Abinitio SHG: Quadrupolar Contribution

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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]

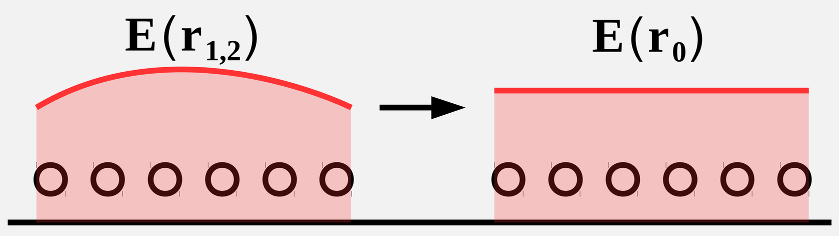
Current implementations of ab-initio SHG assume a rigorous long-wavelength limit, which precludes the calculation of quadrupole contributions.

Macroscopic Symmetry Argument

Microscopically the second-order polarization response reads

$$\mathbf{P}^{(2)}(\mathbf{r}_0) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \chi^{(2)}(\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2) : \mathbf{E}(\mathbf{r}_1)\mathbf{E}(\mathbf{r}_2) \qquad (1)$$

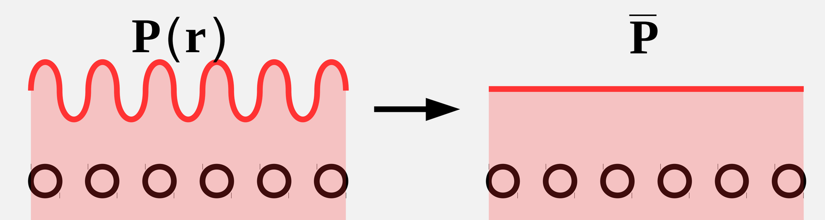
In the (rigorous) **long-wavelength limit** the external electric field $\mathbf{E}$ is constant over the range of the non-locality of $\chi^{(2)}$,



and the response can be described by a purely local response function,

$$\mathbf{P}^{(2)}(\mathbf{r}_0) = \chi^{(2D)}(\mathbf{r}_0) : \mathbf{E}(\mathbf{r}_0)\mathbf{E}(\mathbf{r}_0) \qquad (2)$$

Additionally, microscopic variations in $\mathbf{P}^{(2)}$ 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

$$\mathbf{P}^{(2)} = \chi^{(2D)} : \mathbf{EE} \qquad (3)$$

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

Notation

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

$$P_\alpha^{(2)}(\omega_0) = \sum_{\beta\gamma} \iint d\omega_1 d\omega_2 \chi^{(2)}_{\alpha\beta\gamma} E_\beta(\omega_1) E_\gamma(\omega_2) \qquad (4)$$

Quadrupole Response

The term $\mathbf{E}(\mathbf{r}_0)\mathbf{E}(\mathbf{r}_0)$ in (2) corresponds to zero-order Taylor-expansion of $\mathbf{E}(\mathbf{r}_1)\mathbf{E}(\mathbf{r}_2)$ around $\mathbf{r}_0$. Extending the expansion up to first order yields an additional polarization component

$$\mathbf{P}^{(2Q)}(\mathbf{r}) = \chi^{(2Q)}(\mathbf{r}) : \mathbf{E}(\mathbf{r})\nabla\mathbf{E}(\mathbf{r}) \qquad (5)$$

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 $\partial_t \mathbf{P} = \mathbf{J}$.[3]

In **Fourier space** these long-wavelength response functions are given by the behavior of $\chi^{(2)}(\mathbf{q}_0, \mathbf{q}_1, \mathbf{q}_2)$ around the Γ-point. For the macroscopic components we find

$$\boxed{\begin{aligned} \chi^{(2D)} &= \chi^{(2)}(0,0,0) \\ \chi^{(2Q)} &= -2i\nabla_{\mathbf{k}}\chi^{(2)}(\mathbf{k},0,\mathbf{k})\Big|_{\mathbf{k}=0} \end{aligned}} \qquad (6)$$

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

[a] $\chi^{(2)}$'s physical meaning is defined by the equation $\mathbf{P}^{(2)} = \chi^{(2)} : \mathbf{EE}$, where only the symmetric part of $\chi^{(2)}$ contributes. We can thus always require $\chi^{(2)}_{\alpha\beta\gamma}(\mathbf{q}_0\omega_0\mathbf{q}_1\omega_1\mathbf{q}_2\omega_2) = \chi^{(2)}_{\alpha\gamma\beta}(\mathbf{q}_0\omega_0\mathbf{q}_2\omega_2\mathbf{q}_1\omega_1)$. If $\chi^{(2)}$ *doesn't* fulfill this equation we can discard the antisymmetric part without changing the described physics.

TDPT

In order to obtain the microscopic response function we perform time-dependent perturbation theory (TDPT) for the many-particle system (see e.g. ref. [4]) for the Hamiltonian

$$H = \frac{1}{2m_e}\left(\mathbf{p} - e\mathbf{A}(\mathbf{r},t)\right)^2 + V \qquad (7)$$

where $\mathbf{A}$ is the vector potential, $\mathbf{r}$ is the position operator and V the (generally non-local) potential of the unperturbed Hamiltonian. TDPT up to second order in $\mathbf{A}$ gives the **current-current-current response** function

$$\boxed{\mathbf{J}^{(2)} = \chi^{\mathbf{jjj}} : \mathbf{AA}} \qquad (8)$$

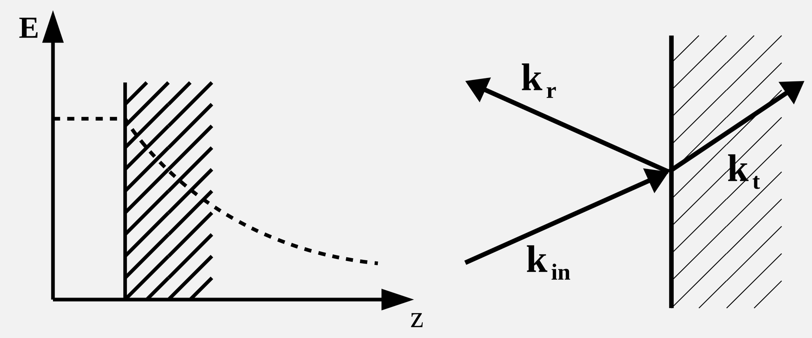
from which $\chi^{(2)}$ can be calculated, presumably without adding scalar-potential terms to the Hamiltonian.[a]

In contrast to existing literature such as ref. [5, 6] we need to preserve position-dependence of the vector field throughout the derivations, which are currently in progress.

[a] Since we can choose a gauge where $\mathbf{A}(t) = \int \mathbf{E}(t)dt$ and $\Phi \equiv 0$, the inclusion of a scalar potential Φ into the Hamiltonian should not be required. If done it gives rise to three additional response functions $\chi^{\mathbf{j}\rho\rho}$, $\chi^{\mathbf{j}\rho\mathbf{j}}$, $\chi^{\mathbf{jj}\rho}$.

Connecting the Scales

From a macroscopic point of view, the total electric field is a plane wave outside the sample with a reflected component. Inside the sample it has a different wave vector (refraction) and decays exponentially.



On this scale the second order polarization is given by

$$\overline{\chi}^{(2D)}(\mathbf{r}) : \overline{\mathbf{E}}^{tot}(\mathbf{r})\overline{\mathbf{E}}^{tot}(\mathbf{r}) + \overline{\chi}^{(2Q)}(\mathbf{r}) : \overline{\mathbf{E}}(\mathbf{r})\nabla\overline{\mathbf{E}}(\mathbf{r}) \qquad (9)$$

where $\overline{\mathbf{E}}$ indicates the macroscopic components. On this scale $\chi^{(2)}, \chi^{(2Q)}$ are constant in the bulk regime, have a $\delta(z)$-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 $\chi^{(2D)}, \chi^{(2Q)}$ calculated from (6) and IPA-TDPT as IPA values for the macroscopic response functions.

Conclusion

- We are deriving a **microscopic 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

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