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

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

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

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

$$+ \chi_{yzx}(-2\omega; \omega, \omega)E^+_z(\omega)E^-_x(\omega)]. \qquad (1.7.2.35)$$

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):

$$\chi^{(2)}_{\mu\alpha\beta}(-\omega_\sigma; \omega_1, \omega_2)$$

$$= \frac{Ne^3}{\varepsilon_o^2\hbar^2}S_T\sum_{abc}\rho_o(a)\frac{r^\mu_{ab}r^\alpha_{bc}r^\beta_{ca}}{(\Omega_{ba} - \omega_1 - \omega_2)(\Omega_{ca} - \omega_1)}, \qquad (1.7.2.36)$$

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

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,

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

where the averaging is performed over a cycle and

$$\mathbf{E}(t) = Re[E_{\omega_i} \exp(-j\omega_i t)]$$
$$\mathbf{P}(t) = Re[P_{\omega_i} \exp(-j\omega_i t)]. \qquad (1.7.2.38)$$

The following expressions can be derived straightforwardly:

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

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

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

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 $\chi^{(2)}_{\mu\alpha\beta}(-2\omega; \omega, \omega)$ or $d^{(2)}_{\mu\alpha\beta}(-2\omega; \omega, \omega)$ 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 $\chi^{(2)}_{ijk}(-2\omega; \omega, \omega)$ and $\chi^{(2)}_{ikj}(-2\omega; \omega, \omega)$ 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:

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

The 27 elements of $\chi^{(2)}_{\mu\alpha\beta}(-2\omega; \omega, \omega)$ 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

$$P^{(2)}_y(2\omega) = \varepsilon_o \chi_{25}(-2\omega; \omega, \omega)[e^+_x(\omega)\mathbf{E}^+(\omega)e^-_z(\omega)\mathbf{E}^-(\omega)$$
$$+ e^+_z(\omega)\mathbf{E}^+(\omega)e^-_x(\omega)\mathbf{E}^-(\omega)]. \qquad (1.7.2.41)$$

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

contracted tensor notation with the following contraction convention:

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

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, yzz, 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 ($\bar{4}$)	$xyz = yxz$, $xzy = yzx$, $xzx = -yzy$, $xxz = -yyz$, $zxx = -zyy$, $zxy = zyx$
D_4 (422)	$xyz = -yxz$, $xzy = -yzx$, $zxy = -zyx$
C_{4v} (4mm)	$xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz
D_{2d} ($\bar{4}2m$)	$xyz = yxz$, $xzy = yzx$, $zxy = zyx$
Hexagonal C_6 (6)	$xyz = -yxz$, $xzy = -yzx$, $xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz, $zxy = -zyx$
C_{3h} ($\bar{6}$)	$xxx = -xyy = -yxy = -yyx$, $yyy = -yxx = -xyx = -xxy$
D_6 (622)	$xyz = -yxz$, $xzy = -yzx$, $zxy = -zyx$
C_{6v} (6mm)	$xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz
D_{3h} ($\bar{6}2m$) (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 ($\bar{4}3m$)	$xyz = xzy = yzx = yxz = zxy = zyx$
O (432)	$xyz = -xzy = yzx = -yxz = zxy = -zyx$

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):

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

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)	$xxx, xyy = yxy = yyx, xzz = zxz = zzx,$ $xyz = xzy = yxz = yzx = zxy = zyx,$ $xxz = xzx = zxx, xxy = xyx = yxx, yyy,$ $yzz = zyz = zzy, yyz = yzy = zyy, zzz$
Monoclinic C_2 (2) (twofold axis parallel to z) C_s (m) (mirror perpendicular to z)	$xyz = xzy = yxz = yzx = zxy = zyx,$ $xxz = xzx = zxx, yyz = yzy = zyy, zzz$ $xxx, xyy = yxy = yyx, xzz = zxz = zzx,$ $xxy = xyx = yxx, yyy, yzz = zyz = zzy$
Orthorhombic C_{2v} ($mm2$) (twofold axis parallel to z) D_2 (222)	$xzx = xxz = zxx, yyz = yzy = zyy, zzz$ $xyz = xzy = yzx = yxz = zxy = zyx$
Tetragonal C_4 (4) S_4 ($\bar{4}$) D_4 (422) C_{4v} ($4mm$) D_{2d} ($\bar{4}2m$)	$xzx = xxz = zxx = yzy = yyz = zyy, zzz$ $xyz = xzy = yzx = yxz = zxy = zyx, xzx =$ $xxz = zxx = -yzy = -yyz = -zyy$ All elements are nil $xzx = xxz = zxx = yyz = yzy = zyy, zzz$ $xyz = xzy = yzx = yxz = zxy = zyx$
Hexagonal C_6 (6) C_{3h} ($\bar{6}$) D_6 (622) C_{6v} ($6mm$) D_{3h} ($\bar{6}2m$) (mirror perpendicular to x)	$xzx = xxz = zxx = yyz = yzy = zyy, zzz$ $xxx = -xyy = -yxy = -yyx, yyy = -yxx =$ $-xyx = -xxy$ 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)	$xxx = -xyy = -yyx = -yxy, xzx = xxz = zxx$ $= yyz = yzy = zyy, yyy = -yxx = -xxy =$ $-xyx, zzz$ $xxx = -xyy = -yyx = -yxy$ $yyy = -yxx = -xxy = -xyx, xzx = xxz = zxx$ $= yyz = yzy = zzy, zzz$
Cubic T (23), T_d ($\bar{4}3m$) O (432)	$xyz = xzy = yzx = yxz = zxy = zyx$ All elements are nil
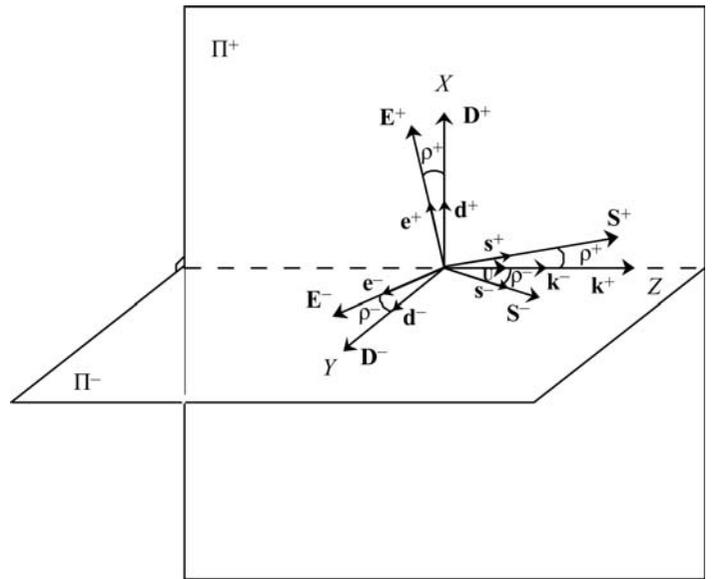
Fig. 1.7.3.1. Field vectors of a plane wave propagating in an anisotropic medium. (X, Y, Z) is the wave frame. Z is along the direction of propagation, X and Y are contained in Π^+ and Π^- respectively, by an arbitrary convention.

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

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

$\varepsilon(\omega) = 1 + \chi^{(1)}(\omega)$ 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):

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

(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 $\mathbf{u}$:

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

(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

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

references