Ab-initio SHG: Quadrupolar Contribution

Klaus-Dieter Bauer1,2, Martin Panholzer1, Kurt Hingerl1
1 Zentrum für Oberflächen- und Nanoanalytik, Johannes Kepler University Linz
2 Christian Doppler Laboratory for Microscopic and Spectroscopic Material Characterisation

June 30, 2015 at OSI-11, Austin

Introduction

Second Harmonic Generation (SHG) has been established as a surface sensitive probe for centrosymmetric materials. In these the usually dominant bulk dipole contribution is symmetry-forbidden and the surface dipole contribution becomes accessible. For a quantitative description of measurements, however, one needs to take into account bulk quadrupole contributions which can be on the same order of magnitude as the surface dipole contribution.1,2

Current implementations of ab-initio SHG assume a rigorous long-wavelength limit, which precludes the calculation of quadrupole contributions.

Macroscopic Symmetry Argument

Microscopically the second-order polarization response reads

\[ P^{(2)}(r_0) = \int d\mathbf{r}_1 d\mathbf{r}_2 \chi^{(2)}(\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2) : \mathbf{E}(\mathbf{r}_1)\mathbf{E}(\mathbf{r}_2) \] (1)

In the (rigorous) long-wavelength limit the external electric field \( \mathbf{E} \) is constant over the range of the non-locality of \( \chi^{(2)} \), and the response can be described by a purely local response function,

\[ P^{(2)}(r_0) = \chi^{(2D)}(r_0) : \mathbf{E}(r_0) \] (2)

Additionally, microscopic variations in \( P^{(2)} \) on a scale smaller than a wavelength don’t contribute to an optical signal, i.e. only the macroscopic components are observable.

Therefore, in a bulk regime we can locally write

\[ P^{(2)} = \chi^{(2D)} : \mathbf{E} \] (3)

without any position variables. In a centrosymmetric bulk the polarization should be invariant under coordinate inversion, yielding \( P^{(2)} = -P^{(2)} \), i.e. \( \chi^{(2D)} \) must vanish.

Notation

Throughout this document we have omitted time-variables and tensor components to avoid distracting verbosity. A form \( P = \chi^{(2)} : \mathbf{E} \) should be read as

\[ P^{(2)}(\omega_0) = \sum \int d\mathbf{q}_2 \chi^{(2)}_2 \mathbf{E}_2(\omega_0) \mathbf{E}_1(\omega_0) \] (4)

Quadrupole Response

The term \( \mathbf{E}(r_0) : \mathbf{E}(r_0) \) in (2) corresponds to zero-order Taylor-expansion of \( \mathbf{E}(\mathbf{r}, \mathbf{r}_0) \) around \( \mathbf{r}_0 \). Extending the expansion up to first order yields an additional polarization component\n
\[ P^{(2Q)}(\mathbf{r}) = \mathbf{\chi}^{(2Q)}(\mathbf{r}) : \mathbf{E}(\mathbf{r})\mathbf{E}(\mathbf{r}) \] (5)

which is equivalent to the more verbose forms in ref.[1] when taking into account that the microscopic polarization field is best defined as time-integral of the current \( \partial \mathbf{j} = \mathbf{J}^{(2)} \) in Fourier space these long-wavelength response functions are given by the behavior of \( \chi^{(2)}(\mathbf{q}, \mathbf{q}_1, \mathbf{q}_2) \) around the \( \mathbf{q} \)-point. For the macroscopic components we find

\[ \chi^{(2D)}(\mathbf{r}) = \chi^{(2)}(0, 0, 0) \] \[ \chi^{(2Q)}(\mathbf{r}) = -2i \mathbf{\nabla} \chi^{(2)}(\mathbf{r}) \] (6)

Here we have used that the only the symmetric part of \( \chi^{(2)} \) is physically relevant and thus assumed the anti-symmetric part to vanish.

[\( \chi^{(2)} \)'s physical meaning is defined by the equation \( H^{(2)}(\mathbf{r}) = \frac{1}{2m_e} (\mathbf{p} - e \mathbf{A}(\mathbf{r}, t))^2 + V \) where \( \mathbf{A} \) is the vector potential, \( \mathbf{p} \) is the momentum operator and \( V \) the (generally non-local) potential of the unperturbed Hamiltonian. TDPT up to second order in \( \mathbf{A} \) gives the current-current response function\n
\[ \mathbf{J}^{(2)} = \chi^{(2)} : \mathbf{A} \] (8)

from which \( \chi^{(2Q)} \) can be calculated, presumably without adding scalar-potential terms to the Hamiltonian.\n
In contrast to existing literature such as ref. [5, 6] we have a \( \delta^3 \)-shaped term describing the interface effects and vanish outside the sample.

On an independent particle approximation (IPA) level, the perturbing field in the TDPT ansatz is the total field, albeit set to an arbitrary function rather than self-consistently determined from linear response.

Hence we attempt to use \( \chi^{(2D)} \) and \( \chi^{(2Q)} \) calculated from (6) and IPA-TDPT as IPA values for the macroscopic response functions.

Conclusion

• We are deriving a macroscopic second-order response function in the independent particle approximation.

• From this we will calculate the macroscopic dipole and quadrupole response functions.

• Inserting these into macroscopic models we hope to demonstrate the influence of the bulk quadrupole term for nonlinear optics in centrosymmetric crystals, providing the first ab-initio calculation thereof.

References


Acknowledgements

Financial support by the Austrian Federal Ministry of Science, Research and Economy and the National Foundation for Research, Technology and Development is gratefully acknowledged.