

1.7. NONLINEAR OPTICAL PROPERTIES

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

Process	Order n	$-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n$	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
n th harmonic generation	n	$-n\omega; \omega, \omega, \dots, \omega$	2^{1-n}

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

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

where p is the number of distinct permutations of $\omega_1, \omega_2, \dots, \omega_n$, 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 $\chi_{\mu\alpha_1\alpha_2\dots\alpha_n}^{(n)}$ 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

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

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 n th harmonic generation induced nonlinear polarization is written

$$P_\mu^{(2)}(n\omega) = \varepsilon_o \sum_{\alpha_1\alpha_2\dots\alpha_n} 2^{n-1} \chi_{\mu\alpha_1\alpha_2\dots\alpha_n}^{(n)}(-n\omega; \omega, \omega, \dots, \omega) \times E_{\alpha_1}(\omega) E_{\alpha_2}(\omega) \dots E_{\alpha_n}(\omega). \quad (1.7.2.32)$$

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

$$P_\mu^{(n)}(\omega_\sigma) = \varepsilon_o \sum_{\alpha_1, \dots, \alpha_n} \chi_{\mu\alpha_1 \dots \alpha_n}^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_n) \times E_{\alpha_1}^\pm(\omega_1) \dots E_{\alpha_n}^\pm(\omega_n), \quad (1.7.2.33)$$

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

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

$$P_\mu^{(n)}(n\omega) = \varepsilon_o \sum_{\alpha_1, \dots, \alpha_n} \chi_{\mu\alpha_1 \dots \alpha_n}^{(n)}(-n\omega; \omega, \dots, \omega) \times E_{\alpha_1}^\pm(\omega_1) \dots E_{\alpha_n}^\pm(\omega_n). \quad (1.7.2.34)$$

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 $\chi_{yij}^{(2)}$ coefficients are χ_{yxz} and χ_{yzx} , (1.7.2.34) gives

$$P_y^{(2)}(2\omega) = \varepsilon_o [\chi_{yxz}(-2\omega; \omega, \omega) E_x^+(\omega) E_z^-(\omega) + \chi_{yzx}(-2\omega; \omega, \omega) E_z^+(\omega) E_x^-(\omega)]. \quad (1.7.2.35)$$

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 $\chi_{\mu\alpha_1 \dots \alpha_n}^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_n)$ changes smoothly to $\chi_{\mu\alpha_1 \dots \alpha_n}^{(n)}(-n\omega; \omega, \dots, \omega)$ when all the $\omega_1, \dots, \omega_n$ 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 n th order susceptibility $\chi_{\mu\alpha_1\alpha_2\dots\alpha_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n)$ 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 occurring 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):

$$\chi_{\mu\alpha\beta}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) = \frac{Ne^3}{\varepsilon_o^2 \hbar^2} S_T \sum_{abc} \rho_o(a) \frac{r_{ab}^\mu r_{bc}^\alpha r_{ca}^\beta}{(\Omega_{ba} - \omega_1 - \omega_2)(\Omega_{ca} - \omega_1)}, \quad (1.7.2.36)$$

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_{ab}^μ 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 $-\omega_\sigma, \omega_1, \omega_2$ 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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permutation of Cartesian indices appearing only in the numerator of (1.7.2.36), regardless of frequency. This property, which can be generalized to higher-order susceptibilities, is known as *Kleinman symmetry*. Its validity can help reduce the number of non-vanishing terms in the susceptibility, as will be shown later.

1.7.2.2.1.2. Manley–Rowe relations

An important consequence of overall permutation symmetry is the *Manley–Rowe* power relations, which account for energy exchange between electromagnetic waves in a purely reactive (e.g. non-dissipative) medium. Calling W_i the power input at frequency ω_i into a unit volume of a dielectric polarizable medium,

$$W_i = \left\langle \mathbf{E}(t) \cdot \frac{d\mathbf{P}}{dt}(t) \right\rangle, \quad (1.7.2.37)$$

where the averaging is performed over a cycle and

$$\begin{aligned} \mathbf{E}(t) &= \text{Re}[E_{\omega_i} \exp(-j\omega_i t)] \\ \mathbf{P}(t) &= \text{Re}[P_{\omega_i} \exp(-j\omega_i t)]. \end{aligned} \quad (1.7.2.38)$$

The following expressions can be derived straightforwardly:

$$W_i = \frac{1}{2} \omega_i \text{Re}(iE_{\omega_i} \cdot P_{\omega_i}) = \frac{1}{2} \omega_i \text{Im}(E_{\omega_i}^* \cdot P_{\omega_i}). \quad (1.7.2.39)$$

Introducing the quadratic induced polarization $P^{(2)}$, Manley–Rowe relations for sum-frequency generation state

$$\frac{W_1}{\omega_1} = \frac{W_2}{\omega_2} = -\frac{W_3}{\omega_3}. \quad (1.7.2.40)$$

Since $\omega_1 + \omega_2 = \omega_3$, (1.7.2.40) leads to an energy conservation condition, namely $W_3 + W_1 + W_2 = 0$, which expresses that the power generated at ω_3 is equal to the sum of the powers lost at ω_1 and ω_2 .

A quantum mechanical interpretation of these expressions in terms of photon fusion or splitting can be given, remembering that $W_i/\hbar\omega_i$ is precisely the number of photons generated or annihilated per unit volume in unit time in the course of the nonlinear interactions.

1.7.2.2.1.3. Contracted notation for susceptibility tensors

The tensors $\chi_{\mu\alpha\beta}^{(2)}(-2\omega; \omega, \omega)$ or $d_{\mu\alpha\beta}^{(2)}(-2\omega; \omega, \omega)$ are invariant with respect to (α, β) permutation as a consequence of the intrinsic permutation symmetry. Independently, it is not possible to distinguish the coefficients $\chi_{ijk}^{(2)}(-2\omega; \omega, \omega)$ and $\chi_{ikj}^{(2)}(-2\omega; \omega, \omega)$ by SHG experiments, even if the two fundamental waves have different directions of polarization.

Therefore, these third-rank tensors can be represented in contracted form as 3×6 matrices $\chi_{\mu m}(-2\omega; \omega, \omega)$ and $d_{\mu m}(-2\omega; \omega, \omega)$, where the suffix m runs over the six possible (α, β) Cartesian index pairs according to the classical convention of contraction:

$$\begin{aligned} \text{for } \mu: & x \rightarrow 1 \quad y \rightarrow 2 \quad z \rightarrow 3 \\ \text{for } m: & xx \rightarrow 1 \quad yy \rightarrow 2 \quad zz \rightarrow 3 \quad yz = zy \rightarrow 4 \\ & xz = zx \rightarrow 5 \quad xy = yx \rightarrow 6. \end{aligned}$$

The 27 elements of $\chi_{\mu\alpha\beta}^{(2)}(-2\omega; \omega, \omega)$ are then reduced to 18 in the $\chi_{\mu m}$ contracted tensor notation (see Section 1.1.4.10).

For example, (1.7.2.35) can be written

$$\begin{aligned} P_y^{(2)}(2\omega) &= \varepsilon_o \chi_{25}(-2\omega; \omega, \omega) [e_x^+(\omega) \mathbf{E}^+(\omega) e_z^-(\omega) \mathbf{E}^-(\omega) \\ &+ e_z^+(\omega) \mathbf{E}^+(\omega) e_x^-(\omega) \mathbf{E}^-(\omega)]. \end{aligned} \quad (1.7.2.41)$$

The same considerations can be applied to THG. Then the 81 elements of $\chi_{\mu\alpha\beta\gamma}^{(3)}(-3\omega; \omega, \omega, \omega)$ can be reduced to 30 in the $\chi_{\mu m}$

contracted tensor notation with the following contraction convention:

$$\begin{aligned} \text{for } \mu: & x \rightarrow 1 \quad y \rightarrow 2 \quad z \rightarrow 3 \\ \text{for } m: & xxx \rightarrow 1 \quad yyy \rightarrow 2 \quad zzz \rightarrow 3 \quad yzz \rightarrow 4 \quad yyz \rightarrow 5 \\ & xzz \rightarrow 6 \quad xxz \rightarrow 7 \quad xyy \rightarrow 8 \quad xxy \rightarrow 9 \quad xyz \rightarrow 0. \end{aligned}$$

If Kleinman symmetry holds, the contracted tensor can be further extended beyond SHG and THG to any other processes where all the frequencies are different.

1.7.2.2.2. Implications of spatial symmetry on the susceptibility tensors

Centrosymmetry is the most detrimental crystalline symmetry constraint that will fully cancel all odd-rank tensors such as the $d^{(2)}$ [or $\chi^{(2)}$] susceptibilities. Intermediate situations, corresponding to noncentrosymmetric crystalline point groups, will reduce the number of nonzero coefficients without fully depleting the tensors.

Tables 1.7.2.2 to 1.7.2.5 detail, for each crystal point group, the remaining nonzero $\chi^{(2)}$ and $\chi^{(3)}$ coefficients and the eventual connections between them. $\chi^{(2)}$ and $\chi^{(3)}$ are expressed in the principal axes x, y and z of the second-rank $\chi^{(1)}$ tensor. (x, y, z) is usually called the optical frame; it is linked to the crystal-

Table 1.7.2.2. Nonzero $\chi^{(2)}$ coefficients and equalities between them in the general case

Symmetry class	$\chi^{(2)}$ nonzero elements
Triclinic C_1 (1)	All 27 elements are independent and nonzero
Monoclinic C_2 (2) (twofold axis parallel to z) C_s (m) (mirror perpendicular to z)	$xyz, xzy, xxz, xzx, yyz, yzy, yxz, yzx, zxx, zyy, zzz, zxy, zyx$ $xxx, xyy, xzz, xxy, xyx, yxx, yyy, yzz, yxy, yyx, zyz, zzy, zxz, zzx$
Orthorhombic C_{2v} ($mm2$) (twofold axis parallel to z) D_2 (222)	$xzx, xxz, yyz, yzy, zxx, zyy, zzz$ $xyz, xzy, yzx, yxz, zxy, zyx$
Tetragonal C_4 (4) S_4 ($\bar{4}$) D_4 (422) C_{4v} ($4mm$) D_{2d} ($42m$)	$xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz, zxx = zyy, zzz, zxy = -zyx$ $xyz = yxz, xzy = yzx, xzx = -yzy, xxz = -yyz, zxx = -zzy, zxy = zyx$ $xyz = -yxz, xzy = -yzx, zxy = -zyx$ $xzx = yzy, xxz = yyz, zxx = zyy, zzz$ $xyz = yxz, xzy = yzx, zxy = zyx$
Hexagonal C_6 (6) C_{3h} ($\bar{6}$) D_6 (622) C_{6v} ($6mm$) D_{3h} ($62m$) (mirror perpendicular to x)	$xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz, zxx = zyy, zzz, zxy = -zyx$ $xxx = -xyy = -yyx = -yxy, yyy = -yxx = -xxy = -xyx, zxx = zyy = -xyx = -xxy$ $xyz = -yxz, xzy = -yzx, zxy = -zyx$ $xzx = yzy, xxz = yyz, zxx = zyy, zzz$ $yyy = -yxx = -xxy = -xyx$
Trigonal C_3 (3) D_3 (32) C_{3v} ($3m$) (mirror perpendicular to x)	$xxx = -xyy = -yyx = -yxy, xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz, yyy = -yxx = -xxy = -xyx, zxx = zyy, zzz, zxy = -zyx$ $xxx = -xyy = -yyx = -yxy, xyz = -yxz, xzy = -yzx, zxy = -zyx$ $yyy = -yxx = -xxy = -xyx, xzx = yzy, xxz = yyz, zxx = zyy, zzz$
Cubic T (23), T_d ($\bar{4}3m$) O (432)	$xyz = xzy = yzx = yxz = zxy = zyx$ $xyz = -xzy = yzx = -yxz = zxy = -zyx$