection and spectroscopy of gold nanoparticles using supercontinuum white light confocal microscopy. *Physical Review Letters*, 93(3):37401, 2004.

[3] H. Haick. Chemical sensors based on molecularly modified metallic nanoparticles. *Journal of Physics D: Applied Physics*, 40:7173, 2007.

[4] S. Berciaud, D. Lasne, G.A. Blab, L. Cognet, and B. Lounis. Photothermal heterodyne imaging of individual metallic nanoparticles: Theory versus experiment. *Physical Review B*, 73(4):045424, 2006.

[5] A. Kamyshny, M. Ben-Moshe, S. Aviezer, and S. Magdassi. Ink-jet printing of metallic nanoparticles and microemulsions. *Macromolecular Rapid Communications*, 26(4):281–288, 2005.

[6] J.R. Krenn, A. Dereux, J.C. Weeber, E. Bourillot, Y. Lacroute, J.P. Goudonnet, G. Schider, W. Gotschy, A. Leitner, and F.R. Aussenegg. Squeezing the optical near-field zone by plasmon coupling of metallic nanoparticles. *Physical Review Letters*, 82(12):2590–2593, 1999.

[7] S. Pillai, K.R. Catchpole, T. Trupke, and M.A. Green. Surface plasmon enhanced silicon solar cells. *Journal of Applied Physics*, 101:093105, 2007.

[8] Z.F. Li and E. Ruckenstein. Water-soluble poly (acrylic acid) grafted luminescent silicon nanoparticles and their use as fluorescent biological staining labels. *Nano Letters*, 4(8):1463–1467, 2004.

[9] P. Figliozzi, L. Sun, Y. Jiang, N. Matlis, B. Mattern, M.C. Downer, S.P. Withrow, C.W. White, W.L. Mochán, and B.S. Mendoza. Single-beam and enhanced two-beam second-harmonic generation from silicon nanocrystals by use of spatially inhomogeneous femtosecond pulses. *Physical Review Letters*, 94(4):47401, 2005.

[10] R.W. Boyd. *Nonlinear Optics*. Academic Press, 2003.

[11] J.C. Diels and W. Rudolph. *Ultrashort Laser Pulse Phenomena*. Academic Press, 2006.

[12] Y.R. Shen. *The Principles of Nonlinear Optics*, volume 1. Wiley-Interscience, 1984.

[13] A.L. Schawlow and C.H. Townes. Infrared and optical masers. *Physical Review*, 112(6):1940–1949, Dec 1958.

[14] P.A. Franken, A.E. Hill, C.W. Peters, and G. Weinreich. Generation of optical harmonics. *Physical Review Letters*, 7(4):118–119, Aug 1961.

[15] J.A. Armstrong, N. Bloembergen, J. Ducuing, and P.S. Pershan. Interactions between light waves in a nonlinear dielectric. *Physical Review*, 127(6):1918–1939, Sep 1962.

[16] N. Bloembergen and P.S. Pershan. Light waves at the boundary of nonlinear media. *Physical Review*, 128(2):606–622, Oct 1962.

[17] R.W. Terhune, P.D. Maker, and C.M. Savage. Optical harmonic generation in calcite. *Physical Review Letters*, 8(10):404–406, May 1962.

[18] B. Lax, J.G. Mavroides, and D.F. Edwards. Nonlinear interband and plasma effects in solids. *Physical Review Letters*, 8(4):166–168, 1962.

[19] N. Bloembergen, R.K. Chang, S.S. Jha, and C.H. Lee. Optical second-harmonic generation in reflection from media with inversion symmetry. *Physical Review*, 174(3):813–822, Oct 1968.

[20] C. Flytzanis and J. Ducuing. Second-order optical susceptibilities of III-V semiconductors. *Physical Review*, 178(3):1218–1228, Feb 1969.

[21] A.E. Siegman. *Lasers*. University Science Books, 1986.

[22] C.K. Chen, A.R.B. de Castro, and Y.R. Shen. Surface-enhanced second-harmonic generation. *Physical Review Letters*, 46(2):145–148, Jan 1981.

[23] P. Guyot-Sionnest and Y.R. Shen. Bulk contribution in surface second-harmonic generation. *Physical Review B*, 38(12):7985–7989, Oct 1988.

[24] Y.R. Shen. Surface properties probed by second-harmonic and sum-frequency generation. *Nature*, 337(6207):519–525, February 1989.

[25] J.L.P. Hughes and J.E. Sipe. Calculation of second-order optical response in semiconductors. *Physical Review B*, 53(16):10751–10763, Apr 1996.

[26] B.S. Mendoza and W.L. Mochán. Exactly solvable model of surface second-harmonic generation. *Physical Review B*, 53(8):4999–5006, Feb 1996.

[27] B.S. Mendoza, W.L. Mochán, and J.A. Maytorena. Visible-infrared sum and difference frequency generation at adsorbate-covered Au. *Physical Review B*, 60(20):14334–14340, Nov 1999.

[28] B.S. Mendoza and W.L. Mochán. Polarizable-bond model for second-harmonic generation. *Physical Review B*, 55(4):2489–2502, Jan 1997.

[29] J.A. Maytorena, B.S. Mendoza, and W.L. Mochán. Theory of surface sum frequency generation spectroscopy. *Physical Review B*, 57(4):2569–2579, Jan 1998.

[30] M.C. Downer, Y. Jiang, D. Lim, L. Mantese, P.T. Wilson, B.S. Mendoza, and V.I. Gavrilenko. Optical second harmonic spectroscopy of silicon surfaces, interfaces and nanocrystals. *Physica Status Solidi A*, 188(4):1371–1381, 2001.

[31] G. Lüpke. Characterization of semiconductor interfaces by second-harmonic generation. *Surface Science Reports*, 35(3-4):75 – 161, 1999.

[32] P.F. Moulton. Spectroscopic and laser characteristics of Ti:Al_2O_3. *Journal of the Optical Society of America B*, 3(1):125–133, Jan 1986.

[33] D. Strickland and G. Mourou. Compression of amplified chirped optical pulses. *Optics Communications*, 55(6):447 – 449, 1985.

[34] A.M. Janner. *Second-Harmonic Generation, a Selective Probe for Excitons*. PhD thesis, 1998.

[35] N. Bloembergen. Surface nonlinear optics: A historical overview. *Applied Physics B: Lasers and Optics*, 68(3):289–293, 1999.

[36] J.E. Sipe, V. Mizrahi, and G.I. Stegeman. Fundamental difficulty in the use of second-harmonic generation as a strictly surface probe. *Physical Review B*, 35(17):9091–9094, 1987.

[37] Y.R. Shen. Surface contribution versus bulk contribution in surface nonlinear optical spectroscopy. *Applied Physics B: Lasers and Optics*, 68(3):295–300, 1999.

[38] J.F. McGilp. A review of optical second-harmonic and sum-frequency generation at surfaces and interfaces. *Journal of Physics D: Applied Physics*, 29:1812, 1996.

[39] J.F. McGilp. Second-harmonic generation at semiconductor and metal surfaces. *Surface Review and Letters*, 6(3-4):529–558, 1999.

[40] O.A. Aktsipetrov, A.A. Fedyanin, A.V. Melnikov, J.I. Dadap, X.F. Hu, M.H. Anderson, M.C. Downer, and J.K. Lowell. D.C. electric field induced second-harmonic generation spectroscopy of the Si(001)-SiO_2 interface: Separation of the bulk and surface non-linear contributions. *Thin Solid Films*, 294(1-2):231–234, 1997.

[41] T. Scheidt, E.G. Rohwer, H.M. von Bergmann, and H. Stafast. Optical second harmonic imaging: A versatile tool to investigate semiconductor surfaces and interfaces. *The European Physical Journal Applied Physics*, 27(1-3):393–397, 2004.

[42] R. Huber, H. Satzger, W. Zinth, and J. Wachtveitl. Noncollinear optical parametric amplifiers with output parameters improved by the application of a white light continuum generated in CaF_2. *Optics Communications*, 194(4-6):443–448, 2001.

[43] J. Wei, A. Wirth, M.C. Downer, and B.S. Mendoza. Second-harmonic and linear optical spectroscopic study of silicon nanocrystals embedded in SiO_2. *Physical Review B*, 84:165316, Oct 2011.

[44] N. Bodnar. A dual-pumping geometry for non-collinear optical parametric amplification. *Electrical Engineering*, 2010.

[45] G.M. Gale, M. Cavallari, T.J. Driscoll, and F. Hache. Sub-20-fs tunable pulses in the visible from an 82-MHz optical parametric oscillator. *Optics Letters*, 20(14):1562–1564, 1995.

[46] T. Wilhelm, J. Piel, and E. Riedle. Sub-20-fs pulses tunable across the visible from a blue-pumped single-pass noncollinear parametric converter. *Optics Letters*, 22(19):1494–1496, 1997.

[47] C.K. Lee. Cascaded nonlinear optical mixing in a noncollinear optical parametric amplifier. *Advances in Optical Amplifiers*, 2011.

[48] J.I. Dadap, J. Shan, K.B. Eisenthal, and T.F. Heinz. Second-harmonic Rayleigh scattering from a sphere of centrosymmetric material. *Physical Review Letters*, 83(20):4045–4048, 1999.

[49] J.I. Dadap, J. Shan, and T.F. Heinz. Theory of optical second-harmonic generation from a sphere of centrosymmetric material: Small-particle limit. *Journal of the Optical Society of America B*, 21(7):1328–1347, 2004.

[50] J. Shan, J.I. Dadap, I. Stiopkin, G.A. Reider, and T.F. Heinz. Experimental study of optical second-harmonic scattering from spherical nanoparticles. *Physical Review A*, 73(2):023819, 2006.

[51] V.L. Brudny, B.S. Mendoza, and W.L. Mochán. Second-harmonic generation from spherical particles. *Physical Review B*, 62(16):11152, 2000.

[52] W.L. Mochán, J.A. Maytorena, B.S. Mendoza, and V.L. Brudny. Second-harmonic generation in arrays of spherical particles. *Physical Review B*, 68(8):085318, 2003.

[53] M.W. Klein, M. Wegener, N. Feth, and S. Linden. Experiments on second-and third-harmonic generation from magnetic metamaterials. *Optics Express*, 15(8):5238–5247, 2007.

[54] N. Feth, S. Linden, M.W. Klein, M. Decker, F.B.P. Niesler, Y. Zeng, W. Hoyer, J. Liu, S.W. Koch, and J.V. Moloney. Second-harmonic generation from complementary split-ring resonators. *Optics Letters*, 33(17):1975–1977, 2008.

[55] Y. Zeng, W. Hoyer, J. Liu, S.W. Koch, and J.V. Moloney. Classical theory for second-harmonic generation from metallic nanoparticles. *Physical Review B*, 79(23):235109, 2009.

[56] S. Link and M.A. El-Sayed. Optical properties and ultrafast dynamics of metallic nanocrystals. *Annual Review of Physical Chemistry*, 54(1):331–366, 2003.

[57] S. Cattaneo and M. Kauranen. Determination of second-order susceptibility components of thin films by two-beam second-harmonic generation. *Optics Letters*, 28(16):1445–1447, 2003.

[58] F.X. Wang, F.J. Rodríguez, W.M. Albers, R. Ahorinta, J.E. Sipe, and M. Kauranen. Surface and bulk contributions to the second-order nonlinear optical response of a gold film. *Physical Review B*, 80(23):233402, 2009.

[59] A. Wirth, J. Wei, J.J.H. Gielis, P. Figliozzi, J. Rafaelsen, Y.Q. An, and M.C. Downer. Second-harmonic spectroscopy of Si nanocrystals embedded in silica. *Physica Status Solidi C*, 5(8):2662–2666, 2008.

[60] L. Sun, P. Figliozzi, Y.Q. An, M.C. Downer, W.L. Mochan, and B.S. Mendoza. Quadrupolar SHG enhancement in isotropic materials using two orthogonally polarized laser beams. In *Quantum Electronics and Laser Science Conference*, volume 1, pages 274–276. IEEE, 2005.

[61] M. C. Downer, B. S. Mendoza, and V. I. Gavrilenko. Optical second harmonic spectroscopy of semiconductor surfaces: advances in microscopic understanding. *Surf. Interface Anal.*, 31(10):966–986, 2001.

[62] G. Lüpke. Characterization of semiconductor interfaces by second-harmonic generation. *Surf. Sci. Rep.*, 35(3):75–161, 1999.

[63] B. S. Mendoza, M. Palummo, G. Onida, and R. Del Sole. Ab initio calculation of second-harmonic-generation at the si(100) surface. *Phys. Rev. B*, 63(20):205406, 2001.

[64] D. Lim, M. C. Downer, J. G. Ekerdt, N. Arzate, B. S. Mendoza, V. I. Gavrilenko, and R. Q. Wu. Optical second harmonic spectroscopy of boron-reconstructed si (001). *Phys. Rev. Lett.*, 84(15):3406fh3409, 2000.

[65] V. I. Gavrilenko, R. Q. Wu, M. C. Downer, J. G. Ekerdt, D. Lim, and P. Parkinson. Optical second harmonic spectra of silicon-adatom surfaces: theory and experiment. *Thin Solid Films*, 364(1):1–5, 2000.

[66] B. S. Mendoza, W. L. Mochán, and J. A. Maytorena. Visible-infrared sum and difference frequency generation at adsorbate-covered au. *Phys. Rev. B*, 60(20):14334, 1999.

[67] B. S. Mendoza, A. Gaggiotti, and R. Del Sole. Microscopic theory of second harmonic generation at si (100) surfaces. *Phys. Rev. Lett.*, 81(17):3781–3784, 1998.

[68] B. S. Mendoza and W. L. Mochán. Local-field effect in the second-harmonic-generation spectra of Si surfaces. *Phys. Rev. B*, 53(16):10473–10476, 1996.

[69] B. S. Mendoza and W. L. Mochán. Polarizable-bond model for second-harmonic generation. *Phys. Rev. B*, 55(4):2489, 1997.

[70] P. Guyot-Sionnest, A. Tadjeddine, and A. Liebsch. Electronic distribution and nonlinear optical response at the metal-electrolyte interface. *Phys. Rev. Lett.*, 64(14):1678–1681, 1990.

[71] B. S. Mendoza. Longitudinal Gauge Theory of Second Harmonic Generation at Semiconductor Surfaces. In *Epioptics-7: Proceedings of the 24th Course of the International School of Solid State Physics: Erice, Italy, 20-26 July 2002*, volume 23, page 52, 2004.

[72] N. Arzate and B. S. Mendoza. Microscopic study of surface second-harmonic generation from a clean si(100) c(4×2) surface. *Phys. Rev. B*, 63(12):125303, 2001.

[73] C. Aversa and J. E. Sipe. Nonlinear optical susceptibilities of semiconductors: Results with a length-gauge analysis. *Phys. Rev. B*, 52(20):14636–14645, 1995.

[74] J. E. Sipe and A. I. Shkrebtii. Second-order optical response in semiconductors. *Phys. Rev. B*, 61(8):5337, 2000.

[75] W. R. L. Lambrecht and S. N. Rashkeev. From band structures to linear and nonlinear optical spectra in semiconductors. *Phys. Status Solidi B*, 217(1):599–640, 2000.

[76] E. N. Adams. The crystal momentum as a quantum mechanical operator. *J. Chem. Phys.*, 21(11):2013–2017, November 1953.

[77] E. I. Blount, F. Seitz, and D. Turnbull. Formalisms of band theory. *Solid State Phys.*, 13:305, 1962.

[78] S. Ismail-Beigi, E. K. Chang, and S. G. Louie. Coupling of nonlocal potentials to electromagnetic fields. *Phys. Rev. Lett.*, 87(8):087402, August 2001.

[79] C. Motta, M. Giantomassi, M. Cazzaniga, K. Gaál-Nagy, and X. Gonze. Implementation of techniques for computing optical properties in ofh3 dimensions, including a real-space cutoff, in ABINIT. *Comput. Mater. Sci.*, 50(2):698–703, 2010.

[80] L. Kleinman and D. M. Bylander. Efficacious form for model pseudopotentials. *Phys. Rev. Lett.*, 48(20):1425–1428, 1982.

[81] B. Adolph, V. I. Gavrilenko, K. Tenelsen, F. Bechstedt, and R. Del Sole. Nonlocality and many-body effects in the optical properties of semiconductors. *Phys. Rev. B*, 53(15):9797–9808, 1996.

[82] L. Reining, R. Del Sole, M. Cini, and J. G. Ping. Microscopic calculation of second-harmonic generation at semiconductor surfaces: As/Si(111) as a test case. *Phys. Rev. B*, 50(12):8411–8422, 1994.

[83] H. Sano, G. Mizutani, W. Wolf, and R. Podloucky. Ab initio study of linear and nonlinear optical responses of si(111) surfaces. *Phys. Rev. B*, 66(19):195338, November 2002.

[84] J. E. Mejía, B. S. Mendoza, and C. Salazar. Layer-by-layer analysis of second harmonic generation at a simple surface. *Revista Mexicana de Física*, 50(2):134–139, 2004.

[85] C. Hogan, R. Del Sole, and G. Onida. Optical properties of real surfaces from microscopic calculations of the dielectric function of finite atomic slabs. *Phys. Rev. B*, 68(3):035405, 2003.

[86] C. Castillo, B. S. Mendoza, W. G. Schmidt, P. H. Hahn, and F. Bechstedt. Layer-by-layer analysis of surface reflectance anisotropy in semiconductors. *Phys. Rev. B*, 68(4):041310, 2003.

[87] B. S. Mendoza, F. Nastos, N. Arzate, and J. Sipe. Layer-by-layer analysis of the linear optical response of clean and hydrogenated si(100) surfaces. *Phys. Rev. B*, 74(7):075318, 2006.

[88] Nicolas Tancogne-Dejean private communication. Indeed, one can compute the layered contribution of the non-local contribution to **v** with an analytic expression. However, one needs to compute this within the DP code.

[89] S. N. Rashkeev, W. R. L. Lambrecht, and B. Segall. Efficient ab initio method for the calculation of frequency-dependent second-order optical response in semiconductors. *Phys. Rev. B*, 57(7):3905–3919, 1998.

[90] Valérie Véniard, E. Luppi, and H. Hübener. unpublished.

[91] Neil W. Ashcroft and N. David Mermin. *Solid State Physics*. Saunders College, Philadelphia, 1976.

[92] Robert W. Boyd. *Nonlinear Optics*. AP, New York, 2007.

[93] Michele Cini. Simple model of electric-dipole second-harmonic generation from interfaces. *Physical Review B*, 43(6):4792–4802, February 1991.

[94] V. Mizrahi and J. E. Sipe. Phenomenological treatment of surface second-harmonic generation. *J. Opt. Soc. Am. B*, 5(3):660–667, 1988.

[95] J. E. Sipe. New Green-function formalism for surface optics. *Journal of the Optical Society of America B*, 4(4):481–489, 1987.

[96] J. E. Sipe, D. J. Moss, and H. M. van Driel. Phenomenological theory of optical second- and third-harmonic generation from cubic centrosymmetric crystals. *Phys. Rev. B*, 35(3):1129–1141, January 1987.

[97] A. B. Gordienko and A. S. Poplavnoi. Influence of the pseudopotential nonlocality on the calculated optical characteristics of crystals. *Russian Physics Journal*, 47(7):687–691, July 2004.

[98] M. Fuchs and M. Scheffler. Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density-functional theory. 119(1):67–98, June 1999.

[99] J. Cabellos, B. Mendoza, M. Escobar, F. Nastos, and J. Sipe. Effects of nonlocality on second-harmonic generation in bulk semiconductors. *Phys. Rev. B*, 80(15):155205, 2009.

[100] Valerio Olevano. Private communication.

[101] F. Nastos, B. Olejnik, K. Schwarz, and J. E. Sipe. Scissors implementation within length-gauge formulations of the frequency-dependent nonlinear optical response of semiconductors. *Phys. Rev. B*, 72(4):045223, 2005.

[102] Nicolas Tancogne-Dejean private communication.