LENGTH VS. TRANSVERSAL GAUGE CALCULATIONS FOR NONLINEAR OPTICS

By

Marco Antonio Escobar Acevedo

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Supervisor:

Dr. Bernardo Mendoza Santoyo

Internal examiners:

Dr. Raúl Alfonso Vázquez Nava

External examiners:

Dr. Eleuterio Castaño Tostado

(UAM-I)

To my family

for their unending support.

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Abstract

We present a comparison of the optical nonlinear response calculations for bulk semiconductors, using length and transversal gauges. *Ab initio* calculations of the second-order optical susceptibilities for GaAs are presented as a case of study; calculations were performed using local density approximation (LDA) and to correct the underestimation of the band gap within density functional theory (DFT) scissors correction was implemented. Both formalisms were derived from the density matrix approach and the problem of gauge invariance is discussed.

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Chapter 1

Introduction

> "...even at the simplest level of approximation – treating electrons as independent particles interacting with the electromagnetic field in the long-wavelength limit and neglecting local field effects – the calculation of nonlinear optical coefficients of semiconductors has been troublesome." [1].

The research activity leading to possible improvements in the field of photonics occupies an important place in the scientific community. In recent years much effort has been done to understand nonlinear optical properties of materials in order to implement photonic devices of practical use.

According to Aversa C. and Sipe J. E. [2] and Sipe and Shkrebtii [3], all-optical generation and control of direct current in semiconductors, can be described within the framework of nonlinear optics using susceptibilities. The use of this perspective leads to general expressions that are independent of the electronic structure models, and give the opportunity to understand the process for resonant and nonresonant excitations. To calculate the generation of current first a reliable frequency dependent susceptibility should be computed and that is the aim of the present thesis.

The interaction of photons and electrons with matter has been a major topic of study. Today, most characterization tools as well as electro-optical devices are based on our understanding of these interactions. Technological applications are rapidly progressing, but many fundamental questions concerning theoretical and numerical descriptions are still open.

In theoretical calculations we can easily change one parameter and find its response. In contrast, in real experiments it is difficult to isolate one variable and measure its particular contribution. Nevertheless, theoretical calculations will not replace traditional techniques. On the contrary, they complement each other, Walter Khon won the 1998 Nobel Prize in Chemistry for his density functional theory (DFT) of many-electron systems, within this theory a numerical barrier was broken an whole new areas of investigation had emerged [4].

Calculations of the optical response occupies and important place in the physical computations. A material interacting with the intense light of a laser beam responds in a "nonlinear" way. Consequences of this are a number of peculiar phenomena, including the generation of optical frequencies that are initially absent. This effect allows the production of laser light at wave lengths normally unattainable by conventional laser techniques. So the application of nonlinear optics (NLO) range from basic research to spectroscopy, telecommunications and astronomy. Second harmonic generation (SHG), in particular, corresponds to the appearance of a frequency component that is exactly twice the input one.

The use of two different approaches to calculate optical response can serve to infer if the calculations are correct. However, it will be demonstrated later on this thesis the gauge invariance is an issue, and we have to be careful in that aspect.

The calculations presented in this thesis were made using pseudopotentials band structures based on the local density approximation (LDA) + scissors corrections, this approach is the most popular to calculate optical properties using full zone band structures.

This work is organized as follows, the second chapter deals with the derivation of the formulae used to calculate the second order non linear susceptibilities of semiconductors, then the formal demonstration of gauge invariance is presented followed by the comptutational details for such calculation, we present our results in the transversal and length gauge and finally our conclusions and observations.

Chapter 2

Optical Response Calculation

"It is my experience that the direct derivation of many simple, well-known formulae from first principles is not easy to find in print. The original papers do not follow the easiest path, the authors of reviews find the necessary exposition too difficult—or beneath their dignity—and the treatises are too self-conscious about completeness and rigour."

–J. M. Ziman, Principles of the Theory of Solids (1998).

2.1 Introduction

Electromagnetic waves cause polarization in a medium, which is interpreted as electronic transitions from unoccupied to occupied states. The effect of the electric field vector $\mathbf{E}(\omega)$ of the incoming light is to polarize the material. This polarization can be calculated using the following relation:

$$P^a(\omega) = \chi^{(1)}_{ab} E^b(\omega) + \chi^{(2)}_{abc} E^b(\omega) E^c(\omega) + ... \tag{2.1}$$

in this expression $\chi^{(1)}_{ab}$ is the linear optical susceptibility and $\chi^{(2)}_{abc}$ is the second order nonlinear optical susceptibility.

In order to calculate the optical properties and optical response of semiconductors a number of formalisms have been proposed [5–10], and for second order response specialized articles can be found [3, 11, 12]. In general susceptibility tensors can be derived using potentials as perturbations, by using standard quantum mechanics perturbation theory which can be reviewed elsewhere [13, 14].

2.2 Gauge transformation

In classical electrodynamics the fields described by the Maxwell equations can be derived from a vector, $\mathbf{A}$, and a scalar, ϕ, potential. Potentials are quantities inferred (within the ambiguity of gauge invariance) by integration of the fields along appropriate paths. In free space [15]:

$$\mathbf{E} = \frac{\partial \mathbf{A}}{\partial t} - \nabla \Phi \tag{2.2a}$$

$$\mathbf{H} = \frac{1}{\mu_0} \nabla \times \mathbf{A} \tag{2.2b}$$

The potentials are not unique since one can add a potential χ as

$$\mathbf{A}' = \mathbf{A} - \nabla \chi \tag{2.3a}$$

$$\Phi' = \Phi + \frac{\partial \chi}{\partial t} \tag{2.3b}$$

A fundamental aspect of the formulation of electrodynamics is the gauge invariance: potentials are not unique but all the derived responses must yield the same results regardless of the gauge [15–18].

Gauge invariance is sometimes taken for granted, when in reality it should be verified due to the fact that in real calculations several approximations are made [1]. Explicit corroborations of gauge invariance in the calculation of optical response are scarce [1, 5, 19], and that is the main reason we decided to confirm numerically the gauge invariance for the second order nonlinear susceptibility in semiconductors.

Let suppose that we know all the details of the ground state of the material, to calculate the optical response we have to consider the interaction of electrons with the incident electromagnetic field and use the minimal coupling principle.*
The electromagnetic fields act as perturbations to the ground state. In general the Hamiltonian of a system can be decomposed as

$$\mathrm{H} = \mathrm{H}_0 + \mathrm{H}', \tag{2.4}$$

where H_0 stands for the ground state Hamiltonian and H' is the perturbative part.

*The coupling between particles and fields depends only on the potentials [20].

In the transversal gauge $\Phi = 0$, $\nabla \cdot \mathbf{A} = 0$ and

$$\mathbf{E} = -\dot{\mathbf{A}}/c, \tag{2.5}$$

so the single particle canonical moment can be written as [21]:

$$\mathbf{P} = \mathbf{p} - \frac{e}{c}\mathbf{A}. \tag{2.6}$$

The Hamiltonian of an electron in the presence of a light field is

$$\mathrm{H} = \frac{1}{2m}(\mathbf{p} - \frac{e}{c}\mathbf{A})^2 + \mathcal{V}, \tag{2.7}$$

where $\mathcal{V}$ is time independent and due to the interaction with the crystal potential. In the long wavelength approximation[†]

$$\mathbf{A} = \mathbf{A}(t) = \mathbf{A}_0 e^{-i\omega t} \tag{2.9}$$

so it commutes with $\mathbf{p}$, also it can be shown that the term $\mathbf{A}^2$ can be neglected [22], so

$$\mathrm{H} = \frac{\mathbf{p}^2}{2m} - \frac{e}{mc}\mathbf{A} \cdot \mathbf{p} + \mathcal{V}, \tag{2.10}$$

and thus the perturbative part is

$$\mathrm{H}' = -\frac{e}{mc}\mathbf{A} \cdot \mathbf{p} \tag{2.11}$$

To get the Hamiltonian in the length gauge we perform a gauge transformation to the transversal gauge [23]:

$$\chi(\mathbf{r}, t) = -\mathbf{r} \cdot \mathbf{A}(t) \tag{2.12}$$

substituting in Equations (2.3a) and (2.3b) leads to

$$H = H_0 - e\mathbf{r} \cdot \mathbf{E} \tag{2.13}$$

[†]We expand $\mathbf{A}(\mathbf{r}, t)$ such that

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} + \frac{1}{2!}(i\mathbf{k} \cdot \mathbf{r})^2 + \ldots \tag{2.8}$$

notice that $|\mathbf{k} \cdot \mathbf{r}| << 1$ so $e^{i\mathbf{k}\cdot\mathbf{r}} \sim 1$

2.3 Quantum Mechanics Formalism

To derive the second order nonlinear susceptibilities we will follow the formalism applied by Aversa C. and Sipe J. E. [1] to the length gauge, that formalism is based on the use of the density matrix. We use the fact that the expectation value of any single particle operator $\mathcal{O}$ can be calculated using the density matrix trough the relation

$$< \mathcal{O} >= \mathrm{Tr}(\rho\mathcal{O}), \tag{2.14}$$

where the trace is defined by

$$\begin{aligned} \mathrm{Tr}(AB) &= \sum_m \langle m|AB|m\rangle \\ &= \sum_{m,n} \langle m|A|n\rangle\langle n|B|m\rangle \\ &= A_{mn}B_{nm} \end{aligned} \tag{2.15}$$

The dynamical equation of motion for ρ is given by

$$i\hbar\frac{\mathrm{d}\rho}{\mathrm{d}t} = [\mathrm{H}, \rho] \tag{2.16}$$

we change to the interaction picture because the equation of motion involving total Hamiltonian simplifies (see Appendix A) to the form given by

$$i\hbar\dot{\tilde{\rho}} = [\tilde{\mathrm{H}}', \tilde{\rho}] \tag{2.17}$$

where only the perturbation term of the Hamiltonian, H', is involved [12]. In the interaction picture the operator $\tilde{\mathcal{O}}$ is defined as

$$\tilde{\mathcal{O}} = U\mathcal{O}U^\dagger, \tag{2.18}$$

with

$$U = \exp(iH_0 t/\hbar). \tag{2.19}$$

Notice that $\tilde{\mathcal{O}}$ has a time dependency even if $\mathcal{O}$ does not. The equation (2.16) leads to

$$i\hbar\frac{\mathrm{d}\tilde{\rho}(t)}{\mathrm{d}t} = [-e\tilde{\mathrm{H}}', \tilde{\rho}(t)], \tag{2.20}$$

that leads to

$$\tilde{\rho}(t) = \tilde{\rho}(t = -\infty) + \frac{ie}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' [\tilde{\mathrm{H}}'(t'), \tilde{\rho}(t')]. \tag{2.21}$$

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

$$\mathbf{E}(t) = \mathbf{E}e^{-i\omega t}e^{\eta t}, \tag{2.22}$$

where $\eta > 0$ assures that at $t = -\infty$ the interaction is zero and has its full strength, $\mathbf{E}$, at $t = 0$. After the required time integrals are done, one takes $\eta \to 0$. Instead of Equation (2.22) we will use implicitly

$$\mathbf{E}(t) = \mathbf{E}e^{-i\tilde{\omega}t}, \tag{2.23}$$

with

$$\tilde{\omega} = \omega + i\eta. \tag{2.24}$$

Also, $\tilde{\rho}(t = -\infty)$ should be independent of time, and thus $[\tilde{\mathrm{H}}, \tilde{\rho}]_{t=-\infty} = 0$, which implies that $\tilde{\rho}(t = -\infty) \equiv \tilde{\rho}_0$, where $\tilde{\rho}_0$ is the density matrix of the unperturbed ground state, such that

$$\langle n\mathbf{k}|\tilde{\rho}_0|m\mathbf{k}'\rangle = f_n(\hbar\omega_n(\mathbf{k}))\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'), \tag{2.25}$$

where $f_n(\hbar\omega_n(\mathbf{k})) = f_{n\mathbf{k}}$ is the Fermi-Dirac distribution function.

We solve Equation (2.21) using the standard iterative solution, for which we write

$$\tilde{\rho} = \tilde{\rho}^{(0)} + \tilde{\rho}^{(1)} + \tilde{\rho}^{(2)} + \cdots, \tag{2.26}$$

where $\tilde{\rho}^{(N)}$ is the density operator to order N in $\mathbf{E}(t)$. Then, Equation (2.21) reads

$$\tilde{\rho}^{(0)} + \tilde{\rho}^{(1)} + \tilde{\rho}^{(2)} + \cdots = \tilde{\rho}_0 + \frac{ie}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' [\mathrm{H}', \tilde{\rho}^{(0)} + \tilde{\rho}^{(1)} + \tilde{\rho}^{(2)} + \cdots], \tag{2.27}$$

where by equating equal orders in the perturbation, we find

$$\tilde{\rho}^{(0)} \equiv \tilde{\rho}_0, \tag{2.28}$$

and

$$\tilde{\rho}^{(N)}(t) = \frac{ie}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' [\tilde{\mathrm{H}}', \tilde{\rho}^{(N-1)}(t')]. \tag{2.29}$$

To calculate the expectation value of the macroscopic current density we use [24]:

$$\mathbf{J} = e\mathrm{Tr}(\rho\mathbf{v}) \tag{2.30}$$

The polarization is related to the microscopic current through

$$\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t} = \mathbf{J}, \tag{2.31}$$

we will demonstrate later that for the transversal and length gauges the polarization of the system can be written as

$$\frac{\mathrm{d}P^a}{\mathrm{d}t} = \frac{e}{m}\sum_{nm\mathbf{k}} p^a_{mn}\rho_{nm}, \tag{2.32}$$

and after integration over time the susceptibility can be obtained; to first order related to $\rho^{(1)}$ and to second order related to $\rho^{(2)}$.

2.4 Transversal Gauge

The operator $\mathbf{v}$ is defined for the transversal gauge as

$$\mathbf{v} = \frac{\mathbf{p}}{m} - \frac{e}{mc}\mathbf{A} \tag{2.33}$$

and thus

$$\mathbf{J} = \frac{e}{m}\mathrm{Tr}(\rho\mathbf{p}) - \frac{e^2}{mc}\mathrm{Tr}(\rho\mathbf{A}), \tag{2.34}$$

the term containing $\mathbf{A}$ cancels (see Appendix B).

In this gauge Equation (2.29) becomes

$$\tilde{\rho}_V^{(N+1)} = \frac{ie}{\hbar mc}\int_{-\infty}^{t} dt'[\tilde{\mathbf{p}}(t')\cdot\mathbf{A}(t'), \tilde{\rho}_V^{(N)}(t')] \tag{2.35}$$

To first and second order we have

$$\tilde{\rho}_V^{(1)}(t) = \frac{ie}{\hbar mc}\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{p}}(t')\cdot\mathbf{A}(t'), \tilde{\rho}_0(t')] \tag{2.36a}$$

$$\tilde{\rho}_V^{(2)}(t) = \frac{ie}{\hbar mc}\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{p}}(t')\cdot\mathbf{A}(t'), \tilde{\rho}_V^{(1)}(t')] \tag{2.36b}$$

using the fact that the ρ_0 matrix elements are

$$\rho_{0,nm} = f_n \delta_{nm} \tag{2.37}$$

where δ_{nm} is the Kronecker delta, and f_n is the fermi occupation level, for a clean cold (T= 0 K) semiconductor it is zero if n is a conduction band and one if n is a valence band.

The matrix elements of (2.36a) are then

$$\begin{aligned} \rho^{(1)}_{nm,V}(\mathbf{k};t) &= \frac{ie}{mc\hbar} f_{mn\mathbf{k}} p^b_{nm}(\mathbf{k}) A^b \int_{-\infty}^{t} \mathrm{d}t' e^{i(\omega_{nm\mathbf{k}}-\omega)t'} \\ &= \frac{e}{mc\hbar} f_{mn\mathbf{k}} p^b_{nm}(\mathbf{k}) A^b \frac{e^{i(\omega_{nm\mathbf{k}}-\omega)t}}{\omega_{nm\mathbf{k}}-\omega} \end{aligned} \tag{2.38}$$

with $f_{nm} \equiv f_n - f_m$.

Replacing (2.38) in (2.36b), and generalizing to two perturbing fields we obtain

$$\tilde{\rho}^{(2)}_{V,nm} = \frac{ie^2}{\hbar^2 m^2 c^2} \int_{-\infty}^{t} \mathrm{d}t' \sum_{\ell} \left(\frac{p^b_{nl} f_{ml} p^c_{nm}}{\omega_{\ell m} - \omega} - \frac{f_{\ell n} p^b_{n\ell} p^c_{\ell m}}{\omega_{n\ell} - \omega} \right) e^{i\omega_{nm} t'} A^b(t') A^c(t'), \tag{2.39}$$

performing the integral and using $\mathbf{A} = c\mathbf{E}/i\omega$ we arrive to the final form of the second order density matrix elements

$$\rho^{(2)}_{V,nm} = -\frac{e^2}{\hbar^2 m^2 \omega^2} \frac{1}{\omega_{nm} - 2\omega} \sum_{\ell} \left[\frac{p^a_{n\ell} f_{m\ell} p^c_{\ell m}}{\omega_{\ell m} - \omega} - \frac{f_{\ell n} p^c_{n\ell} p^b_{\ell m}}{\omega_{n\ell} - \omega} \right] E^b E^c \tag{2.40}$$

Substituting (2.40) into (2.32) we obtain

$$\frac{\mathrm{d}P^a}{\mathrm{d}t} = -\frac{e^3}{\hbar^2 m^3 \omega^2} \sum_{n,m,\ell,\mathbf{k}} \left[\frac{p^a_{mn} p^b_{n\ell} f_{m\ell} p^c_{\ell m}}{(\omega_{nm} - 2\omega)(\omega_{\ell m - \omega})} - \frac{p^a_{mn} f_{\ell m} p^c_{n\ell} p^c_{\ell m}}{(\omega_{nm} - 2\omega)(\omega_{n\ell} - \omega)} \right] E^b E^c \tag{2.41}$$

and after integration over time and comparing with Equation (2.1) we get

$$\chi^{(2)}_{abc} = \frac{-ie^3}{2\hbar^2 m^3 \omega^3} \sum_{n,m,\ell,\mathbf{k}} \left[\frac{p^a_{mn} p^b_{n\ell} f_{m\ell} p^c_{\ell m}}{(\omega_{nm} - 2\omega)(\omega_{\ell m - \omega})} - \frac{p^a_{mn} f_{\ell m} p^c_{n\ell} p^c_{\ell m}}{(\omega_{nm} - 2\omega)(\omega_{n\ell} - \omega)} \right] \tag{2.42}$$

using the identity

$$\frac{1}{(\omega_{nm} - 2\omega)(\omega_{n\ell} - \omega)} = \frac{2}{\omega_{nm} - 2\omega_{n\ell}} \frac{1}{\omega_{nm} - 2\omega} + \frac{1}{\omega_{nm} - 2\omega_{n\ell}} \frac{1}{\omega_{n\ell} - \omega} \tag{2.43}$$

the expression (2.42) can be rewritten as

$$\chi^{(2)}_{abc} = \frac{ie^3}{2\hbar^2 m^3\omega^3}\sum_{\ell,m,n,\mathbf{k}} \left[\frac{p^a_{mn}p^b_{m\ell}p^c_{\ell n}f_{n\ell}}{\omega_{mn}-2\omega_{\ell n}}\left(\frac{1}{\omega_{\ell n}-\omega}-\frac{2}{\omega_{mn}-2\omega}\right) - \frac{p^a_{m\ell}p^b_{nm}p^c_{\ell n}f_{n\ell}}{\omega_{\ell n}-2\omega_{\ell n}}\left(\frac{1}{\omega_{\ell n}-\omega}-\frac{2}{\omega_{\ell m}-2\omega}\right)\right] \quad (2.44)$$

In these expressions, ω is really $\omega + i\eta$ where η is a small positive number,[‡] in the limit $\eta \to 0$

$$\lim_{\eta\to 0}\frac{1}{\omega_{mn}-\omega-i\eta} = \mathcal{P}\left(\frac{1}{\omega_{mn}-\omega}\right) + i\pi\delta(\omega_{mn}-\omega) \quad (2.45)$$

where $\mathcal{P}$ denotes the Cauchy principal value.

Using the relation (2.45) into (2.44) we get

$$\chi^{(2)}_{abc} = -\frac{\pi e^3}{2\hbar^2 m^3\omega^3}\sum_{\ell,m,n,\mathbf{k}}\left[\frac{p^a_{mn}p^b_{m\ell}p^c_{\ell n}f_{n\ell}}{\omega_{mn}-2\omega_{\ell n}}\Big(\delta(\omega_{\ell n}-\omega)-2\delta(\omega_{mn}-2\omega)\Big) - \frac{p^a_{m\ell}p^b_{nm}p^c_{\ell n}f_{n\ell}}{\omega_{\ell n}-2\omega_{\ell n}}\Big(\delta(\omega_{\ell n}-\omega)-2\delta(\omega_{\ell m}-2\omega)\Big)\right] \quad (2.46)$$

Notice the fact that in expressions like $\delta(\omega_{\ell m}-2\omega)$, $\omega_{\ell m}$ must be positive in order for the delta to resonate, imposing that condition, and $f_{nn} = 0$, we can change ℓ, m, n to valence or conduction bands, and then it is straightforward to arrive to the expression derived by Mendoza, Gaggiotti, and del Sole [25] for the imaginary part of the second order susceptibility.

The expression Equation (2.46) was derived whitout knowledge that the result was previously reported by Ghahramani, Moss, and Sipe [26] although the procedure was not presented in that paper. It is important to notice that we arrived to the same results that are obtained following the formalism of Reining et al. [6], which is based on time dependent perturbation theory and second quantization.

It is clear that expression (2.44) has a divergence at zero frequency. It was demonstrated by Aspnes and Studna [27] that such divergence do not exists for cubic crystals, but it was until the work by Ghahramani et al. [26], nine years later,

‡This is due to the adiabatic switch-on

that a sum rule to demonstrate that the divergence does not exist, independent of the crystal symmetry, was stated.

The basic idea is to expand (2.44) into partial fractions

$$\frac{1}{\omega^3(2\omega-\omega_{ji})}\left[\frac{f_{il}}{\omega-\omega_{li}}+\frac{f_{jl}}{\omega-\omega_{jl}}\right]=\frac{\mathcal{A}}{\omega^3}+\frac{\mathcal{B}}{\omega^2}+\frac{\mathcal{C}}{E}+\mathcal{F}(\omega) \tag{2.47}$$

where

$$\mathcal{A} = \frac{1}{\omega_{ji}}\left(\frac{f_{il}}{\omega_{li}}+\frac{f_{jl}}{\omega_{jl}}\right) \tag{2.48a}$$

$$\mathcal{B} = \frac{f_{il}}{\omega_{ji}\omega_{li}}\left(\frac{2}{\omega_{ji}}+\frac{1}{\omega_{li}}\right)+\frac{f_{jl}}{\omega_{ji}\omega_{jl}}\left(\frac{2}{\omega_{ji}}+\frac{1}{\omega_{jl}}\right) \tag{2.48b}$$

$$\mathcal{C} = \frac{f_{il}}{\omega_{jl}\omega_{li}}\left(\frac{4}{\omega_{ji}^2}+\frac{2}{\omega_{ji}\omega_{li}}+\frac{1}{\omega_{li}^2}\right)+\frac{f_{jl}}{\omega_{ji}\omega_{jl}}\left(\frac{4}{\omega_{ji}^2}+\frac{2}{\omega_{ji}\omega_{jl}}+\frac{1}{\omega_{jl}^2}\right) \tag{2.48c}$$

$$\mathcal{F} = \frac{16}{\omega_{ji}^3(2\omega-\omega_{ji})}\left(\frac{f_{il}}{\omega_{ji}-2\omega_{li}}+\frac{f_{jl}}{\omega_{ji}-2\omega_{jl}}\right)+\frac{f_{il}}{\omega_{li}^3(2\omega_{li}-\omega_{ji})(\omega-\omega_{li})} + \frac{f_{jl}}{\omega_{jl}^3(2\omega_{jl}-\omega_{ji})(\omega-\omega_{jl})} \tag{2.48d}$$

By taking advantage of the time reversal symmetry, whose main results are summarized in the following relations [26, 28]:

$$f_{ij}(\mathbf{k}) = f_{ij}(-\mathbf{k}) \tag{2.49a}$$

$$\omega_{ij}(\mathbf{k}) = \omega_{ij}(-\mathbf{k}) \tag{2.49b}$$

$$p_{ij}(\mathbf{k}) = -p_{ji}(-\mathbf{k}) \tag{2.49c}$$

$$r_{ij}(\mathbf{k}) = r_{ji}(-\mathbf{k}) \tag{2.49d}$$

and the intrinsic permutation symmetry,[§] the only nonvanishing term is $\mathcal{F}$, so

$$\begin{aligned}
\chi^{(2)}_{abc} = & -\frac{\pi e^3}{2m^3\hbar^2}\sum_{i,j,l,\mathbf{k}} p^a_{ij}p^b_{jl}p^c_{\ell i}\Big[\frac{16}{\omega^3_{ji}}\left(\frac{f_{il}}{\omega_{ji}-2\omega_{li}}+\frac{f_{jl}}{\omega_{ji}-2\omega_{jl}}\right)\delta(2\omega-\omega_{ji}) \\
& + \frac{f_{il}}{\omega^3_{li}(2\omega_{li}-\omega_{ji})}\delta(\omega-\omega_{li}) \\
& + \frac{f_{jl}}{\omega^3_{jl}(2\omega_{jl}-\omega_{ji})}\delta(\omega-\omega_{jl})\Big],
\end{aligned} \tag{2.51}$$

and this expression has not divergence at zero frecuency.

It is important to mention that the real and imaginary parts of the susceptibility are related through the *Kramers-Krönig* relations [30], in general the imaginary part of the susceptibilities is calculated, and from it the real part is computed. To our specific case [31]:

$$\mathrm{Re}\chi^{(2)}(\omega,\omega) = \frac{2}{\pi}\int_0^\infty \frac{\omega' \mathrm{Im}\chi^{(2)}(\omega',\omega')}{\omega'^2-\omega^2}\mathrm{d}\omega' \tag{2.52}$$

2.5 Length Gauge

The formalisms to find the nonlinear optical susceptibilities of semiconductors by length gauge analysis was proposed by Aversa C. and Sipe J. E. [1], more recent derivations can be found in References [3, 12], A detailed discussion can be found in Reference [32]. Here we will highlight the most important steps.

H_0 has eigenvalues $\hbar\omega_n(\mathbf{k})$ and eigenvectors $|n\mathbf{k}\rangle$ (Bloch states) labeled by a band index n and crystal momentum $\mathbf{k}$. The r representation of the Bloch states is given by

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r}|n\mathbf{k}\rangle = \sqrt{\frac{\Omega}{8\pi^3}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}), \tag{2.53}$$

[§]To fullfill intrinsic permutation symmetry, a symmetrization of the last two indices (b, c) should be made. The intrinsic permutation symmetry states that the susceptibility must be invariant under permutation of the incoming fields, thus [29]

$$P^a = \chi^{abc}E^bE^c = (\frac{\chi^{abc}+\chi^{acb}}{2})E^bE^c \tag{2.50}$$

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

$$\int_\Omega d^3r\, u^*_{n\mathbf{k}}(\mathbf{r}) u_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm}\delta_{\mathbf{k},\mathbf{q}}, \tag{2.54}$$

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

$$\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{2.55}$$

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

$$\frac{\partial}{\partial\mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\frac{\partial}{\partial\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}'), \tag{2.56}$$

on the other,

$$\begin{aligned}\frac{\partial}{\partial\mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \frac{\partial}{\partial\mathbf{k}}\int d\mathbf{r}\langle n\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|m\mathbf{k}'\rangle \\ &= \int d\mathbf{r}\left(\frac{\partial}{\partial\mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r})\right)\psi_{m\mathbf{k}'}(\mathbf{r}),\end{aligned} \tag{2.57}$$

the derivative of the wavefunction is simply given by

$$\frac{\partial}{\partial\mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{\Omega}{8\pi^3}}\left(\frac{\partial}{\partial\mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)e^{-i\mathbf{k}\cdot\mathbf{r}} - i\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r}). \tag{2.58}$$

We take this back into Equation (2.57), to obtain

$$\begin{aligned}\frac{\partial}{\partial\mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \sqrt{\frac{\Omega}{8\pi^3}}\int d\mathbf{r}\left(\frac{\partial}{\partial\mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{m\mathbf{k}'}(\mathbf{r}) \\ &\quad -i\int d\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r})\mathbf{r}\psi_{m\mathbf{k}'}(\mathbf{r}) \\ &= \frac{\Omega}{8\pi^3}\int d\mathbf{r}\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\left(\frac{\partial}{\partial\mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)u_{m\mathbf{k}'}(\mathbf{r}) \\ &\quad -i\langle n\mathbf{k}|\mathbf{r}|m\mathbf{k}'\rangle.\end{aligned} \tag{2.59}$$

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

$$\int d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) = \frac{8\pi^3}{\Omega}\delta(\mathbf{q}-\mathbf{k}) \int_\Omega d^3r\, f(\mathbf{r}), \tag{2.60}$$

to finally write,

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \delta(\mathbf{k}-\mathbf{k}') \int_\Omega d\mathbf{r}\, \left(\frac{\partial}{\partial \mathbf{k}} u^*_{n\mathbf{k}}(\mathbf{r})\right) u_{m\mathbf{k}}(\mathbf{r}) \\ &\quad -i\langle n\mathbf{k}|\mathbf{r}|m\mathbf{k}'\rangle. \end{aligned}\tag{2.61}$$

where Ω is the volume of the unit cell. From

$$\int_\Omega u_{m\mathbf{k}} u^*_{n\mathbf{k}} d\mathbf{r} = \delta_{nm}, \tag{2.62}$$

we easily find that

$$\int_\Omega d\mathbf{r} \left(\frac{\partial}{\partial \mathbf{k}} u_{m\mathbf{k}}(\mathbf{r})\right) u^*_{n\mathbf{k}}(\mathbf{r}) = -\int_\Omega d\mathbf{r}\, u_{m\mathbf{k}}(\mathbf{r}) \left(\frac{\partial}{\partial \mathbf{k}} u^*_{n\mathbf{k}}(\mathbf{r})\right). \tag{2.63}$$

Therefore, we define

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i \int_\Omega d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r}) \nabla_\mathbf{k} u_{m\mathbf{k}}(\mathbf{r}), \tag{2.64}$$

with $\partial/\partial\mathbf{k} = \nabla_\mathbf{k}$. Now, from Equations (2.56), (2.59), and (2.64), we have that the matrix elements of the position operator of the electron are given by

$$\langle n\mathbf{k}|\mathbf{r}|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}) + i\delta_{nm}\nabla_\mathbf{k}\delta(\mathbf{k}-\mathbf{k}'), \tag{2.65}$$

Then, from Eq. (2.65), and writing $\mathbf{r} = \mathbf{r}_e + \mathbf{r}_i$, with $\mathbf{r}_e$ ($\mathbf{r}_i$) the interband (intraband) part, we obtain that

$$\langle n\mathbf{k}|\mathbf{r}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_\mathbf{k}\delta(\mathbf{k}-\mathbf{k}')\right], \tag{2.66}$$

$$\langle n\mathbf{k}|\mathbf{r}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}). \tag{2.67}$$

To proceed, we relate Equation (2.67) to the matrix elements of the momentum operator as follows. We start from the basic relation,

$$\mathbf{v} = \frac{1}{i\hbar}[\mathbf{r}, \mathrm{H}_0], \tag{2.68}$$

with $\mathbf{v}$ the velocity operator. Neglecting nonlocal potentials in H_0 we obtain, on one hand

$$[\mathbf{r}, H_0] = i\hbar \frac{\mathbf{p}}{m}, \tag{2.69}$$

with $\mathbf{p}$ the momentum operator, with m the mass of the electron. On the other hand,

$$\langle n\mathbf{k}|[\mathbf{r}, H_0]|m\mathbf{k}\rangle = \langle n\mathbf{k}|\mathbf{r}H_0 - H_0\mathbf{r}|m\mathbf{k}\rangle = (\hbar\omega_m(\mathbf{k}) - \hbar\omega_n(\mathbf{k}))\langle n\mathbf{k}|\mathbf{r}|m\mathbf{k}\rangle, \tag{2.70}$$

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

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{p}_{nm}(\mathbf{k})}{im\omega_{nm}(\mathbf{k})} = \frac{\mathbf{v}_{nm}(\mathbf{k})}{i\omega_{nm}(\mathbf{k})} \qquad n \neq m. \tag{2.71}$$

Comparing above result with Equation (2.67), we can identify

$$(1 - \delta_{nm})\boldsymbol{\xi}_{nm} \equiv \mathbf{r}_{nm}, \tag{2.72}$$

and the we can write

$$\langle n\mathbf{k}|\mathbf{r}_e|m\mathbf{k}\rangle = \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{p}_{nm}(\mathbf{k})}{im\omega_{nm}(\mathbf{k})} \qquad n \neq m, \tag{2.73}$$

which gives the interband matrix elements of the position operator in terms of the matrix elements of the well defined momentum operator.

For the intraband part, we derive the following general result,

$$\begin{aligned}
\langle n\mathbf{k}|[\mathbf{r}_i, \mathcal{O}]|m\mathbf{k}'\rangle &= \sum_{\ell,\mathbf{k}''} \big(\langle n\mathbf{k}|\mathbf{r}_i|\ell\mathbf{k}''\rangle\langle \ell\mathbf{k}''|\mathcal{O}|m\mathbf{k}'\rangle \\
&\quad - \langle n\mathbf{k}|\mathcal{O}|\ell\mathbf{k}''\rangle\langle \ell\mathbf{k}''|\mathbf{r}_i|m\mathbf{k}'\rangle\big) \\
&= \sum_{\ell} \big(\langle n\mathbf{k}|\mathbf{r}_i|\ell\mathbf{k}'\rangle\mathcal{O}_{\ell m}(\mathbf{k}') \\
&\quad - \mathcal{O}_{n\ell}(\mathbf{k})|\ell\mathbf{k}\rangle\langle \ell\mathbf{k}|\mathbf{r}_i|m\mathbf{k}'\rangle\big),
\end{aligned} \tag{2.74}$$

where we have taken $\langle n\mathbf{k}|\mathcal{O}|\ell\mathbf{k}''\rangle = \delta(\mathbf{k}-\mathbf{k}'')\mathcal{O}_{n\ell}(\mathbf{k})$. We substitute Equation (2.66), to obtain

$$
\begin{aligned}
\sum_\ell \quad & \left(\delta_{n\ell}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{\ell m}(\mathbf{k}')\right. \\
& \left. -\mathcal{O}_{n\ell}(\mathbf{k})\delta_{\ell m}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\right) \\
= \quad & \left(\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{nm}(\mathbf{k}')\right. \\
& \left. -\ \mathcal{O}_{nm}(\mathbf{k})\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\right) \\
= \quad & \delta(\mathbf{k}-\mathbf{k}')\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right) + i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\
& + i\delta(\mathbf{k}-\mathbf{k}')\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\
= \quad & i\delta(\mathbf{k}-\mathbf{k}')\Big(\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right)\Big) \\
\equiv \quad & i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}.
\end{aligned} \tag{2.75}
$$

Then,

$$\langle n\mathbf{k}|[\mathbf{r}_i,\mathcal{O}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{2.76}$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right), \tag{2.77}$$

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 Equation (2.75), thus giving a well defined commutator of the intraband position operator with an arbitrary operator $\mathcal{O}$.

Summarizing, the position operator can be decomposed in

$$\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e \tag{2.78}$$

where $\mathbf{r}_i$ stands for the intraband and $\mathbf{r}_e$ for the interband. The matrix elements of the interband part are simply defined by

$$\mathbf{r}_{nm} = \frac{\mathbf{p}_{nm}}{im\omega_{nm}} \tag{2.79}$$

for $n \neq m$ and $\mathbf{r}_{nn} = 0$, while we will only deal with the intraband term trough commutators with simple operators,[¶] $\mathcal{O}$, in which the following equality stands

$$\langle n\mathbf{k}|[\mathbf{r}_i,\mathcal{O}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}} \tag{2.80}$$

[¶] A simple operator is defined as one whose Bloch state matrix elements involve only $\delta(\mathbf{k}-\mathbf{k}')$.

where the $;\mathbf{k}$ operator represents a generalized derivative. With the aid of equation (2.77) and commutator relations it can be shown that [32]

$$(r^b_{nm})_{;k^a} = \frac{r^a_{nm}\Delta^b_{mn} + r^b_{nm}\Delta^a_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_l(\omega_{lm}r^a_{nl}r^b_{lm} - \omega_{nl}r^b_{nl}r^a_{lm}) \qquad (2.81)$$

defining Δ by

$$\Delta^a_{nm} \equiv \frac{p^a_{nn} - p^a_{mm}}{m} \qquad (2.82)$$

The equivalent of equation (2.35) in the length gauge is

$$\tilde{\rho}^{(N+1)}_L = \int_{-\infty}^t \frac{ie}{\hbar}[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), \tilde{\rho}^{(N)}_L] \qquad (2.83)$$

to first and second order yields explicity

$$\begin{aligned}\tilde{\rho}^{(1)}_L(t) &= \frac{ie}{\hbar}\int_{-\infty}^t dt'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), \rho_0] &\quad (2.84a)\\ \tilde{\rho}^{(2)}_L(t) &= \frac{ie}{\hbar}\int_{-\infty}^t dt'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), \tilde{\rho}^{(1)}_L] &\quad (2.84b)\end{aligned}$$

By decomposing the $\mathbf{r}$ operator into $\mathbf{r}_i$ and $\mathbf{r}_e$ from (2.83) and considering the matrix elements we get

$$\tilde{\rho}^{(N+1)}_{nm,L}(t) = \frac{ie}{\hbar}\int_{-\infty}^t dt' e^{i\omega_{nm}t'}\mathbf{E}(t')\cdot[\mathbf{R}^{(N)}_e(t') + \mathbf{R}^{(N)}_i(t')], \qquad (2.85)$$

where

$$\begin{aligned}\mathbf{R}^{(N)}_e &= \sum_l(r_{nl}\rho^{(N)}_{lm,L} - \rho^{(N)}_{nl,L}r_{lm}) &\quad (2.86a)\\ \mathbf{R}^{(N)}_i &= (\rho^{(N)}_{nm,L})_{;\mathbf{k}} &\quad (2.86b)\end{aligned}$$

To second order

$$\rho^{(2)}_{nm,L}(t) = \frac{e}{i\hbar}\frac{1}{\omega_{nm} - 2\omega}\Big[-(B^b_{nm})_{;\mathbf{k}} + i\sum_\ell(r^c_{n\ell}B^b_{\ell m} - B^b_{n\ell}r^c_{\ell m})\Big]E^bE^ce^{-2i\omega t} \quad (2.87)$$

with

$$B^b_{nm} = \frac{e}{\hbar}\frac{f_{nm} r^b_{nm}}{\omega_{nm} - \omega} \tag{2.88}$$

For the length gauge the velocity operator is

$$\mathbf{v} = \mathbf{p}/m, \tag{2.89}$$

thus we can substitute (2.87) into (2.32) to obtain the second harmonic tensor, even more it can be written in terms of intraband and interband contributions [10]:

$$\chi^{abc}(-2\omega;\omega,\omega) = \chi^{abc}_e(-2\omega;\omega,\omega) + \chi^{abc}_i(-2\omega;\omega,\omega), \tag{2.90}$$

where

$$\chi^{abc}_i = -\frac{e^3}{2m\hbar^2\omega}\sum_{m,n,\mathbf{k}} \frac{p^a_{mn}}{\omega_{nm} - 2\omega}\left(\frac{f_{mn} r^b_{nm}}{\omega_{nm} - \omega}\right)_{;k^c} \tag{2.91a}$$

$$\chi^{abc}_e = -\frac{e^3}{2m\hbar^2\omega}\sum_{\ell,m,n,\mathbf{k}} \frac{p^a_{mn}}{\omega_{nm} - 2\omega}\left(\frac{f_{m\ell} r^b_{n\ell} r^b_{\ell m}}{\omega_{\ell m} - \omega} - \frac{f_{\ell n} r^b_{n\ell} r^c_{\ell m}}{\omega_{n\ell} - \omega}\right) \tag{2.91b}$$

Equation (2.91a) can be simplified by the chain rule

$$\left(\frac{f_{mn} r^b_{nm}}{\omega_{nm} - \omega}\right)_{;k^c} = \frac{f_{mn}}{\omega_{nm} - \omega}(r^b_{nm})_{;k^c} - \frac{f_{nm} r^b_{nm}}{(\omega_{nm} - \omega)^2}(\omega_{nm})_{;k^c} \tag{2.92}$$

here

$$(\omega_{nm})_{;k^a} = \frac{p^a_{nn} - p^a_{mn}}{m} \tag{2.93}$$

now we can rewrite Equations (2.91a) and (2.91b) to

$$\chi^{abc}_e = \frac{e^3}{\hbar^2}\sum_{m,n,\ell,\mathbf{k}} \frac{r^a_{nm}\left(r^b_{m\ell} r^c_{\ell n} + r^c_{m\ell} r^b_{\ell n}\right)}{2(\omega_{\ell n} - \omega_{m\ell})}\left[\frac{2f_{nm}}{\omega_{mn} - 2\omega} - \frac{f_{n\ell}}{\omega_{\ell n} - \omega} - \frac{f_{\ell m}}{\omega_{m\ell} - \omega}\right] \tag{2.94}$$

and

$$
\begin{aligned}
\chi_i^{abc} = \quad & \frac{i}{2}\frac{e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} \frac{2f_{nm}r^a_{nm}\big((r_{mn})^b_{;k^c} + (r^c_{mn})_{;k^b}\big)}{\omega_{nm}(\omega_{mn}-2\omega)} \\
+ \quad & \frac{i}{2}\frac{e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} \frac{f_{nm}\big((r^a_{nm})_{;k^c}r^b_{mn} + (r^a_{nm})_{;k^b}r^c_{mn}\big)}{\omega_{mn}(\omega_{mn}-\omega)} \\
+ \quad & \frac{i}{2}\frac{e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} \frac{f_{nm}}{\omega^2_{nm}}\left(\frac{1}{\omega_{mn}-\omega} - \frac{4}{\omega_{mn}-2\omega}\right) r^a_{nm}(r^b_{mn}\Delta^c_{mn} + r^c_{mn}\Delta^b_{mn}) \\
- \quad & \frac{i}{2}\frac{e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} \frac{f_{nm}}{2\omega_{mn}}(\frac{1}{\omega_{mn}-\omega})((r^b_{nm})_{;k^a}r^c_{mn} + (r^c_{nm})_{;k^a}r^b_{mn}). \qquad (2.95)
\end{aligned}
$$

Separating the contributions of ω, I, and 2ω, II, and using (2.45) we arrive to our final expressions for the imaginary part of the secon harmonic suceptibility tensors:

$$
\begin{aligned}
\chi_{e\mathrm{I}}^{abc} = \quad - \quad & \frac{i\pi e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} f_{nm}\left[\frac{r^c_{mn}}{2}\sum_p\left(\frac{r^a_{np}r^b_{pm}}{\omega_{mn}-\omega_{pm}} + \frac{r^b_{np}r^a_{pm}}{\omega_{np}-\omega_{mn}}\right)\right. \\
+ \quad & \left.\frac{r^b_{mn}}{2}\sum_p\left(\frac{r^a_{np}r^c_{pm}}{\omega_{mn}-\omega_{pm}} + \frac{r^c_{np}r^a_{pm}}{\omega_{np}-\omega_{mn}}\right)\right]\delta(\omega_{mn}-\omega) \qquad (2.96)
\end{aligned}
$$

$$
\chi_{e\mathrm{II}}^{abc} = \frac{i\pi e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} f_{nm}r^a_{nm}\sum_p \frac{\big(r^b_{mp}r^c_{pn} + r^c_{mp}r^b_{pn}\big)}{(\omega_{pn}-\omega_{mp})}\delta(\omega_{mn}-2\omega) \qquad (2.97)
$$

and

$$
\begin{aligned}
\chi_{i\mathrm{I}}^{abc} = \quad - \quad & \frac{\pi e^3}{\hbar^2}\sum_{mn} f_{nm}\frac{(r^a_{nm})_{;k^c}(r^b_{mn} + (r^a_{nm})_{;k^b}r^c_{mn})}{2\omega_{mn}}\delta(\omega_{mn}-\omega) \\
- \quad & \frac{\pi e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} f_{nm}\frac{r^a_{nm}(r^b_{mn}\Delta^c_{mn} + r^c_{mn}\Delta^b_{mn})}{2\omega^2_{mn}}\delta(\omega_{mn}-\omega) \\
+ \quad & \frac{\pi e^3}{\hbar^2}\sum_{m,n,\mathbf{k}} f_{nm}\frac{\big((r^b_{nm})_{;k^a}r^c_{mn} + (r^c_{nm})_{;k^a}r^b_{mn}\big)}{4\omega_{mn}}\delta(\omega_{mn}-\omega) \quad (2.98)
\end{aligned}
$$

$$\begin{aligned}\chi_{i\mathrm{II}}^{abc} = & - \frac{\pi e^3}{\hbar^2} \sum_{m,n,\mathbf{k}} f_{nm} \frac{r_{nm}^a \big((r_{mn}^b)_{;k^c} + (r_{mn}^c)_{;k^b} \big)}{\omega_{mn}} \delta(\omega_{mn} - 2\omega) \\ & + \frac{\pi e^3}{\hbar^2} \sum_{m,n,\mathbf{k}} f_{nm} \frac{2 r_{nm}^a (r_{mn}^b \Delta_{mn}^c + r_{mn}^c \Delta_{mn}^b)}{\omega_{mn}^2} \delta(\omega_{mn} - 2\omega). \end{aligned} \quad (2.99)$$

Chapter 3

Analitical Demonstration of Gauge Invariance

> "The good news is that the formulation of nonlinear optical response of extended systems... is approaching a satisfactory state. The reference here is not to the recent advances... in formulating and calculating many-body effects such as local field and excitonic corrections, but rather the formulation of the very basic structure of the nonlinear optical response coefficients even in the independent particle approximation. The uninitiated might find it surprising that there could be any problems here." [24].

In this section we demonstrate explicitly the gauge invariance of the expressions. For this purpose we have to choices: To demonstrate by algebraic manipulation that the expressions (2.96) to (2.99) are equal to (2.51), or to find a relation between $\chi_L^{(2)}$ and $\chi_V^{(2)}$, we chose the second one.

3.1 Equivalence of Expressions

We present a general procedure to establish the equivalence between the longitudinal and the transverse or velocity gauge, based on the article by Aversa C. and Sipe J. E. [1]. In the velocity gauge Equation (2.20) leads to

$$i\hbar(\tilde{\rho}_V(t) - \rho_0) = \frac{-e}{mc}\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{p}}(t') \cdot \mathbf{A}(t'), \tilde{\rho}_V(t')], \tag{3.1}$$

where V denotes the velocity gauge. From $\tilde{\mathbf{p}} = m\dot{\tilde{\mathbf{r}}}$ an integration by parts gives

$$i\hbar(\tilde{\rho}_V(t) - \rho_0) = - \frac{e}{c}[\tilde{\mathbf{r}}(t)\cdot\mathbf{A}(t), \tilde{\rho}_V(t)] - e\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{r}}\cdot\mathbf{E}(t'), \tilde{\rho}_V(t')] + \frac{e}{c}\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{r}}\cdot\mathbf{A}(t'), \dot{\tilde{\rho}}_V(t')]. \tag{3.2}$$

We take

$$\rho_V = \rho_0 + \rho_V^{(1)} + \rho_V^{(2)} + \cdots, \tag{3.3}$$

where $\rho_V^{(N)}$ goes with the N-th power of the perturbation $\mathbf{E}(t)$. Then, to first order we get

$$i\hbar\tilde{\rho}_V^{(1)}(t) = - \frac{e}{c}[\tilde{\mathbf{r}}(t)\cdot\mathbf{A}(t), \tilde{\rho}_0(t)] - e\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{r}}\cdot\mathbf{E}(t'), \tilde{\rho}_0(t')] + \frac{e}{c}\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{r}}\cdot\mathbf{A}(t'), \dot{\tilde{\rho}}_0(t')]. \tag{3.4}$$

where $\dot{\tilde{\rho}}_0 = 0$, and thus

$$\tilde{\rho}_V^{(1)}(t) = \tilde{\rho}_L^{(1)}(t) - \frac{e}{i\hbar c}[\tilde{\mathbf{r}}(t)\cdot\mathbf{A}(t), \tilde{\rho}_0], \tag{3.5}$$

with

$$\tilde{\rho}_L^{(1)}(t) = \frac{-e}{i\hbar}\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{r}}\cdot\mathbf{E}(t'), \tilde{\rho}_0(t')], \tag{3.6}$$

where L denotes the longitudinal gauge, since $\mathrm{H}'(t) = -e\mathbf{r}\cdot\mathbf{E}$ in this gauge.

Now, we move to the second-order response, from Equation (3.2) we obtain

$$i\hbar\tilde{\rho}_V^{(2)}(t) = - \frac{e}{c}[\tilde{\mathbf{r}}(t)\cdot\mathbf{A}(t), \tilde{\rho}_V^{(1)}(t)] - e\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), \tilde{\rho}_V^{(1)}(t')] + \frac{e}{c}\int_{-\infty}^{t} \mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{A}(t'), \dot{\tilde{\rho}}_V^{(1)}(t')]. \tag{3.7}$$

From Equation (2.20) and (2.17) we have that

$$i\hbar\dot{\tilde{\rho}}_V^{(1)} = -\frac{e}{mc}[\tilde{\mathbf{p}}\cdot\mathbf{A}, \tilde{\rho}_0]. \tag{3.8}$$

Substituting Equation (3.8) and Equation (3.5) into Equation (3.7) we obtain

$$
\begin{aligned}
i\hbar\tilde{\rho}_V^{(2)}(t) = & - \frac{e}{c}[\tilde{\mathbf{r}}(t)\cdot\mathbf{A}(t), \tilde{\rho}_L^{(1)}(t)] + \frac{e^2}{i\hbar c^2}[\tilde{\mathbf{r}}(t)\cdot\mathbf{A}(t), [\tilde{\mathbf{r}}(t)\cdot\mathbf{A}(t), \tilde{\rho}_0]] \quad (3.9)\\
& - e\int_{-\infty}^{t}\mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), \tilde{\rho}_L^{(1)}(t')]\\
& + \frac{e^2}{i\hbar c}\int_{-\infty}^{t}\mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), [\tilde{\mathbf{r}}(t')\cdot\mathbf{A}(t'), \tilde{\rho}_0]] \quad (3.10)\\
& - \frac{e^2}{i\hbar mc^2}\int_{-\infty}^{t}\mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{A}(t'), [\tilde{\mathbf{p}}(t')\cdot\mathbf{A}(t'), \tilde{\rho}_0]].
\end{aligned}
$$

We use harmonic fields to write $\mathbf{A}(t) = (c/i\omega)\mathbf{E}(t)$, then

$$
\begin{aligned}
\tilde{\rho}_V^{(2)}(t) = & \quad \tilde{\rho}_L^{(2)}(t) + \frac{e}{\hbar\omega}[\tilde{\mathbf{r}}(t)\cdot\mathbf{E}(t), \tilde{\rho}_L^{(1)}(t)] \quad (3.11)\\
& + \frac{e^2}{\hbar^2\omega^2}[\tilde{\mathbf{r}}(t)\cdot\mathbf{E}(t), [\tilde{\mathbf{r}}(t)\cdot\mathbf{E}(t), \tilde{\rho}_0]]\\
& - \frac{e^2}{i\hbar^2\omega}\int_{-\infty}^{t}\mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), [\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), \tilde{\rho}_0]]\\
& - \frac{e^2}{m\hbar^2\omega^2}\int_{-\infty}^{t}\mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), [\tilde{\mathbf{p}}(t')\cdot\mathbf{E}(t'), \tilde{\rho}_0]],
\end{aligned}
$$

where

$$
\tilde{\rho}_L^{(2)} = -e\int_{-\infty}^{t}\mathrm{d}t'[\tilde{\mathbf{r}}(t')\cdot\mathbf{E}(t'), \tilde{\rho}_L^{(1)}(t')]\ , \quad (3.12)
$$

using the with the velocity operator in Equation (2.30) $\mathbf{v} = \mathbf{p}/m - e\mathbf{A}/mc$, we get

$$
\mathbf{J}_V^{(2)}(t) = \frac{e}{m}\mathrm{Tr}(\tilde{\rho}_V^{(2)}\tilde{\mathbf{p}}) - \frac{e^2}{mc}\mathrm{Tr}(\tilde{\rho}_V^{(1)}\mathbf{A}). \quad (3.13)
$$

Using Equation (3.11) we get (roman superscripts are Cartesian directions)

$$
\begin{aligned}
J_V^{a(2)}(t) = \quad & \frac{e}{m}\Bigg(\mathrm{Tr}\big(\tilde{\rho}_L^{(2)}(t)\tilde{p}^a(t)\big) + \frac{e}{\hbar\omega}E^b(t)\mathrm{Tr}\big([\tilde{r}^b(t), \tilde{\rho}_L^{(1)}(t)]\tilde{p}^a(t)\big) \\
+ \quad & \frac{e^2}{\hbar^2\omega^2}E^b(t)E^c(t)\mathrm{Tr}\big([\tilde{r}^b(t), [\tilde{r}^c(t), \tilde{\rho}_0]]\tilde{p}^a(t)\big) \\
- \quad & \frac{e^2}{i\hbar^2\omega}\int_{-\infty}^{t} \mathrm{d}t' E^b(t')E^c(t')\mathrm{Tr}\big([\tilde{r}^b(t'), [\tilde{r}^c(t'), \tilde{\rho}_0]]\tilde{p}^a(t)\big) \\
- \quad & \frac{e^2}{m\hbar^2\omega^2}\int_{-\infty}^{t} \mathrm{d}t' E^b(t')E^c(t')\mathrm{Tr}\big([\tilde{r}^b(t'), [\tilde{p}^c(t'), \tilde{\rho}_0]]\tilde{p}^a(t)\big)\Bigg) \\
- \quad & \frac{e^2}{mc}A^a(t)\mathrm{Tr}(\tilde{\rho}_L^{(1)}) + \frac{e^3}{i\hbar mc^2}A^a(t)A^b(t)\mathrm{Tr}([\tilde{r}^b(t), \tilde{\rho}_0]).
\end{aligned}
\tag{3.14}
$$

From the Appendix B

$$
\mathrm{Tr}(\tilde{\rho}_L^{(1)}) = 0, \tag{3.15}
$$

and using the well known properties of the trace

$$
\mathrm{Tr}(\tilde{a}\tilde{b}) = \mathrm{Tr}(ab) = \mathrm{Tr}(ba), \tag{3.16}
$$

we get

$$
\mathrm{Tr}([\tilde{r}^b(t), \tilde{\rho}_0]) = \mathrm{Tr}([r^b, \rho_0]) = \mathrm{Tr}(r^b\rho_0) - \mathrm{Tr}(\rho_0 r^b) = 0. \tag{3.17}
$$

Also,

$$
\begin{aligned}
J_V^{a(2)}(t) = \quad & J_L^{a(2)}(t) + \frac{e}{m}\Bigg(\frac{e}{\hbar\omega}E^b(t)\mathrm{Tr}\big([\tilde{p}^a(t), \tilde{r}^b(t)]\tilde{\rho}_L^{(1)}(t)\big) \\
+ \quad & \frac{e^2}{\hbar^2\omega^2}E^b(t)E^c(t)\mathrm{Tr}\big([\tilde{p}^a(t), [\tilde{r}^b(t), \tilde{r}^c(t)]]\tilde{\rho}_0(t)\big) \\
- \quad & \frac{e^2}{i\hbar^2\omega}\int_{-\infty}^{t} \mathrm{d}t' E^b(t')E^c(t')\mathrm{Tr}\big([[\tilde{p}^a(t), \tilde{r}^b(t')], \tilde{r}^c(t')]\tilde{\rho}_0(t')\big) \\
- \quad & \frac{e^2}{m\hbar^2\omega^2}\int_{-\infty}^{t} \mathrm{d}t' E^b(t')E^c(t')\mathrm{Tr}\big([[\tilde{p}^a(t), \tilde{r}^b(t')], \tilde{p}^c(t')]\tilde{\rho}_0(t')\big)\Bigg),
\end{aligned}
\tag{3.18}
$$

where

$$
J_L^{a(2)}(t) = \frac{e}{m}\mathrm{Tr}\big(\tilde{\rho}_L^{(2)}(t)\tilde{p}^a(t)\big). \tag{3.19}
$$

From Equation (3.15) and Equation (3.16) we get

$$\mathrm{Tr}\big([\tilde{p}^a(t),\tilde{r}^b(t)]\tilde{\rho}^{(1)}_L(t)\big) = \mathrm{Tr}\big([p^a,r^b]\rho^{(1)}_L\big) = -i\hbar\delta_{ab}\mathrm{Tr}\big(\rho^{(1)}_L\big) = 0, \tag{3.20}$$

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

$$\mathrm{Tr}\big([\tilde{p}^a(t),[\tilde{r}^b(t),\tilde{r}^c(t)]]\tilde{\rho}_0(t)\big) = \mathrm{Tr}\big([p^a,[r^b,r^c]]\rho_0\big) = 0, \tag{3.21}$$

from the fact that $[r^b,r^c]=0$.

Then, the Equation (3.18) reduces to

$$\begin{aligned} J^{a(2)}_V(t) &= J^{a(2)}_L(t) - \frac{e^3}{im\hbar^2\omega}\int_{-\infty}^{t}\mathrm{d}t' E^b(t')E^c(t')\mathrm{Tr}\big([[\tilde{p}^a(t),\tilde{r}^b(t')],\tilde{r}^c(t')]\tilde{\rho}_0(t')\big) \\ &\quad -\frac{e^3}{m^2\hbar^2\omega^2}\int_{-\infty}^{t}\mathrm{d}t' E^b(t')E^c(t')\mathrm{Tr}\big([[\tilde{p}^a(t),\tilde{r}^b(t')],\tilde{p}^c(t')]\tilde{\rho}_0(t')\big) \\ &= J^{a(2)}_L(t) + \mathcal{R}^{a(2)}, \end{aligned} \tag{3.22}$$

with

$$\begin{aligned} \mathcal{R}^{a(2)}(t) &= -\frac{e^2}{i\hbar^2\omega}\int_{-\infty}^{t}\mathrm{d}t' E^b(t')E^c(t')\Big(\mathrm{Tr}\big([\tilde{r}^b(t'),[\tilde{r}^c(t'),\tilde{\rho}_0(t')]]\tilde{p}^a(t)\big) \\ &\quad +\frac{1}{im\omega}\mathrm{Tr}\big([\tilde{r}^b(t'),[\tilde{p}^c(t'),\tilde{\rho}_0(t')]]\tilde{p}^a(t)\big)\Big). \end{aligned} \tag{3.23}$$

Take

$$\begin{aligned} \mathrm{Tr}\big([\tilde{r}^b(t'),[\tilde{r}^c(t'),\tilde{\rho}_0(t')]]\tilde{p}^a(t)\big) &= \mathrm{Tr}\big(U(t')[r^b,[r^c,\rho_0]]U^\dagger(t')U(t)p^aU^\dagger(t)\big) \qquad (3.24) \\ &= \sum_{mn}\langle m|U(t')[r^b,[r^c,\rho_0]]U^\dagger(t')|n\rangle\langle n|U(t)p^aU^\dagger(t)|m\rangle \\ &= \sum_{mn} e^{i\omega_{nm}t}e^{i\omega_{mn}t'}\langle m|[r^b,[r^c,\rho_0]]|n\rangle p^a_{nm}. \end{aligned}$$

Now, let's take matrix elements of

$$\begin{aligned} \langle m|[r^c,\rho_0]|n\rangle &= \langle m|[r^c_e,\rho_0]+[r^c_i,\rho_0]|n\rangle \\ &= \sum_\ell \big(r^c_{m\ell}\rho_{0,\ell n} - \rho_{0,m\ell}r^c_{\ell n}\big) + (\rho_{0,mn})_{;k^c}, \end{aligned} \tag{3.25}$$

where is understood that $\mathbf{r}_{mn}$ are the interband, $m \neq n$, matrix elements related to the momentum matrix elements by Equation (2.71). Also, the unperturbed zero order density matrix satisfies $\rho_{0,mn} = f_m\delta_{mn}$, so at $T = 0$, $(\rho_{0,mn})_{;k^c} = 0$, and then

$$\langle m|[r^c, \rho_0]|n\rangle = f_{nm} r^c_{mn}. \tag{3.26}$$

Finally,

$$\begin{aligned} \langle m|[r^b, [r^c, \rho_0]]|n\rangle &= \langle m|[r^b_e, [r^c, \rho_0]] + [r^b_i, [r^c, \rho_0]]|n\rangle \\ &= \sum_\ell \left(f_{n\ell} r^b_{m\ell} r^c_{\ell n} - f_{\ell m} r^c_{m\ell} r^b_{\ell n}\right) + i f_{nm} (r^c_{mn})_{;k^b}. \end{aligned} \tag{3.27}$$

Likewise,

$$\mathrm{Tr}\big([\tilde{r}^b(t'), [\tilde{p}^c(t'), \tilde{\rho}_0(t')]]\tilde{p}^a(t)\big) = \sum_{mn} e^{i\omega_{nm}t} e^{i\omega_{mn}t'} \langle m|[r^b, [p^c, \rho_0]]|n\rangle p^a_{nm}. \tag{3.28}$$

Now,

$$\begin{aligned} \langle m|[p^c, \rho_0]|n\rangle &= \sum_\ell \left(p^c_{m\ell}\rho_{0,\ell n} - \rho_{0,m\ell} p^c_{\ell n}\right) \\ &= f_{nm} p^c_{mn}, \end{aligned} \tag{3.29}$$

and finally

$$\begin{aligned} \langle m|[r^b, [p^c, \rho_0]]|n\rangle &= \langle m|[r^b_e, [p^c, \rho_0]] + [r^b_i, [p^c, \rho_0]]|n\rangle \\ &= \sum_\ell \left(f_{n\ell} r^b_{m\ell} p^c_{\ell n} - f_{\ell m} p^c_{m\ell} r^b_{\ell n}\right) + i f_{nm} (p^c_{mn})_{;k^b}. \end{aligned} \tag{3.30}$$

From Equation (2.71) we have that

$$\begin{aligned} (p^c_{mn})_{;k^b} &= i m r^c_{mn} (\omega_{mn})_{;k^b} + i m \omega_{mn} (r^c_{mn})_{;k^b} \\ &= i m \Delta^b_{mn} r^c_{mn} + i m \omega_{mn} (r^c_{mn})_{;k^b}, \end{aligned} \tag{3.31}$$

with Δ defined by Equation (2.82). We assume $\mathbf{E}(t) = \mathbf{E}_\omega e^{i\omega t}$, then the time integral of Equation (3.23), using Equation (3.24) and Equation (3.28), reduces to

$$e^{i\omega_{nm}t} E^b_\omega E^c_\omega \int_{-\infty}^t \mathrm{d}t' e^{i(\omega_{mn} - 2\omega)t'} = \frac{e^{-i2\omega t}}{i(\omega_{mn} - 2\omega)} E^b_\omega E^c_\omega. \tag{3.32}$$

Using this into Equation (3.23) we obtain

$$\begin{aligned}
\mathcal{R}^{a(2)}(t) = & - \frac{e^2}{i\hbar^2\omega}\sum_{mn}\Bigg[\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}r^c_{\ell n} - f_{\ell m}r^c_{m\ell}r^b_{\ell n}\right) + if_{nm}(r^c_{mn})_{;k^b} \\
& + \frac{1}{im\omega}\Bigg(\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}p^c_{\ell n} - f_{\ell m}p^c_{m\ell}r^b_{\ell n}\right) \\
& + if_{nm}(p^c_{mn})_{;k^b}\Bigg)\Bigg] \\
& \times \frac{p^a_{nm}}{i(\omega_{mn}-2\omega)}E^b_\omega E^c_\omega e^{-i2\omega t}. \qquad (3.33)
\end{aligned}$$

To obtain the non-linear susceptibility we use Equation (2.30), $\mathbf{P}(t) = \mathbf{P}(2\omega)e^{-i2\omega t}$ and $P^a(2\omega) = \chi^{abc}(2\omega)E^b_\omega E^c_\omega$ to obtain that

$$\begin{aligned}
\chi^{abc}_V(2\omega) &= \chi^{abc}_L(2\omega) - \frac{e^2}{i2\hbar^2\omega^2}\sum_{mn}\Bigg[\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}r^c_{\ell n} - f_{\ell m}r^c_{m\ell}r^b_{\ell n}\right) + if_{nm}(r^c_{mn})_{;k^b} \\
&+ \frac{1}{im\omega}\Bigg(\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}p^c_{\ell n} - f_{\ell m}p^c_{m\ell}r^b_{\ell n}\right) + if_{nm}(p^c_{mn})_{;k^b}\Bigg)\Bigg] \\
&\times \frac{p^a_{nm}}{(\omega_{mn}-2\omega)}. \qquad (3.34)
\end{aligned}$$

Then, we define

$$\begin{aligned}
R^{abc} &= -\frac{e^2}{i2\hbar^2\omega^2}\sum_{mn}\Bigg[\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}r^c_{\ell n} - f_{\ell m}r^c_{m\ell}r^b_{\ell n}\right) + if_{nm}(r^c_{mn})_{;k^b} \qquad (3.35) \\
&+ \frac{1}{im\omega}\Bigg(\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}p^c_{\ell n} - f_{\ell m}p^c_{m\ell}r^b_{\ell n}\right) + if_{nm}(p^c_{mn})_{;k^b}\Bigg)\Bigg]\frac{p^a_{nm}}{(\omega_{mn}-2\omega)} \\
&= \frac{e^2}{i4\hbar^2\omega^3}\sum_{\ell m} f_{m\ell}\Big[\left(r^b_{m\ell}r^c_{\ell m} + r^c_{m\ell}r^b_{\ell m}\right) + \frac{1}{im\omega}\left(r^b_{m\ell}p^c_{\ell m} + p^c_{m\ell}r^b_{\ell m}\right)\Big]p^a_{mm} \\
&- \frac{e^2}{i2\hbar^2\omega^2}\sum_{m\neq n}\Bigg[\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}r^c_{\ell n} - f_{\ell m}r^c_{m\ell}r^b_{\ell n}\right) + if_{nm}(r^c_{mn})_{;k^b} \\
&+ \frac{1}{im\omega}\Bigg(\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}p^c_{\ell n} - f_{\ell m}p^c_{m\ell}r^b_{\ell n}\right) + if_{nm}(p^c_{mn})_{;k^b}\Bigg)\Bigg]\frac{p^a_{nm}}{(\omega_{mn}-2\omega)},
\end{aligned}$$

Where we can safely use Equation (2.71) to write

$$
\begin{aligned}
R^{abc} &= \frac{e^3}{i4m\hbar^2\omega^3}\sum_{\ell m} f_{m\ell}\left[\left(r^b_{m\ell}r^c_{\ell m}+r^c_{m\ell}r^b_{\ell m}\right)+\frac{\omega_{\ell m}}{\omega}\left(r^b_{m\ell}r^c_{\ell m}-r^c_{m\ell}r^b_{\ell m}\right)\right]p^a_{mm} \quad (3.36)\\
&- \frac{e^3}{2m\hbar^2}\sum_{m\neq n}\left[\left(\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}r^c_{\ell n}-f_{\ell m}r^c_{m\ell}r^b_{\ell n}\right)+if_{nm}(r^c_{mn})_{;k^b}\right)\frac{\omega_{mn}r^a_{nm}}{\omega^2(\omega_{mn}-2\omega)}\right.\\
&+ \left.\left(\sum_{\ell}\left(f_{n\ell}r^b_{m\ell}\omega_{\ell n}r^c_{\ell n}-f_{\ell m}\omega_{m\ell}r^c_{m\ell}r^b_{\ell n}\right)+if_{nm}(\omega_{mn}r^c_{mn})_{;k^b}\right)\frac{\omega_{mn}r^a_{nm}}{\omega^3(\omega_{mn}-2\omega)}\right].
\end{aligned}
$$

We analyze each term separately, and add the sum over $\mathbf{k}$ that we have omitted for brevity thus far. First term in right hand side (r.h.s.):

$$
\begin{aligned}
\sum_{\mathbf{k}\ell m} f_{m\ell}\left[\left(r^b_{m\ell}r^c_{\ell m}+r^c_{m\ell}r^b_{\ell m}\right)p^a_{mm}\right. &= \sum_{\mathbf{k}>0\ell m} f_{m\ell}\left[\left(r^b_{m\ell}(\mathbf{k})r^c_{\ell m}(\mathbf{k})+r^c_{m\ell}(\mathbf{k})r^b_{\ell m}(\mathbf{k})\right)p^a_{mm}(\mathbf{k})\right.\\
&\quad \left.+\left(r^b_{m\ell}(-\mathbf{k})r^c_{\ell m}(-\mathbf{k})+r^c_{m\ell}(-\mathbf{k})r^b_{\ell m}(-\mathbf{k})\right)p^a_{mm}(-\mathbf{k})\right]\\
&= \sum_{\mathbf{k}>0\ell m} f_{m\ell}\left[\left(r^b_{m\ell}(\mathbf{k})r^c_{\ell m}(\mathbf{k})+r^c_{m\ell}(\mathbf{k})r^b_{\ell m}(\mathbf{k})\right)\right. \quad (3.37)\\
&\quad \left.-\left(r^b_{\ell m}(\mathbf{k})r^c_{m\ell}(\mathbf{k})+r^c_{\ell m}(\mathbf{k})r^b_{m\ell}(\mathbf{k})\right)\right]p^a_{mm}(\mathbf{k})=0,
\end{aligned}
$$

where we used $\mathbf{r}_{mn}(-\mathbf{k})=\mathbf{r}_{nm}(\mathbf{k})$ and $\mathbf{p}_{mn}(-\mathbf{k})=-\mathbf{p}_{nm}(\mathbf{k})$. Second term in r.h.s: we obtain its real part

$$
\begin{aligned}
\frac{\omega_{\ell m}}{2\omega}p^a_{mm}\left[\left(r^b_{m\ell}r^c_{\ell m}-r^c_{m\ell}r^b_{\ell m}\right)+\left(r^b_{m\ell}r^c_{\ell m}-r^c_{m\ell}r^b_{\ell m}\right)^*\right] &= \frac{2\omega_{\ell m}}{\omega}p^a_{mm}\left[\left(r^b_{m\ell}r^c_{\ell m}-r^c_{m\ell}r^b_{\ell m}\right)\right.\\
&+ \left.\left(r^b_{\ell m}r^c_{m\ell}-r^c_{\ell m}r^b_{m\ell}\right)\right] \quad (3.38)\\
&= 0,
\end{aligned}
$$

where we used $\mathbf{r}^*_{mn}=\mathbf{r}_{nm}$ and the fact the expectation value $\mathbf{p}_{mm}$ is be real. Note that this means that the contribution of the second term to the imaginary part of R^{abc} is zero.

For the last two terms we use partial fractions for

$$
\frac{\omega_{mn}}{\omega^2(\omega_{mn}-2\omega)}=\frac{1}{\omega^2}+\frac{2}{\omega\omega_{mn}}+\frac{4}{\omega_{mn}(\omega_{mn}-2\omega)}, \quad (3.39)
$$

and

$$
\frac{\omega_{mn}}{\omega^3(\omega_{mn}-2\omega)}=\frac{1}{\omega^3}+\frac{4}{\omega\omega^2_{mn}}+\frac{2}{\omega^2\omega_{mn}}+\frac{8}{\omega^2_{mn}(\omega_{mn}-2\omega)}, \quad (3.40)
$$

then, we obtain the following terms

$$\mathcal{A} = \Big(\quad \big(f_{n\ell} r^b_{m\ell} r^c_{\ell n} - f_{\ell m} r^c_{m\ell} r^b_{\ell n}\big) + i f_{nm} (r^c_{mn})_{;k^b} \Big) \\ \times \quad (\frac{1}{\omega^2} + \frac{2}{\omega\omega_{mn}} + \frac{4}{\omega_{mn}(\omega_{mn} - 2\omega)}), \tag{3.41}$$

and

$$\mathcal{B} = \Big(\quad \big(f_{n\ell} r^b_{m\ell} \omega_{\ell n} r^c_{\ell n} - f_{\ell m} \omega_{m\ell} r^c_{m\ell} r^b_{\ell n}\big) + i f_{nm} (\omega_{mn} r^c_{mn})_{;k^b} \Big) \\ \times \quad (\frac{1}{\omega^3} + \frac{4}{\omega\omega^2_{mn}} + \frac{2}{\omega^2\omega_{mn}} + \frac{8}{\omega^2_{mn}(\omega_{mn} - 2\omega)}). \tag{3.42}$$

We expand to obtain 6 terms for $\mathcal{A}$ and 8 terms for $\mathcal{B}$, and call these terms $\mathcal{A}_i$ and $\mathcal{B}_i$, so for instance

$$\mathcal{A}_2 = \big(f_{n\ell} r^b_{m\ell} r^c_{\ell n} - f_{\ell m} r^c_{m\ell} r^b_{\ell n}\big) \frac{2}{\omega\omega_{mn}}, \tag{3.43}$$

and

$$\mathcal{B}_8 = i f_{nm} (\omega_{mn} r^c_{mn})_{;k^b} \frac{8}{\omega^2_{mn}(\omega_{mn} - 2\omega)}, \tag{3.44}$$

and so forth. We look for the imaginary part of each term, since we would like to get $\mathrm{Im}(R^{abc})$, and use

$$(r^a_{mn})^*_{;k^b} = (r^a_{nm})_{;k^b} \quad (r^a_{mn}(-\mathbf{k}))_{;k^b} = -(r^a_{nm}(\mathbf{k}))_{;k^b}, \tag{3.45}$$

to get that $\mathrm{Im}(\mathcal{A}) = 0$, and $\mathrm{Im}(\mathcal{B}) = 0$. They way that the imaginary part of each $\mathcal{A}_i$ and $\mathcal{B}_i$ is zero depends on several steps, that we proceed to mention but leave the details of the straightforward calculation to the reader:

- $\mathcal{A}_1$ exchange $m \leftrightarrow n$, and the term is real.
- $\mathcal{A}_2$ exchange $m \leftrightarrow n$, add the $\mathbf{k}$ and $-\mathbf{k}$ contributions, and the term is zero.
- $\mathcal{A}_3$ exchange $m \leftrightarrow n$, calculate the imaginary part, add the $\mathbf{k}$ and $-\mathbf{k}$ contributions, and the term is zero.
- $\mathcal{A}_{4,5,6}$ calculate the imaginary part, add the $\mathbf{k}$ and $-\mathbf{k}$ contributions, and the term is zero.

$\mathcal{B}_{1,2}$ exchange $m \leftrightarrow n$, add the $\mathbf{k}$ and $-\mathbf{k}$ contributions, and the term is zero.

$\mathcal{B}_3$ exchange $m \leftrightarrow n$, and the term is real.

$\mathcal{B}_4$ exchange $m \leftrightarrow n$, calculate the imaginary part, add the $\mathbf{k}$ and $-\mathbf{k}$ contributions, and the term is zero.

$\mathcal{B}_{5,6,7,8}$ calculate the imaginary part, add the $\mathbf{k}$ and $-\mathbf{k}$ contributions, and the term is zero.

Then, we have that $\mathrm{Im}(R^{abc}) = 0$, and from Equation (3.34)

$$\mathrm{Im}(\chi_V^{abc}) = \mathrm{Im}(\chi_L^{abc}). \tag{3.46}$$

Using the Kramers-Kronig relations we finally get that $\chi_V^{abc} = \chi_L^{abc}$. If we go back to Equation (3.14), we realize that the time integral terms contribute zero, and then the equality between the velocity and longitudinal gauges depends on $[r^a, p^b] = i\hbar\delta_{ab}$ and $[r^a, r^b] = 0$ being satisfied. Of course, they are formally satisfied, but when a numerical calculation is done, both the numerical accuracy and the approximations of the method itself, do not a priory guarantee the fulfillment of the commutation relationships.

3.2 Commutator Relations

In order to see the fulfillment of the commutation relationships, we take as an example the matrix elements of $[r^a, p^b] = i\hbar\delta_{ab}$, then

$$\langle n\mathbf{k}|[r^a, p^b]|m\mathbf{k}'\rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{3.47}$$

so

$$\langle n\mathbf{k}|[r_i^a, p^b]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|[r_e^a, p^b]|m\mathbf{k}'\rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'). \tag{3.48}$$

From Ref. [32]

$$\langle n\mathbf{k}|[r_i^a, p^b]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(p^b_{nm})_{;k^a} \tag{3.49}$$

$$(p^b_{nm})_{;k^a} = \nabla_{k^a} p^b_{nm}(\mathbf{k}) - i p^b_{nm}(\mathbf{k})\left(\xi^a_{nn}(\mathbf{k}) - \xi^a_{mm}(\mathbf{k})\right), \tag{3.50}$$

and

$$\begin{aligned}
\langle n\mathbf{k}|[r_e^a, p^b]|m\mathbf{k}'\rangle &= \sum_{\ell\mathbf{k}''}\Bigg(\langle n\mathbf{k}|r_e^a|\ell\mathbf{k}''\rangle\langle \ell\mathbf{k}''|p^b|m\mathbf{k}'\rangle \\
&\quad -\langle n\mathbf{k}|p^b|\ell\mathbf{k}''\rangle\langle \ell\mathbf{k}''|r_e^a|m\mathbf{k}'\rangle\Bigg) \\
&= \sum_{\ell\mathbf{k}''}\Bigg((1-\delta_{n\ell})\delta(\mathbf{k}-\mathbf{k}'')\xi_{n\ell}^a\delta(\mathbf{k}''-\mathbf{k}')p_{\ell m}^b \\
&\quad -\delta(\mathbf{k}-\mathbf{k}'')p_{n\ell}^b(1-\delta_{\ell m})\delta(\mathbf{k}''-\mathbf{k}')\xi_{\ell m}^a\Bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\sum_{\ell}\Bigg((1-\delta_{n\ell})\xi_{n\ell}^a p_{\ell m}^b \\
&\quad -(1-\delta_{\ell m})p_{n\ell}^b\xi_{\ell m}^a\Bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\sum_{\ell}\Bigg(r_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b r_{\ell m}^a\Bigg), \qquad (3.51)
\end{aligned}$$

where we use the fact that the interband matrix elements of $\mathbf{r}$ are defined by Equation (2.72), where we see that r_{nm}^a intrinsically have $n \neq m$. Also, from the previous to the last step of Equation (3.51), we could obtain that

$$\langle n\mathbf{k}|[r_e^a, p^b]|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\Bigg(\sum_{\ell}\Bigg(\xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b\xi_{\ell m}^a\Bigg) + p_{nm}^b(\xi_{mm}^a - \xi_{nn}^a)\Bigg). \qquad (3.52)$$

Using Equations (3.49) and (3.52) into Equation (3.48) gives

$$\begin{aligned}
i\delta(\mathbf{k}-\mathbf{k}')\Bigg((p_{nm}^b)_{;k^a} &\quad -i\sum_{\ell}\Bigg(\xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b\xi_{\ell m}^a\Bigg) \\
&\quad -ip_{nm}^b(\xi_{mm}^a - \xi_{nn}^a)\Bigg) = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \qquad (3.53)
\end{aligned}$$

then

$$\begin{aligned}
(p_{nm}^b)_{;k^a} &= \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell}\Bigg(\xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b\xi_{\ell m}^a\Bigg) \\
&\quad + ip_{nm}^b(\xi_{mm}^a - \xi_{nn}^a), \qquad (3.54)
\end{aligned}$$

and from Equation (3.50),

$$\nabla_{k^a} p^b_{nm} = \hbar\delta_{ab}\delta_{nm} + i\sum_\ell \Bigg(\xi^a_{n\ell}p^b_{\ell m} - p^b_{n\ell}\xi^a_{\ell m}\Bigg). \tag{3.55}$$

Now, there are two cases. We use Equations (2.72) and (2.71).
Case $n = m$

$$\frac{1}{\hbar}\nabla_{k^a} p^b_{nn} = \delta_{ab} - \frac{m}{\hbar}\sum_\ell \omega_{\ell n}\Bigg(r^a_{n\ell}r^b_{\ell n} + r^b_{n\ell}r^a_{\ell n}\Bigg), \tag{3.56}$$

that gives the familiar expansion for the inverse effective mass tensor $(m_n^{-1})_{ab}$ [33].
Case $n \neq m$

$$\begin{aligned}
(p^b_{nm})_{;k^a} &= \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell\neq m\neq n}\Bigg(\xi^a_{n\ell}p^b_{\ell m} - p^b_{n\ell}\xi^a_{\ell m}\Bigg) \\
&\quad + i\Bigg(\xi^a_{nm}p^b_{mm} - p^b_{nm}\xi^a_{mm}\Bigg) \\
&\quad + i\Bigg(\xi^a_{nn}p^b_{nm} - p^b_{nn}\xi^a_{nm}\Bigg) + ip^b_{nm}(\xi^a_{mm} - \xi^a_{nn}) \\
&= -m\sum_\ell\Bigg(\omega_{\ell m}r^a_{n\ell}r^b_{\ell m} - \omega_{n\ell}r^b_{n\ell}r^a_{\ell m}\Bigg) + i\xi^a_{nm}(p^b_{mm} - p^b_{nn}) \\
&= -m\sum_\ell\Bigg(\omega_{\ell m}r^a_{n\ell}r^b_{\ell m} - \omega_{n\ell}r^b_{n\ell}r^a_{\ell m}\Bigg) + imr^a_{nm}\Delta^b_{mn},
\end{aligned} \tag{3.57}$$

where Δ is defined by Equation (2.82). Going back to Equation (3.47), we also have two cases *Case* $n = m$

$$\begin{aligned}
\langle n|[r^a,p^b]|n\rangle &= \sum_{\ell\neq n}\left(r^a_{n\ell}p^b_{\ell n}-p^b_{n\ell}r^a_{\ell n}\right)+i\nabla_{k^a}p^b_{nn} \\
&= \sum_{\ell\neq n}\left(r^a_{n\ell}p^b_{\ell n}-p^b_{n\ell}r^a_{\ell n}\right)+i\hbar\delta_{ab}-im\sum_{\ell}\omega_{\ell n}\left(r^a_{n\ell}r^b_{\ell n}+r^b_{n\ell}r^a_{\ell n}\right) \\
&= \sum_{\ell\neq n}\left(r^a_{n\ell}p^b_{\ell n}-p^b_{n\ell}r^a_{\ell n}\right)+i\hbar\delta_{ab}-\sum_{\ell\neq n}\left(r^a_{n\ell}p^b_{\ell n}+r^b_{n\ell}p^a_{\ell n}\right) \\
&= -\sum_{\ell\neq n}\left(p^b_{n\ell}r^a_{\ell n}+r^b_{n\ell}p^a_{\ell n}\right)+i\hbar\delta_{ab} \\
&= i\hbar\delta_{ab},
\end{aligned} \tag{3.58}$$

where the last equality is simple given by Equation (3.47), and we used Equations (3.51) and (3.56), also the **k** dependence is understood. Above equation leads to

$$\sum_{\ell\neq n}\left(p^b_{n\ell}r^a_{\ell n}+r^b_{n\ell}p^a_{\ell n}\right)=0,\quad \forall\, n. \tag{3.59}$$

Case $n\neq m$

$$\begin{aligned}
\langle n|[r^a,p^b]|n\rangle &= \sum_{\ell\neq m\neq n}\left(r^a_{n\ell}p^b_{\ell m}-p^b_{m\ell}r^a_{\ell n}\right)+i(p^b_{nm})_{;k^a} \\
&= \sum_{\ell\neq m\neq n}\left(r^a_{n\ell}p^b_{\ell m}-p^b_{m\ell}r^a_{\ell n}\right) \\
&- im\sum_{\ell\neq m\neq n}\left(\omega_{\ell m}r^a_{n\ell}r^b_{\ell m}-\omega_{n\ell}r^b_{n\ell}r^a_{\ell m}\right)-mr^a_{nm}\Delta^b_{mn} \\
&= \sum_{\ell\neq m\neq n}\left(r^a_{n\ell}p^b_{\ell m}-p^b_{m\ell}r^a_{\ell n}\right)-\sum_{\ell\neq m\neq n}\left(r^a_{n\ell}p^b_{\ell m}-p^b_{n\ell}r^a_{\ell m}\right)-mr^a_{nm}\Delta^b_{mn} \\
&= \\
&= \sum_{\ell\neq m\neq n}\left(p^b_{n\ell}r^a_{\ell m}-p^b_{m\ell}r^a_{\ell n}\right)-mr^a_{nm}\Delta^b_{mn} \\
&= 0,
\end{aligned} \tag{3.60}$$

where the last equality is simple given by Equation (3.47), and we used Equations (3.51) and (3.57), also the $\mathbf{k}$ dependence is understood. Above equation leads to

$$\sum_{\ell \neq m \neq n} \left(p^b_{n\ell} r^a_{\ell m} - p^b_{m\ell} r^a_{\ell n} \right) - m r^a_{nm} \Delta^b_{mn} = 0, \quad \forall\, n \neq m. \tag{3.61}$$

Equation (3.59) and (3.61) could be numerically verified in order to see weather or not the commutator $[r^a, p^b] = i\hbar\delta_{ab}$ is satisfied or not. In a similar way we could verify other commutators like $[r^a, r^b] = 0$, etc.

Chapter 4

Results

> "...the brevity of life does not allow us the luxury of spending time on problems which will lead to no new results..."
>
> –Landau, 1959.

In the first section we explain the computational details for the calculation of the second order nonlinear optical response for bulk GaAs, subsequently we show the results obtained for the transversal gauge and the length gauge calculations.

4.1 Computational Details

The ground state results have been obtained thanks to the use of the ABINIT code [34], that is based on pseudopotentials and planewaves. The ABINIT program is mostly based on DFT and we use it to calculate the energy eigenvalues and wave function (WF) of the system, from these data we can calculate the momentum and position matrix elements [35].

Due to the fact that bulk semiconductors are periodic, we expect the WF to be periodic and thus a infinite number of plane waves is necessary to expand it in a Fourier like expansion. The plane waves are a particular well suited set of basis functions for extended systems and its simplicity leads to very efficient numerical schemes for solving KS equations [36].

Pseudopotentials replace the true valence WF by pseudo wave-functions which match exactly the true valence WFs outside the ionic core region, the direct implication of this is to reduce the number of planewaves. Hartwigsen, Goedecker,

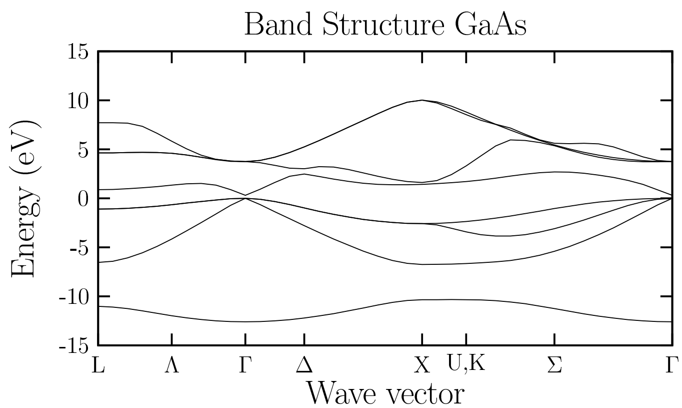

Figure 4.1 : Calculation of the Band Structure for GaAs without the scissors correction, the band gap calculated is .34 eV when the theoretical value is 1.519 eV. The theoretical value of 10.45 a_0 for the lattice constant is used [28].

Hutter pseudopotentials where used [37], such potentials take into account the spin orbit effect.

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}} C_{i,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{4.1}$$

The coefficients $C_{i,\mathbf{k}+\mathbf{G}}$ used to expand a wave function with small kinetic energy are more important than those with large kinetic energy [38]. Therefore, we will only consider the plane waves with coefficients having a kinetic energy no longer than a *cutoff energy* [39]. That is, we will truncate our calculations when we reach the *cutoff energy*. It is important to choose the minimum cutoff energy at which the results converge in order to save computing resources and time.

To correct the underestimation of the band gap within the DFT, as shown in Figure 4.1, a "Scissors" correction is implemented, Figure 4.2. This correction is a modification of the KS-LDA Hamiltonian to include a term that rigidly shifts the conduction band energies up in energy so that the band gap is correct.

We must take into account that the scissors operator modifies the value of the interband momentum matrix elements connecting occupied to unoccupied states; the effect over the matrix elements is important in the evaluation of nonlinear response. We use the Scissors implementation as proposed by Nastos F., Olejnik B., Schwarz K., and Sipe J. E. [40] for the position matrix elements and as stated

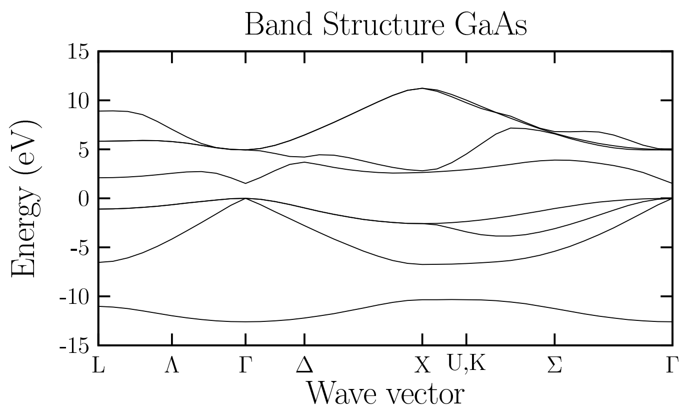

Figure 4.2 : Calculation of the Band Structure for GaAs with scissors correction, the band gap was adjusted to 1.519 eV.

by Del Sole and Girlanda [5] for momentum matrix elements.

Momentum matrix elements are calculated from the WF output of the ABINIT code, which is expressed as in Equation (4.1), so the momentum matrix elements are [41]

$$\langle\psi_m|\mathbf{p}|\psi_n\rangle_{\mathbf{k}} = -i\int d\mathbf{r}\psi^*_{m,\mathbf{k}}\hbar\nabla\psi_{n,\mathbf{k}} \tag{4.2}$$

where m, n stand for the band index. After straightforward algebraic manipulation we get the following result

$$\mathbf{p}_{mn,\mathbf{k}} = \hbar\sum_{\mathbf{G}} C^*_{\mathbf{k},m}(\mathbf{G})C_{\mathbf{k},n}(\mathbf{G})(\mathbf{k}+\mathbf{G}) \tag{4.3}$$

When the scissors operator is applied the momentum matrix elements must be renormalized, [42]:

$$\mathbf{p}_{CV} = \mathbf{p}^{\mathrm{LDA}}_{CV}\frac{E_C(\mathbf{k}) - E_V(\mathbf{k}) + \Delta}{E_C(\mathbf{k}) - E_V(\mathbf{k})}, \tag{4.4}$$

where Δ is the energy shift and C and V stand for conduction and valence bands.

The contributions to the momentum matrix elements from the non-local part of the pseudopotential is excluded, as is usually done, see derivation fo Equation (2.69).

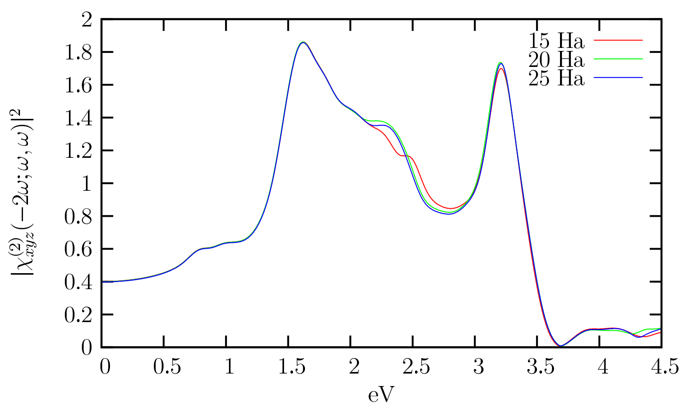

Figure 4.3 : Ecut convergence test for the transversal gauge, at 20 Ha convergence was achieved, the total band number is set to 24 and the number of kpoints to 11480.

As stated by Nastos F. et al. [40], $\mathbf{r}^a_{nm}(\mathbf{k})$ and $(\mathbf{r}^a_{nm})_{;k^b}$ are written in terms of the momentum matrix elements and energy eigenvalues of the KS-LDA by

$$\mathbf{r}_{mn}(\mathbf{k}) = \frac{\mathbf{v}^{\mathrm{LDA}}_{mn}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{mn}} \tag{4.5}$$

where $\omega_{mn} = \omega_m - \omega_n$. So the position matrix elements must be calculated before the renormalization of the momentum matrix elements and before the scissors correction is applied to the energy eigenvalues.

4.2 Transversal Gauge Results

The results are in CGS units and scaled by a factor of 10^6. We observe that the transversal gauge convergence was achieved at an ecut of 20 Ha, Figure (4.3) and it slowly converges at around 16200 kpts of equi-spaced sampling in the irreducible Brillouin zone, Figure 4.4. The convergence in bands took place at 24 bands; 8 valence bands and 16 conduction bands, Figure 4.5.

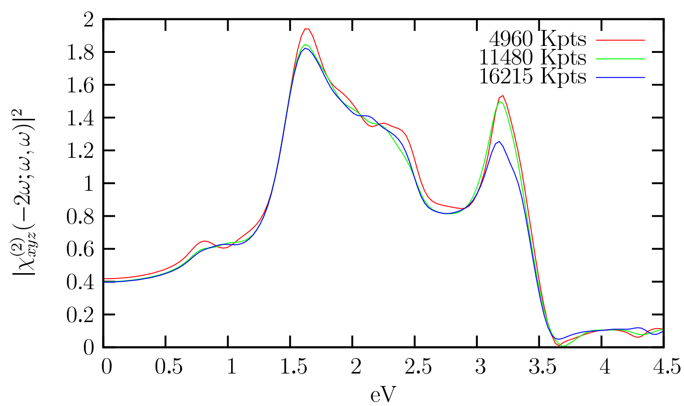

Figure 4.4 : Kpoints convergence test for the transversal gauge, it converges for more than 16000 kpoints, the ecut is set to 20 Ha and the band number to 24.

4.3 Length Gauge Results

The length gauge convergence was much more cumbersome: the convergence on ecut was not achieved to any value, Figure 4.8, the kpoints convergence could not been achieved by equidistant sampling, Figure 4.7, but the band convergence was achieved at 24 bands, Figure 4.6.

The convergence of the kpoints in the length gauge was not achieved by standard procedures, the use of an adaptive approach for the kpoints sampling, such approach is proposed by Nastos et al. [28]. The number of **k** points can be significantly reduced if one does not restrict oneself to an equi-spaced mesh of kpoints, the adaptive scheme more **k** points are added around a targeted kpoints to produce a finer mesh without augmenting significantly the overall number of kpoints, this scheme is very efficient to save computer time.

Using adaptive sampling we were able to obtain kpoints converged susceptibilities, Figure 4.9. Once the convergence in kpoints was achieved we were able to achieve convergence in ecut, Figure 4.10, at 24 Ha.

We use the adaptive sampling to perform another transversal gauge calculation, Figure 4.11, with the same results obtained previously for equi-spaced sampling, Figure 4.4.

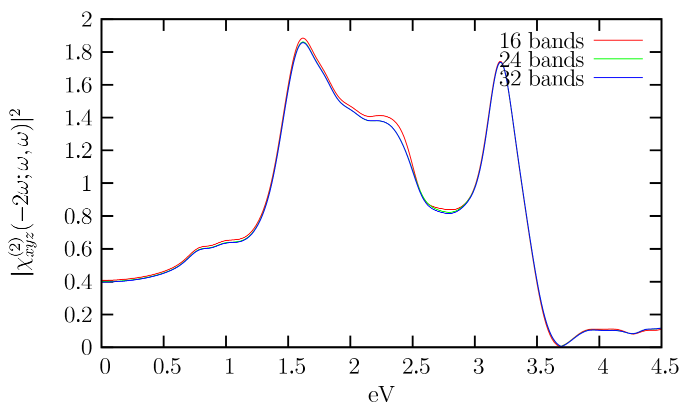

Figure 4.5 : Bands convergence test for the transversal gauge, it converges for 24 bands total bands: 8 valence bands and 16 conduction bands. The ecut is set to 20 Ha and the number of kpoints to 11480.

4.4 Transversal vs. Length Gauge Results

When we compare the two gauges we notices that they slightly differ, Figure 4.12 although in both the peaks of $\chi^{(2)}$ take place at eV values of half the band gap, the band gap and twice the band gap.

The unphysical differences between both gauges calculations are from the expressions

$$\mathrm{Tr}\big([\tilde{p}^a(t), \tilde{r}^b(t)]\tilde{\rho}^{(1)}_L(t)\big) = 0, \tag{4.6}$$

and,

$$\mathrm{Tr}\big([\tilde{p}^a(t), [\tilde{r}^b(t), \tilde{r}^c(t)]]\tilde{\rho}_0(t)\big) = \mathrm{Tr}\big([p^a, [r^b, r^c]]\rho_0\big) = 0, \tag{4.7}$$

that appears in Equation (3.18), the terms must be zero due to the fact that the commutators are formally a constant or zero, Equations (3.20) and (3.21). However when the term is numerically evaluated we find that it is different from zero, Figure 4.13. The unfullfillment of the commutator relations are attributed to exclusion of the non-local part of the pseudopotential contributions to the momentum matrix elements, Equation (2.69).

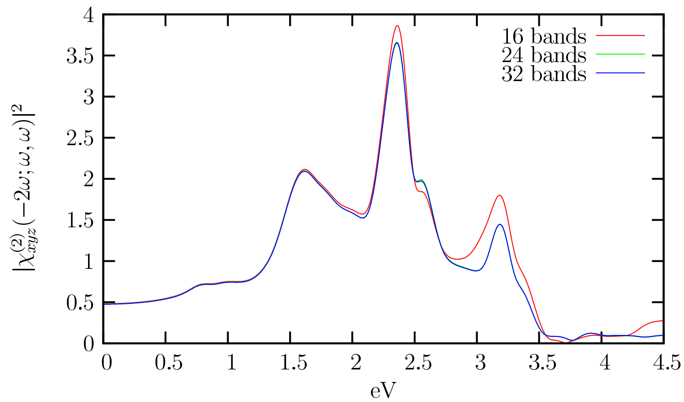

Figure 4.6 : Bands convergence test for the length gauge, it converges for 24 bands. The ecut is set to 20 Ha and the number of kpoints to 11480

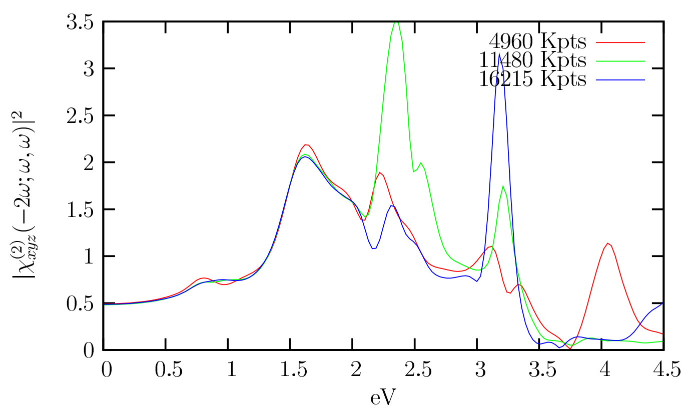

Figure 4.7 : Kpoints convergence test for the transversal gauge, convergence could not been achieved even at 16000 kpoints. The number of bands is set to 24 and the ecut to 20 Ha.

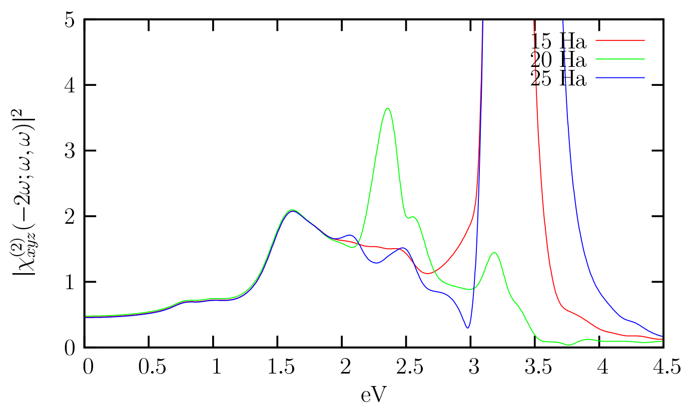

Figure 4.8 : Ecut convergence test for the length gauge, the convergence is not achived at any value. The number of bands is set to 24 and the number of kpoints to 11480.

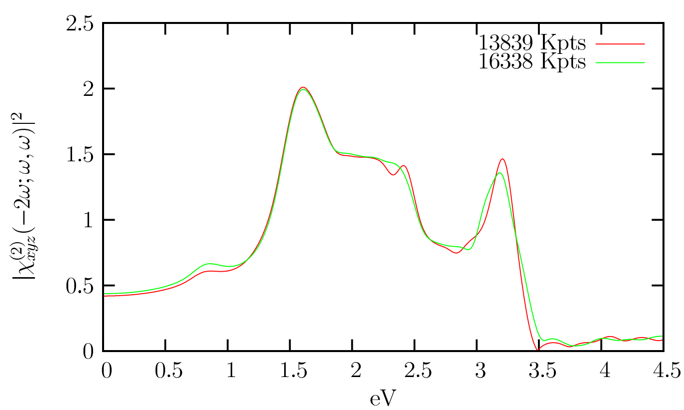

Figure 4.9 : Convergence is achieved at 16338 kpoints using the adaptive sampling, energies below 5eV are targeted. The number of bands is set to 24 and the ecut to 20 Ha.

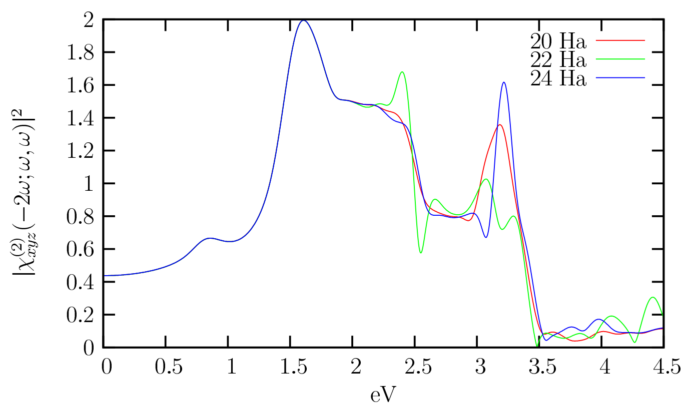

Figure 4.10 : Ecut convergence test length gauge, the kpoints convergence was achieved trough adaptive sampling, 16338, and now we see the ecut converge at 24 Ha.

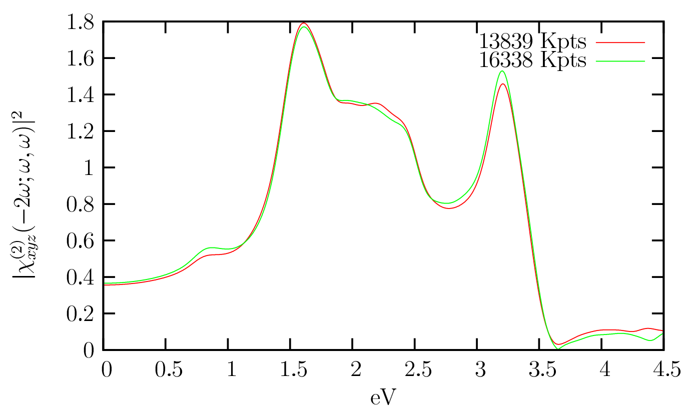

Figure 4.11 : Kpoints convergence test transversal gauge, adaptive sampling, although convergence was achieved before we wanted to compare the results with the adaptive sampling.

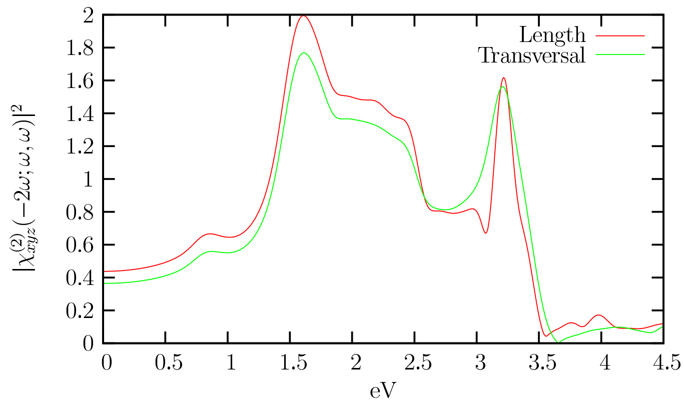

Figure 4.12 : Comparison Length vs. Transversal, results should be identical, the causes of the differences are the unfullfillment of commutation relations.

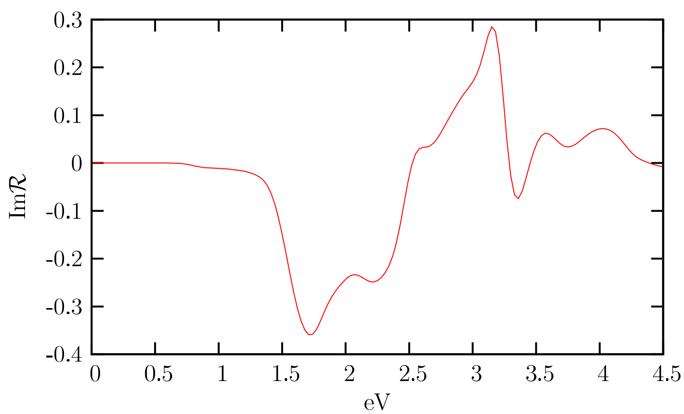

Figure 4.13 : The term presented is formally zero but when evaluated a numerical error is detected.

Chapter 5

Conclusions

In this chapter we present our conclusions and observations on the use of the two different gauges to calculate the second order nonlinear optical response, conclusions and observations are organized as they appear during the thesis.

The second order non linear susceptibility using the transversal gauge was deduced within the matrix density formalism. To our knowledge this procedure has not been published.

A FORTRAN code to calculate the non linear susceptibilities using the length and transversal gauges was implemented, and convergence tests were made for bulk GaAs in the number of plane waves used to represent the wave function, ecut, the number of conduction and valence bands and the sampling of the irreducible Brillouin zone, kpoints.

From our results we found that the susceptibilities calculated with the length gauge are more difficult to converge than the transversal ones this observation opposes to the expected by Aversa C. and Sipe J. E. [1], where they predicted that the length gauge should converge easily. In our work we find that while the transversal susceptibilities can converge independently in ecut and kpoints, the length susceptibilities must converge first in kpoints before converge in ecut.

For the first time to our knowledge gauge invariance for second order nonlinear susceptibilities was formally demonstrated, such demonstration is independent of the crystal symmetry.

Using LDA + pseudopotentials in the calculation of nonlinear response has important consequences in the gauge invariance, as the commutator relations present a numerical error which is the source of gauge variance.

The immediate future work includes the calculation of the nonlinear optical response using all electron software like the Wien2k. This could serve to corroborate that the unfulfillment of the commutation relations is in part due to the use of pseudopotentials.

Appendix A

Equation of Motion in the Interaction Picture

In general

$$i\hbar\frac{d\rho}{dt} = [H,\rho] = [H_0,\rho] + [H',\rho], \tag{A.1}$$

in the interaction picture

$$\begin{aligned} i\hbar\frac{d\tilde{\rho}}{dt} &= i\hbar[\frac{i}{\hbar}H_0 U\rho U^\dagger - \frac{i}{\hbar}U\rho H_0 U^\dagger + U\frac{d\rho}{dt}U^\dagger] \\ &= i\hbar U\frac{d\rho}{dt}U^\dagger + U[\rho, H_0]U^\dagger, \end{aligned} \tag{A.2}$$

and

$$i\hbar U\frac{d\rho}{dt}U^\dagger = U[H_0,\rho]U^\dagger + U[H',\rho]U^\dagger \tag{A.3}$$

thus

$$i\hbar\frac{d\tilde{\rho}}{dt} = [\tilde{H}', \tilde{\rho}] \tag{A.4}$$

Appendix B

Trace vanishing terms

We present the proof that the $\mathbf{A}$ term of the Equation (2.34) vanishes

The veolocity operator in the transverse gauge is

$$\mathbf{v} = \frac{\mathbf{p}}{m} - \frac{e\mathbf{A}}{mc} \tag{B.1}$$

Thus, formally

$$\mathbf{J} = \frac{e}{m} Tr(\mathbf{p}\rho_V^{(2)}) - \frac{e^2}{mc} Tr(\rho_V^{(1)})\mathbf{A} \tag{B.2}$$

However

$$Tr(\rho_V^{(1)}) = 0 \tag{B.3}$$

Because $\mathbf{r}_{mm} = 0$ and $f_{mm} = 0$

$$\begin{aligned} Tr(\rho_L^{(1)}) &= \frac{ie}{\hbar c} \int_{-\infty}^{t} dt' \sum_l (\mathbf{r}_{ml} f_m \delta_{ml} - f_m \delta_{ml} \mathbf{r}_{lm}) \cdot \mathbf{E} \qquad \text{(B.4)} \\ &= \frac{ie}{\hbar c} \int_{-\infty}^{t} dt' \sum_l (\mathbf{r}_{mm} f_m - f_m \mathbf{r}_{mm}) \cdot \mathbf{E} = 0 \end{aligned}$$

Appendix C

List of abbreviations

DFT	Density Functional Theory
ecut	Energy cutoff
EM	Electro Magnetic
KS	Kohn-Sham
LDA	Local Density Approximation
nkpt	Number of **k**-points
QM	Quantum Mechanics
SCF	Self Consistent Field
PT	Perturbation Theory
WF	Wave Function

Appendix D

List of symbols

$\mathbf{A}$	Magnetic vector potential
c	Speed of light
e	Electron charge
E	Energy
$\mathbf{E}$	Electric field vector
$\mathbf{G}$	Reciprocal lattice vector
$\mathcal{O}$	Arbitrary operator used to represent an observable
$\mathbf{r}$,$\mathbf{R}$	Position vector
t	Time
U	Unitary operator
$\mathcal{V}$	Electro-magnetic potential
δ_{ab}	Kronecker's delta
ψ,Ψ	Wave function
Φ	Scalar potential
Ω	Volume

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