

LONGITUDINAL GAUGE THEORY OF SURFACE SECOND HARMONIC GENERATION

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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

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

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

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

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

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

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

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

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

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

on the other,

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

the derivative of the wavefunction is simply given by

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

We take this back into Eq. 6, to obtain

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

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),

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

to finally write,¹⁴

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

where Ω is the volume of the unit cell. From

$$\int_{\Omega} u_{m\mathbf{k}} u_{n\mathbf{k}}^* d\mathbf{r} = \delta_{nm}, \quad (11)$$

we easily find that

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

Therefore, we define

$$\xi_{nm}(\mathbf{k}) \equiv i \int_{\Omega} d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}), \quad (13)$$

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

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

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

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm} [\delta(\mathbf{k} - \mathbf{k}')\xi_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k} - \mathbf{k}')], \quad (15)$$

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

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

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

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

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

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

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

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

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

Comparing above result with Eq. 16, we can identify

$$(1 - \delta_{nm})\xi_{nm} \equiv \mathbf{r}_{nm}, \quad (21)$$

and the we can write

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

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,

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

where we have taken $\langle n\mathbf{k} | \hat{O} | \ell\mathbf{k}'' \rangle = \delta(\mathbf{k} - \mathbf{k}'') \mathcal{O}_{n\ell}(\mathbf{k})$. We substitute Eq. 15, to obtain

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

Then,

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

with

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

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{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

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

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

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

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

$$\hat{\mathcal{O}}_I = \hat{U} \hat{\mathcal{O}} \hat{U}^\dagger, \quad (29)$$

where

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

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

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

that leads to

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

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

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

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 $\eta \rightarrow 0$. Instead of Eq. 33 we use

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

with

$$\tilde{\omega} = \omega + i\eta. \quad (35)$$

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

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

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

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

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

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

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,

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

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

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

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,

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

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

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

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

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

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

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

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. $\mathbf{E}(t) = \mathbf{E}_{\omega_\alpha} e^{-i\bar{\omega}_\alpha t}$, then

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

with

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

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

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

and from Eq. 44

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

^afrom 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

$$\begin{aligned}
\rho_{I,nm}^{(2)}(\mathbf{k}; t) &= \frac{ie}{\hbar} \left[\sum_{\ell} \left(r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k}, \omega_{\beta}) - B_{n\ell}^c(\mathbf{k}, \omega_{\beta}) r_{\ell m}^b(\mathbf{k}) \right) \right. \\
&\quad \left. + i(B_{nm}^c(\mathbf{k}, \omega_{\beta}))_{;kb} \right] E_{\omega_{\alpha}}^b E_{\omega_{\beta}}^c \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}} - \tilde{\omega}_{\alpha} - \tilde{\omega}_{\beta})t'} \\
&= \frac{e}{\hbar} \left[\sum_{\ell} \left(r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k}, \omega_{\beta}) - B_{n\ell}^c(\mathbf{k}, \omega_{\beta}) r_{\ell m}^b(\mathbf{k}) \right) \right. \\
&\quad \left. + i(B_{nm}^c(\mathbf{k}, \omega_{\beta}))_{;kb} \right] E_{\omega_{\alpha}}^b E_{\omega_{\beta}}^c \frac{e^{i(\omega_{nm\mathbf{k}} - \tilde{\omega}_3)t}}{\omega_{nm\mathbf{k}} - \tilde{\omega}_3} \\
&= e^{i\omega_{nm\mathbf{k}}t} \rho_{nm}^{(2)}(\mathbf{k}; t). \tag{53}
\end{aligned}$$

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

$$\begin{aligned}
\rho_{nm}^{(2)}(\mathbf{k}; \omega_3) &= \frac{e}{i\hbar \omega_{nm\mathbf{k}} - \tilde{\omega}_3} \left[- (B_{nm}^c(\mathbf{k}, \omega_{\beta}))_{;kb} \right. \\
&\quad \left. + i \sum_{\ell} \left(r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega_{\beta}) - B_{n\ell}^c(\mathbf{k}, \omega_{\beta}) r_{\ell m}^b \right) \right] E_{\omega_{\alpha}}^b E_{\omega_{\beta}}^c \tag{54}
\end{aligned}$$

where $\tilde{\omega}_3 = \tilde{\omega}_{\alpha} + \tilde{\omega}_{\beta}$ and \mathbf{E}_{ω_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 $\chi_{abc}^{slab} = 0$, and thus we must devise a way in which this artifact of a centrosymmetric

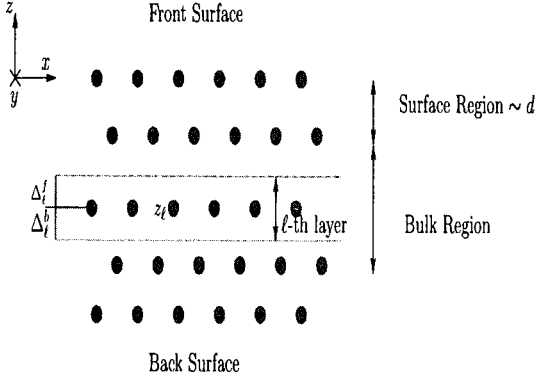


Figure 1. We show a sketch of the slab, where the small circles represent the atoms. See the text for the details.

slab is bypassed in order to have a finite χ_{abc}^s 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 $\chi_{abc}^{slab} \neq 0$, we need a procedure to extract the front surface χ_{abc}^f and the back surface χ_{abc}^b from the slab non-linear susceptibility χ_{abc}^{slab} .

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,

$$S_\ell(z) = \Theta(z - z_\ell + \Delta_\ell^b)\Theta(z_\ell - z + \Delta_\ell^f), \quad (55)$$

where Θ is the Heaviside function. Here, $\Delta_\ell^{f/b}$ is the distance that the ℓ -th layer extends towards the front (f) or back (b) from its z_ℓ position. Thus $\Delta_\ell^f + \Delta_\ell^b$ 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

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

where the operator for the electron’s current is

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

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

trace to write

$$\begin{aligned}
Tr(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)) &= Tr(\hat{\rho}(t)\hat{\mathbf{j}}(\mathbf{r})) = \frac{1}{2} (Tr(\hat{\rho}\hat{\mathbf{v}}\hat{\mu}) + Tr(\hat{\rho}\hat{\mu}\hat{\mathbf{v}})) \\
&= \frac{1}{2} \sum_{n\mathbf{k}} (\langle n\mathbf{k}|\hat{\rho}\hat{\mathbf{v}}\hat{\mu}|n\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\rho}\hat{\mu}\hat{\mathbf{v}}|n\mathbf{k}\rangle) \\
&= \frac{1}{2} \sum_{nm\mathbf{k}} \langle n\mathbf{k}|\hat{\rho}|m\mathbf{k}\rangle (\langle m\mathbf{k}|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle) \\
\mathbf{j}(\mathbf{r}, t) &= e \sum_{nm\mathbf{k}} \rho_{nm}(\mathbf{k}; t) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}), \tag{58}
\end{aligned}$$

where

$$\mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}) = \frac{1}{2} (\langle m\mathbf{k}|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle), \tag{59}$$

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

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

$$\frac{1}{\Omega} \int d^3r S_\ell(z) \mathbf{j}(\mathbf{r}, t) \equiv \mathbf{J}^{(\ell)}(t), \tag{60}$$

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

$$\mathcal{V}_{mn}^{(\ell)}(\mathbf{k}) \equiv \frac{1}{\Omega} \int d^3r S_\ell(z) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}), \tag{61}$$

to write

$$J_a^{(N, \ell)}(t) = e \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{a(\ell)}(\mathbf{k}) \rho_{nm}^{(N)}(\mathbf{k}; t), \tag{62}$$

as the induced macroscopic current, to order N -th in the external perturbation, of the ℓ -th layer. The matrix elements of the density operator for $N = 1, 2$ are given by Eqs. 50 and 54, respectively. Also, the roman superindices a, b, c denote Cartesian components.

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

$$\begin{aligned}
i\hbar\hat{\mathbf{v}} &= [\hat{\mathbf{r}}, \hat{H}_0] \\
&= [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}(\mathbf{r}) + \hat{v}(\mathbf{r}, \hat{\mathbf{p}})] \approx [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m}] = i\hbar \frac{\hat{\mathbf{p}}}{m}, \tag{63}
\end{aligned}$$

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

$$m\hat{\mathbf{v}} \approx \hat{\mathbf{p}} = -i\hbar\nabla, \quad (64)$$

is the explicit functional form of the velocity or momentum operator. From Eq. 59, we need

$$\langle \mathbf{r} | \hat{\mathbf{v}} | n\mathbf{k} \rangle = \int d^3r' \langle \mathbf{r} | \hat{\mathbf{v}} | \mathbf{r}' \rangle \langle \mathbf{r}' | n\mathbf{k} \rangle \approx \frac{1}{m} \hat{\mathbf{p}} \psi_{n\mathbf{k}}(\mathbf{r}), \quad (65)$$

where we used

$$\langle \mathbf{r} | \hat{v}^x | \mathbf{r}' \rangle \approx \frac{1}{m} \langle \mathbf{r} | \hat{p}^x | \mathbf{r}' \rangle = \delta(y - y') \delta(z - z') \left(-i\hbar \frac{\partial}{\partial x} \delta(x - x') \right), \quad (66)$$

with similar results for the y and z Cartesian directions. Now, from Eqs. 61 and 59 we obtain

$$\mathcal{V}_{mn}^{(\ell)}(\mathbf{k}) = \frac{1}{2} \int d^3r S_\ell(z) \left[\langle m\mathbf{k} | \mathbf{v} | \mathbf{r} \rangle \langle \mathbf{r} | n\mathbf{k} \rangle + \langle m\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{v} | n\mathbf{k} \rangle \right], \quad (67)$$

and using Eq. 65, we can write, for any function $S(z)$ used to identify the response from a region of the slab, that

$$\mathcal{V}_{mn}(\mathbf{k}) \approx \frac{1}{2m} \int d^3r S(z) \left[\psi_{n\mathbf{k}}(\mathbf{r}) \hat{\mathbf{p}}^* \psi_{m\mathbf{k}}^*(\mathbf{r}) + \psi_{m\mathbf{k}}^*(\mathbf{r}) \hat{\mathbf{p}} \psi_{n\mathbf{k}}(\mathbf{r}) \right], \quad (68)$$

$$= \frac{1}{m} \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \left[\frac{S(z)\mathbf{p} + \mathbf{p}S(z)}{2} \right] \psi_{n\mathbf{k}}(\mathbf{r}), \quad (69)$$

$$= \frac{1}{m} \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \hat{\mathcal{P}} \psi_{n\mathbf{k}}(\mathbf{r}) \equiv \frac{1}{m} \mathcal{P}_{mn}(\mathbf{k}). \quad (70)$$

Here an integration by parts is performed on the first term of the right hand side of Eq. 68; since the $e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r})$ are periodic over the unit cell, the surface term vanishes. From Eqs. 68 we see that the replacement

$$\hat{\mathbf{p}} \rightarrow \hat{\mathcal{P}} = \left[\frac{S(z)\hat{\mathbf{p}} + \hat{\mathbf{p}}S(z)}{2} \right], \quad (71)$$

is what it takes to change the momentum operator of the electron, $\hat{\mathbf{p}}$, to the new momentum operator $\hat{\mathcal{P}}$ that implicitly takes into account the contribution of the region of the slab given by $S(z)$. Note that $\hat{\mathcal{P}}$ is properly symmetrized.

Finally, the Fourier component of macroscopic current of Eq. 62 is given by

$$J_a^{(N,\ell)}(\omega_3) = \frac{e}{m} \sum_{mn\mathbf{k}} \mathcal{P}_{mn}^{a(\ell)}(\mathbf{k}) \rho_{nm}^{(N)}(\mathbf{k}; \omega_3), \quad (72)$$

where the non-local contribution of H_0 is neglected, and from Eq. 69

$$\mathcal{P}_{mn}^{\alpha(\ell)} = \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \left[\frac{S_\ell(z)p^\alpha + p^\alpha S_\ell(z)}{2} \right] \psi_{n\mathbf{k}}(\mathbf{r}). \quad (73)$$

Actually, to limit the response to one surface, the Eq. 71 was proposed in Ref. ¹⁵, and latter used in Refs. ¹⁶ and ¹⁷ in the context of SHG. Then, the layer-by-layer analysis of Refs. ¹⁸ and ¹⁹ actually used Eq. 55 thus limiting the current response to a particular layer of the slab, and used it to obtain the anisotropic linear optical response of semiconductor surfaces. However, the first formal derivation of this scheme is presented in Ref. ²⁰ for the linear optical response, and here for the non-linear optical response of semiconductors.

5. Non-linear Susceptibility

In this section we obtain the expressions for the non-linear surface susceptibility tensor to second order in the perturbing fields. We start with the non-linear polarization \mathbf{P} written as

$$P_a(\omega_3) = \chi_{abc}(-\omega_3; \omega_1, \omega_2) E_b(\omega_1) E_c(\omega_2) + \chi_{abcd}(-\omega_3; \omega_1, \omega_2) E_b(\omega_1) \nabla_c E_l(\omega_2) + \dots, \quad (74)$$

where χ_{abc} and χ_{abcd} , correspond to the dipolar and quadrupolar susceptibilities, respectively, and the sum continues with higher multipolar terms. If we consider a semi-infinite system with a centrosymmetric bulk, above equation splits, due to symmetry considerations alone, into two contributions, one from the surface of the system and the other from the bulk of the system. Indeed, let's take

$$P_a(\mathbf{r}) = \chi_{abc} E_b(\mathbf{r}) E_c(\mathbf{r}) + \chi_{abcd} E_b(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}_c} E_l(\mathbf{r}) + \dots, \quad (75)$$

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

$$P_a(-\mathbf{r}) = \chi_{abc} E_b(-\mathbf{r}) E_c(-\mathbf{r}) + \chi_{abcd} E_b(-\mathbf{r}) \frac{\partial}{\partial (-\mathbf{r}_c)} E_l(-\mathbf{r}) + \dots, \quad (76)$$

as the polarization in the coordinate system where inversion is taken, i.e. $\mathbf{r} \rightarrow -\mathbf{r}$. Note that we have kept the same susceptibility tensors, since as the system is centrosymmetric, they must be invariant under $\mathbf{r} \rightarrow -\mathbf{r}$. Recalling that $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$, are polar vectors,²¹ we have that Eq. 76 reduces to

$$-P_a(\mathbf{r}) = \chi_{abc}(-E_b(\mathbf{r}))(-E_c(\mathbf{r})) - \chi_{abcd}(-E_b(\mathbf{r}))\left(-\frac{\partial}{\partial \mathbf{r}_c}\right)(-E_l(\mathbf{r})) + \dots,$$

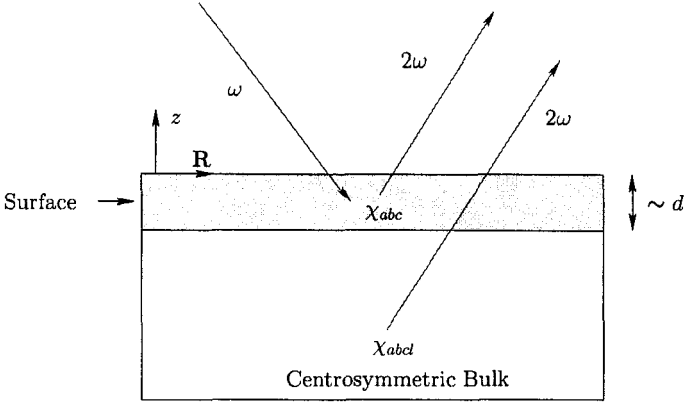


Figure 2. (color online) We show a sketch of the semi-infinite system with a centrosymmetric bulk. The surface region is of width $\sim d$. The incoming photon of frequency ω is represented by a downward red arrow, whereas both the surface and bulk created second harmonic photons of frequency 2ω are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

$$P_a(\mathbf{r}) = -\chi_{abc}E_b(\mathbf{r})E_c(\mathbf{r}) + \chi_{abcl}E_b(\mathbf{r})\frac{\partial}{\partial r_c}E_l(\mathbf{r}) + \dots, \quad (77)$$

that when compared with Eq. 75 leads to the conclusion that

$$\chi_{abc} = 0 \quad \text{for a centrosymmetric bulk.} \quad (78)$$

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

$$\begin{aligned} \int d\mathbf{R} \int dz P_a(\mathbf{R}, z) &\approx S d P_a \\ &= S P_a^s \\ &= \chi_{abc} E_b E_c, \end{aligned} \quad (79)$$

where \mathbf{R} is a vector parallel to the surface which is perpendicular to z , S is the surface area of the unit cell that characterizes the surface of the system, and d is the surface region from which the dipolar signal of \mathbf{P} is different from zero (see Fig. 2). Also, $d\mathbf{P} \equiv \mathbf{P}^{(s)}$ is the surface SH polarization, given by

$$P_a^s = \frac{1}{S} \chi_{abc} E_b E_c = \chi_{abc}^s E_b E_c, \quad (80)$$

with $\chi_{abc}^s = \chi_{abc}/\mathcal{S}$ the surface non-linear susceptibility. On the other hand,

$$P_a^b(\mathbf{r}) = \chi_{abcl} E_b(\mathbf{r}) \nabla_c E_l(\mathbf{r}), \quad (81)$$

gives the bulk polarization. Immediately we see that the surface polarization is of dipolar order, whereas the bulk polarization is of quadrupolar order, and that the rank of the susceptibility tensors is 3 for the surface, i.e. χ_{abc} , and 4 for the bulk, i.e. χ_{abcl} . Although the bulk generated SH is in itself a very important optical phenomena, in here we concentrate only in the surface generated SH. Indeed, in centrosymmetric systems for which the quadrupolar bulk response is much smaller than the dipolar surface response, SH is readily used as a very useful and powerful optical surface probe.¹

To calculate χ_{abc}^s , we start from the basic relation, $\mathbf{J} = d\mathbf{P}/dt$ with \mathbf{J} the current calculated in Sec. 4, and from Eq. 72 we obtain

$$J_a^{(2,\ell)}(\omega_3) = -i\omega_3 P_a(\omega_3) = \frac{e}{m} \sum_{mnk} \mathcal{P}_{mn}^{a(\ell)}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k}; \omega_3), \quad (82)$$

which upon using Eqs. 54 and 80 leads to

$$\begin{aligned} \chi_{abc}^{s(\ell)}(-\omega_3; \omega_1, \omega_2) &= \frac{ie}{mE_1^b E_2^c \mathcal{S} \omega_3} \sum_{mnk} \mathcal{P}_{mn}^{a(\ell)}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k}; \omega_3) \\ &= \frac{e^2}{Sm\hbar\omega_3} \sum_{mnk} \frac{\mathcal{P}_{mn}^{a(\ell)}(\mathbf{k})}{\omega_{nmk} - \bar{\omega}_3} \left[- (B_{nm}^c(\mathbf{k}, \omega_\beta))_{;kb} \right. \\ &\quad \left. + i \sum_{\ell} (r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega_\beta) - B_{n\ell}^c(\mathbf{k}, \omega_\beta) r_{\ell m}^b) \right], \quad (83) \end{aligned}$$

which gives the surface susceptibility of layer ℓ -th. As can be seen from Eq. (54), $\chi_{abc}^{s(\ell)}$ can be split into two terms, one coming from the first term of Eq. (54) and the other from the second term of the same equation. Then we have, after substituting Eq. 50, that

$$\chi_{i,abc}^{s(\ell)} = -\frac{e^3}{m\hbar^2\omega_3} \sum_{mnk} \frac{\mathcal{P}_{mn}^{a(\ell)}}{\omega_{nm} - \omega_3} \left(\frac{f_{mn} r_{nm}^b}{\omega_{nm} - \omega_\beta} \right)_{;kc}, \quad (84)$$

and

$$\chi_{e,abc}^{s(\ell)} = \frac{ie^3}{m\hbar^2\omega_3} \sum_{\ell mnk} \frac{\mathcal{P}_{mn}^{a(\ell)}}{\omega_{nm} - \omega_3} \left(\frac{r_{n\ell}^c r_{\ell m}^b f_{m\ell}}{\omega_{\ell m} - \omega_\beta} - \frac{r_{n\ell}^b r_{\ell m}^c f_{\ell n}}{\omega_{n\ell} - \omega_\beta} \right), \quad (85)$$

where $\chi_i^{s(\ell)}$ is related to intraband transitions and $\chi_e^{s(\ell)}$ to interband transitions. We mention that Eq. (84) and Eq. (85) need to be symmetrized for intrinsic permutation symmetry, i.e. $\chi^{abc}(-\omega_3; \omega_1, \omega_2) = \chi^{acb}(-\omega_3; \omega_2, \omega_1)$,²² and that for SHG $\omega_1 = \omega_2 = \omega$ and $\omega_3 = 2\omega$.

The generalized derivative in Eq. (84) is obtained from the chain rule as

$$\left(\frac{f_{mn} r_{nm}^b}{\omega_{nm} - \omega_2} \right)_{;k^c} = \frac{f_{mn}}{\omega_{nm} - \omega} (r_{nm}^b)_{;k^c} - \frac{f_{mn} r_{nm}^b}{(\omega_{nm} - \omega)^2} (\omega_{nm})_{;k^c}, \quad (86)$$

here $(\omega_{nm})_{;k^a} = (\omega_n)_{;k^a} - (\omega_m)_{;k^a}$. In the appendices we show that

$$(\omega_{nm})_{;k^c} = \frac{p_{nn}^c - p_{mm}^c}{m} \equiv \Delta_{nm}^c, \quad (87)$$

and that

$$(r_{nm}^b)_{;k^c} = \frac{r_{nm}^c \Delta_{mn}^b + r_{nm}^b \Delta_{mn}^c}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{\ell} (\omega_{\ell m} r_{n\ell}^c r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^c). \quad (88)$$

Above formulas give a complete set of relationships in order to calculate the nonlinear susceptibility of any given layer ℓ as $\chi^{s(\ell)} = \chi_e^{s(\ell)} + \chi_i^{s(\ell)}$. Then, we can calculate the surface susceptibility as

$$\chi_{abc}^s(2\omega) \equiv \sum_{\ell_0}^{\ell_d} \chi_{abc}^{(\ell)}(2\omega), \quad (89)$$

where ℓ_0 represents the first layer right at the surface, and ℓ_d the layer at a distance $\sim d$ from the surface (see Fig. 2). Of course we can use Eq. 89 for either the front or the back surface. Likewise

$$\chi_{abc}^{(\ell_f)}(2\omega) \equiv \sum_{\ell_d}^{\ell_f} \chi_{abc}^{(\ell)}(2\omega), \quad (90)$$

is a dipolar bulk susceptibility, with the property that,

$$\chi_{abc}^{(\ell_f)}(2\omega) \stackrel{\ell_f \rightarrow \ell_b}{=} 0, \quad (91)$$

where ℓ_b is a bulk layer such that the bulk centrosymmetry is fully established and the dipolar non-linear susceptibility is identically zero, in accordance with Eq. 78. We remark that ℓ_d is not universal, and ℓ_b should be found according to Eq. 91.

In the next section we show that the longitudinal and transverse gauge formally give the same result for any order N , and present a simple relationship that can be checked numerically.

6. Gauge Invariance

We present a general procedure to establish the equivalence between the longitudinal and the transverse gauge. In the transverse gauge the interaction hamiltonian is given by $\hat{H}^I = (-e/mc)\hat{\mathbf{p}} \cdot \mathbf{A}$. Within the long wavelength

approximation, \mathbf{A} is constant through out space, and since we are working in the semiclassical approximation, \mathbf{A} is not an operator. From Eq. 28 we can get

$$i\hbar(\hat{\rho}_{I,T}(t) - \rho_0) = \frac{-e}{mc} \int_{-\infty}^t dt' [\hat{\mathbf{p}}_I(t') \cdot \mathbf{A}(t'), \hat{\rho}_{I,T}(t')], \quad (92)$$

where T denotes the transverse gauge. An integration by parts gives

$$\begin{aligned} i\hbar(\hat{\rho}_{I,T}(t) - \rho_0) &= \frac{-e}{c} [\hat{\mathbf{r}}_I(t) \cdot \mathbf{A}(t), \hat{\rho}_{I,T}(t)] - e \int_{-\infty}^t dt' [\hat{\mathbf{r}}_I \cdot \mathbf{E}, \hat{\rho}_{I,T}(t')] \\ &\quad - \frac{e}{c} \int_{-\infty}^t dt' [\hat{\mathbf{r}}_I \cdot \mathbf{A}, \dot{\hat{\rho}}_{I,T}(t')]. \end{aligned} \quad (93)$$

To first order we get

$$\hat{\rho}_{I,T}^{(1)}(t) = \hat{\rho}_{I,L}^{(1)}(t) - \frac{e}{i\hbar c} [\hat{\mathbf{r}}_I(t) \cdot \mathbf{A}(t), \rho_0], \quad (94)$$

where L denotes the longitudinal gauge. With the velocity operator (T-gauge) $\mathbf{v} = \mathbf{p}/m - e\mathbf{A}/mc$, Eq. (72) gives $\chi_T^{(1)} = \chi_L^{(1)} + S^{(1)}$, where for a harmonic perturbation,

$$S^{(1)} = \frac{-ic^2}{\omega^2 m \hbar} \sum_{mn} (C_1)_{mn} (\rho_0)_{nm}, \quad (95)$$

with $C_1 = [r^a, p^b] - i\hbar\delta^{ab}$. Therefore, since formally $[r^a, p^b] = i\hbar\delta^{ab}$, $S^{(1)} = 0$, and $\chi_T^{(1)} = \chi_L^{(1)}$, which shows gauge invariance. From Eq. (94) one can show to any order that $\chi_T^{(N)} = \chi_L^{(N)} + S^{(N)}$, where again $S^{(N)} = 0$, due to commutator identities. Therefore, the gauge invariance relies on the fulfillment of the commutator relationships, and thus one has to check this for the particular system in question. As an example, we can take matrix elements of the simple commutator

$$([r^a, p^b])_{nn} = \sum_m (r_{nm}^a p_{mn}^b - p_{nm}^b r_{mn}^a) = \sum_m \frac{p_{nm}^a p_{mn}^b - p_{nm}^b p_{mn}^a}{im\omega_{nm}}, \quad (96)$$

to obtain

$$\sum_m \frac{p_{nm}^a p_{mn}^b - p_{nm}^b p_{mn}^a}{\omega_{nm}} = m\hbar\delta^{ab}, \quad \forall n \neq m \quad (97)$$

which is a relationship that can be numerically verified.

7. SHG Radiation

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

$$R(\omega) = I(2\omega)/I^2(\omega), \quad (98)$$

with the intensity

$$I(\omega) = c/8\pi|E(\omega)|^2. \quad (99)$$

There are several ways to calculate R , one of which is the procedure followed by Cini.²³ This approach calculates the non-linear susceptibility and at the same time the radiated fields. However, we present an alternative derivation based in the work of Mizrahi and Sipe,²⁴ since the derivation of the so called three-layer-model is straightforward. Within our level of approximation this is the best model that we can use. In this scheme, we assume that the SH conversion takes place in a thin layer, just below the surface, that is characterized by a surface dielectric function $\epsilon_\ell(\omega)$. This layer is below vacuum and sits on top of the bulk characterized by $\epsilon_b(\omega)$ (see Fig. 3). The non-linear polarization immersed in the thin layer, will radiate an electric field directly into vacuum and also into the bulk. This bulk directed field, will be reflected back into vacuum. Thus, the total field radiated into vacuum will be the sum of these two contributions (see Fig. 3). We decompose the field into s and p polarizations, then the electric field radiated by a polarization sheet of the form given by Eq. 80, $\mathcal{P}_i = \chi_{ijk}E_j(\omega)E_k(\omega)$,^b is given by,²⁴

$$(E_{p\pm}, E_s) = \left(\frac{2\pi i\tilde{\omega}^2}{w} \hat{\mathbf{p}}_{\pm} \cdot \mathcal{P}, \frac{2\pi i\tilde{\omega}^2}{w} \hat{\mathbf{s}} \cdot \mathcal{P} \right), \quad (100)$$

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

$$k_z(\omega) = \sqrt{\epsilon(\omega) - \sin^2\theta}, \quad (101)$$

and $\hat{\mathbf{p}}_{\pm} = \mathbf{p}_{\pm}/\sqrt{\epsilon}$, with

$$\mathbf{p}_{\pm} = \mp k_z \hat{\mathbf{x}} - \sin\theta \hat{\mathbf{z}}. \quad (102)$$

In the above equations z is the direction perpendicular to the surface that points towards the bulk, x is parallel to the surface, and θ is the angle of incidence, where the plane of incidence is chosen as the xz plane (see

^bFor convenience of notation we now use subscripts i, j, k as Cartesian indices.

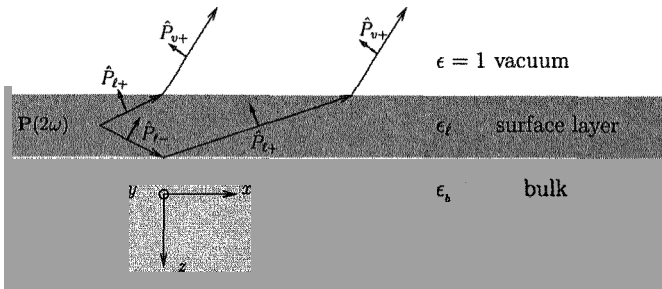


Figure 3. Sketch of the three layer model for SHG. Vacuum is on top with $\epsilon = 1$, the layer with non-linear polarization \mathbf{P} is characterized with $\epsilon_\ell(\omega)$ and the bulk with $\epsilon_b(\omega)$. In the dipolar approximation the bulk does not radiate SHG. The thin arrows are along the direction of propagation, and the unit vectors for p -polarization are denoted with thick arrows (capital letters denote SH components). The unit vector for s -polarization points along y (out of the page).

Fig. 3), thus $\hat{\mathbf{s}} = \hat{\mathbf{y}}$. The function $k_z(\omega)$ is the projection of the wave vector perpendicular to the surface. As we see from Fig. 3, the SH field is refracted at the layer-vacuum interface (lv), and reflected from the layer-bulk (lb) interface, thus we can define the transmission, \mathbf{T} , and reflection, \mathbf{R} , tensors as,

$$\mathbf{T}_{lv} = \hat{\mathbf{s}}T_s^{\ell v}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{v+}\tilde{T}_p^{\ell v}\hat{\mathbf{P}}_{\ell+}, \quad (103)$$

and

$$\mathbf{R}_{lb} = \hat{\mathbf{s}}R_s^{\ell b}\hat{\mathbf{s}} + \hat{\mathbf{P}}_{\ell+}R_p^{\ell b}\hat{\mathbf{P}}_{\ell-}, \quad (104)$$

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

$$\begin{aligned} \mathbf{E}(2\omega) = & E_s(2\omega) (\mathbf{T}_{lv} + \mathbf{T}_{lv} \cdot \mathbf{R}_{lb}) \cdot \hat{\mathbf{s}} \\ & + E_{p+}(2\omega) \mathbf{T}_{lv} \cdot \hat{\mathbf{P}}_{\ell+} + E_{p-}(2\omega) \mathbf{T}_{lv} \cdot \mathbf{R}_{lb} \cdot \hat{\mathbf{P}}_{\ell-}. \end{aligned} \quad (105)$$

The first term is the transmitted s -polarized field, the second one is the reflected and then transmitted s -polarized field and the third and fourth terms are the equivalent fields for p -polarization. The transmission is from

the layer into vacuum, and the reflection between the layer and the bulk. After some simple algebra, we obtain

$$\mathbf{E}(2\omega) = \frac{4\pi i\tilde{\omega}}{K_{z\ell}} \mathbf{H} \cdot \mathcal{P}, \quad (106)$$

where,

$$\mathbf{H} = \hat{s} T_s^{\ell v} (1 + R_s^{\ell b}) \hat{s} + \hat{\mathbf{P}}_{v+} \tilde{T}_p^{\ell v} \left(\hat{\mathbf{P}}_{\ell+} + R_p^{\ell b} \hat{\mathbf{P}}_{\ell-} \right). \quad (107)$$

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

$$E(2\omega) = \frac{4\pi i\omega}{c} \mathbf{e}^{2\omega} \cdot \mathcal{P}. \quad (108)$$

Using the above equations and the following simple relationships between T and R ,

$$T_s^{\ell v} = \frac{K_{z\ell}}{\cos\theta} T_s^{v\ell}, \quad \tilde{T}_p^{\ell v} = \frac{\sqrt{\epsilon_\ell(2\omega)} K_{z\ell}}{\cos\theta} T_p^{v\ell}, \quad (109)$$

$$1 - R_p^{\ell b} = \frac{\epsilon_\ell(2\omega) K_{zb}}{K_{z\ell}} T_p^{\ell b}, \quad 1 + R_p^{\ell b} = \epsilon_b(2\omega) T_p^{\ell b}, \quad (110)$$

we obtain

$$\mathbf{e}^{2\omega} = \frac{1}{\cos\theta} \hat{\mathbf{e}}^{out} \cdot \left[\hat{s} T_s^{v\ell} T_s^{\ell b} \hat{s} - \hat{\mathbf{P}}_{v+} T_p^{v\ell} T_p^{\ell b} (\epsilon_\ell(2\omega) K_{zb} \hat{\mathbf{x}} + \epsilon_b(2\omega) \sin\theta \hat{\mathbf{z}}) \right], \quad (111)$$

and then we write from Eq. (108)

$$E_s(2\omega) = \frac{4\pi i\omega}{c \cos\theta} T_s^{v\ell} T_s^{\ell b} \chi_{yij} E_i(\omega) E_j(\omega), \quad (112)$$

and

$$E_p(2\omega) = \frac{-4\pi i\omega}{c \cos\theta} T_p^{v\ell} T_p^{\ell b} [\epsilon_\ell(2\omega) K_{zb} \chi_{xij} + \epsilon_b(2\omega) \sin\theta \chi_{zij}] E_i(\omega) E_j(\omega). \quad (113)$$

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

$$\mathbf{E}_s(\omega) = E_o t_s^{v\ell} (1 + r_s^{\ell b}) \hat{\mathbf{y}}, \quad (114)$$

and

$$\mathbf{E}_p(\omega) = E_o [\tilde{t}_p^{v\ell} (1 - r_p^{\ell b}) \cos\theta_\ell \hat{\mathbf{x}} - \tilde{t}_p^{v\ell} (1 + r_p^{\ell b}) \sin\theta_\ell \hat{\mathbf{z}}], \quad (115)$$

where E_o is the incoming amplitude and θ_ℓ is the angle of refraction in the layer. Notice that the transmitted and reflected fields in the layer are taken into \mathbf{E}_s and \mathbf{E}_p . From Eqs. (109-110) we get

$$\mathbf{E}_s(\omega) = E_o t_s^{v\ell} t_s^{\ell b} \hat{\mathbf{y}}, \quad (116)$$

and

$$\mathbf{E}_p(\omega) = E_o t_p^{vl} t_p^{\ell b} (\epsilon_\ell(\omega) k_{zb} \hat{\mathbf{x}} - \epsilon_b(\omega) \sin \theta \hat{\mathbf{z}}). \quad (117)$$

Using Eqs. (112), (113), (116), (117), into R , we finally write

$$R_{iF} = \frac{32\pi^3 \omega^2}{(n_o e)^2 c^3 \cos^2 \theta} |T_F^{vl} T_F^{\ell b} (t_i^{vl} t_i^{\ell b})^2 r_{iF}|^2, \quad (118)$$

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

$$r_{iP} = (K_{zb} \chi_{xjk} + \sin \theta \chi_{zjk}) E_j^i E_k^i, \quad (119)$$

and

$$r_{iS} = \chi_{yjk} E_j^i E_k^i, \quad (120)$$

where from Eqs. (116-117), $\mathbf{E}^s = \hat{\mathbf{y}}$, and

$$\mathbf{E}^p = \epsilon_\ell(\omega) k_{zb} \hat{\mathbf{x}} - \epsilon_b(\omega) \sin \theta \hat{\mathbf{z}}. \quad (121)$$

The $n_o e$ factor in Eq. (118), with n_o the electronic density, renders χ dimensionless. To complete the required formulas, we write down the Fresnel factors,

$$t_s^{vl} = \frac{2 \cos \theta}{\cos \theta + k_{z\ell}}, \quad t_p^{vl} = \frac{2 \cos \theta}{\epsilon_\ell(\omega) \cos \theta + k_{z\ell}}, \quad (122)$$

$$t_s^{\ell b} = \frac{2k_{z\ell}}{k_{z\ell} + k_{zb}}, \quad t_p^{\ell b} = \frac{2k_{z\ell}}{\epsilon_b(\omega) k_{z\ell} + \epsilon_s(\omega) k_{zb}}, \quad (123)$$

where the appropriate term $\sqrt{\epsilon(\omega)}$ from the usual definition of t_p ,²¹ has been taken out to give Eqs. (119) and (120). For a given surface symmetry and its corresponding non-zero tensor elements of χ_{ijk} , Eq. (118) can be calculated explicitly through Eqs. (119) and (120)^{6,25}. With the three-layer model we can get two opposite cases, one in which the SH conversion takes places in vacuum for which we simply put $\epsilon_\ell = 1$, and the other case where the layer is identical to the bulk, or $\epsilon_\ell = \epsilon_b$. The former case corresponds to no screening and the latter to the usual Fresnel screening.

8. Conclusions

We have presented a complete derivation of the required elements to calculate the surface SHG radiated from a semiconductor within the dipole approximation, and showed how to calculate the layer-by-layer contribution to the optical signal. We derived the nonlinear surface susceptibility tensor χ within the longitudinal gauge and thus we decomposed χ into intraband

and interband one-electron transitions. We showed that the longitudinal and transverse gauges give the same result, and a simple expression was presented in order to check the numerical accuracy of this equivalency. Also, we calculated the radiated efficiency R within the three layer model. The combination of χ and R allow us to study this fascinating surface optical phenomena.

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Appendix A.

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

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

and

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

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

$$\int_V d^3r \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{q}}(\mathbf{r}) = \frac{V}{8\pi^3} \delta_{nm} \delta_{\mathbf{k},\mathbf{q}}, \quad (\text{A.3})$$

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

$$\int d^3r \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm} \delta(\mathbf{k} - \mathbf{q}), \quad (\text{A.4})$$

for which the Kronecker- δ is replaced by

$$\delta_{\mathbf{k},\mathbf{q}} \rightarrow \frac{8\pi^3}{V} \delta(\mathbf{k} - \mathbf{q}), \quad (\text{A.5})$$

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

$$\int d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) = \sum_j^{\text{unit cells}} \int_{\Omega} d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{r}+\mathbf{R}_j)} f(\mathbf{r} + \mathbf{R}_j),$$

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

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

Appendix B.

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

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

then Eq. 26 gives

$$\begin{aligned}
(H_{0,nm})_{;\mathbf{k}} &= \nabla_{\mathbf{k}} H_{0,nm}(\mathbf{k}) - iH_{0,nm}(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})) \\
&= \delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m(\mathbf{k}), \tag{B.2}
\end{aligned}$$

where from Eq. 25,

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

then

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

Now, from Eq. 19

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{H}_0]|m\mathbf{k}\rangle = i\hbar \frac{\mathbf{p}_{nm}(\mathbf{k})}{m} \quad n \neq m, \tag{B.5}$$

and from Eq. 18

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0]|m\mathbf{k}\rangle = i\hbar \frac{\mathbf{p}_{nm}(\mathbf{k})}{m}, \tag{B.6}$$

therefore, substituting above into

$$\langle n\mathbf{k} | [\hat{\mathbf{r}}, \hat{H}_0] | m\mathbf{k} \rangle = \langle n\mathbf{k} | [\hat{\mathbf{r}}_i, \hat{H}_0] | m\mathbf{k} \rangle + \langle n\mathbf{k} | [\hat{\mathbf{r}}_e, \hat{H}_0] | m\mathbf{k} \rangle, \quad (\text{B.7})$$

we get

$$i\hbar \frac{\mathbf{p}_{nm}(\mathbf{k})}{m} = i\delta_{nm} \hbar \nabla_{\mathbf{k}} \omega_m(\mathbf{k}) + i\hbar(1 - \delta_{nm}) \frac{\mathbf{p}_{nm}(\mathbf{k})}{m}, \quad (\text{B.8})$$

from where

$$\frac{\mathbf{p}_{nm}(\mathbf{k})}{m} = \nabla_{\mathbf{k}} \omega_n(\mathbf{k}), \quad (\text{B.9})$$

so from Eq. B.4

$$(\omega_n(\mathbf{k}))_{;k^a} = \frac{p_{nn}^a(\mathbf{k})}{m}. \quad (\text{B.10})$$

Appendix C.

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

$$[r^a, p^b] = i\hbar \delta_{ab}, \quad (\text{C.1})$$

then

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

so

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

From Eq. 25 and 26

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

$$(p_{nm}^b)_{;k^a} = \nabla_{k^a} p_{nm}^b(\mathbf{k}) - ip_{nm}^b(\mathbf{k}) (\xi_{nn}^a(\mathbf{k}) - \xi_{mm}^a(\mathbf{k})), \quad (\text{C.5})$$

and

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

$$\begin{aligned}
&= \delta(\mathbf{k} - \mathbf{k}') \sum_{\ell} \left((1 - \delta_{n\ell}) \xi_{n\ell}^a p_{\ell m}^b \right. \\
&\quad \left. - (1 - \delta_{\ell m}) p_{n\ell}^b \xi_{\ell m}^a \right) \\
&= \delta(\mathbf{k} - \mathbf{k}') \left(\sum_{\ell} \left(\xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right) \right. \\
&\quad \left. + p_{nm}^b (\xi_{mm}^a - \xi_{nn}^a) \right). \tag{C.6}
\end{aligned}$$

Using Eqs. C.4 and C.6 into Eq. C.3 gives

$$\begin{aligned}
i\delta(\mathbf{k} - \mathbf{k}') \left((p_{nm}^b)_{;k^a} - i \sum_{\ell} \left(\xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right) \right. \\
\left. - i p_{nm}^b (\xi_{mm}^a - \xi_{nn}^a) \right) = i\hbar \delta_{ab} \delta_{nm} \delta(\mathbf{k} - \mathbf{k}'), \tag{C.7}
\end{aligned}$$

then

$$\begin{aligned}
(p_{nm}^b)_{;k^a} &= \hbar \delta_{ab} \delta_{nm} + i \sum_{\ell} \left(\xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right) \\
&\quad + i p_{nm}^b (\xi_{mm}^a - \xi_{nn}^a), \tag{C.8}
\end{aligned}$$

and from Eq. C.5,

$$\nabla_{k^a} p_{nm}^b = \hbar \delta_{ab} \delta_{nm} + i \sum_{\ell} \left(\xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right). \tag{C.9}$$

Now, there are two cases. We use Eqs. 21 and 22.

Case $n = m$

$$\frac{1}{\hbar} \nabla_{k^a} p_{nn}^b = \delta_{ab} - \frac{m}{\hbar} \sum_{\ell} \omega_{\ell n} \left(r_{n\ell}^a r_{\ell n}^b + r_{n\ell}^b r_{\ell n}^a \right), \tag{C.10}$$

that gives the familiar expansion for the inverse effective mass tensor $(m_n^{-1})_{ab}$ ²⁶.

Case $n \neq m$

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

$$\begin{aligned}
&= -m \sum_{\ell} \left(\omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + i \xi_{nm}^a (p_{mm}^b - p_{nn}^b) \\
&= -m \sum_{\ell} \left(\omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + i m r_{nm}^a \Delta_{mn}^b, \quad (\text{C.11})
\end{aligned}$$

where

$$\Delta_{mn}^b = \frac{p_{mm}^b - p_{nn}^b}{m}. \quad (\text{C.12})$$

Now, for $n \neq m$, Eqs. 22, B.10 and C.11 and the chain rule, give

$$\begin{aligned}
(r_{nm}^b)_{;k^a} &= \left(\frac{p_{nm}^b}{i m \omega_{nm}} \right)_{;k^a} = \frac{1}{i m \omega_{nm}} (p_{nm}^b)_{;k^a} - \frac{p_{nm}^b}{i m \omega_{nm}^2} (\omega_{nm})_{;k^a} \\
&= \frac{i}{\omega_{nm}} \sum_{\ell} \left(\omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + \frac{r_{nm}^a \Delta_{mn}^b}{\omega_{nm}} \\
&\quad - \frac{r_{nm}^b}{\omega_{nm}} (\omega_{nm})_{;k^a} \\
&= \frac{i}{\omega_{nm}} \sum_{\ell} \left(\omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + \frac{r_{nm}^a \Delta_{mn}^b}{\omega_{nm}} \\
&\quad - \frac{r_{nm}^b p_{nn}^a - p_{mm}^a}{\omega_{nm} m} \\
&= \frac{r_{nm}^a \Delta_{mn}^b + r_{nm}^b \Delta_{mn}^a}{\omega_{nm}} \\
&\quad + \frac{i}{\omega_{nm}} \sum_{\ell} \left(\omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) \quad (\text{C.13})
\end{aligned}$$

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