1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

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

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

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

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

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

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

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

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

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

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

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

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

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

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):

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

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

references