1.7. Nonlinear optical properties

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1.7.1. Introduction

The first nonlinear optical phenomenon was observed by Franken *et al.* (1961): ultraviolet radiation at 0.3471 µm was detected at the exit of a quartz crystal illuminated with a ruby laser beam at 0.6942 µm. This was the first demonstration of second harmonic generation at optical wavelengths. A coherent light of a few W cm^{-2} is necessary for the observation of nonlinear optical interactions, which thus requires the use of laser beams.

The basis of nonlinear optics, including quantum-mechanical perturbation theory and Maxwell equations, is given in the paper published by Armstrong *et al.* (1962).

It would take too long here to give a complete historical account of nonlinear optics, because it involves an impressive range of different aspects, from theory to applications, from physics to chemistry, from microscopic to macroscopic aspects, from quantum mechanics of materials to classical and quantum electrodynamics, from gases to solids, from mineral to organic compounds, from bulk to surface, from waveguides to fibres and so on.

Among the main nonlinear optical effects are harmonic generation, parametric wave mixing, stimulated Raman scattering, self-focusing, multiphoton absorption, optical bistability, phase conjugation and optical solitons.

This chapter deals mainly with harmonic generation and parametric interactions in anisotropic crystals, which stand out as one of the most important fields in nonlinear optics and certainly one of its oldest and most rigorously treated topics. Indeed, there is a great deal of interest in the development of solid-state laser sources, be they tunable or not, in the ultraviolet, visible and infrared ranges. Spectroscopy, telecommunications, telemetry and optical storage are some of the numerous applications.

The electric field of light interacts with the electric field of matter by inducing a dipole due to the displacement of the electron density away from its equilibrium position. The induced dipole moment is termed polarization and is a vector: it is related to the applied electric field *via* the dielectric susceptibility tensor. For fields with small to moderate amplitude, the polarization remains linearly proportional to the field magnitude and defines the linear optical properties. For increasing field amplitudes, the polarization is a nonlinear function of the applied electric field and gives rise to nonlinear optical effects. The polarization is properly modelled by a Taylor power series of the applied electric field if its strength does not exceed the atomic electric field (10^8–10^9 V cm^{-1}) and if the frequency of the electric field is far away from the resonance frequencies of matter. Our purpose lies within this framework because it encompasses the most frequently encountered cases, in which laser intensities remain in the kW to MW per cm^2 range, that is to say with electric fields from 10^3 to 10^4 V cm^{-1}. The electric field products appearing in the Taylor series express the interactions of different optical waves. Indeed, a wave at the circular frequency ω can be radiated by the second-order polarization induced by two waves at ω_a and ω_b such as $\omega = \omega_a \pm \omega_b$: these interactions correspond to sum-frequency generation ($\omega = \omega_a + \omega_b$), with the particular cases of second harmonic generation ($2\omega_a = \omega_a + \omega_a$) and indirect third harmonic generation ($3\omega_a = \omega_a + 2\omega_a$); the other three-wave process is difference-frequency generation, including optical parametric amplification and optical parametric oscillation. In the same way, the third-order polarization governs four-wave mixing: direct third harmonic generation ($3\omega_a = \omega_a + \omega_a + \omega_a$)

and more generally sum- and difference-frequency generations ($\omega = \omega_a \pm \omega_b \pm \omega_c$).

Here, we do not consider optical interactions at the microscopic level, and we ignore the way in which the atomic or molecular dielectric susceptibility determines the macroscopic optical properties. Microscopic solid-state considerations and the relations between microscopic and macroscopic optical properties, particularly successful in the realm of organic crystals, play a considerable role in materials engineering and optimization. This important topic, known as molecular and crystalline engineering, lies beyond the scope of this chapter. Therefore, all the phenomena studied here are connected to the macroscopic first-, second- and third-order dielectric susceptibility tensors $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$, respectively; we give these tensors for all the crystal point groups.

We shall mainly emphasize propagation aspects, on the basis of Maxwell equations which are expressed for each Fourier component of the optical field in the nonlinear crystal. The reader will then follow how the linear optical properties come to play a pivotal role in the nonlinear optical interactions. Indeed, an efficient quadratic or cubic interaction requires not only a high magnitude of $\chi^{(2)}$ or $\chi^{(3)}$, respectively, but also specific conditions governed by $\chi^{(1)}$: existence of phase matching between the induced nonlinear polarization and the radiated wave; suitable symmetry of the field tensor, which is defined by the tensor product of the electric field vectors of the interacting waves; and small or nil double refraction angles. Quadratic and cubic processes cannot be considered as fully independent in the context of cascading. Significant phase shifts driven by a sequence of sum- and difference-frequency generation processes attached to a $\chi^{(2)} \cdot \chi^{(2)}$ contracted tensor expression have been reported (Bosshard, 2000). These results point out the relevance of polar structures to cubic phenomena in both inorganic and organic structures, thus somewhat blurring the borders between quadratic and cubic NLO.

We analyse in detail second harmonic generation, which is the prototypical interaction of frequency conversion. We also present indirect and direct third harmonic generations, sum-frequency generation and difference-frequency generation, with the specific cases of optical parametric amplification and optical parametric oscillation.

An overview of the methods of measurement of the nonlinear optical properties is provided, and the chapter concludes with a comparison of the main mineral and organic crystals showing nonlinear optical properties.

1.7.2. Origin and symmetry of optical nonlinearities

1.7.2.1. *Induced polarization and susceptibility*

The macroscopic electronic polarization of a unit volume of the material system is classically expanded in a Taylor power series of the applied electric field $\mathbf{E}$, according to Bloembergen (1965):

$$\mathbf{P} = \mathbf{P}_0 + \varepsilon_o(\chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{E}^2 + \ldots + \chi^{(n)} \cdot \mathbf{E}^n + \ldots),$$

$$(1.7.2.1)$$

where $\chi^{(n)}$ is a tensor of rank $n + 1$, $\mathbf{E}^n$ is a shorthand abbreviation for the *n*th order tensor product $\mathbf{E} \otimes \mathbf{E} \otimes \ldots \otimes \mathbf{E} = \otimes^n \mathbf{E}$ and the dot stands for the contraction of the last n indices of the

tensor $\chi^{(n)}$ with the full $\mathbf{E}^n$ tensor. More details on tensor algebra can be found in Chapter 1.1 and in Schwartz (1981).

A more compact expression for (1.7.2.1) is

$$\mathbf{P} = \mathbf{P}_0 + \mathbf{P}_1(t) + \mathbf{P}_2(t) + \ldots + \mathbf{P}_n(t) + \ldots, \qquad (1.7.2.2)$$

where $\mathbf{P}_0$ represents the static polarization and $\mathbf{P}_n$ represents the nth order polarization. The properties of the linear and nonlinear responses will be assumed in the following to comply with time invariance and locality. In other words, time displacement of the applied fields will lead to a corresponding time displacement of the induced polarizations and the polarization effects are assumed to occur at the site of the polarizing field with no remote interactions. In the following, we shall refer to the classical formalism and related notations developed in Butcher (1965) and Butcher & Cotter (1990).

Tensorial expressions will be formulated within the Cartesian formalism and subsequent multiple lower index notation. The alternative irreducible tensor representation, as initially implemented in the domain of nonlinear optics by Jerphagnon *et al.* (1978) and more recently revived by Brasselet & Zyss (1998) in the realm of molecular-engineering studies, is particularly advantageous for connecting the nonlinear hyperpolarizabilities of microscopic (*e.g.* molecular) building blocks of molecular materials to the macroscopic (*e.g.* crystalline) susceptibility level. Such considerations fall beyond the scope of the present chapter, which concentrates mainly on the crystalline level, regardless of the microscopic origin of phenomena.

1.7.2.1.1. Linear and nonlinear responses

1.7.2.1.1.1. Linear response

Let us first consider the first-order linear response in (1.7.2.1) and (1.7.2.2): the most general possible linear relation between $\mathbf{P}(t)$ and $\mathbf{E}(t)$ is

$$\mathbf{P}^{(1)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau \; T^{(1)}(t, \tau) \cdot \mathbf{E}(\tau), \qquad (1.7.2.3)$$

where $T^{(1)}$ is a rank-two tensor, or in Cartesian index notation

$$P_\mu^{(1)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau \; T_{\mu\alpha}^{(1)}(t, \tau) E_\alpha(\tau). \qquad (1.7.2.4)$$

Applying the time-invariance assumption to (1.7.2.4) leads to

$$\begin{aligned}
\mathbf{P}^{(1)}(t + t_0) &= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau \; T^{(1)}(t + t_0, \tau) \cdot \mathbf{E}(\tau) \\
&= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau \; T^{(1)}(t, \tau + t_0) \cdot \mathbf{E}(\tau) \\
&= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau' \; T^{(1)}(t, \tau' - t_0) \cdot \mathbf{E}(\tau'), \qquad (1.7.2.5)
\end{aligned}$$

hence $T^{(1)}(t + t_0, \tau) = T^{(1)}(t, \tau - t_0)$ or, setting $t = 0$ and $t_0 = t$,

$$T^{(1)}(t, \tau) = T^{(1)}(0, \tau - t) = R^{(1)}(t - \tau), \qquad (1.7.2.6)$$

where $R^{(1)}$ is a rank-two tensor referred to as the linear polarization response function, which depends only on the time difference $t - \tau$. Substitution in (1.7.2.5) leads to

$$\begin{aligned}
\mathbf{P}^{(1)}(t) &= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau \; R^{(1)}(t - \tau) \mathbf{E}(\tau) \\
&= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau \; R^{(1)}(\tau) \mathbf{E}(t - \tau). \qquad (1.7.2.7)
\end{aligned}$$

$R^{(1)}$ can be viewed as the tensorial analogue of the linear impulse function in electric circuit theory. The causality principle imposes that $R^{(1)}(\tau)$ should vanish for $\tau < 0$ so that $\mathbf{P}^{(1)}(t)$ at time t will depend only on polarizing field values before t. $R^{(1)}$, $\mathbf{P}^{(1)}$ and $\mathbf{E}$ are real functions of time.

1.7.2.1.1.2. Quadratic response

The most general expression for $\mathbf{P}^{(2)}(t)$ which is quadratic in $\mathbf{E}(t)$ is

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \; \mathrm{d}\tau_2 \; T^{(2)}(t, \tau_1, \tau_2) \cdot \mathbf{E}(\tau_1) \otimes \mathbf{E}(\tau_2) \qquad (1.7.2.8)$$

or in Cartesian notation

$$P_\mu^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \; \mathrm{d}\tau_2 \; T_{\mu\alpha\beta}^{(2)}(t, \tau_1, \tau_2) E_\alpha(\tau_1) E_\beta(\tau_2). \qquad (1.7.2.9)$$

It can easily be proved by decomposition of $T^{(2)}$ into symmetric and antisymmetric parts and permutation of dummy variables (α, τ_1) and (β, τ_2), that $T^{(2)}$ can be reduced to its symmetric part, satisfying

$$T_{\mu\alpha\beta}^{(2)}(t, \tau_1, \tau_2) = T_{\mu\alpha\beta}^{(2)}(t, \tau_2, \tau_1). \qquad (1.7.2.10)$$

From time invariance

$$T^{(2)}(t, \tau_1, \tau_2) = R^{(2)}(t - \tau_1, t - \tau_2), \qquad (1.7.2.11)$$

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \; \mathrm{d}\tau_2 \; R^{(2)}(t - \tau_1, t - \tau_2) \cdot \mathbf{E}(\tau_1) \otimes \mathbf{E}(\tau_2),$$

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \; \mathrm{d}\tau_2 \; R^{(2)}(\tau_1, \tau_2) \cdot \mathbf{E}(t - \tau_1) \otimes \mathbf{E}(t - \tau_2). \qquad (1.7.2.12)$$

Causality demands that $R^{(2)}(\tau_1, \tau_2)$ cancels for either τ_1 or τ_2 negative while $R^{(2)}$ is real. Intrinsic permutation symmetry implies that $R_{\mu\alpha\beta}^{(2)}(\tau_1, \tau_2)$ is invariant by interchange of (α, τ_1) and (β, τ_2) pairs.

1.7.2.1.1.3. Higher-order response

The nth order polarization can be expressed in terms of the $(n + 1)$-rank tensor $T^{(n)}(t, \tau_1, \tau_2, \ldots, \tau_n)$ as

$$\begin{aligned}
\mathbf{P}^{(n)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \int_{-\infty}^{+\infty} \mathrm{d}\tau_2 \ldots \int_{-\infty}^{+\infty} \mathrm{d}\tau_n \; T^{(n)}(t, \tau_1, \tau_2, \ldots, \tau_n) \\
\cdot \mathbf{E}(\tau_1) \otimes \mathbf{E}(\tau_2) \otimes \ldots \otimes \mathbf{E}(\tau_n). \qquad (1.7.2.13)
\end{aligned}$$

For similar reasons to those previously stated, it is sufficient to consider the symmetric part of $T^{(n)}$ with respect to the $n!$ permutations of the n pairs $(\alpha_1, \tau_1), (\alpha_2, \tau_2) \ldots (\alpha_n, \tau_n)$. The $T^{(n)}$ tensor will then exhibit intrinsic permutation symmetry at the nth order. Time-invariance considerations will then allow the introduction of the $(n + 1)$th-rank real tensor $R^{(n)}$, which generalizes the previously introduced R operators:

$$\begin{aligned}
P_\mu^{(n)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \int_{-\infty}^{+\infty} \mathrm{d}\tau_2 \ldots \int_{-\infty}^{+\infty} \mathrm{d}\tau_n \; R_{\mu\alpha_1\alpha_2\ldots\alpha_n}^{(n)}(\tau_1, \tau_2, \ldots \tau_n) \\
\times E_{\alpha_1}(t - \tau_1) E_{\alpha_2}(t - \tau_2) \ldots E_{\alpha_n}(t - \tau_n). \qquad (1.7.2.14)
\end{aligned}$$

$R^{(n)}$ cancels when one of the τ_i's is negative and is invariant under any of the $n!$ permutations of the (α_i, τ_i) pairs.

1.7.2.1.2. Linear and nonlinear susceptibilities

Whereas the polarization response has been expressed so far in the time domain, in which causality and time invariance are most naturally expressed, Fourier transformation into the frequency domain permits further simplification of the equations given above and the introduction of the susceptibility tensors according to the following derivation.

The direct and inverse Fourier transforms of the field are defined as

$$\mathbf{E}(t) = \int_{-\infty}^{+\infty} d\omega \; \mathbf{E}(\omega) \exp(-i\omega t) \qquad (1.7.2.15)$$

$$\mathbf{E}(\omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt \; \mathbf{E}(t) \exp(i\omega t), \qquad (1.7.2.16)$$

where $\mathbf{E}(\omega)^* = \mathbf{E}(-\omega)$ as $\mathbf{E}(t)$ is real.

1.7.2.1.2.1. Linear susceptibility

By substitution of (1.7.2.15) in (1.7.2.7),

$$\mathbf{P}^{(1)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\tau \; R^{(1)}(\tau) \cdot \mathbf{E}(\omega) \exp[-i\omega(t-\tau)]$$

$$\mathbf{P}^{(1)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} d\omega \; \chi^{(1)}(-\omega_\sigma; \omega) \mathbf{E}(\omega) \exp(-i\omega_\sigma t),$$
$$(1.7.2.17)$$

where

$$\chi^{(1)}(-\omega_\sigma; \omega) = \int_{-\infty}^{+\infty} d\tau \; R^{(1)}(\tau) \exp(i\omega\tau).$$

In these equations, $\omega_\sigma = \omega$ to satisfy the energy conservation condition that will be generalized in the following. In order to ensure convergence of $\chi^{(1)}$, ω has to be taken in the upper half plane of the complex plane. The reality of $R^{(1)}$ implies that $\chi^{(1)}(-\omega_\sigma; \omega)^* = \chi^{(1)}(\omega_\sigma^*; -\omega^*)$.

1.7.2.1.2.2. Second-order susceptibility

Substitution of (1.7.2.15) in (1.7.2.12) yields

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 \; R^{(2)}(\tau_1, \tau_2)$$
$$\cdot \mathbf{E}(\omega_1) \otimes \mathbf{E}(\omega_2) \exp\{-i[\omega_1(t-\tau_1) + \omega_2(t-\tau_2)]\}$$
$$(1.7.2.18)$$

or

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \; \chi^{(2)}(-\omega_\sigma; \omega_1, \omega_2) \cdot \mathbf{E}(\omega_1) \otimes \mathbf{E}(\omega_2)$$
$$\times \exp(-i\omega_\sigma t) \qquad (1.7.2.19)$$

with

$$\chi^{(2)}(-\omega_\sigma; \omega_1, \omega_2) = \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 \; R^{(2)}(\tau_1, \tau_2)$$
$$\times \exp[i(\omega_1\tau_1 + \omega_2\tau_2)]$$

and $\omega_\sigma = \omega_1 + \omega_2$. Frequencies ω_1 and ω_2 must be in the upper half of the complex plane to ensure convergence. Reality of $R^{(2)}$ implies $\chi^{(2)}(-\omega_\sigma; \omega_1, \omega_2)^* = \chi^{(2)}(\omega_\sigma^*; -\omega_1^*, -\omega_2^*)$. $\chi^{(2)}_{\mu\alpha\beta}(-\omega_\sigma; \omega_1, \omega_2)$ is invariant under the interchange of the (α, ω_1) and (β, ω_2) pairs.

1.7.2.1.2.3. nth-order susceptibility

Substitution of (1.7.2.15) in (1.7.2.14) provides

$$\mathbf{P}^{(n)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \ldots \int_{-\infty}^{+\infty} d\omega_n \; \chi^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \ldots \omega_n)$$
$$\cdot \mathbf{E}(\omega_1) \otimes \mathbf{E}(\omega_2) \otimes \ldots \otimes \mathbf{E}(\omega_n) \exp(-i\omega_\sigma t)$$
$$(1.7.2.20)$$

where

$$\chi^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n)$$
$$= \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 \ldots \int_{-\infty}^{+\infty} d\tau_n \; R^{(n)}(\tau_1, \tau_2, \ldots, \tau_n) \exp\left(i\sum_{j=1}^{n} \omega_j\tau_j\right)$$
$$(1.7.2.21)$$

and $\omega_\sigma = \omega_1 + \omega_2 + \ldots + \omega_n$.

All frequencies must lie in the upper half complex plane and reality of $\chi^{(n)}$ imposes

$$\chi^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n)^* = \chi^{(n)}(\omega_\sigma^*; -\omega_1^*, -\omega_2^*, \ldots, -\omega_n^*).$$
$$(1.7.2.22)$$

Intrinsic permutation symmetry implies that $\chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n)$ is invariant with respect to the $n!$ permutations of the (α_i, ω_i) pairs.

1.7.2.1.3. Superposition of monochromatic waves

Optical fields are often superpositions of monochromatic waves which, due to spectral discretization, will introduce considerable simplifications in previous expressions such as (1.7.2.20) relating the induced polarization to a continuous spectral distribution of polarizing field amplitudes.

The Fourier transform of the induced polarization is given by

$$\mathbf{P}^{(n)}(\omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt \; \mathbf{P}^{(n)}(t) \exp(i\omega t). \qquad (1.7.2.23)$$

Replacing $\mathbf{P}^{(n)}(t)$ by its expression as from (1.7.2.20) and applying the well known identity

$$(1/2\pi) \int_{-\infty}^{+\infty} dt \; \exp[i(\omega - \omega_\sigma)t] = \delta(\omega - \omega_\sigma) \qquad (1.7.2.24)$$

leads to

$$\mathbf{P}^{(n)}(\omega) = \varepsilon_o \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \ldots \int_{-\infty}^{+\infty} d\omega_n \; \chi^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \ldots \omega_n)$$
$$\times \mathbf{E}(\omega_1)\mathbf{E}(\omega_2) \ldots \mathbf{E}(\omega_n)\delta(\omega - \omega_\sigma). \qquad (1.7.2.25)$$

In practical cases where the applied field is a superposition of monochromatic waves

$$\mathbf{E}(t) = (1/2) \sum_{\omega'} [E_{\omega'} \exp(-i\omega' t) + E_{-\omega'} \exp(i\omega' t)] \qquad (1.7.2.26)$$

with $E_{-\omega'} = E_{\omega'}^*$. By Fourier transformation of (1.7.2.26)

$$\mathbf{E}(\omega) = (1/2) \sum_{\omega'} [E_{\omega'}\delta(\omega - \omega') + E_{-\omega'}\delta(\omega + \omega')]. \qquad (1.7.2.27)$$

The optical intensity for a wave at frequency ω' is related to the squared field amplitude by

$$I_{\omega'} = \varepsilon_o cn(\omega')\langle \mathbf{E}^2(t)\rangle_t = \tfrac{1}{2}\varepsilon_o cn(\omega')|E_{\omega'}|^2. \qquad (1.7.2.28)$$

The averaging as represented above by brackets is performed over a time cycle and $n(\omega')$ is the index of refraction at frequency ω'.

1.7.2.1.4. Conventions for nonlinear susceptibilities
1.7.2.1.4.1. Classical convention

Insertion of (1.7.2.26) in (1.7.2.25) together with permutation symmetry provides

$$P_\mu^{(n)}(\omega_\sigma) = \varepsilon_o \sum_{\alpha_1\alpha_2\ldots\alpha_n} \sum_\omega K(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n)$$
$$\times \chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n)$$
$$\times E_{\alpha_1}(\omega_1)E_{\alpha_2}(\omega_2) \ldots E_{\alpha_n}(\omega_n), \qquad (1.7.2.29)$$

Table 1.7.2.1. *The most common nonlinear effects and the corresponding susceptibility tensors in the frequency domain*

Process	Order n	$-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n$	K
Linear absorption	1	$-\omega; \omega$	1
Optical rectification	2	$0; -\omega, \omega$	1/2
Linear electro-optic effect	2	$-\omega; \omega, 0$	2
Second harmonic generation	2	$-2\omega; \omega, \omega$	1/2
Three-wave mixing	2	$-\omega_3; \omega_1, \omega_2$	1
D.c. Kerr effect	3	$-\omega; \omega, 0, 0$	3
D.c. induced second harmonic generation	3	$-2\omega; \omega, \omega, 0$	3/2
Third harmonic generation	3	$-3\omega; \omega, \omega, \omega$	1/4
Four-wave mixing	3	$-\omega_4; \omega_1, \omega_2, \omega_3$	3/2
Coherent anti-Stokes Raman scattering	3	$-\omega_{as}; \omega_p, -\omega_p, -\omega_s$	3/4
Intensity-dependent refractive index	3	$-\omega; \omega, -\omega, \omega$	3/4
nth harmonic generation	n	$-n\omega; \omega, \omega, \ldots, \omega$	2^{1-n}

where the summation over ω stands for all distinguishable permutation of $\omega_1, \omega_2, \ldots, \omega_n$, K being a numerical factor given by

$$K(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n) = 2^{s+m-n}p, \qquad (1.7.2.30)$$

where p is the number of distinct permutations of $\omega_1, \omega_2, \ldots, \omega_n$, n is the order of the nonlinear process, m is the number of d.c. fields (*e.g.* corresponding to $\omega_i = 0$) within the n frequencies and $s = 0$ when $\omega_\sigma = 0$, otherwise $s = 1$. For example, in the absence of a d.c. field and when the ω_i's are different, $K = 2^{s-n}n!$.

The K factor allows the avoidance of discontinuous jumps in magnitude of the $\chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}$ elements when some frequencies are equal or tend to zero, which is not the case for the other conventions (Shen, 1984).

The induced nonlinear polarization is often expressed in terms of a tensor $d^{(n)}$ by replacing $\chi^{(n)}$ in (1.7.2.29) by

$$\chi^{(n)} = 2^{-s-m+n}d^{(n)}. \qquad (1.7.2.31)$$

Table 1.7.2.1 summarizes the most common classical nonlinear phenomena, following the notations defined above. Then, according to Table 1.7.2.1, the nth harmonic generation induced nonlinear polarization is written

$$P^{(2)}_\mu(n\omega) = \varepsilon_o \sum_{\alpha_1\alpha_2\ldots\alpha_n} 2^{n-1} \chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-n\omega; \omega, \omega, \ldots, \omega)$$
$$\times E_{\alpha_1}(\omega)E_{\alpha_2}(\omega)\ldots E_{\alpha_n}(\omega). \qquad (1.7.2.32)$$

The E_{α_i} are the components of the total electric field $\mathbf{E}(\omega)$.

1.7.2.1.4.2. *Convention used in this chapter*

The K convention described above is often used, but may lead to errors in cases where two of the interacting waves have the same frequency but different polarization states. Indeed, as demonstrated in Chapter 1.6 and recalled in Section 1.7.3, a direction of propagation in an anisotropic crystal allows in the general case two different directions of polarization of the electric field vector, written $\mathbf{E}^+$ and $\mathbf{E}^-$. Then any nonlinear coupling in this medium occurs necessarily between these eigen modes at the frequencies concerned.

Because of the possible non-degeneracy with respect to the direction of polarization of the electric fields at the same frequency, it is suitable to consider a harmonic generation process, second harmonic generation (SHG) or third harmonic generation (THG) for example, like any other non-degenerated interaction. We do so for the rest of this chapter. Then all terms derived from the permutation of the fields with the same frequency are taken into account in the expression of the induced nonlinear polarization and the K factor in equation (1.7.2.29) disappears: hence, in the general case, the induced nonlinear polarization is written

$$P^{(n)}_\mu(\omega_\sigma) = \varepsilon_o \sum_{\alpha_1,\ldots,\alpha_n} \chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-\omega_\sigma; \omega_1, \ldots, \omega_n)$$
$$\times E^\pm_{\alpha_1}(\omega_1)\ldots E^\pm_{\alpha_n}(\omega_n), \qquad (1.7.2.33)$$

where $+$ and $-$ refer to the eigen polarization modes.

According to (1.7.2.33), the nth harmonic generation induced polarization is expressed as

$$P^{(n)}_\mu(n\omega) = \varepsilon_o \sum_{\alpha_1,\ldots,\alpha_n} \chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-n\omega; \omega, \ldots, \omega)$$
$$\times E^\pm_{\alpha_1}(\omega_1)\ldots E^\pm_{\alpha_n}(\omega_n). \qquad (1.7.2.34)$$

For example, in the particular case of SHG where the two waves at ω have different directions of polarization $\mathbf{E}^+(\omega)$ and $\mathbf{E}^-(\omega)$ and where the only nonzero $\chi^{(2)}_{yij}$ coefficients are χ_{yxz} and χ_{yzx}, (1.7.2.34) gives

$$P^{(2)}_y(2\omega) = \varepsilon_o[\chi_{yxz}(-2\omega; \omega, \omega)E^+_x(\omega)E^-_z(\omega)$$
$$+ \chi_{yzx}(-2\omega; \omega, \omega)E^+_z(\omega)E^-_x(\omega)]. $$
$$(1.7.2.35)$$

The two field component products are equal only if the two eigen modes are the same, *i.e.* $+$ or $-$.

According to (1.7.2.33) and (1.7.2.34), we note that $\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-\omega_\sigma; \omega_1, \ldots, \omega_n)$ changes smoothly to $\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-n\omega; \omega, \ldots, \omega)$ when all the $\omega_1, \ldots \omega_n$ approach continuously the same value ω.

1.7.2.2. *Symmetry properties*

1.7.2.2.1. *Intrinsic permutation symmetry*

1.7.2.2.1.1. *ABDP and Kleinman symmetries*

Intrinsic permutation symmetry, as already discussed, imposes the condition that the nth order susceptibility $\chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n)$ be invariant under the $n!$ permutations of the (α_i, ω_i) pairs as a result of time invariance and causality. Furthermore, the overall permutation symmetry, *i.e.* the invariance over the $(n + 1)!$ permutations of the (α_i, ω_i) and $(\mu, -\omega_\sigma)$ pairs, may be valid when all the optical frequencies occuring in the susceptibility and combinations of these appearing in the denominators of quantum expressions are far removed from the transitions, making the medium transparent at these frequencies. This property is termed *ABDP symmetry*, from the initials of the authors of the pioneering article by Armstrong *et al.* (1962).

Let us consider as an application the quantum expression of the quadratic susceptibility (with damping factors neglected), the derivation of which being beyond the scope of this chapter, but which can be found in nonlinear optics treatises dealing with microscopic interactions, such as in Boyd (1992):

$$\chi^{(2)}_{\mu\alpha\beta}(-\omega_\sigma; \omega_1, \omega_2)$$
$$= \frac{Ne^3}{\varepsilon_o^2\hbar^2} S_T \sum_{abc} \rho_o(a) \frac{r^\mu_{ab}r^\alpha_{bc}r^\beta_{ca}}{(\Omega_{ba} - \omega_1 - \omega_2)(\Omega_{ca} - \omega_1)},$$
$$(1.7.2.36)$$

where N is the number of microscopic units (*e.g.* molecules in the case of organic crystals) per unit volume, a, b and c are the eigen states of the system, Ω_{ba} and Ω_{ca} are transition energies, r^μ_{ab} is the μ component of the transition dipole connecting states a and b, and $\rho_o(a)$ is the population of level a as given by the corresponding diagonal term of the density operator. S_T is the summation operator over the six permutations of the $(\mu, -\omega_\sigma)$, (α, ω_1), (β, ω_2). Provided all frequencies at the denominator are much smaller than the transition frequencies Ω_{ba} and Ω_{ca}, the optical frequencies $-\omega_\sigma$, ω_1, ω_2 can be permuted without significant variation of the susceptibility. It follows correspondingly that the susceptibility is invariant with respect to the

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