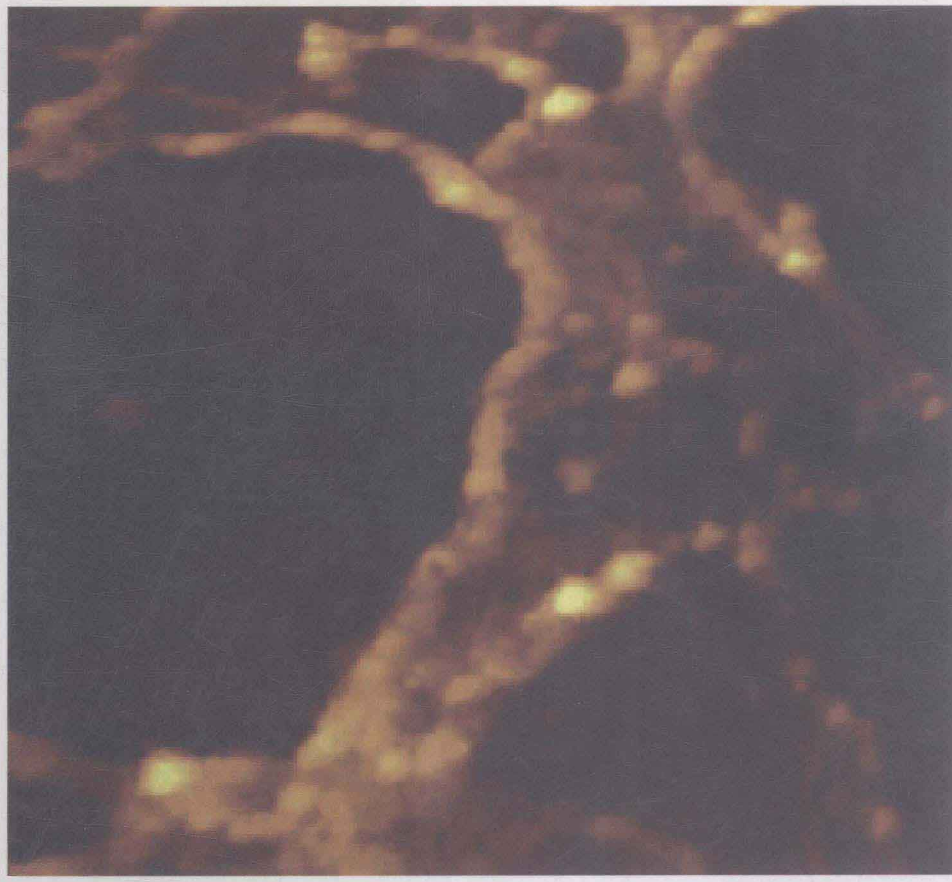
THE SCIENCE AND CULTURE SERIES — PHYSICS

Series Editor: A. Zichichi

Proceedings of the 39th Course of the International School of Solid State Physics

EPIOPTICS-9



Editor

Antonio Cricenti

THE SCIENCE AND CULTURE SERIES — PHYSICS

EPIOPTICS-9

Proceedings of the 39th Course of the
International School of Solid State Physics

Erice, Italy 20 — 26 July 2006

Editor
Antonio Cricenti

Series Editor
A. Zichichi

World Scientific

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI

Published by

World Scientific Publishing Co. Pte. Ltd.
5 Toh Tuck Link, Singapore 596224
USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601
UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

The Science and Culture Series — Physics
EPIOPTICS-9
Proceedings of the 39th Course of the International School of Solid State Physics

ISBN-13 978-981-279-402-4
ISBN-10 981-279-402-6

Printed in Singapore by B & JO Enterprise

PREFACE

This special volume contains the Proceedings of the 9th Epioptics Workshop, held in the Ettore Majorana Foundation and Centre for Scientific Culture, Erice, Sicily, from July 20 to 26, 2006. The Workshop was the 9th in the Epioptics series and the 39th of the International School of Solid State Physics. Antonio Cricenti from CNR Istituto di Struttura della Materia and Theo Rasing from the University of Njimegen, were the Directors of the Workshop. The Advisory Committee of the Workshop included Y. Borensztein from U. Paris VII (F), R. Del Sole from U. Roma II Tor Vergata (I), D. Aspnes from NCSU (USA), O. Hunderi from U. Trondheim (N), J. McGilp from Trinity College Dublin (Eire), W. Richter from TU Berlin (D), N. Tolk from Vanderbilt University (USA), and P. Weightman from University Liverpool (UK). Fifty five scientists from sixteen countries attended the Workshop.

The Workshop has brought together researchers from universities and research institutes who work in the fields of (semiconductor) surface science, epitaxial growth, materials deposition and optical diagnostics relevant to (semiconductor) materials and structures of interest for present and anticipated (spin) electronic devices. The Workshop was aimed at assessing the capabilities of state-of-the-art optical techniques in elucidating the fundamental electronic and structural properties of semiconductor and metal surfaces, interfaces, thin layers, and layer structures, and assessing the usefulness of these techniques for optimization of high quality multilayer samples through feedback control during materials growth and processing. Particular emphasis is dedicated to theory of non-linear optics and to dynamical processes through the use of pump-probe techniques together with the search for new optical sources. Some new applications of Scanning Probe Microscopy to material science and biological samples, dried and *in vivo*, with the use of different laser sources have also been presented. Materials of particular interest have been silicon, semiconductor-metal interfaces, semiconductor and magnetic multi-layers and III-V compound semiconductors. The Workshop is characterized by the adequate collection of notes in this volume, combined with the tutorials in some of the most advanced topics in the field.

This book is dedicated to Professor Gianfranco Chiarotti for his fundamental contributions to the development of Optical Spectroscopy as a tool to study Surface States: these studies have paved the way to the establishment of our Epioptics Community. During the School Prof. Chiarotti has been awarded the diploma of Father of Epioptics School, for the lecture regarding his contribution to the discovery of "Optical transition between semiconductor surface states". Prof. Giorgio Benedek was also awarded in the occasion of his 65th birthday for his strong and successful effort in running the International School of Solid State Physics.

I want personally to thank Prof. Chiarotti for giving me the opportunity to start this wonderful trip in science and as an example of rigour and dedication in the endeavour of scientific research. It is sad to remember that during the editing of these Proceedings two of our colleagues passed away: Dr. Marco Fabio Righini, who started his research at CNR in our optical group becoming an excellent scientist and with whom I shared the optical set-up for several years, and Prof. Carlo Coluzza, who was a very intuitive scientist in many different fields of science and a very good friend. I want also to remember my father-in-law Benito Cello, who had been very special to me, and my father Domenico, who also passed away recently: he was an untiring worker all his life, who has been exemplary and has been a great resource for me.

I wish to thank our sponsors, the Italian National Research Council (CNR) and the Sicilian Regional Government for facilitating a most successful Workshop. We wish to thank Prof. A. Zichichi, the President of the Ettore Majorana Foundation and Director of the Ettore Majorana Centre for Scientific Culture in Erice, and all the staff members of the Centre for the excellent support, organization and hospitality provided.

Antonio Cricenti

CONTENTS

LONGITUDINAL GAUGE THEORY OF SURFACE SECOND HARMONIC GENERATION

BERNARDO S. MENDOZA
Centro de Investigaciones en Optica
León, Guanajuato, México
bms@cio.mx

A theoretical review of surface second harmonic generation from semiconductor surfaces based on the longitudinal gauge is presented. The so called, layer-by-layer analysis is carefully presented in order to show how a surface calculation of second harmonic generation (SHG) can readily be carried out. The nonlinear susceptibility tensor χ is split into two terms, one that is related to inter-band one-electron transitions, and the other is related to intra-band one-electron transitions. The equivalence of this formulation to the transverse gauge approach is shown and the possibility of confirming its numerical accuracy is discussed. Also, the calculation of the surface second harmonic radiated intensity R within the three-layer-model is derived. With χ and R one has a complete description of this fascinating optical phenomena.

1. Introduction

Second harmonic generation (SHG) has become a powerful spectroscopic tool to study optical properties of surfaces and interfaces since it has the advantage of being surface sensitive. For centrosymmetric materials inversion symmetry forbids, within the dipole approximation, SHG from the bulk, but it is allowed at the surface, where the inversion symmetry is broken. Therefore, SHG should necessarily come from a localized surface region. SHG allows to study the structural atomic arrangement and phase transitions of clean and adsorbate covered surfaces, and since it is an optical probe, it can be used out of UHV conditions, and is non-invasive and non-destructive. On the experimental side, the new tunable high intensity laser systems have made SHG spectroscopy readily accessible and applicable to a wide range of systems.[1] However, the theoretical development of the field is still an ongoing subject of research. Some recent advances for the case of semiconducting and metallic systems have appeared in the literature, where the confrontation of theoretical models with experiment has yield correct physical interpretations for the SHG spectra. [1,2,3,4,5,6,7,8]

In a previous article,[9] we reviewed some of the recent results in the study of SHG using the transverse gauge for the coupling between the electromagnetic field and the electron. In particular, we showed a method to systematically investigate the different contributions to the observed peaks in SHG.[10] The approach consisted in the separation of the different contributions to the nonlinear susceptibility according to 1ω and 2ω transitions and to the surface or bulk character of the states among which the transitions take place. To complement above results, on this article we review the calculation of the nonlinear susceptibility using the longitudinal gauge, and show that both gauges give, as they should, the same result. We discuss a possible numerical check up on this equivalency. Also, the so called three-layer-model for the calculation of the surface radiated SH efficiency is presented.

2. Longitudinal Gauge

To calculate the optical properties of a given system within the longitudinal gauge, we follow the article by Aversa and Sipe.[11] A more recent derivation can also be found in Ref. [12] and [13]. Assuming the long-wavelength approximation, which implies a position independent electric field, the hamiltonian in the so called length gauge approximation is given by

$$\hat{H} = \hat{H}_0 - e\hat{\mathbf{r}} \cdot \mathbf{E}, \tag{1}$$

where $H_0 = p^2/2m + V(\mathbf{r})$, where $V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$ is the periodic crystal potential, with $\mathbf{R}$ the real-space lattice vector. The electric field $\mathbf{E} = -\dot{\mathbf{A}}/c$, with $\mathbf{A}$ the vector potential. 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

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r}|n\mathbf{k}\rangle = \sqrt{\frac{\Omega}{8\pi^3}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \tag{2}$$

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

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

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

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

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

$$\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\frac{\partial}{\partial \mathbf{k}}\delta(\mathbf{k}-\mathbf{k}'), \tag{5}$$

on the other,

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \frac{\partial}{\partial \mathbf{k}}\int d\mathbf{r}\langle n\mathbf{k}|\mathbf{r}\rangle\langle \mathbf{r}|m\mathbf{k}'\rangle \\ &= \int d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r})\right)\psi_{m\mathbf{k}'}(\mathbf{r}),\end{aligned} \tag{6}$$

the derivative of the wavefunction is simply given by

$$\frac{\partial}{\partial \mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{\Omega}{8\pi^3}}\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)e^{-i\mathbf{k}\cdot\mathbf{r}} - i\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r}). \tag{7}$$

We take this back into Eq. 6, to obtain

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

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

$$\int d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}}f(\mathbf{r}) = \frac{8\pi^3}{\Omega}\delta(\mathbf{q}-\mathbf{k})\int_\Omega d^3r\, f(\mathbf{r}), \tag{9}$$

to finally write,[14]

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \delta(\mathbf{k}-\mathbf{k}')\int_\Omega d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)u_{m\mathbf{k}}(\mathbf{r}) \\ &\quad -i\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle.\end{aligned} \tag{10}$$

where Ω is the volume of the unit cell. From

$$\int_\Omega u_{m\mathbf{k}}u^*_{n\mathbf{k}}d\mathbf{r} = \delta_{nm}, \tag{11}$$

we easily find that

$$\int_\Omega d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}u_{m\mathbf{k}}(\mathbf{r})\right)u^*_{n\mathbf{k}}(\mathbf{r}) = -\int_\Omega d\mathbf{r}\, u_{m\mathbf{k}}(\mathbf{r})\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right). \tag{12}$$

Therefore, we define

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i \int_{\Omega} d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r}) \nabla_{\mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}), \tag{13}$$

with $\partial/\partial\mathbf{k} = \nabla_{\mathbf{k}}$. Now, from Eqs. 5, 8, and 13, we have that the matrix elements of the position operator of the electron are given by

$$\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}) + i\delta_{nm}\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}'), \tag{14}$$

Then, from Eq. (14), 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

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right], \tag{15}$$

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}). \tag{16}$$

To proceed, we relate Eq. 16 to the matrix elements of the momentum operator as follows. We start from the basic relation,

$$\hat{\mathbf{v}} = \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{H}_0], \tag{17}$$

with $\hat{\mathbf{v}}$ the velocity operator. Neglecting nonlocal potentials in $\hat{H}_0$ we obtain, on one hand

$$[\hat{\mathbf{r}}, \hat{H}_0] = i\hbar\frac{\hat{\mathbf{p}}}{m}, \tag{18}$$

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

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0]|m\mathbf{k}\rangle = \langle n\mathbf{k}|\hat{\mathbf{r}}\hat{H}_0 - \hat{H}_0\hat{\mathbf{r}}|m\mathbf{k}\rangle = (\hbar\omega_m(\mathbf{k}) - \hbar\omega_n(\mathbf{k}))\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}\rangle, \tag{19}$$

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

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{p}_{nm}(\mathbf{k})}{im\omega_{nm}(\mathbf{k})} = \frac{\mathbf{v}_{nm}(\mathbf{k})}{i\omega_{nm}(\mathbf{k})} \qquad n \neq m. \tag{20}$$

Comparing above result with Eq. 16, we can identify

$$(1-\delta_{nm})\boldsymbol{\xi}_{nm} \equiv \mathbf{r}_{nm}, \tag{21}$$

and the we can write

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle = \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{p}_{nm}(\mathbf{k})}{im\omega_{nm}(\mathbf{k})} \qquad n \neq m, \tag{22}$$

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,

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{\mathcal{O}}]|m\mathbf{k}'\rangle &= \sum_{\ell,\mathbf{k}''}\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_i|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|\hat{\mathcal{O}}|m\mathbf{k}'\rangle \\ &\quad -\langle n\mathbf{k}|\hat{\mathcal{O}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle\Big) \\ &= \sum_{\ell}\big(\langle n\mathbf{k}|\hat{\mathbf{r}}_i|\ell\mathbf{k}'\rangle\mathcal{O}_{\ell m}(\mathbf{k}') \\ &\quad -\mathcal{O}_{n\ell}(\mathbf{k})|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle\big)\,, \end{aligned} \tag{23}$$

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. 15, to obtain

$$\begin{aligned}\sum_{\ell} &\quad \big(\delta_{n\ell}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{\ell m}(\mathbf{k}') \\ &\quad -\mathcal{O}_{n\ell}(\mathbf{k})\delta_{\ell m}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\big) \\ &= \big(\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{nm}(\mathbf{k}') \\ &\quad -\mathcal{O}_{nm}(\mathbf{k})\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\big) \\ &= \delta(\mathbf{k}-\mathbf{k}')\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right) + i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\ &\quad +i\delta(\mathbf{k}-\mathbf{k}')\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\ &= i\delta(\mathbf{k}-\mathbf{k}')\Big(\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right)\Big) \\ &\equiv i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}. \end{aligned} \tag{24}$$

Then,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{\mathcal{O}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{25}$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right), \tag{26}$$

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. 24, thus giving a well defined commutator of the intraband position operator with an arbitrary operator $\hat{\mathcal{O}}$. We use Eq. 22 and 25 in the next section.

3. Time-dependent Perturbation Theory

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

$$\mathcal{O} = Tr(\hat{\mathcal{O}}\hat{\rho}) = Tr(\hat{\rho}\hat{\mathcal{O}}), \tag{27}$$

where Tr is the trace, that as we have shown has the property of being invariant under cyclic permutations. The dynamical equation of motion for ρ is given by

$$i\hbar\frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}], \tag{28}$$

where it is more convenient to work in the interaction picture, for which we transform all the operators according to

$$\hat{\mathcal{O}}_I = \hat{U}\hat{\mathcal{O}}\hat{U}^\dagger, \tag{29}$$

where

$$\hat{U} = e^{i\hat{H}_0 t/\hbar}, \tag{30}$$

is the unitary operator that take 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. 28 into

$$i\hbar\frac{d\hat{\rho}_I(t)}{dt} = [-e\hat{\mathbf{r}}_I(t)\cdot\mathbf{E}(t), \hat{\rho}_I(t)], \tag{31}$$

that leads to

$$\hat{\rho}_I(t) = \hat{\rho}_I(t=-\infty) + \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I(t')]. \tag{32}$$

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

$$\mathbf{E}(t) = \mathbf{E}e^{-i\omega t}e^{\eta t}, \tag{33}$$

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 Eq. 33 we use

$$\mathbf{E}(t) = \mathbf{E}e^{-i\tilde{\omega}t}, \tag{34}$$

with

$$\tilde{\omega} = \omega + i\eta. \tag{35}$$

Also, $\hat{\rho}_I(t=-\infty)$ should be independent of time, and thus $[\hat{H}, \hat{\rho}]_{t=-\infty} = 0$, which 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

$$\langle n\mathbf{k}|\hat{\rho}_0|m\mathbf{k}'\rangle = f_n(\hbar\omega_n(\mathbf{k}))\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{36}$$

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

We solve Eq. 32 using the standard iterative solution, for which we write

$$\hat{\rho}_I = \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots, \tag{37}$$

where $\hat{\rho}_I^{(N)}$ is the density operator to order N in $\mathbf{E}(t)$. Then, Eq. 32 reads

$$\hat{\rho}_I^{(0)}+\hat{\rho}_I^{(1)}+\hat{\rho}_I^{(2)}+\cdots = \hat{\rho}_0+\frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'),\hat{\rho}_I^{(0)}+\hat{\rho}_I^{(1)}+\hat{\rho}_I^{(2)}+\cdots], \quad (38)$$

where by equating equal orders in the perturbation, we find

$$\hat{\rho}_I^{(0)} \equiv \hat{\rho}_0, \quad (39)$$

and

$$\hat{\rho}_I^{(N)}(t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'),\hat{\rho}_I^{(N-1)}(t')]. \quad (40)$$

It is simple to show that matrix elements of Eq. (40) satisfy $\langle n\mathbf{k}|\rho_I^{(N+1)}(t)|m\mathbf{k}'\rangle = \rho_{I,nm}^{(N+1)}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')$, with

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt'\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t'),\hat{\rho}_I^{(N)}(t')]|m\mathbf{k}\rangle\cdot\mathbf{E}(t'). \quad (41)$$

Now we work out the commutator of Eq. 41. Then,

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t),\hat{\rho}_I^{(N)}(t)]|m\mathbf{k}\rangle &= \langle n\mathbf{k}|[\hat{U}\hat{\mathbf{r}}\hat{U}^\dagger,\hat{U}\hat{\rho}^{(N)}(t)\hat{U}^\dagger]|m\mathbf{k}\rangle\\ &= \langle n\mathbf{k}|\hat{U}[\hat{\mathbf{r}},\hat{\rho}^{(N)}(t)]\hat{U}^\dagger|m\mathbf{k}\rangle \quad (42)\\ &= e^{i\omega_{nm\mathbf{k}}t}\left(\langle n\mathbf{k}|[\hat{\mathbf{r}}_e,\hat{\rho}^{(N)}(t)]+[\hat{\mathbf{r}}_i,\hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle\right),\end{aligned}$$

where the time dependence of operator's interaction picture is explicitly shown by the exponential factor, and the implicit dependence of $\hat{\rho}^{(N)}$ inherited from Eq. 28 is shown by its t argument. We calculate the interband term first, so using Eq. 22 we obtain

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_e,\hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle &= \sum_\ell\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_e|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\rho}^{(N)}(t)|m\mathbf{k}\rangle\\ &\quad -\langle n\mathbf{k}|\hat{\rho}^{(N)}(t)|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle\Big)\\ &= \sum_{\ell\neq n,m}\left(\mathbf{r}_{n\ell}(\mathbf{k})\rho_{\ell m}^{(N)}(\mathbf{k};t)-\rho_{n\ell}^{(N)}(\mathbf{k};t)\mathbf{r}_{\ell m}(\mathbf{k})\right)\\ &\equiv \mathbf{R}_e^{(N)}(\mathbf{k};t). \quad (43)\end{aligned}$$

Now, from Eq. 25 we simply obtain,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{\rho}^{(N)}(t)]|m\mathbf{k}'\rangle = i(\rho_{nm}^{(N)}(t))_{;\mathbf{k}} \equiv \mathbf{R}_i^{(N)}(\mathbf{k};t). \quad (44)$$

Then Eq. 41 becomes,

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega})t'}\left[R_e^{b(N)}(\mathbf{k};t')+R_i^{b(N)}(\mathbf{k};t')\right]E^b, \quad (45)$$

where, the roman superindices a, b, c denote Cartesian components that are summed over if repeated. We start with the linear response, then from Eq. 36 and 43,[a]

$$
\begin{aligned}
R_e^{b(0)}(\mathbf{k};t) &= \sum_\ell \left(r_{n\ell}^b(\mathbf{k})\rho_{\ell m}^{(0)}(\mathbf{k}) - \rho_{n\ell}^{(0)}(\mathbf{k})r_{\ell m}^b(\mathbf{k})\right) \\
&= \sum_\ell \left(r_{n\ell}^b(\mathbf{k})\delta_{\ell m} f_m(\hbar\omega_m(\mathbf{k})) - \delta_{n\ell} f_n(\hbar\omega_n(\mathbf{k}))r_{\ell m}^b(\mathbf{k})\right) \\
&= f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k}),
\end{aligned} \tag{46}
$$

where $f_{mn\mathbf{k}} = f_{m\mathbf{k}} - f_{n\mathbf{k}}$. Also, from Eq. 44 and Eq. 26

$$
R_i^{b(0)}(\mathbf{k}) = i(\rho_{nm}^{(0)})_{;k^b} = i\delta_{nm}(f_{n\mathbf{k}})_{;k^b} = i\delta_{nm}\nabla_{k^b} f_{n\mathbf{k}}. \tag{47}
$$

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 $\mathbf{R}_i^{(0)} = 0$. Therefore the linear response has no contribution from intraband transitions. Then,

$$
\begin{aligned}
\rho_{I,nm}^{(1)}(\mathbf{k};t) &= \frac{ie}{\hbar} f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k}) E^b \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega})t'} \\
&= \frac{e}{\hbar} f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k}) E^b \frac{e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega})t}}{\omega_{nm\mathbf{k}}-\tilde{\omega}} \\
&= e^{i\omega_{nm\mathbf{k}}t} B_{mn}^b(\mathbf{k}) E^b(t) \\
&= e^{i\omega_{nm\mathbf{k}}t} \rho_{nm}^{(1)}(\mathbf{k};t).
\end{aligned} \tag{48}
$$

We generalize this result since we need it for the non-linear response. In general we could have several perturbing fields with different frequencies, i.e. $\mathbf{E}(t) = \mathbf{E}_{\omega_\alpha} e^{-i\tilde{\omega}_\alpha t}$, then

$$
\rho_{nm}^{(1)}(\mathbf{k};t) = B_{mn}^b(\mathbf{k},\omega_\alpha) E_{\omega_\alpha}^b e^{-i\tilde{\omega}_\alpha t}, \tag{49}
$$

with

$$
B_{nm}^b(\mathbf{k},\omega_\alpha) = \frac{e}{\hbar}\frac{f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k})}{\omega_{nm\mathbf{k}}-\tilde{\omega}_\alpha}. \tag{50}
$$

Now, we calculate the second-order response. Then, from Eq. 43

$$
\begin{aligned}
R_e^{b(1)}(\mathbf{k};t) &= \sum_\ell \left(r_{n\ell}^b(\mathbf{k})\rho_{\ell m}^{(1)}(\mathbf{k};t) - \rho_{n\ell}^{(1)}(\mathbf{k};t) r_{\ell m}^b(\mathbf{k})\right) \\
&= \sum_\ell \left(r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k},\omega_\beta) - B_{n\ell}^c(\mathbf{k},\omega_\beta) r_{\ell m}^b(\mathbf{k})\right) E_{\omega_\beta}^c(t),
\end{aligned} \tag{51}
$$

and from Eq. 44

$$
R_i^{b(1)}(\mathbf{k};t) = i(\rho_{nm}^{(1)}(t))_{;k^b} = iE_{\omega_\beta}^c(t)(B_{nm}^c(\mathbf{k},\omega_\beta))_{;k^b}. \tag{52}
$$

[a] from now on, it should be clear that the matrix elements of $\mathbf{r}_{nm}$ imply $n \neq m$.

Using Eqs. 51 and 52 in Eq. (45), and generalizing to two different perturbing fields, we obtain

$$
\begin{aligned}
\rho^{(2)}_{I,nm}(\mathbf{k};t) &= \frac{ie}{\hbar}\Bigg[\sum_{\ell}\Big(r^b_{n\ell}(\mathbf{k})B^c_{\ell m}(\mathbf{k},\omega_\beta) - B^c_{n\ell}(\mathbf{k},\omega_\beta)r^b_{\ell m}(\mathbf{k})\Big) \\
&\quad + i(B^c_{nm}(\mathbf{k},\omega_\beta))_{;k^b}\Bigg]E^b_{\omega_\alpha}E^c_{\omega_\beta}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega}_\alpha-\tilde{\omega}_\beta)t'} \\
&= \frac{e}{\hbar}\Bigg[\sum_{\ell}\Big(r^b_{n\ell}(\mathbf{k})B^c_{\ell m}(\mathbf{k},\omega_\beta) - B^c_{n\ell}(\mathbf{k},\omega_\beta)r^b_{\ell m}(\mathbf{k})\Big) \\
&\quad + i(B^c_{nm}(\mathbf{k},\omega_\beta))_{;k^b}\Bigg]E^b_{\omega_\alpha}E^c_{\omega_\beta}\frac{e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega}_3)t}}{\omega_{nm\mathbf{k}}-\tilde{\omega}_3} \\
&= e^{i\omega_{nm\mathbf{k}}t}\rho^{(2)}_{nm}(\mathbf{k};t).
\end{aligned} \tag{53}
$$

Now, we write $\rho^{(2)}_{nm}(\mathbf{k};t) = \rho^{(2)}_{nm}(\mathbf{k};\omega_3)e^{-i\tilde{\omega}_3 t}$, with

$$
\begin{aligned}
\rho^{(2)}_{nm}(\mathbf{k};\omega_3) &= \frac{e}{i\hbar}\frac{1}{\omega_{nm\mathbf{k}}-\tilde{\omega}_3}\Bigg[-(B^c_{nm}(\mathbf{k},\omega_\beta)_{;k^b} \\
&\quad + i\sum_{\ell}\Big(r^b_{n\ell}B^c_{\ell m}(\mathbf{k},\omega_\beta) - B^c_{n\ell}(\mathbf{k},\omega_\beta)r^b_{\ell m}\Big)\Bigg]E^b_{\omega_\alpha}E^c_{\omega_\beta}
\end{aligned} \tag{54}
$$

where $\tilde{\omega}_3 = \tilde{\omega}_\alpha + \tilde{\omega}_\beta$ and $\mathbf{E}_{\omega_i}$ is the amplitude of the perturbing field with ω_i for $i = \alpha, \beta$. We use Eq. 54 in section 5.

4. Layered Current Density

In this section, we derive the expressions for the macroscopic current density of a given layer in the unit cell of the system. The approach we use to study the surface of a semi-infinite semiconductor crystal is as follows. Instead of using a semi-infinite system, we replace it by a slab (see Fig. 1). The slab consists of two surfaces, say the front and the back surface, and in between these two surfaces the bulk of the system. In general the surface of a crystal reconstructs 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 any more their bulk partner atoms, since these, by definition, are absent above (below) the front (back) surface of the slab. Therefore, to take the reconstruction into account, by surface we really mean the true surface that consists of the very first relaxed layer of atoms, and some of the sub-true-surface relaxed atomic layers. Since the front and the back surfaces of the slab are usually identical, the total slab is centrosymmetric. This fact (see Sec. 4), will imply $\chi^{slab}_{abc} = 0$, and thus we must device a way in which this artifact of a centrosymmetric

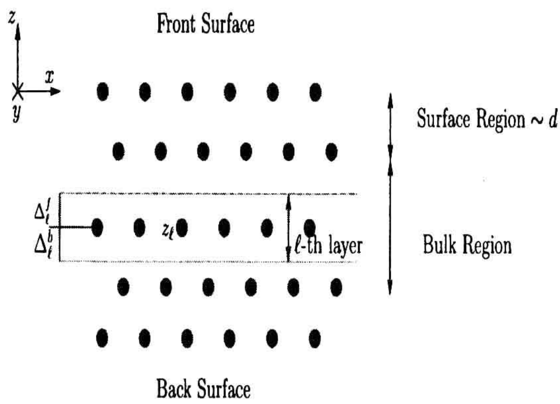


Figure 1. We show a sketch of the slab, where the small circles represent the atoms. See the text for the details.

slab is bypassed 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, thus breaking the centrosymmetry and therefore giving an overall $\chi^{slab}_{abc} \neq 0$, we need a procedure to extract the front surface χ^f_{abc} and the back surface χ^b_{abc} from the slab non-linear susceptibility χ^{slab}_{abc}.

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

$$S_\ell(z) = \Theta(z - z_\ell + \Delta^b_\ell)\Theta(z_\ell - z + \Delta^f_\ell), \tag{55}$$

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. Thus $\Delta^f_\ell + \Delta^b_\ell$ is the thickness of layer ℓ (see Fig. 1).

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

$$\mathbf{j}(\mathbf{r}, t) = eTr(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)), \tag{56}$$

where the operator for the electron's current is

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2}\left(\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}\right), \tag{57}$$

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