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tensor $\chi^{(n)}$ with the full $\mathbf{E}^n$ tensor. More details on tensor algebra can be found in Chapter 1.1 and in Schwartz (1981).

A more compact expression for (1.7.2.1) is

$$\mathbf{P} = \mathbf{P}_0 + \mathbf{P}_1(t) + \mathbf{P}_2(t) + \ldots + \mathbf{P}_n(t) + \ldots, \quad (1.7.2.2)$$

where $\mathbf{P}_0$ represents the static polarization and $\mathbf{P}_n$ represents the nth order polarization. The properties of the linear and nonlinear responses will be assumed in the following to comply with time invariance and locality. In other words, time displacement of the applied fields will lead to a corresponding time displacement of the induced polarizations and the polarization effects are assumed to occur at the site of the polarizing field with no remote interactions. In the following, we shall refer to the classical formalism and related notations developed in Butcher (1965) and Butcher & Cotter (1990).

Tensorial expressions will be formulated within the Cartesian formalism and subsequent multiple lower index notation. The alternative irreducible tensor representation, as initially implemented in the domain of nonlinear optics by Jerphagnon *et al.* (1978) and more recently revived by Brasselet & Zyss (1998) in the realm of molecular-engineering studies, is particularly advantageous for connecting the nonlinear hyperpolarizabilities of microscopic (*e.g.* molecular) building blocks of molecular materials to the macroscopic (*e.g.* crystalline) susceptibility level. Such considerations fall beyond the scope of the present chapter, which concentrates mainly on the crystalline level, regardless of the microscopic origin of phenomena.

1.7.2.1.1. *Linear and nonlinear responses*

1.7.2.1.1.1. *Linear response*

Let us first consider the first-order linear response in (1.7.2.1) and (1.7.2.2): the most general possible linear relation between $\mathbf{P}(t)$ and $\mathbf{E}(t)$ is

$$\mathbf{P}^{(1)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau\, T^{(1)}(t, \tau) \cdot \mathbf{E}(\tau), \quad (1.7.2.3)$$

where $T^{(1)}$ is a rank-two tensor, or in Cartesian index notation

$$P^{(1)}_{\mu}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau\, T^{(1)}_{\mu\alpha}(t, \tau) E_{\alpha}(\tau). \quad (1.7.2.4)$$

Applying the time-invariance assumption to (1.7.2.4) leads to

$$\begin{aligned}\mathbf{P}^{(1)}(t+t_0) &= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau\, T^{(1)}(t+t_0, \tau) \cdot \mathbf{E}(\tau)\\ &= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau\, T^{(1)}(t, \tau+t_0) \cdot \mathbf{E}(\tau)\\ &= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau'\, T^{(1)}(t, \tau'-t_0) \cdot \mathbf{E}(\tau'), \quad (1.7.2.5)\end{aligned}$$

hence $T^{(1)}(t+t_0, \tau) = T^{(1)}(t, \tau - t_0)$ or, setting $t = 0$ and $t_0 = t$,

$$T^{(1)}(t, \tau) = T^{(1)}(0, \tau - t) = R^{(1)}(t - \tau), \quad (1.7.2.6)$$

where $R^{(1)}$ is a rank-two tensor referred to as the linear polarization response function, which depends only on the time difference $t - \tau$. Substitution in (1.7.2.5) leads to

$$\begin{aligned}\mathbf{P}^{(1)}(t) &= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau\, R^{(1)}(t-\tau)\mathbf{E}(\tau)\\ &= \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\tau\, R^{(1)}(\tau)\mathbf{E}(t-\tau). \quad (1.7.2.7)\end{aligned}$$

$R^{(1)}$ can be viewed as the tensorial analogue of the linear impulse function in electric circuit theory. The causality principle imposes that $R^{(1)}(\tau)$ should vanish for $\tau < 0$ so that $\mathbf{P}^{(1)}(t)$ at time t will depend only on polarizing field values before t. $R^{(1)}$, $\mathbf{P}^{(1)}$ and $\mathbf{E}$ are real functions of time.

1.7.2.1.1.2. *Quadratic response*

The most general expression for $\mathbf{P}^{(2)}(t)$ which is quadratic in $\mathbf{E}(t)$ is

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}\tau_1\, \mathrm{d}\tau_2\, T^{(2)}(t, \tau_1, \tau_2) \cdot \mathbf{E}(\tau_1) \otimes \mathbf{E}(\tau_2) \quad (1.7.2.8)$$

or in Cartesian notation

$$P^{(2)}_{\mu}(t) = \varepsilon_o \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}\tau_1\, \mathrm{d}\tau_2\, T^{(2)}_{\mu\alpha\beta}(t, \tau_1, \tau_2) E_{\alpha}(\tau_1) E_{\beta}(\tau_2). \quad (1.7.2.9)$$

It can easily be proved by decomposition of $T^{(2)}$ into symmetric and antisymmetric parts and permutation of dummy variables (α, τ_1) and (β, τ_2), that $T^{(2)}$ can be reduced to its symmetric part, satisfying

$$T^{(2)}_{\mu\alpha\beta}(t, \tau_1, \tau_2) = T^{(2)}_{\mu\alpha\beta}(t, \tau_2, \tau_1). \quad (1.7.2.10)$$

From time invariance

$$T^{(2)}(t, \tau_1, \tau_2) = R^{(2)}(t - \tau_1, t - \tau_2), \quad (1.7.2.11)$$

$$\begin{aligned}\mathbf{P}^{(2)}(t) &= \varepsilon_o \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}\tau_1\, \mathrm{d}\tau_2\, R^{(2)}(t-\tau_1, t-\tau_2) \cdot \mathbf{E}(\tau_1) \otimes \mathbf{E}(\tau_2),\\ \mathbf{P}^{(2)}(t) &= \varepsilon_o \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}\tau_1\, \mathrm{d}\tau_2\, R^{(2)}(\tau_1, \tau_2) \cdot \mathbf{E}(t-\tau_1) \otimes \mathbf{E}(t-\tau_2). \quad (1.7.2.12)\end{aligned}$$

Causality demands that $R^{(2)}(\tau_1, \tau_2)$ cancels for either τ_1 or τ_2 negative while $R^{(2)}$ is real. Intrinsic permutation symmetry implies that $R_{\mu\alpha\beta}{}^{(2)}(\tau_1, \tau_2)$ is invariant by interchange of (α, τ_1) and (β, τ_2) pairs.

1.7.2.1.1.3. *Higher-order response*

The nth order polarization can be expressed in terms of the $(n+1)$-rank tensor $T^{(n)}(t, \tau_1, \tau_2, \ldots, \tau_n)$ as

$$\begin{aligned}\mathbf{P}^{(n)}(t) = \varepsilon_o &\int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \int_{-\infty}^{+\infty} \mathrm{d}\tau_2 \ldots \int_{-\infty}^{+\infty} \mathrm{d}\tau_n\, T^{(n)}(t, \tau_1, \tau_2, \ldots, \tau_n)\\ &\cdot \mathbf{E}(\tau_1) \otimes \mathbf{E}(\tau_2) \otimes \ldots \otimes \mathbf{E}(\tau_n). \quad (1.7.2.13)\end{aligned}$$

For similar reasons to those previously stated, it is sufficient to consider the symmetric part of $T^{(n)}$ with respect to the $n!$ permutations of the n pairs $(\alpha_1, \tau_1), (\alpha_2, \tau_2) \ldots (\alpha_n, \tau_n)$. The $T^{(n)}$ tensor will then exhibit intrinsic permutation symmetry at the nth order. Time-invariance considerations will then allow the introduction of the $(n+1)$th-rank real tensor $R^{(n)}$, which generalizes the previously introduced R operators:

$$\begin{aligned}\mathbf{P}^{(n)}_{\mu}(t) = \varepsilon_o &\int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \int_{-\infty}^{+\infty} \mathrm{d}\tau_2 \ldots \int_{-\infty}^{+\infty} \mathrm{d}\tau_n\, R^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(\tau_1, \tau_2, \ldots \tau_n)\\ &\times E_{\alpha_1}(t-\tau_1) E_{\alpha_2}(t-\tau_2) \ldots E_{\alpha_n}(t-\tau_n). \quad (1.7.2.14)\end{aligned}$$

$R^{(n)}$ cancels when one of the τ_i's is negative and is invariant under any of the $n!$ permutations of the (α_i, τ_i) pairs.

1.7.2.1.2. *Linear and nonlinear susceptibilities*

Whereas the polarization response has been expressed so far in the time domain, in which causality and time invariance are most naturally expressed, Fourier transformation into the frequency domain permits further simplification of the equations given above and the introduction of the susceptibility tensors according to the following derivation.

The direct and inverse Fourier transforms of the field are defined as

$$\mathbf{E}(t) = \int_{-\infty}^{+\infty} \mathrm{d}\omega\ \mathbf{E}(\omega)\exp(-i\omega t) \qquad (1.7.2.15)$$

$$\mathbf{E}(\omega) = (1/2\pi)\int_{-\infty}^{+\infty} \mathrm{d}t\ \mathbf{E}(t)\exp(i\omega t), \qquad (1.7.2.16)$$

where $\mathbf{E}(\omega)^* = \mathbf{E}(-\omega)$ as $\mathbf{E}(t)$ is real.

1.7.2.1.2.1. *Linear susceptibility*

By substitution of (1.7.2.15) in (1.7.2.7),

$$\mathbf{P}^{(1)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\omega \int_{-\infty}^{+\infty} \mathrm{d}\tau\ R^{(1)}(\tau)\cdot\mathbf{E}(\omega)\exp[-i\omega(t-\tau)]$$

$$\mathbf{P}^{(1)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\omega\ \chi^{(1)}(-\omega_\sigma;\omega)\mathbf{E}(\omega)\exp(-i\omega_\sigma t), \qquad (1.7.2.17)$$

where

$$\chi^{(1)}(-\omega_\sigma;\omega) = \int_{-\infty}^{+\infty} \mathrm{d}\tau\ R^{(1)}(\tau)\exp(i\omega\tau).$$

In these equations, $\omega_\sigma = \omega$ to satisfy the energy conservation condition that will be generalized in the following. In order to ensure convergence of $\chi^{(1)}$, ω has to be taken in the upper half plane of the complex plane. The reality of $R^{(1)}$ implies that $\chi^{(1)}(-\omega_\sigma;\omega)^* = \chi^{(1)}(\omega_\sigma^*;-\omega^*)$.

1.7.2.1.2.2. *Second-order susceptibility*

Substitution of (1.7.2.15) in (1.7.2.12) yields

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\omega_1 \int_{-\infty}^{+\infty} \mathrm{d}\omega_2 \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \int_{-\infty}^{+\infty} \mathrm{d}\tau_2\ R^{(2)}(\tau_1,\tau_2) \cdot \mathbf{E}(\omega_1)\otimes\mathbf{E}(\omega_2)\exp\{-i[\omega_1(t-\tau_1)+\omega_2(t-\tau_2)]\} \qquad (1.7.2.18)$$

or

$$\mathbf{P}^{(2)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\omega_1 \int_{-\infty}^{+\infty} \mathrm{d}\omega_2\ \chi^{(2)}(-\omega_\sigma;\omega_1,\omega_2)\cdot\mathbf{E}(\omega_1)\otimes\mathbf{E}(\omega_2) \times \exp(-i\omega_\sigma t) \qquad (1.7.2.19)$$

with

$$\chi^{(2)}(-\omega_\sigma;\omega_1,\omega_2) = \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \int_{-\infty}^{+\infty} \mathrm{d}\tau_2\ R^{(2)}(\tau_1,\tau_2) \times \exp[i(\omega_1\tau_1+\omega_2\tau_2)]$$

and $\omega_\sigma = \omega_1 + \omega_2$. Frequencies ω_1 and ω_2 must be in the upper half of the complex plane to ensure convergence. Reality of $R^{(2)}$ implies $\chi^{(2)}(-\omega_\sigma;\omega_1,\omega_2)^* = \chi^{(2)}(\omega_\sigma^*;-\omega_1^*,-\omega_2^*)$. $\chi^{(2)}_{\mu\alpha\beta}(-\omega_\sigma;\omega_1,\omega_2)$ is invariant under the interchange of the (α,ω_1) and (β,ω_2) pairs.

1.7.2.1.2.3. *nth-order susceptibility*

Substitution of (1.7.2.15) in (1.7.2.14) provides

$$\mathbf{P}^{(n)}(t) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\omega_1 \int_{-\infty}^{+\infty} \mathrm{d}\omega_2 \ldots \int_{-\infty}^{+\infty} \mathrm{d}\omega_n\ \chi^{(n)}(-\omega_\sigma;\omega_1,\omega_2,\ldots\omega_n) \cdot \mathbf{E}(\omega_1)\otimes\mathbf{E}(\omega_2)\otimes\ldots\otimes\mathbf{E}(\omega_n)\exp(-i\omega_\sigma t) \qquad (1.7.2.20)$$

where

$$\chi^{(n)}(-\omega_\sigma;\omega_1,\omega_2,\ldots,\omega_n) = \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \int_{-\infty}^{+\infty} \mathrm{d}\tau_2 \ldots \int_{-\infty}^{+\infty} \mathrm{d}\tau_n\ R^{(n)}(\tau_1,\tau_2,\ldots,\tau_n)\exp\Big(i\sum_{j=1}^{n}\omega_j\tau_j\Big) \qquad (1.7.2.21)$$

and $\omega_\sigma = \omega_1 + \omega_2 + \ldots + \omega_n$.

All frequencies must lie in the upper half complex plane and reality of $\chi^{(n)}$ imposes

$$\chi^{(n)}(-\omega_\sigma;\omega_1,\omega_2,\ldots,\omega_n)^* = \chi^{(n)}(\omega_\sigma^*;-\omega_1^*,-\omega_2^*,\ldots,-\omega_n^*). \qquad (1.7.2.22)$$

Intrinsic permutation symmetry implies that $\chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-\omega_\sigma;\omega_1,\omega_2,\ldots,\omega_n)$ is invariant with respect to the $n!$ permutations of the (α_i,ω_i) pairs.

1.7.2.1.3. *Superposition of monochromatic waves*

Optical fields are often superpositions of monochromatic waves which, due to spectral discretization, will introduce considerable simplifications in previous expressions such as (1.7.2.20) relating the induced polarization to a continuous spectral distribution of polarizing field amplitudes.

The Fourier transform of the induced polarization is given by

$$\mathbf{P}^{(n)}(\omega) = (1/2\pi)\int_{-\infty}^{+\infty} \mathrm{d}t\ \mathbf{P}^{(n)}(t)\exp(i\omega t). \qquad (1.7.2.23)$$

Replacing $\mathbf{P}^{(n)}(t)$ by its expression as from (1.7.2.20) and applying the well known identity

$$(1/2\pi)\int_{-\infty}^{+\infty} \mathrm{d}t\ \exp[i(\omega-\omega_\sigma)t] = \delta(\omega-\omega_\sigma) \qquad (1.7.2.24)$$

leads to

$$\mathbf{P}^{(n)}(\omega) = \varepsilon_o \int_{-\infty}^{+\infty} \mathrm{d}\omega_1 \int_{-\infty}^{+\infty} \mathrm{d}\omega_2 \ldots \int_{-\infty}^{+\infty} \mathrm{d}\omega_n\ \chi^{(n)}(-\omega_\sigma;\omega_1,\omega_2,\ldots\omega_n) \times \mathbf{E}(\omega_1)\mathbf{E}(\omega_2)\ldots\mathbf{E}(\omega_n)\delta(\omega-\omega_\sigma). \qquad (1.7.2.25)$$

In practical cases where the applied field is a superposition of monochromatic waves

$$\mathbf{E}(t) = (1/2)\sum_{\omega'}[E_{\omega'}\exp(-i\omega' t) + E_{-\omega'}\exp(i\omega' t)] \qquad (1.7.2.26)$$

with $E_{-\omega'} = E^*_{\omega'}$. By Fourier transformation of (1.7.2.26)

$$\mathbf{E}(\omega) = (1/2)\sum_{\omega'}[E_{\omega'}\delta(\omega-\omega') + E_{-\omega'}\delta(\omega+\omega')]. \qquad (1.7.2.27)$$

The optical intensity for a wave at frequency ω' is related to the squared field amplitude by

$$I_{\omega'} = \varepsilon_o c n(\omega')\langle\mathbf{E}^2(t)\rangle_t = \tfrac{1}{2}\varepsilon_o c n(\omega')|E_{\omega'}|^2. \qquad (1.7.2.28)$$

The averaging as represented above by brackets is performed over a time cycle and $n(\omega')$ is the index of refraction at frequency ω'.

1.7.2.1.4. *Conventions for nonlinear susceptibilities*

1.7.2.1.4.1. *Classical convention*

Insertion of (1.7.2.26) in (1.7.2.25) together with permutation symmetry provides

$$P^{(n)}_\mu(\omega_\sigma) = \varepsilon_o \sum_{\alpha_1\alpha_2\ldots\alpha_n}\sum_{\omega} K(-\omega_\sigma;\omega_1,\omega_2,\ldots,\omega_n) \times \chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-\omega_\sigma;\omega_1,\omega_2,\ldots,\omega_n) \times E_{\alpha_1}(\omega_1)E_{\alpha_2}(\omega_2)\ldots E_{\alpha_n}(\omega_n), \qquad (1.7.2.29)$$

references