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,

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

where the averaging is performed over a cycle and

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

The following expressions can be derived straightforwardly:

$$W_i = \tfrac{1}{2}\omega_i\, Re(iE_{\omega_i}\cdot P_{\omega_i}) = \tfrac{1}{2}\omega_i\, Im(E^*_{\omega_i}\cdot P_{\omega_i}). \quad (1.7.2.39)$$

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 $\chi^{(2)}_{\mu\alpha\beta}(-2\omega;\omega,\omega)$ 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:

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

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

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

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:

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

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)	$xxx, xyy, xzz, xxy, xyx, yxx, yyy, yzz, yxy, yyx, zyz, zzy, zxz, zzx$
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 ($\bar{4}$)	$xyz=yxz, xzy=yzx, xzx=-yzy, xxz=-yyz, zxx=-zyy, zxy=zyx$
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)	$xyz=-xzy=yzx=-yxz=zxy=-zyx$