

1.7. NONLINEAR OPTICAL PROPERTIES

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

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lographical frame by the standard conventions given in Chapter 1.6.

1.7.3. Propagation phenomena

1.7.3.1. Crystalline linear optical properties

We summarize here the main linear optical properties that govern the nonlinear propagation phenomena. The reader may refer to Chapter 1.6 for the basic equations.

1.7.3.1.1. Index surface and electric field vectors

The relations between the different field vectors relative to a propagating electromagnetic wave are obtained from the constitutive relations of the medium and from Maxwell equations.

In the case of a non-magnetic and non-conducting medium, Maxwell equations lead to the following wave propagation equation for the Fourier component at the circular frequency ω defined by (1.7.2.15) and (1.7.2.16) (Butcher & Cotter, 1990):

$$\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}\mathbf{E}(\omega) = (\omega^2/c^2)\mathbf{E}(\omega) + \omega^2\mu_0\mathbf{P}(\omega), \quad (1.7.3.1)$$

where $\omega = 2\pi c/\lambda$, λ is the wavelength and c is the velocity of light in a vacuum; μ_0 is the free-space permeability, $\mathbf{E}(\omega)$ is the electric field vector and $\mathbf{P}(\omega)$ is the polarization vector.

Table 1.7.2.3. Nonzero $\chi^{(2)}$ coefficients and equalities between them under the Kleinman symmetry assumption

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

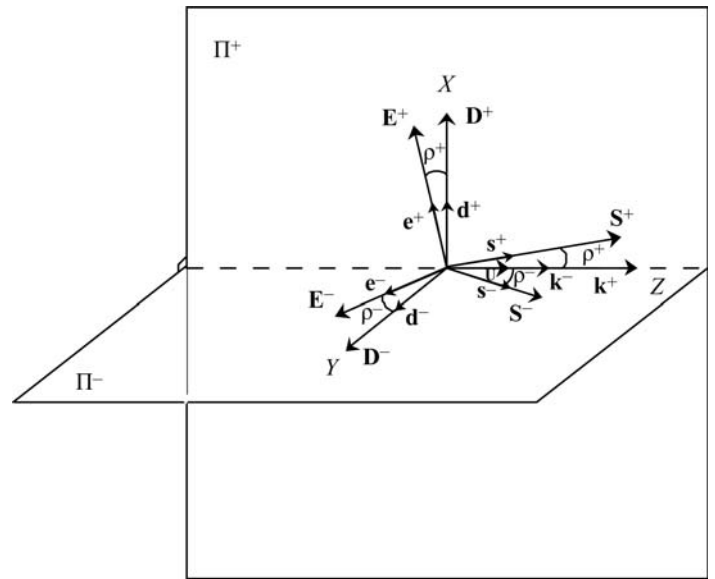


Fig. 1.7.3.1. Field vectors of a plane wave propagating in an anisotropic medium. (X, Y, Z) is the wave frame. Z is along the direction of propagation, X and Y are contained in Π^+ and Π^- respectively, by an arbitrary convention.

In the linear regime, $\mathbf{P}(\omega) = \varepsilon_0\chi^{(1)}(\omega)\mathbf{E}(\omega)$, where ε_0 is the free-space permittivity and $\chi^{(1)}(\omega)$ is the first-order electric susceptibility tensor. Then (1.7.3.1) becomes

$$\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}\mathbf{E}(\omega) = (\omega^2/c^2)\varepsilon(\omega)\mathbf{E}(\omega). \quad (1.7.3.2)$$

$\varepsilon(\omega) = 1 + \chi^{(1)}(\omega)$ is the dielectric tensor. In the general case, $\chi^{(1)}(\omega)$ is a complex quantity i.e. $\chi^{(1)} = \chi^{(1)'} + i\chi^{(1)''}$. For the following, we consider a medium for which the losses are small ($\chi^{(1)'} \gg \chi^{(1)''}$); it is one of the necessary characteristics of an efficient nonlinear medium. In this case, the dielectric tensor is real: $\varepsilon = 1 + \chi^{(1)'}$.

The plane wave is a solution of equation (1.7.3.2):

$$\mathbf{E}(\omega, X, Y, Z) = \mathbf{e}(\omega)\mathbf{E}(\omega, X, Y, Z) \exp[\pm ik(\omega)Z]. \quad (1.7.3.3)$$

(X, Y, Z) is the orthonormal frame linked to the wave, where Z is along the direction of propagation.

We consider a linearly polarized wave so that the unit vector \mathbf{e} of the electric field is real ($\mathbf{e} = \mathbf{e}^*$), contained in the XZ or YZ planes.

$\mathbf{E}(\omega, X, Y, Z) = A(\omega, X, Y, Z) \exp[i\Phi(\omega, Z)]$ is the scalar complex amplitude of the electric field where $\Phi(\omega, Z)$ is the phase, and $\mathbf{E}^*(-\omega, X, Y, Z) = \mathbf{E}(\omega, X, Y, Z)$. In the linear regime, the amplitude of the electric field varies with Z only if there is absorption.

k is the modulus of the wavevector, real in a lossless medium: $+kZ$ corresponds to forward propagation along Z , and $-kZ$ to backward propagation. We consider that the plane wave propagates in an anisotropic medium, so there are two possible wavevectors, \mathbf{k}^+ and \mathbf{k}^- , for a given direction of propagation of unit vector \mathbf{u} :

$$\mathbf{k}^{\pm}(\omega, \theta, \varphi) = (\omega/c)n^{\pm}(\omega, \theta, \varphi)\mathbf{u}(\theta, \varphi). \quad (1.7.3.4)$$

(θ, φ) are the spherical coordinates of the direction of the unit wavevector \mathbf{u} in the optical frame; (x, y, z) is the optical frame defined in Section 1.7.2.

The spherical coordinates are related to the Cartesian coordinates (u_x, u_y, u_z) by

$$u_x = \cos \varphi \sin \theta \quad u_y = \sin \varphi \sin \theta \quad u_z = \cos \theta. \quad (1.7.3.5)$$