FREQUENCY- AND SPATIALLY VARIABLE ELECTRIC AND MAGNETIC POLARIZATIONS INDUCED IN NONLINEAR MEDIA BY ELECTROMAGNETIC FIELDS

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Vectors of the electric and magnetic polarization of the medium containing multipolar and nonlinear contributions of arbitrary order are introduced into Maxwell's equations and the wave equations resulting from them. The operators of multipolar electric and magnetic polarization are discussed in consecutive approximations of the first, second, third and higher orders in a phenomenological and, further on, quantum-mechanical approach. In particular, quantum-mechanical expressions are derived for the tensors of electric and magnetic multipole susceptibility of the first, second, third and quite generally arbitrary order, valid in the entire frequency range including the region of resonance. The formalism proposed is applied to the quantitative description of various frequency- and spatially variable nonlinear optical processes of arbitrary order as *e.g.* optical mixing of frequencies between several laser beams and higher harmonics generation, usual and *DC* field induced optical activity as well as other electro- and magneto-optical effects of higher orders.

1. Introduction and formal theory

It is well-known that in the case when the electric field strength $\boldsymbol{E}$ is small the dipole electric polarization vector of a medium $\boldsymbol{P}_e$ arising from the external field is a linear function of $\boldsymbol{E}$ (the spontaneous polarization of a medium in the absence of an applied field is not considered here)

$$\boldsymbol{P}_e = \boldsymbol{\chi}_e \cdot \boldsymbol{E}, \tag{1.1}$$

where $\boldsymbol{\chi}_e$ is the usual electric susceptibility tensor of the medium.

If, however, the applied electric field is of very great strength, the linear relation of (1.1) will no longer be adequate, since the polarization vector $\boldsymbol{P}_e$ is now a generally nonlinear function of the field $\boldsymbol{E}$ and has to be replaced by the following nonlinear expansion:

$$\boldsymbol{P}_e = \sum_{r=1}^{\infty} \frac{1}{r!} \overset{(r)}{\boldsymbol{\chi}_e}[r]\boldsymbol{E}^r = \sum_{r=1}^{\infty} \overset{(r)}{\boldsymbol{P}_e}, \tag{1.2}$$

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in which

$$\overset{(r)}{\boldsymbol{P}}_e = \frac{1}{r!}\overset{(r)}{\chi}_e[r]\boldsymbol{E}^r \tag{1.3}$$

and $\overset{(r)}{\chi}_e$ are the r-th order electric dipole polarization and susceptibility tensor, respectively; the symbol $[r]$ stands for r contractions of the tensor $\overset{(r)}{\chi}_e$ and polyad $\boldsymbol{E}^r$ of r factors.

An entirely different picture results if an oscillating (with frequency ω) electrical field is applied to the medium,

$$\boldsymbol{E}(t) = \boldsymbol{E}_0 \cos \omega t. \tag{1.4}$$

In this case, the electric susceptibility tensor of order r becomes a function of the frequency ω, in general of r-harmonic frequencies $r\omega$, and the r-th order electric polarization vector (1.3) has now to be separated into even- and odd-order parts given as

$$\overset{(2r)}{\boldsymbol{P}}_e(\omega) = \frac{1}{2^{2r}(2r)!}\left\{\binom{2r}{r}\overset{(2r)}{\chi}_e(0)[2r]\boldsymbol{E}_0^{2r} + \right.$$

$$\left. + 2\sum_{s=0}^{r-1}\binom{2r}{s}\overset{(2r)}{\chi}_e(2r\omega-2s\omega)[2r]\boldsymbol{E}_0^{2r}\cos 2(r-s)\omega t\right\}, \tag{1.5}$$

$$\overset{(2r-1)}{\boldsymbol{P}}_e(\omega) = \frac{1}{2^{2r-2}(2r-1)!}\sum_{s=0}^{r-1}\binom{2r-1}{s}\overset{(2r-1)}{\chi}_e(2r\omega-2s\omega-\omega)[2r-1]\boldsymbol{E}_0^{2r-1}\cos(2r-2s-1)\omega t. \tag{1.6}$$

We see from (1.5) that the even-order polarization vector contains the zero-frequency contribution corresponding to a *DC* polarization effect within the medium and the frequency-dependent polarization responsible for the radiation of even $2(r-s)$-harmonics from the medium. The odd-order polarization vector of (1.6) consists only of frequency-dependent contributions corresponding to generation of odd $2(r-s)-1$ -harmonics.

In particular we obtain from (1.5) and (1.6) for the first, second-, third- and fourth-order electric polarization vectors

$$\overset{(1)}{\boldsymbol{P}}_e(\omega) = \overset{(1)}{\chi}_e(\omega)\cdot\boldsymbol{E}_0\cos\omega t,$$

$$\overset{(2)}{\boldsymbol{P}}_e(\omega) = \frac{1}{4}\{\overset{(2)}{\chi}_e(0):\boldsymbol{E}_0^2 + \overset{(2)}{\chi}_e(2\omega):\boldsymbol{E}_0^2\cos 2\omega t\},$$

$$\overset{(3)}{\boldsymbol{P}}_e(\omega) = \frac{1}{24}\{3\overset{(3)}{\chi}_e(\omega)\vdots\boldsymbol{E}_0^3\cos\omega t + \overset{(3)}{\chi}_e(3\omega)\vdots\boldsymbol{E}_0^3\cos 3\omega t\},$$

$$\overset{(4)}{\boldsymbol{P}}_e(\omega) = \frac{1}{192}\{3\overset{(4)}{\chi}_e(0)::\boldsymbol{E}_0^4 + 4\overset{(4)}{\chi}(2\omega)::\boldsymbol{E}_0^4\cos 2\omega t + \overset{(4)}{\chi}_e(4\omega)::\boldsymbol{E}_0^4\cos 4\omega t\},\ldots \tag{1.7}$$

The above expressions show that the second-order polarization which is the sum of the *DC* quadratic polarization and of the polarization at frequency 2ω represents a second-harmonic generation, whereas the third-order polarization represents a fundamental frequency contribution and third-harmonic generation. When using laser beams in experiments the second harmonic generation has been observed in many materials *e.g.* in quartz and triglycine sulfate [1], potassium dihydrogen phosphate [2, 3, 6] and other piezoelectric and ferroelectric crystals lacking inversion symmetry [4—7]. Third-harmonic generation has also been observed in centrosymmetric materials [8].

In the case when additionally a *DC* electric field is applied to the medium, the third-order electric polarization is of the form

$$\overset{(3)}{\boldsymbol{P}}_e(\omega) = \frac{1}{4}\{\overset{(3)}{\chi}_e(0):\boldsymbol{E}_0^2+\overset{(3)}{\chi}_e(2\omega):\boldsymbol{E}_0^2\cos 2\omega t\}\cdot\boldsymbol{E}_{DC}, \tag{1.8}$$

where the first term represents the zero-frequency cubic polarization, whereas the second term represents the *DC* electric field induced second-harmonic generation [8, 9].

The theory of optical harmonics generation has been discussed by many authors from different points of view [10—20].

By (1.5) and (1.6) we obtain for the time-averaged polarization vectors

$$\overline{\overset{(2r)}{\boldsymbol{P}}_e(\omega)}^t = \frac{1}{2^{2r}(r!)^2}\overset{(2r)}{\chi}_e(0)[2r]\boldsymbol{E}_0^{2r} = \frac{1}{(2r)!}\overset{(2r)}{\chi}_e(0)[2r]\overline{\boldsymbol{E}_0^{2r}}^t,\quad \overline{\overset{(2r-1)}{\boldsymbol{P}}_e(\omega)}^t = 0, \tag{1.9}$$

since we have

$$\overline{\boldsymbol{E}^p}^t = \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}\boldsymbol{E}^p(t)dt = \begin{cases}\dfrac{(2r)!}{2^{2r}(r!)^2}\boldsymbol{E}_0^{2r}, & \text{for } p=2r,\\ 0, & \text{for } p=2r-1,\end{cases}$$

and $\overline{\cos p\omega t}^t = 0$.

If, in general, the medium under consideration is acted on simultaneously by an external electric $\boldsymbol{E}$ and magnetic $\boldsymbol{H}$ field, the dipole electric polarization vector of order r can be expanded as follows:

$$\overset{(r)}{\boldsymbol{P}}_e = \frac{1}{r!}\sum_{s=0}^{r}\binom{r}{s}\overset{(r-s,\,s)}{\chi}_{em}[r]\boldsymbol{E}^{r-s}\boldsymbol{H}^s, \tag{1.10}$$

where the r-th-order susceptibility tensor $\overset{(r-s,s)}{\chi}_{em}$ has the order $r-s$ in electric and s in magnetic properties.

For the case of oscillating electric and magnetic fields we have by (1.4) instead of (1.10) the following expressions:

$$\overset{(2r)}{\boldsymbol{P}}_e(\omega) = \frac{1}{2^{2r}(2r)!}\sum_{s=0}^{2r}\binom{2r}{s}\left\{\binom{2r}{s}\overset{(2r-s,\,s)}{\chi}_{em}(0)[2r]\boldsymbol{E}_0^{2r-s}\boldsymbol{H}_0^s+\right.$$

$$+2\sum_{u=0}^{r-1}\binom{2r}{u}\overset{(2r-s,\,s)}{\chi_{em}}(2r\omega-2u\omega)\,[2r]\,\boldsymbol{E}_0^{2r-s}\boldsymbol{H}_0^s\cos 2(r-u)\,\omega t\Big\}, \tag{1.11}$$

$$\overset{(2r-1)}{\boldsymbol{P}_e}(\omega)=\frac{1}{2^{2r-2}(2r-1)!}\sum_{s=0}^{2r-1}\binom{2r-1}{s}\sum_{u=0}^{r-1}\binom{2r-1}{s}\times$$

$$\times\overset{(2r-s-1,\,s)}{\chi_{em}}(2r\omega-2u\omega-\omega)\,[2r-1]\,\boldsymbol{E}_0^{2r-s-1}\boldsymbol{H}_0^s\cos(2r-2u-1)\omega t, \tag{1.12}$$

which yield for the first-, second-, and third-order electric polarization vectors

$$\overset{(1)}{\boldsymbol{P}_e}(\omega)=\overset{(1,0)}{\chi_{ee}}(\omega)\cdot\boldsymbol{E}_0\cos\omega t+\overset{(0,1)}{\chi_{em}}(\omega)\cdot\boldsymbol{H}_0\cos\omega t,$$

$$\overset{(2)}{\boldsymbol{P}_e}(\omega)=\frac{1}{4}\{\overset{(2,0)}{\chi_{ee}}(0):\boldsymbol{E}_0^2+2\overset{(1,1)}{\chi_{em}}(0):\boldsymbol{E}_0\boldsymbol{H}_0+\overset{(0,2)}{\chi_{em}}(0):\boldsymbol{H}_0^2+\overset{(2,0)}{\chi_{ee}}(2\omega):\boldsymbol{E}_0^2\cos 2\omega t+$$

$$+2\overset{(1,1)}{\chi_{em}}(2\omega):\boldsymbol{E}_0\boldsymbol{H}_0\cos 2\omega t+\overset{(0,2)}{\chi_{em}}(2\omega):\boldsymbol{H}_0^2\cos 2\omega t\},$$

$$\overset{(3)}{\boldsymbol{P}_e}(\omega)=\frac{1}{8}\{\overset{(3,0)}{\chi_{ee}}(\omega)\vdots\boldsymbol{E}_0^3\cos\omega t+3\overset{(2,1)}{\chi_{em}}(\omega)\vdots\boldsymbol{E}_0^2\boldsymbol{H}_0\cos\omega t+3\overset{(1,2)}{\chi_{em}}(\omega)\vdots\boldsymbol{E}_0\boldsymbol{H}_0^2\cos\omega t+$$

$$+\overset{(0,3)}{\chi_{em}}(\omega)\vdots\boldsymbol{H}_0^3\cos\omega t\}+\frac{1}{24}\{\overset{(3,0)}{\chi_{ee}}(3\omega)\vdots\boldsymbol{E}_0^3\cos 3\omega t+3\overset{(2,1)}{\chi_{em}}(3\,\omega)\vdots\boldsymbol{E}_0^2\boldsymbol{H}_0\cos 3\omega t+$$

$$+3\overset{(1,2)}{\chi_{em}}(3\,\omega)\vdots\boldsymbol{E}_0\boldsymbol{H}_0^2\cos 3\omega t+\overset{(0,3)}{\chi_{em}}(3\omega)\vdots\boldsymbol{H}_0^3\cos 3\omega t\},\ldots \tag{1.13}$$

Analogous expressions can be written for the magnetic dipole polarization vector $\boldsymbol{P}_m$ of the first, second, *etc.* orders.

We shall now consider in brief the case when the electric field is not only time-variable but is also spatially variable; namely we have at position $\boldsymbol{r}$ and time t

$$\boldsymbol{E}(\boldsymbol{r},t)=\boldsymbol{E}_0\cos(\omega t-\boldsymbol{k}\cdot\boldsymbol{r}), \tag{1.14}$$

where $\boldsymbol{k}$ is the wave vector.

By (1.14), the first-order electric polarization vector is of the following form in the presence of spatial dispersion:

$$\overset{(1)}{\boldsymbol{P}_e}(\omega,\boldsymbol{k})=\sum_{s=0}^{\infty}(-1)^s\Big\{\frac{1}{(2s)!}\overset{(1)}{\chi_e^{(2s)}}(\omega)[2s-1]\boldsymbol{k}^{2s}\boldsymbol{E}_0\cos\omega t+$$

$$+\frac{1}{(2s-1)!}\overset{(1)}{\chi_e^{(2s-1)}}(\omega)[2s-2]\boldsymbol{k}^{2s-1}\boldsymbol{E}_0\sin\omega t\Big\}, \tag{1.15}$$

where we have denoted by $\overset{(1)}{\chi_e^{(2s)}}(\omega)=\overset{(1)}{\chi_e}(\omega)\boldsymbol{r}^{2s}$ the susceptibility tensor of rank $2s+2$.

From the above expression we obtain for the case of weak spatial dispersion

$$\overset{(1)}{\boldsymbol{P}}_e(\omega, \boldsymbol{k}) = \left\{\overset{(1)}{\chi}{}_e^{(0)}(\omega) - \frac{1}{2}\overset{(1)}{\chi}{}_e^{(2)}(\omega):\boldsymbol{k}^2 + \frac{1}{24}\overset{(1)}{\chi}{}_e^{(4)}(\omega)::\boldsymbol{k}^4 - \ldots\right\}\cdot \boldsymbol{E}_0 \cos\omega t +$$

$$+ \left\{\overset{(1)}{\chi}{}_e^{(1)}(\omega)\cdot\boldsymbol{k} - \frac{1}{6}\overset{(1)}{\chi}{}_e^{(3)}(\omega)\vdots\boldsymbol{k}^3 + \ldots\right\}\cdot \boldsymbol{E}_0 \sin\omega t. \qquad (1.16)$$

The phenomenological expansions (1.15) and (1.16) determine the linear (or first--order) optics with frequency- and spatial dispersion.

Similarly, the second-order electric polarization vector can be given by the expansion

$$\overset{(2)}{\boldsymbol{P}}_e(\omega, \boldsymbol{k}) = \overset{(2)}{\boldsymbol{P}}_e(\omega) + \frac{1}{2}\overset{(2)}{\chi}{}_e^{(1)}(2\omega)\vdots\boldsymbol{k}\boldsymbol{E}_0^2 \sin 2\omega t +$$

$$+ \frac{1}{2}\sum_{s=1}^{\infty}(-1)^s\left\{\frac{2^{2s-1}}{(2s)!}\overset{(2)}{\chi}{}_e^{(2s)}(2\omega)[2s+2]\boldsymbol{k}^{2s}\boldsymbol{E}_0^2\cos 2\omega t +\right.$$

$$\left. + \frac{2^{2s}}{(2s+1)!}\overset{(2)}{\chi}{}_e^{(2s+1)}(2\omega)\,[2s+3]\boldsymbol{k}^{2s+1}\boldsymbol{E}_0^2 \sin 2\omega t\right\}, \qquad (1.17)$$

in which one has a part independent of $\boldsymbol{k}$ and a series in powers of $\boldsymbol{k}$.

In a good approximation we obtain from (1.17)

$$\overset{(2)}{\boldsymbol{P}}_e(\omega, \boldsymbol{k}) = \overset{(2)}{\boldsymbol{P}}_e(\omega) + \frac{1}{2}\overset{(2)}{\chi}{}_e^{(1)}(2\omega)\vdots\boldsymbol{k}\boldsymbol{E}_0^2 \sin 2\omega t -$$

$$- \frac{1}{2}\overset{(2)}{\chi}{}_e^{(2)}(2\omega)::\boldsymbol{k}^2\boldsymbol{E}_0^2\cos 2\omega t - \ldots \qquad (1.18)$$

with $\overset{(2)}{\boldsymbol{P}}_e(\omega)$ defined in the expressions of (1.7).

In (1.18) the first part of the second-order polarization independent of the wave vector $\boldsymbol{k}$ vanishes if the material has inversion symmetry, but the second term proportional to $\boldsymbol{k}\boldsymbol{E}_0^2 \sin 2\omega t$ is not zero and yields the second-harmonic generation in a crystal with inversion symmetry [8, 16]. There exist in the literature several papers in which nonlinear interaction of time- and spatially variable electromagnetic fields with matter is discussed [19—22]. Also the frequency-dependence of the various nonlinear processes has been discussed both on a classical and quantum-mechanical level [4, 11—18, 20—23].

In this paper we develop nonlinear optics in which the electromagnetic fields are not only time-variable but are also spatially variable. To do this we shall start from the Lorentz microscopic field equations [24] and by a suitable averaging procedure [25, 26] derive the Maxwell macroscopic field equations for nonlinear media. These equations contain in general electric and magnetic multipole polarization operators $\boldsymbol{P}_e^{(n)}$ and $\boldsymbol{P}_m^{(n)}$ of all orders [27—29]. In our approach of the present theory the first-order multipole electric and magnetic polarizations yield with the electromagnetic field equations the basis of the linear optics, whereas the second-, third- and r-th-order multipole polarizations yield the nonlinear optics, or optics of higher orders. The 2^n-pole polarizations $\boldsymbol{P}_e^{(n)}$ and $\boldsymbol{P}_m^{(n)}$ are in general nonlinear functions of the electromagnetic field strengths and can be expressed in terms of multipole susceptibility tensors of appropriate orders in two steps: first macroscopically with phenomenological susceptibility tensors, then microscopically using a quantal perturbation method yielding the quantum-mechanical expressions for the multipole susceptibility tensors. This consistent and general tensor formalism can be used for the quantitative determination of various nonlinear optical phenomena involving interaction effects not only dipolar but also quadrupolar, octopolar *etc.* between micro-systems and electromagnetic fields.

2. *General foundations of the nonlinear optics*

Born and Infeld [30] evolved a nonlinear, relativistically invariant electrodynamics which in a linear approximation goes over into Maxwell's electrodynamics for vacuum or an isotropic medium. In the case of an arbitrary continuous medium Maxwell's macroscopic electromagnetic field equations

$$\nabla\times\boldsymbol{E} = -\frac{1}{c}\frac{\partial\boldsymbol{B}}{\partial t}, \qquad \nabla\cdot\boldsymbol{B} = 0, \tag{2.1}$$

$$\nabla\times\boldsymbol{H} = \frac{1}{c}\frac{\partial\boldsymbol{D}}{\partial t} + \frac{4\pi}{c}\boldsymbol{J}, \qquad \nabla\cdot\boldsymbol{D} = 4\pi\varrho_e, \tag{2.2}$$

can be derived from the well-known Lorentz microscopic field equations [24] by applying a suitable statistical averaging procedure [25, 26]. Generally, in this case, the electric and magnetic displacement vectors at position $\boldsymbol{r}$ and time t can be obtained in the form of the following multipole expansions [29]:

$$\boldsymbol{D}(\boldsymbol{r}, t) = \boldsymbol{E}(\boldsymbol{r}, t) - 4\pi\sum_{n=1}^{\infty}(-1)^n\frac{2^n n!}{(2n)!}\nabla^{n-1}[n-1]\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t), \tag{2.3}$$

$$\boldsymbol{H}(\boldsymbol{r}, t) = \boldsymbol{B}(\boldsymbol{r}, t) + 4\pi\sum_{n=1}^{\infty}(-1)^n\frac{2^n n!}{(2n)!}\nabla^{n-1}[n-1]\boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t). \tag{2.4}$$

These equations contain the electric $\boldsymbol{P}_e^{(n)}$ and magnetic $\boldsymbol{P}_m^{(n)}$ multipole polarization operators (or moment densities) of arbitrary order given by the expressions [29]

$$\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t) = \langle\sum_{p=1}^{N}\boldsymbol{M}_{ep}^{(n)}\delta(\boldsymbol{r}_p - \boldsymbol{r})\rangle, \tag{2.5}$$

$$\boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t) = \langle\sum_{p=1}^{N}\boldsymbol{M}_{mp}^{(n)}\delta(\boldsymbol{r}_p - \boldsymbol{r})\rangle, \tag{2.6}$$

in which

$$\boldsymbol{M}_{ep}^{(n)} = \sum_{i=1}^{\nu_p} e_{pi} r_{pi}^n \boldsymbol{Y}_{pi}^{(n)}, \tag{2.7}$$

$$\boldsymbol{M}_{mp}^{(n)} = \frac{n}{(n+1)c}\sum_{i=1}^{\nu_p} e_{pi} r_{pi}^n \boldsymbol{Y}_{pi}^{(n)} \times \dot{\boldsymbol{r}}_{pi}, \tag{2.8}$$

define respectively the 2^n-pole electric and magnetic moment operators of a p-th microsystem consisting of ν_p point particles (nuclei and electrons) of electric charges e_{pi} and positional vectors $\boldsymbol{r}_{pi}$ with origin in the centre of mass whose position is $\boldsymbol{r}_p$; $\boldsymbol{Y}^{(n)}$ is an operator of order n having the properties of spherical harmonics [22].

Similarly to (2.5) and (2.6) we can also write the multipole expansion for the total electromagnetic force density $\boldsymbol{F}$ [31] which, in the general case considered here, is of the form (if a suitable gauge transformation is used) at the space-time point $(\boldsymbol{r}, t)$

$$\boldsymbol{F}(\boldsymbol{r}, t) = \boldsymbol{F}_L + \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \{\boldsymbol{P}_e^{(n)}[n]\boldsymbol{E}^{(n+1)} + \boldsymbol{P}_m^{(n)}[n]\boldsymbol{H}^{(n+1)}\}, \tag{2.9}$$

where

$$\boldsymbol{F}_L = \varrho_e \boldsymbol{E} + \frac{1}{c} \boldsymbol{J}\times\boldsymbol{H} \tag{2.10}$$

is the well-known Lorentz external electromagnetic force density acting on the system, with

$$\varrho_e(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \sum_{i=1}^{\nu_p} e_{pi} \delta(\boldsymbol{r}_p - \boldsymbol{r}) \rangle, \tag{2.11}$$

$$\boldsymbol{J}(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \sum_{i=1}^{\nu_p} e_{pi} \dot{\boldsymbol{r}}_p \delta(\boldsymbol{r}_p - \boldsymbol{r}) \rangle, \tag{2.12}$$

denoting the average (true) electric charge and current densities at position $\boldsymbol{r}$ and time t.

The general Equation (2.9) beyond the uniform Lorentz force density (2.10) contains additionally all contributions arising from the interaction between the electric 2^n-pole moment density $\boldsymbol{P}_e^{(n)}$ and an electric field strength (in Coulomb gauge)

$$\boldsymbol{E}^{(n+1)} = -\frac{1}{c} \nabla^n \frac{\partial \boldsymbol{A}}{\partial t} \tag{2.13}$$

of order $n+1$, and from interaction between the magnetic 2^n-pole moment density $\boldsymbol{P}_m^{(n)}$ and magnetic field strength (traditionally we now denote the magnetic field strength by $\boldsymbol{H}$)

$$\boldsymbol{H}^{(n+1)} = \nabla^{n+1} \times \boldsymbol{A} \tag{2.14}$$

of order $n+1$; $\boldsymbol{A}$ is the vector potential of the external electromagnetic field.

By using the well-known equations

$$\boldsymbol{D}(\boldsymbol{r}, t) = \boldsymbol{\epsilon} \cdot \boldsymbol{E}(\boldsymbol{r}, t), \qquad \boldsymbol{B}(\boldsymbol{r}, t) = \boldsymbol{\mu} \cdot \boldsymbol{H}(\boldsymbol{r}, t), \tag{2.15}$$

we obtain by (2.3) and (2.4) the following general equations for the electric and magnetic permittivity tensors:

$$(\boldsymbol{\epsilon} - \boldsymbol{U}) \cdot \boldsymbol{E}(\boldsymbol{r}, t) = 4\pi \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t), \tag{2.16}$$

$$(\boldsymbol{\mu} - \boldsymbol{U}) \cdot \boldsymbol{H}(\boldsymbol{r}, t) = 4\pi \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t), \tag{2.17}$$

in which $\boldsymbol{U}$ is the second-rank unit tensor.

In the well-known way we obtain from Eqs (2.1)—(2.4) the following electromagnetic wave equations:

$$\Box \boldsymbol{E}(\boldsymbol{r}, t)+4\pi \boxdot \cdot \boldsymbol{P}_e(\boldsymbol{r}, t) = 4\pi\left\{\nabla \varrho_e(\boldsymbol{r}, t)+\frac{1}{c}\frac{\partial \boldsymbol{J}(\boldsymbol{r}, t)}{\partial t}+\frac{1}{c}\nabla\times\frac{\partial \boldsymbol{P}_m(\boldsymbol{r}, t)}{\partial t}\right\}, \quad (2.18)$$

$$\Box \boldsymbol{H}(\boldsymbol{r}, t)+4\pi \boxdot \cdot \boldsymbol{P}_m(\boldsymbol{r}, t) = -\frac{4\pi}{c}\nabla\times\left\{\boldsymbol{J}(\boldsymbol{r}, t)+\frac{\partial \boldsymbol{P}_e(\boldsymbol{r}, t)}{\partial t}\right\}, \quad (2.19)$$

where we have introduced the total electric and magnetic polarization vectors

$$\boldsymbol{P}_e(\boldsymbol{r}, t) = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{2^n n!}{(2n)!}\nabla^{n-1}[n-1]\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t), \quad (2.20)$$

$$\boldsymbol{P}_m(\boldsymbol{r}, t) = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{2^n n!}{(2n)!}\nabla^{n-1}[n-1]\boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t), \quad (2.21)$$

which contain all multipole contributions; $\Box = \nabla^2-(1/c^2)\partial^2/\partial t^2$ is the d'Alambert operator and $\boxdot = \nabla\nabla-(1/c^2)\boldsymbol{U}\partial^2/\partial t^2$.

Generally, in the case of a nonlinear medium to be subjected to a strong electromagnetic field the electric and magnetic multipole polarization operators can be expanded as follows:

$$\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t) = \sum_{s=1}^{\infty}\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r}, t), \qquad \boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t) = \sum_{s=1}^{\infty}\overset{(s)}{\boldsymbol{P}}{}_m^{(n)}(\boldsymbol{r}, t), \quad (2.22)$$

whence we have excluded the multipole polarization operators of zeroth order when the external electromagnetic field is absent.

Consider first the special case when only the electric oscillating field is present in a medium. We can formally write the electric multipole polarization operator of order s in the following concise form:

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r}, t) = \frac{1}{s!}\sum_{n_1=1}^{\infty}\cdots\sum_{n_s=1}^{\infty}\frac{2^{n_1+\ldots+n_s}n_1!\ldots n_s!}{(2n_1)!\ldots(2n_s)!}\times$$

$$\times\,{}^{(n)}\chi_e^{(n_1+\ldots+n_s)}[n_1+\ldots+n_s]\boldsymbol{E}^{(n_1)}(\boldsymbol{r}, t)\ldots\boldsymbol{E}^{(n_s)}(\boldsymbol{r}, t), \quad (2.23)$$

where the electric susceptibility tensor ${}^{(n)}\chi_e^{(n_1+\ldots+n_s)}$ describes the s-th-order multipole polarization of the medium caused by the s-th-power electric field strength of degree n.

In the general case of an electromagnetic field we can write for the first, second, third, *etc.* -order multipole electric polarization operators

$$\overset{(1)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r}, t) = \sum_{n_1=1}^{\infty}\frac{2^{n_1}n_1!}{(2n_1)!}\{{}^{(n)}_{\ e}\chi_e^{(n_1)}[n_1]\boldsymbol{E}^{(n_1)}(\boldsymbol{r}, t)+{}^{(n)}_{\ e}\chi_m^{(n_1)}[n_1]\boldsymbol{H}^{(n_1)}(\boldsymbol{r}, t)\},$$

$$\overset{(2)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r}, t) = \frac{1}{2}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{2^{n_1+n_2}n_1!\,n_2!}{(2n_1)!\,(2n_2)!}\{{}^{(n)}_{\ e}\chi_{ee}^{(n_1+n_2)}[n_1+n_2]\boldsymbol{E}^{(n_1)}(\boldsymbol{r}, t)\boldsymbol{E}^{(n_2)}(\boldsymbol{r}, t)+$$

$$+{}^{(n)}_{e}\chi^{(n_1+n_2)}_{em}[n_1+n_2]\,\boldsymbol{E}^{(n_1)}(\boldsymbol{r},t)\boldsymbol{H}^{(n_2)}(\boldsymbol{r},t)+{}^{(n)}_{e}\chi^{(n_1+n_2)}_{me}[n_1+n_2]\boldsymbol{H}^{(n_1)}(\boldsymbol{r},t)\,\boldsymbol{E}^{(n_2)}(\boldsymbol{r},t)+$$

$$+{}^{(n)}_{e}\chi^{(n_1+n_2)}_{mm}[n_1+n_2]\,\boldsymbol{H}^{(n_1)}(\boldsymbol{r},t)\boldsymbol{H}^{(n_2)}(\boldsymbol{r},t)\},$$

$$\overset{(3)}{\boldsymbol{P}}{}^{(n)}_{e}(\boldsymbol{r},t)=\frac{1}{6}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\frac{2^{n_1+n_2+n_3}n_1!\,n_2!\,n_3!}{(2n_1)!\,(2n_2)!\,(2n_3)!}\times$$

$$\times\{{}^{(n)}_{e}\chi^{(n_1+n_2+n_3)}_{eee}[n_1+n_2+n_3]\,\boldsymbol{E}^{(n_1)}(\boldsymbol{r},t)\,\boldsymbol{E}^{(n_2)}(\boldsymbol{r},t)\boldsymbol{E}^{(n_3)}(\boldsymbol{r},t)+$$

$$+{}^{(n)}_{e}\chi^{(n_1+n_2+n_3)}_{eem}[n_1+n_2+n_3]\,\boldsymbol{E}^{(n_1)}(\boldsymbol{r},t)\,\boldsymbol{E}^{(n_2)}(\boldsymbol{r},t)\,\boldsymbol{H}^{(n_3)}(\boldsymbol{r},t)+\ldots\}. \tag{2.24}$$

We have the here Fourier transform

$$\boldsymbol{E}(\boldsymbol{r},t)=\int\int\boldsymbol{E}(\omega,\boldsymbol{k})e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}d\omega d\boldsymbol{k}, \tag{2.25}$$

and similar Equations for $\boldsymbol{H}(\boldsymbol{r},t)$, $\boldsymbol{P}_e(\boldsymbol{r},t)$ *etc.* in which ω is the angular frequency and $\boldsymbol{k}$ is the wave vector.

The Maxwell Equations of (2.1) and (2.2) with the electric and magnetic strength vectors (2.3) and (2.4), as well as the wave Equations (2.18) and (2.19) with the electric and magnetic polarization vectors (2.20) and (2.21), together with the expansions (2.23) or (2.24) jointly determine the general fundamentals of nonlinear optics with time- and spatially variable electromagnetic fields.

In preceding papers [29, 32] the general Equations (2.16) and (2.17) for the electric and magnetic permittivity tensors were discussed for the case of *DC* electric or magnetic fields applied to a medium. In the present paper these equations will be discussed for the general case of time- and spatially variable electric and magnetic fields as *e.g.* conveyed by a light wave from a laser.

3. *Linear optics with spatial dispersion*

In the first approximation we have the case of linear optics (or first-order optics) for which the electric multipole polarization operator is

$${}_{e}\overset{(1)}{\boldsymbol{P}}{}^{(n)}_{e}(\boldsymbol{r},t)=\frac{1}{2}\{{}_{e}\overset{(1)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega,\boldsymbol{k})+{}_{e}\overset{(1)}{\boldsymbol{P}}{}^{(n)}_{e}(-\omega,-\boldsymbol{k})\}, \tag{3.1}$$

where, by the general expansion of (2.19), we have

$${}_{e}\overset{(1)}{\boldsymbol{P}}{}_{e}^{(n)}(\omega,\boldsymbol{k})=\sum_{n_1=1}^{\infty}\frac{2^{n_1}n_1!}{(2n_1)!}\,{}^{(n)}_{e}\chi^{(n_1)}_{e}(\omega)\,[n_1]\,\boldsymbol{E}^{(n_1)}(\omega,\boldsymbol{k}), \tag{3.2}$$

with ${}^{(n)}_{e}\chi^{(n_1)}_{e}(\omega)$ denoting the electric multipole susceptibility tensor of first order at the fundamental frequency ω.

Since

$$\boldsymbol{E}(\boldsymbol{r},t)=-\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A}(\boldsymbol{r},t)=\frac{1}{2}\{\boldsymbol{E}(\omega,\boldsymbol{k})+\boldsymbol{E}^*(-\omega,-\boldsymbol{k})\}$$

$$\boldsymbol{E}(\omega,\boldsymbol{k})=\boldsymbol{E}_0e^{i(\omega t-\boldsymbol{k}\cdot\boldsymbol{r})}, \tag{3.3}$$

we have by (2.13)

$$\boldsymbol{E}^{(n_1)} = (-i\boldsymbol{k})^{n_1-1}\boldsymbol{E}(\omega, \boldsymbol{k}) \tag{3.4}$$

and the expansion (3.2) can be rewritten as

$$ {}_e^{(1)}\boldsymbol{P}_e^{(n)}(\omega, \boldsymbol{k}) = \sum_{n_1=1}^{\infty} (-i)^{n_1-1} \frac{2^{n_1} n_1!}{(2n_1)!} \, {}_e^{(n)}\chi_e^{(n_1)}(\omega)[n_1]\boldsymbol{k}^{n_1-1}\boldsymbol{E}(\omega, \boldsymbol{k}). \tag{3.5}$$

With respect to the expansion (3.4) we obtain from (2.16) for the tensor of electric permittivity

$$\boldsymbol{\epsilon}(\omega, \boldsymbol{k}) - \boldsymbol{U} = 4\pi \sum_{n=1}^{\infty}\sum_{n_1=1}^{\infty} i^n(-i)^{n_1} \frac{2^{n+n_1} n!\, n_1!}{(2n)!(2n_1)!} \boldsymbol{k}^{n-1}[n-1]\, {}_e^{(n)}\chi_e^{(n_1)}(\omega)[n_1-1]\boldsymbol{k}^{n_1-1}, \tag{3.6}$$

or, with the accuracy up to the term with $\boldsymbol{k}^2$,

$$\boldsymbol{\epsilon}(\omega, \boldsymbol{k}) - \boldsymbol{U} = 4\pi \Big\{ {}_e^{(1)}\chi_e^{(1)}(\omega) - \frac{i}{3}[{}_e^{(1)}\chi_e^{(2)}(\omega)\cdot \boldsymbol{k} - \boldsymbol{k}\cdot {}_e^{(2)}\chi_e^{(1)}(\omega)] -$$

$$- \frac{1}{45}[3\, {}_e^{(1)}\chi_e^{(3)}(\omega) : \boldsymbol{k}\boldsymbol{k} - 5\boldsymbol{k}\cdot {}_e^{(2)}\chi_e^{(2)}(\omega)\cdot \boldsymbol{k} + 3\boldsymbol{k}\boldsymbol{k} : {}_e^{(3)}\chi_e^{(1)}(\omega)] + \ldots \Big\} \tag{3.7}$$

Mechanisms of various optical phenomena can be explained within the framework of the atomic-molecular theory of the structure of the medium. Obviously, the microscopic picture of a material system can only be described fully by quantum theory and the optical processes by the method of quantum electrodynamics. However, when the number of photons in the radiation field is large, we can use the method of semiclassical theory [33] in which the photon fields are described by electromagnetic waves and a micro-system (atoms, molecules or their ions) is treated quantum-mechanically. This semiclassical method will be adhered to in the present paper.

Using the Hamiltonian $H = H^{(0)} + H^{(1)}$, in which $H^{(0)}$ is the nonperturbated part of H and [22]

$$H^{(1)} = -\sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \{\boldsymbol{M}_e^{(n)}[n]\boldsymbol{E}^{(n)} + \boldsymbol{M}_m^{(n)}[n]\boldsymbol{H}^{(n)}\} \tag{3.8}$$

is the first-order perturbation Hamiltonian resulting from interaction between a micro--system and the electromagnetic field, we obtain with the help of first-order quantal perturbation method (the magnetic part is omitted)

$$ {}_e^{(n)}\chi_e^{(n_1)}(\omega) = \frac{\varrho}{\hbar}\sum_{klr} \varrho_{kl} \left\{ \frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle\langle r|\boldsymbol{M}_e^{(n_1)}|1\rangle}{\omega_{rl}+\omega+i\Gamma_{rl}} + \frac{\langle k|\boldsymbol{M}_e^{(n_1)}|r\rangle\langle r|\boldsymbol{M}_e^{(n)}|1\rangle}{\omega_{rk}-\omega+i\Gamma_{rk}} \right\}. \tag{3.9}$$

where ϱ is the number density of the medium, and ϱ_{kl} the statistical matrix for the transition $k\to l$ with Bohr frequency ω_{kl} and relaxation time Γ_{kl}^{-1}.

In the general case the first-order perturbation (3.8) contains both an electric and magnetic part and we obtain the additional contribution to the electric multipole polarization of first order

$$ {}_e\overset{(1)}{P}{}^{(n)}_m(\omega, \boldsymbol{k}) = \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} \, {}^{(n)}_{e}\chi^{(n_1)}_{m}(\omega)[n_1]\boldsymbol{H}^{(n_1)}(\omega, \boldsymbol{k}), \tag{3.10} $$

determining the effect of induction in the medium of the electric polarization due to the magnetic vector of the electromagnetic wave.

In the quantum-mechanical description the mixed electro-magnetic multipole susceptibility pseudo-tensor is of the form

$$ {}^{(n)}_{e}\chi^{(n_1)}_{e}(\omega) = \frac{\varrho}{\hbar} \sum_{klr} \varrho_{kl} \left\{ \frac{\langle k|\boldsymbol{M}^{(n)}_e|r\rangle\langle r|\boldsymbol{M}^{(n_1)}_m|1\rangle}{\omega_{rl}+\omega+i\Gamma_{rl}} + \frac{\langle k|\boldsymbol{M}^{(n_1)}_m|r\rangle\langle r|\boldsymbol{M}^{(n)}_e|1\rangle}{\omega_{rk}-\omega+i\Gamma_{rk}} \right\}. \tag{3.11} $$

By (3.2) and (3.10) the total electric multipole polarization of first order is

$$ {}_e\overset{(1)}{P}{}^{(n)}_T(\omega, \boldsymbol{k}) = \sum_{n_1=1}^{\infty} (-1)^{n_1-1} \frac{2^{n_1} n_1!}{(2n_1)!} \{ {}^{(n)}_{e}\chi^{(n_1)}_{e}(\omega)[n_1]\boldsymbol{k}^{n_1-1}\boldsymbol{E}(\omega, \boldsymbol{k}) + $$

$$ + {}^{(n)}_{e}\chi^{(n_1)}_{m}(\omega)[n_1]\boldsymbol{k}^{n_1-1}\boldsymbol{H}(\omega, \boldsymbol{k})\}, \tag{3.12} $$

or, in the case of small spatial dispersion,

$$ {}_e\overset{(1)}{P}{}^{(n)}_T(\omega, \boldsymbol{k}) = \left\{ {}^{(n)}_{e}\chi^{(1)}_{e}(\omega) - \frac{i}{3} \, {}^{(n)}_{e}\chi^{(2)}_{e}(\omega) \cdot \boldsymbol{k} - \frac{1}{15} \, {}^{(n)}_{e}\chi^{(3)}_{e}(\omega) : \boldsymbol{kk} + \ldots \right\} \cdot \boldsymbol{E}(\omega, \boldsymbol{k}) + $$

$$ + \left\{ {}^{(n)}_{e}\chi^{(1)}_{m}(\omega) - \frac{i}{3} \, {}^{(n)}_{e}\chi^{(2)}_{m}(\omega) \cdot \boldsymbol{k} - \frac{1}{15} \, {}^{(n)}_{e}\chi^{(3)}_{m}(\omega) : \boldsymbol{kk} + \ldots \right\} \cdot \boldsymbol{H}(\omega, \boldsymbol{k}). \tag{3.13} $$

In the dipole approximation ($n = 1$) the terms independent of $\boldsymbol{k}$ determine the linear dipole optical polarization (refraction). The terms linear in $\boldsymbol{k}$ describe the linear and dipolar optical activity appearing in crystals without inversion symmetry, whereas the terms quadratic in $\boldsymbol{k}$ — that in material systems with inversion symmetry. In contradistinction to dipolar-quadrupolar optical activity, the linear quadrupolar polarization ($n = 2$) involves terms

$$ -\frac{i}{3} \{ {}^{(2)}_{e}\chi^{(2)}_{e}(\omega) \cdot \boldsymbol{E}(\omega, \boldsymbol{k}) + {}^{(2)}_{e}\chi^{(2)}_{m}(\omega, \boldsymbol{k}) \cdot \boldsymbol{H}(\omega, \boldsymbol{k})\} \cdot \boldsymbol{k} $$

linear in $\boldsymbol{k}$ accounting for the linear quadrupolar-quadrupolar optical activity which can in general exist in all material systems, irrespective of their symmetry.

Similarly, for magnetic multipole polarization of first order, one obtains by (2.24) and (3.8)

$$ {}_m\overset{(1)}{P}{}^{(n)}_T(\omega, \boldsymbol{k}) = \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} \{ {}^{(n)}_{m}\chi^{(n_1)}_{m}(\omega)[n_1]\boldsymbol{H}^{(n_1)}(\omega, \boldsymbol{k}) + {}^{(n)}_{m}\chi^{(n_1)}_{e}(\omega)[n_1]\boldsymbol{E}^{(n_1)}(\omega, \boldsymbol{k})\}, \tag{3.14} $$

where the first part is the magnetic polarization induced in the medium by the magnetic field, whereas the second is that induced by the electric field conveyed by an electromagnetic wave. The quantum-mechanical expression of the pure magnetic multipole susceptibility tensor ${}^{(n)}_{m}\chi^{(n_1)}_{m}$ is given by (3.9) if the electric multipole moments are replaced by magnetic multipole moments and the mixed magneto-electric multipole susceptibility pseudo-tensor ${}^{(n)}_{m}\chi^{(n_1)}_{e}$ has the form of (3.11) by replacing therein $\boldsymbol{M}^{(n)}_{e}$ by $\boldsymbol{M}^{(n)}_{m}$ and $\boldsymbol{M}^{(n_1)}_{e}$ by $\boldsymbol{M}^{(n_1)}_{m}$.

By (2.13), (2.14) and (3.3) we can rewrite the expansion of (3.14) as

$$ {}_{m}\overset{(1)}{\boldsymbol{P}}{}^{(n)}_{T}(\omega,\boldsymbol{k}) = \sum_{n_1=1}^{\infty} (-i)^{n_1-1} \frac{2^{n_1} n_1!}{(2n_1)!} \{ {}^{(n)}_{m}\chi^{(n_1)}_{m}(\omega)[n_1]\boldsymbol{k}^{n_1-1}\boldsymbol{H}(\omega,\boldsymbol{k}) + $$
$$ + {}^{(n)}_{m}\chi^{(n_1)}_{e}(\omega)[n_1]\boldsymbol{k}^{n_1-1}\boldsymbol{E}(\omega,\boldsymbol{k})\}. \qquad (3.15) $$

4. *Second-order optical processes*

If, in general, the radiation field consists of several monochromatic components *i.e.*

$$ \boldsymbol{F}(\boldsymbol{r},t) = \frac{1}{2}\sum_{a} \{\boldsymbol{F}_a e^{i(\omega_a t - \boldsymbol{k}_a\cdot\boldsymbol{r})} + \boldsymbol{F}^*_a e^{-i(\omega_a t-\boldsymbol{k}_a\cdot\boldsymbol{r})}\} $$

$$ = \frac{1}{2}\sum_{a} \{\boldsymbol{F}(\omega_a,\boldsymbol{k}_a) + \boldsymbol{F}^*(-\omega_a,-\boldsymbol{k}_a)\}, \qquad (4.1) $$

the second-order multipole electric polarization can be written as

$$ \overset{(2)}{\boldsymbol{P}}{}^{(n)}_{e}(\boldsymbol{r},t) = \frac{1}{4}\sum_{ab}\{\overset{(2)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega_a,\omega_b,\boldsymbol{k}_a,\boldsymbol{k}_b) + \ldots + \overset{(2)}{\boldsymbol{P}}{}^{(n)}_{e}(-\omega_a,-\omega_b,-\boldsymbol{k}_a,-\boldsymbol{k}_b)\}. \qquad (4.2) $$

where for the pure electric part we have by (2.23)

$$ \overset{(2)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega_a,\omega_b,\boldsymbol{k}_a,\boldsymbol{k}_b) = \frac{1}{2}\sum_{n_a=1}^{\infty}\sum_{n_b=1}^{\infty} \frac{2^{n_a+n_b} n_a! n_b!}{(2n_a)!(2n_b)!} \times $$
$$ \times {}^{(n)}_{e}\chi^{(n_a+n_b)}_{e}(\omega_a,\omega_b)[n_a+n_b]\boldsymbol{E}^{(n_a)}(\omega_a,\boldsymbol{k}_a)\boldsymbol{E}^{(n_b)}(\omega_b,\boldsymbol{k}_b). \qquad (4.3) $$

With regard to (3.3), the expression (4.3) can be put in the form

$$ \overset{(2)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega_a,\omega_b,\boldsymbol{k}_a,\boldsymbol{k}_b) = \frac{1}{2}\sum_{n_a=1}^{\infty}\sum_{n_b=1}^{\infty} (-i)^{n_a+n_b-2} \frac{2^{n_a+n_b} n_a! n_b!}{(2n_a)!(2n_b)!} \times $$
$$ \times {}^{(n)}_{e}\chi^{(n_a+n_b)}_{e}(\omega_a,\omega_b)[n_a+n_b]\boldsymbol{k}^{n_a-1}_a\boldsymbol{k}^{n_b-1}_b\boldsymbol{E}(\omega_a,\boldsymbol{k}_a)\boldsymbol{E}(\omega_b,\boldsymbol{k}_b), \qquad (4.4) $$

which, in the case of small spatial dispersion, yields in a good approximation

$$ \overset{(2)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega_a,\omega_b,\boldsymbol{k}_a,\boldsymbol{k}_b) = \frac{1}{2}\Big\{ {}^{(n)}_{e}\chi^{(1+1)}_{e}(\omega_a,\omega_b) - \frac{i}{3}[{}^{(n)}_{e}\chi^{(1+2)}_{e}(\omega_a,\omega_b)\cdot\boldsymbol{k}_b + {}^{(n)}_{e}\chi^{(2+1)}_{e}(\omega_a,\omega_b)\cdot\boldsymbol{k}_a] - $$
$$ \frac{1}{9}\, {}^{(n)}_{e}\chi^{(2+2)}_{e}(\omega_a,\omega_b):\boldsymbol{k}_a\boldsymbol{k}_b + \ldots\Big\} : \boldsymbol{E}(\omega_a,\boldsymbol{k}_a)\boldsymbol{E}(\omega_b,\boldsymbol{k}_b). \qquad (4.5) $$

In the dipole approximation ($n = 1$) the expansion (4.5) yields

$$\overset{(2)}{\boldsymbol{P}}{}_e^{(1)}(\omega_a, \omega_b, \boldsymbol{k}_a, \boldsymbol{k}_b) = \frac{1}{2}\Big\{ {}^{(1)}_{e}\chi_e^{(1+1)}(\omega_a, \omega_b) - \frac{i}{3}\,[{}^{(1)}_{e}\chi_e^{(1+2)}(\omega_a, \omega_b)\cdot \boldsymbol{k}_b + {}^{(1)}_{e}\chi_e^{(2+1)}(\omega_a, \omega_b)\cdot \boldsymbol{k}_a] - \frac{1}{9}\,{}^{(1)}_{e}\chi_e^{(2+2)}(\omega_a, \omega_b): \boldsymbol{k}_a\boldsymbol{k}_b + \ldots\Big\} : \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\boldsymbol{E}(\omega_b, \boldsymbol{k}_b). \quad (4.6)$$

The first term in the foregoing expansion (the electric dipole-dipole contribution) determines sum-frequency generation in crystals lacking inversion symmetry, whereas the second term linear in $\boldsymbol{k}$ (electric dipole-quadrupole contributions) that in material media having a centre of symmetry. The subsequent terms characterize the higher-order processes related with spatial variations of the electric fields.

If in (4.6) ω_b is replaced by $-\omega_b$ we have the case of difference-frequency generation.

The second-order polarization of (4.5) becomes in the quadrupole approximation ($n = 2$)

$$\overset{(2)}{\boldsymbol{P}}{}_e^{(2)}(\omega_a, \omega_b, \boldsymbol{k}_a, \boldsymbol{k}_b) = \frac{1}{2}\Big\{ {}^{(2)}_{e}\chi_e^{(1+1)}(\omega_a, \omega_b) - \frac{i}{3}\,[{}^{(2)}_{e}\chi_e^{(1+2)}(\omega_a, \omega_b)\cdot \boldsymbol{k}_b + {}^{(2)}_{e}\chi_e^{(2+1)}(\omega_a, \omega_b)\cdot \boldsymbol{k}_a] - \ldots\Big\} : \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\,\boldsymbol{E}(\omega_b, \boldsymbol{k}_b), \quad (4.7)$$

where the first term is responsible for second-harmonic radiation from material systems irrespective of their symmetry.

If a DC electric field is applied to the medium we obtain for the second-order multipole polarization

$$\overset{(2)}{\boldsymbol{P}}{}_e^{(n)}(\omega_a, 0_b, \boldsymbol{k}_a, 0_b) = {}^{(n)}_{e}\chi_e^{(1+1)}(\omega_a, 0_b): \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\boldsymbol{E}(0_b, 0_b) + \frac{1}{3}\,{}^{(n)}_{e}\chi_e^{(1+2)}(\omega_a, 0_b) \vdots \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\nabla\boldsymbol{E}(0_b, 0_b) - \frac{i}{3}\,{}^{(n)}_{e}\chi_e^{(2+1)}(\omega_a, 0_b) \vdots \boldsymbol{k}_a\boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\boldsymbol{E}(0_b, 0_b) + \ldots \quad (4.8)$$

Here, the first term describes the linear electro-optic effect without spatial dispersion, the second term — the optical anisotropy induced in a medium by a DC electric field gradient, whereas the third term — the optical activity induced in a medium by a DC homogeneous electric field.

The quantum-mechanical expression of the second-order multipole electric susceptibility is given by

$${}^{(n)}_{e}\chi_e^{(na+nb)}(\omega_a, \omega_b) = \frac{\varrho}{\hbar^2}\, S(n_a, n_b) \sum_{klrs} \varrho_{kl} \Bigg\{ \frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle\langle r|\boldsymbol{M}_e^{(na)}|s\rangle\langle s|\boldsymbol{M}_e^{(nb)}|l\rangle}{(\omega_{rl}+\omega_a+\omega_b+i\Gamma_{rl})(\omega_{sl}+\omega_b+i\Gamma_{sl})} + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle\langle r|\boldsymbol{M}_e^{(n)}|s\rangle\langle s|\boldsymbol{M}_e^{(nb)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sl}+\omega_b+i\Gamma_{sl})} + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle\langle r|\boldsymbol{M}_e^{(nb)}|s\rangle\langle s|\boldsymbol{M}_e^{(n)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})} \Bigg\}, \quad (4.9)$$

where $S(n_a, n_b, \ldots)$ is a symmetrizing operator consisting in summation over all permutations of $n_a\omega_a$, $n_b\omega_b$, ...

On replacing in the above expressions the electric fields $\boldsymbol{E}^{(n_a)}(\omega_a, \boldsymbol{k}_a), \ldots$ by magnetic fields $\boldsymbol{H}^{(n_a)}(\omega_a, \boldsymbol{k}_a), \ldots$ and the electric multipole moment operators $\boldsymbol{M}_e^{(n)}, \ldots$, by the magnetic multipole moments $\boldsymbol{M}_m^{(n)}, \ldots$, we obtain automatically expressions for the second-order magnetic multipole polarization $\boldsymbol{P}_m^{(n)}$ and multipole susceptibility ${}^{(n)}_{m}\chi_m^{(n_a+n_b)}$). Since the electric and magnetic vectors are associated with the radiation field simultaneously, one has to take into consideration in Equation (3.8) both the electric and magnetic parts of the first-order perturbation Hamiltonian as well as the additional second-order perturbation Hamiltonian given as [22]

$$\overset{(2)}{H} = -\frac{1}{2}\sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}\frac{2^{n+n'}n!\,n'!}{(2n)!\,(2n')!}\boldsymbol{H}^{(n)}(\boldsymbol{r}, t)[n]^{(n)}\boldsymbol{A}_m^{(n')}[n']\boldsymbol{H}^{(n')}(\boldsymbol{r}, t), \tag{4.10}$$

where the tensor of rank $n+n'$

$$^{(n)}\boldsymbol{A}_m^{(n')} = \frac{nn'}{(n+1)\,(n'+1)c^2}\sum_{i=1}^{\nu}\frac{e_i^2}{m_i}r_i^{n+n'}(\boldsymbol{Y}_i^{(n)}\boldsymbol{Y}_i^{(n')} - \boldsymbol{Y}_i^{(n)}\cdot\boldsymbol{Y}_i^{(n')}\boldsymbol{U}) \tag{4.11}$$

determines the multipole (dia) magnetic polarizability operator of a micro-system.

In this general case, as a result, in addition to pure electric and magnetic multipole polarizations $\boldsymbol{P}_e^{(n)}$ and $\boldsymbol{P}_m^{(n)}$, one obtains respectively the additional mixed multipole polarizations $\boldsymbol{P}_{em}^{(n)}$ and $\boldsymbol{P}_{me}^{(n)}$. The electro-magnetic part of the second-order multipole polarization $\boldsymbol{P}_{em}^{(n)}$ consists of three terms given as follows:

$$_e\overset{(2)}{\boldsymbol{P}}{}_{em}^{(n)}(\omega_a, \omega_b, \boldsymbol{k}_a, \boldsymbol{k}_b) = {}_e\overset{(2)}{\boldsymbol{P}}{}_{me}^{(n)}(\omega_a, \omega_b, \boldsymbol{k}_a, \boldsymbol{k}_b)$$

$$= \frac{1}{2}\sum_{n_a=1}^{\infty}\sum_{n_b=1}^{\infty}\frac{2^{n_a+n_b}n_a!\,n_b!}{(2n_a)!\,(2n_b)!}\,{}^{(n)}_{e}\chi_{em}^{(n_a+n_b)}(\omega_a, \omega_b)\,[n_a+n_b]\boldsymbol{E}^{(n_a)}(\omega_a, \boldsymbol{k}_a)\boldsymbol{H}^{(n_b)}(\omega_b, \boldsymbol{k}_b) \tag{4.12}$$

$$_e\overset{(2)}{\boldsymbol{P}}{}_{mm}^{(n)}(\omega_a, \omega_b, \boldsymbol{k}_a, \boldsymbol{k}_b) = \frac{1}{2}\sum_{n_a=1}^{\infty}\sum_{n_b=1}^{\infty}\frac{2^{n_a+n_b}n_a!\,n_b!}{(2n_a)!\,(2n_b)!}\times$$

$$\times\,{}^{(n)}_{e}\chi_{mm}^{(n_a+n_b)}(\omega_a, \omega_b)[n_a+n_b]\boldsymbol{H}^{(n_a)}(\omega_a, \boldsymbol{k}_a)\boldsymbol{H}^{(n_b)}(\omega_b, \boldsymbol{k}_b), \tag{4.13}$$

where the multipole susceptibility pseudo-tensor ${}^{(n)}_{e}\chi_{em}^{(n_a+n_b)}$ is given by (4.9) if the electric multipole moment $\boldsymbol{M}_e^{(n_b)}$ is replaced by the magnetic multipole moment $\boldsymbol{M}_m^{(n_b)}$, whereas

$$\begin{aligned}{}^{(n)}_{e}\chi_{mm}^{(n_a+n_b)} &= \frac{\varrho}{\hbar}\sum_{klr}\varrho_{kl}\left\{\frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle\langle r|^{(n_a)}\boldsymbol{A}_m^{(n_b)}|l\rangle}{(\omega_{rl}+\omega_a+\omega_b+i\Gamma_{rl})} + \frac{\langle k|^{(n_a)}\boldsymbol{A}_m^{(n_b)}|r\rangle\langle r|\boldsymbol{M}_e^{(n)}|l\rangle}{(\omega_{rk}-\omega_a-\omega_b+i\Gamma_{rk})}\right\} + \\ &+ \frac{\varrho}{\hbar^2}S(n_a, n_b)\sum_{klrs}\varrho_{kl}\left\{\frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle\langle r|\boldsymbol{M}_m^{(n_a)}|s\rangle\langle s|\boldsymbol{M}_m^{(n_b)}|l\rangle}{(\omega_{rl}+\omega_a+\omega_b+i\Gamma_{rl})(\omega_{sl}+\omega_b+i\Gamma_{sl})} + \right. \\ &+ \left.\frac{\langle k|\boldsymbol{M}_m^{(n_a)}|r\rangle\langle r|\boldsymbol{M}_e^{(n)}|s\rangle\langle s|\boldsymbol{M}_m^{(n_b)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sl}+\omega_b+i\Gamma_{sl})} + \frac{\langle k|\boldsymbol{M}_m^{(n_a)}|r\rangle\langle r|\boldsymbol{M}_m^{(n_b)}|s\rangle\langle s|\boldsymbol{M}_e^{(n)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})\,(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})}\right\}.\end{aligned} \tag{4.14}$$

Here the first diamagnetic part (term in $\hbar^{-1}$) results from first-order perturbation theory with the second-order perturbation Hamiltonian of (4.10), whereas the second (paramagnetic) part (term in $\hbar^{-2}$) results from second-order perturbation theory when only the first-order perturbation Hamiltonian of (3.8) is used.

By replacing in (4.14) the electric multipole moment $\boldsymbol{M}_e^{(n)}$ by the magnetic multipole moment $\boldsymbol{M}_m^{(n)}$ we obtain immediately the explicite quantal form of the pure second-order magnetic multipole susceptibility ${}^{(n)}_{m}\chi^{(n_a)}_{m}(\omega_a, \omega_b)$.

For the special case of small spatial dispersion we have from (4.12)

$$\overset{(2)}{{}_e\boldsymbol{P}}{}^{(n)}_{em}(\omega_a, \omega_b, \boldsymbol{k}_a, \boldsymbol{k}_b) = \frac{1}{2}\Big\{{}^{(n)}_{e}\chi^{(1+1)}_{em}(\omega_a, \omega_b) -$$

$$-\frac{i}{3}[{}^{(n)}_{e}\chi^{(1+2)}_{em}(\omega_a, \omega_b)\cdot\boldsymbol{k}_b + {}^{(n)}_{e}\chi^{(2+1)}_{em}(\omega_a, \omega_b)\cdot\boldsymbol{k}_a] + \dots\Big\} : \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\boldsymbol{H}(\omega_b, \boldsymbol{k}_b). \quad (4.15)$$

In the presence of a *DC* homogeneous magnetic field the second-order multipole polarization is of the form

$$\overset{(2)}{{}_e\boldsymbol{P}}{}^{(n)}_{em}(\omega_a, 0_b, \boldsymbol{k}_a, 0_b) = \frac{1}{2}\,{}^{(n)}_{e}\chi^{(1+1)}_{em}(\omega_a, 0_b) : \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\boldsymbol{H}(0_b, 0_b) +$$

$$+\frac{1}{3}\,{}^{(n)}_{e}\chi^{(1+2)}_{em}(\omega_a, 0_b) \vdots \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\nabla\boldsymbol{H}(0_b, 0_b) -$$

$$-\frac{i}{3}\,{}^{(n)}_{e}\chi^{(2+1)}_{em}(\omega_a, 0_b) \vdots \boldsymbol{k}_a\boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\boldsymbol{H}(0_b, 0_b) + \dots, \quad (4.16)$$

where the first term represents the well-known Faraday effect, the second term — the *DC* magnetic field gradient induced optical anisotropy, and the third term — the optical activity induced in the medium by a *DC* homogeneous magnetic field.

Similarly, we could discuss the magnetic multipole polarization of the second-order as well as the various processes resulting from it.

5. *Third-order optical processes*

By (2.23) and (4.1) third-order multipole electric polarization is given by

$$\overset{(3)}{\boldsymbol{P}}_e(\boldsymbol{r}, t) = \frac{1}{8}\sum_{abc}\{\overset{(3)}{\boldsymbol{P}}{}^{(n)}_e(\omega_a, \omega_b, \omega_c, \boldsymbol{k}_a, \boldsymbol{k}_b, \boldsymbol{k}_c) + \dots$$

$$+\overset{(3)}{\boldsymbol{P}}{}^{(n)}_e(-\omega_a, -\omega_b, -\omega_c, -\boldsymbol{k}_a, -\boldsymbol{k}_b - \boldsymbol{k}_c)\} \quad (5.1)$$

with

$$\overset{(3)}{\boldsymbol{P}}{}^{(n)}_e(\omega_a, \omega_b, \omega_c, \boldsymbol{k}_a, \boldsymbol{k}_b, \boldsymbol{k}_c) = \frac{1}{6}\sum_{n_a=1}^{\infty}\sum_{n_b=1}^{\infty}\sum_{n_c=1}^{\infty}\frac{2^{n_a+n_b+n_c}n_a!\,n_b!\,n_c!}{(2n_a)!\,(2n_b)!\,(2n_c)!}\times$$

$$\times\,{}^{(n)}_{e}\chi^{(n_a+n_b+n_c)}_{e}(\omega_a, \omega_b, \omega_c)[n_a + n_b + n_c]\boldsymbol{E}^{(n_a)}(\omega_a, \boldsymbol{k}_a]\boldsymbol{E}^{(n_b)}(\omega_b, \boldsymbol{k}_b)\boldsymbol{E}^{(n_c)}(\omega_c, \boldsymbol{k}_c). \quad (5.2)$$

In third-order quantal perturbation theory we obtain for the third-order electric multipole susceptibility tensor

$$ {}^{(n)}_{e}\chi_{e}^{(na+nb+nc)}(\omega_a, \omega_b, \omega_c) = \frac{\varrho}{\hbar^3} S(a, b, c) \sum_{klrst} \varrho_{kl} \times $$

$$ \times \left\{ \frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle \langle r|\boldsymbol{M}_e^{(na)}|s\rangle \langle s|\boldsymbol{M}_e^{(nb)}|t\rangle \langle t|\boldsymbol{M}_e^{(nc)}|l\rangle}{(\omega_{rl}+\omega_a+\omega_b+\omega_c+i\Gamma_{rl})\,(\omega_{sl}+\omega_b+\omega_c+i\Gamma_{sl})\,(\omega_{tl}+\omega_c+i\Gamma_{tl})} + \right. $$

$$ + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle \langle r|\boldsymbol{M}_e^{(n)}|s\rangle \langle s|\boldsymbol{M}_e^{(nb)}|t\rangle \langle t|\boldsymbol{M}_e^{(nc)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})\,(\omega_{sl}+\omega_b+\omega_c+i\Gamma_{sl})\,(\omega_{tl}+\omega_c+i\Gamma_{tl})} + $$

$$ + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle \langle r|\boldsymbol{M}_e^{(nb)}|s\rangle \langle s|\boldsymbol{M}_e^{(n)}|t\rangle \langle t|\boldsymbol{M}_e^{(nc)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})\,(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})\,(\omega_{tl}+\omega_c+i\Gamma_{tl})} + $$

$$ \left. + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle \langle r|\boldsymbol{M}_e^{(nb)}|s\rangle \langle s|\boldsymbol{M}_e^{(nc)}|t\rangle \langle t|\boldsymbol{M}_e^{(n)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})\,(\omega_{tk}-\omega_a-\omega_b-\omega_c+i\Gamma_{tk})} \right\}. \tag{5.3} $$

We will now proceed to the discussion of the expression of (5.2) for several special cases.

In the first step we consider the special case when a weak and homogeneous *DC* electric field is applied to the medium, *i.e.* when all $\omega_c = 0$, and obtain from (5.2)

$$ \overset{(3)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega_a, \omega_b, 0_c, \boldsymbol{k}_a, \boldsymbol{k}_b, 0_c) = \frac{1}{6} \left\{ {}^{(n)}_{e}\chi_{e}^{(1+1+1)}(\omega_a, \omega_b, 0_c) - \right. $$

$$ - \frac{i}{3} \left[{}^{(n)}_{e}\chi_{e}^{(1+2+1)}(\omega_a, \omega_b, 0_c) \cdot \boldsymbol{k}_b + {}^{(n)}_{e}\chi_{e}^{(2+1+1)}(\omega_a, \omega_b, 0_c) \cdot \boldsymbol{k}_a \right] + $$

$$ \left. + \ldots \right\} \vdots \boldsymbol{E}(\omega_a, \boldsymbol{k}_a) \boldsymbol{E}(\omega_b, \boldsymbol{k}_b) \boldsymbol{E}(0_c). \tag{5.4} $$

Here the first term describes the *DC* electric-field induced multipole sum-frequency generation whereas the further terms account for the spatial variation of this effect.

If the homogeneous *DC* electric field is very strong the expression (5.2) yields (all $\omega_b = \omega_c = 0$)

$$ \overset{(3)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega_a, 0_b, 0_c, \boldsymbol{k}_a, 0_b, 0_c) = \frac{1}{6} \left\{ {}^{(n)}_{e}\chi_{e}^{(1+1+1)}\omega_a, 0_b, 0_c) - \right. $$

$$ \left. - \frac{i}{3}\, {}^{(n)}_{e}\chi_{e}^{(2+1+1)}(\omega_a, 0_b, 0_c) \cdot \boldsymbol{k}_a + \ldots \right\} \vdots \boldsymbol{E}(\omega_a, \boldsymbol{k}_a) \boldsymbol{E}(0_b) \boldsymbol{E}(0_c) \tag{5.5} $$

for the multipole electric double refraction. In the dipole approximation ($n = 1$) the first term of Eq. (5.5) describes the well-known Kerr effect whereas the second term — the optical activity induced by the square of the *DC* electric field.

In the general case when all the electric fields are time- and spatially variable, the expression (5.2) becomes in a good approximation

$$ \overset{(3)}{\boldsymbol{P}}{}^{(n)}_{e}(\omega_a, \omega_b, \omega_c, \boldsymbol{k}_a, \boldsymbol{k}_b, \boldsymbol{k}_c) = \frac{1}{6} \left\{ {}^{(n)}_{e}\chi_{e}^{(1+1+1)}(\omega_a, \omega_b, \omega_c) - \right. $$

$$-\frac{i}{3}\left[{}^{(n)}_{e}\chi_{e}^{(2+1+1)}(\omega_a,\omega_b,\omega_c)\cdot\boldsymbol{k}_a+{}^{(n)}_{e}\chi_{e}^{(1+2+1)}(\omega_a,\omega_b,\omega_c)\cdot\boldsymbol{k}_b+\right.$$

$$\left.+{}^{(n)}_{e}\chi_{e}^{(1+1+2)}(\omega_a,\omega_b,\omega_c)\cdot\boldsymbol{k}_c\right]+\ldots\Big\}\vdots\,\boldsymbol{E}(\omega_a,\boldsymbol{k}_a)\boldsymbol{E}(\omega_b,\boldsymbol{k}_b)\boldsymbol{E}(\omega_c,\boldsymbol{k}_c). \tag{5.6}$$

If we take into account both the electric and magnetic part of the first-order perturbation Hamiltonian of (3.8), we obtain further contributions to the third-order electric multipole polarization, one of which is of the form

$$\overset{(3)}{{}_{e}\boldsymbol{P}}{}^{(n)}_{eem}(\omega_a,\omega_b,\omega_c,\boldsymbol{k}_a,\boldsymbol{k}_b,\boldsymbol{k}_c)=\frac{1}{2}\sum_{n_a=1}^{\infty}\sum_{n_b=1}^{\infty}\sum_{n_c=1}^{\infty}\frac{2^{n_a+n_b+n_c}n_a!\,n_b!\,n_c!}{(2n_a)!\,(2n_b)!\,(2n_c)!}\times$$

$$\times{}^{(n)}_{e}\chi_{eem}^{(n_a+n_b+n_c)}(\omega_a,\omega_b,\omega_c)\,[n_a+n_b+n_c]\,\boldsymbol{E}^{(n_a)}(\omega_a,\boldsymbol{k}_a)\,\boldsymbol{E}^{(n_b)}(\omega_b,\boldsymbol{k}_b)\,\boldsymbol{H}^{(n_c)}(\omega_c,\boldsymbol{k}_c), \tag{5.7}$$

where the third-order multipole susceptibility pseudo-tensor ${}^{(n)}_{e}\chi_{eem}^{(n_a+n_b+n_c)}$ is given by (5.3) if the electric multipole moment $\boldsymbol{M}_e^{(n_c)}$ is replaced by the magnetic multipole moment $\boldsymbol{M}_m^{(n_c)}$.

For weak spatial dispersion Eq. (5.7) yields

$$\overset{(3)}{{}_{e}\boldsymbol{P}}{}^{(n)}_{eem}(\omega_a,\omega_b,\omega_c,\boldsymbol{k}_a,\boldsymbol{k}_b,\boldsymbol{k}_c)=\frac{1}{2}\Big\{{}^{(n)}_{e}\chi_{eem}^{(1+1+1)}(\omega_a,\omega_b,\omega_c)-$$

$$-\frac{i}{3}\left[{}^{(n)}_{e}\chi_{eem}^{(2+1+1)}(\omega_a,\omega_b,\omega_c)\cdot\boldsymbol{k}_a+{}^{(n)}_{e}\chi_{eem}^{(1+2+1)}(\omega_a,\omega_b,\omega_c)\cdot\boldsymbol{k}_b+\right.$$

$$\left.+{}^{(n)}_{e}\chi_{eem}^{(1+1+2)}(\omega_a,\omega_b,\omega_c)\cdot\boldsymbol{k}_c\right]+\ldots\Big\}\vdots\,\boldsymbol{E}(\omega_a,\boldsymbol{k}_a)\,\boldsymbol{E}(\omega_b,\boldsymbol{k}_b)\,\boldsymbol{H}(\omega_c,\boldsymbol{k}_c). \tag{5.8}$$

In the case of a zero-frequency magnetic field ($\omega_c = 0$, $\boldsymbol{k}_c = 0$), the expansion (5.8) yields

$$\overset{(3)}{{}_{e}\boldsymbol{P}}{}^{(n)}_{eem}(\omega_a,\omega_b,0_c,\boldsymbol{k}_a,\boldsymbol{k}_b,0_c)=\frac{1}{2}\Big\{{}^{(n)}_{e}\chi_{eem}^{(1+1+1)}(\omega_a,\omega_b,0_c)-$$

$$-\frac{i}{3}\left[{}^{(n)}_{e}\chi_{eem}^{(2+1+1)}(\omega_a,\omega_b,0_c)\cdot\boldsymbol{k}_a+{}^{(n)}_{e}\chi_{eem}^{(1+2+1)}(\omega_a,\omega_b,0_c)\cdot\boldsymbol{k}_b\right]+$$

$$+\ldots\Big\}\vdots\,\boldsymbol{E}(\omega_a,\boldsymbol{k}_a)\,\boldsymbol{E}(\omega_b,\boldsymbol{k}_b)\,\boldsymbol{H}(0_c) \tag{5.9}$$

for the *DC* magnetic-field induced multipole sum-frequency generation effect and its spatial variations.

Similarly we have the further contribution to the third-order multipole electric polarization:

$$\overset{(3)}{{}_{e}\boldsymbol{P}}{}^{(n)}_{emm}(\omega_a,\omega_b,\omega_c,\boldsymbol{k}_a,\boldsymbol{k}_b,\boldsymbol{k}_c)=\frac{1}{2}\sum_{n_a=1}^{\infty}\sum_{n_b=1}^{\infty}\sum_{n_c=1}^{\infty}\frac{2^{n_a+n_b+n_c}n_a!\,n_b!\,n_c!}{(2n_a)!\,(2n_b)!\,(2n_c)!}\times$$

$$\times{}^{(n)}_{e}\chi_{emm}^{(n_a+n_b+n_c)}(\omega_a,\omega_b,\omega_c)\,[n_a+n_b+n_c]\,\boldsymbol{E}^{(n_a)}(\omega_a,\boldsymbol{k}_a)\,\boldsymbol{H}^{(n_b)}(\omega_b,\boldsymbol{k}_b)\,\boldsymbol{H}^{(n_c)}(\omega_c,\boldsymbol{k}_c), \tag{5.10}$$

where, by (3.8) and (4.10),

$$ {}^{(n)}_{e}\chi_{emm}^{(na+nb+nc)}(\omega_a, \omega_b, \omega_c) = {}^{(n)}_{e}\chi_{emm}^{(na+nb+nc)}(\omega_a, \omega_b, \omega_c)_D + $$

$$ + {}^{(n)}_{e}\chi_{emm}^{(na+nb+nc)}(-\omega_a, -\omega_b, -\omega_c)_D + \frac{\varrho}{\hbar^3} S(a, b, c) \sum_{klrst} \varrho_{kl} \times $$

$$ \times \left\{ \frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle\langle r|\boldsymbol{M}_e^{(na)}|s\rangle\langle s|\boldsymbol{M}_m^{(nb)}|t\rangle\langle t|\boldsymbol{M}_m^{(nc)}|l\rangle}{(\omega_{rl}+\omega_a+\omega_b+\omega_c+i\Gamma_{rl})(\omega_{sl}+\omega_b+\omega_c+i\Gamma_{sl})(\omega_{tl}+\omega_c+i\Gamma_{tl})} + \right. $$

$$ + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle\langle r|\boldsymbol{M}_e^{(n)}|s\rangle\langle s|\boldsymbol{M}_m^{(nb)}|t\rangle\langle t|\boldsymbol{M}_m^{(nc)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sl}+\omega_b+\omega_c+i\Gamma_{sl})(\omega_{tl}+\omega_c+i\Gamma_{tl})} + $$

$$ + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle\langle r|\boldsymbol{M}_m^{(nb)}|s\rangle\langle s|\boldsymbol{M}_e^{(n)}|t\rangle\langle t|\boldsymbol{M}_m^{(nc)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})(\omega_{tl}+\omega_c+i\Gamma_{tl})} + $$

$$ \left. + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle\langle r|\boldsymbol{M}_m^{(nb)}|s\rangle\langle s|\boldsymbol{M}_m^{(nc)}|t\rangle\langle t|\boldsymbol{M}_e^{(n)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})(\omega_{tk}-\omega_a-\omega_b-\omega_c+i\Gamma_{tk})} \right\} \tag{5.11} $$

with the following diamagnetic contribution:

$$ {}^{(n)}_{e}\chi_{emm}^{(na+nb+nc)}(\omega_a, \omega_b, \omega_c)_D = \frac{\varrho}{\hbar^2} S(a, b, c) \sum_{klrs} \varrho_{kl} \times $$

$$ \times \left\{ \frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle\langle r|\boldsymbol{M}_e^{(na)}|s\rangle\langle s|{}^{(nb)}\boldsymbol{A}_m^{(nc)}|l\rangle}{(\omega_{rl}+\omega_a+\omega_b+\omega_c+i\Gamma_{rl})(\omega_{sl}+\omega_b+\omega_c+i\Gamma_{sl})} + \right. $$

$$ + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle\langle r|\boldsymbol{M}_e^{(n)}|s\rangle\langle s|{}^{(nb)}\boldsymbol{A}_m^{(nc)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sl}+\omega_b+\omega_c+i\Gamma_{sl})} + $$

$$ \left. + \frac{\langle k|\boldsymbol{M}_e^{(na)}|r\rangle\langle r|{}^{(nb)}\boldsymbol{A}_m^{(nc)}|s\rangle\langle s|\boldsymbol{M}_e^{(n)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sk}-\omega_a-\omega_b-\omega_c+i\Gamma_{sk})} \right\} \tag{5.12} $$

which can be obtained in second-order perturbation theory if the first- and second-order perturbations Hamiltonians of (3.8) and (4.10) are used.

We now assume that the electric field strength $\boldsymbol{E}(\omega_a, \boldsymbol{k}_a)$ conveyed by the wave of frequency ω_a is small and assign to it the role of measuring field, whereas the *DC* uniform magnetic field is of very high intensity, sufficient for producing non-linear polarization of the medium. In this case we have by (5.10)

$$ {}_{e}\overset{(3)}{\boldsymbol{P}}{}^{(n)}_{emm}(\omega_a, 0_b, 0_c, \boldsymbol{k}_a, 0_b, 0_c) = \frac{1}{2}\left\{ {}^{(n)}_{e}\chi_{emm}^{(1+1+1)}(\omega_a, 0_b, 0_c) - \right. $$

$$ \left. - \frac{i}{3}\, {}^{(n)}_{e}\chi_{emm}^{(2+1+1)}(\omega_a, 0_b, 0_c) \cdot \boldsymbol{k}_a + \dots \right\} : \boldsymbol{E}(\omega_a, \boldsymbol{k}_a)\boldsymbol{H}(0_b)\boldsymbol{H}(0_c), \tag{5.13} $$

where, in the dipole approximation, the first term accounts for the Cotton-Mouton effect and the second term for the optical activity induced in a medium by the square of the *DC* magnetic field (or the quadratic change in optical activity).

6. Higher-order optical processes

We now generalize the foregoing considerations to the case of multipole polarization operators of arbitrary order. Namely, the s-th-order multipole electric polarization can be written as

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r}, t) = \frac{1}{2^s} \sum_{a_1 \dots a_s} \{ \overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\omega_{a_1}, \dots \omega_{a_s}, \boldsymbol{k}_{a_1}, \dots \boldsymbol{k}_{a_s}) + \dots$$
$$\dots + \overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(-\omega_{a_1}, \dots -\omega_{a_s}, -\boldsymbol{k}_{a_1}, \dots -\boldsymbol{k}_{a_s})\}, \tag{6.1}$$

wherein the brackets $\{\ \}$ contain 2^s terms which can be derived from the first one

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\omega_{a_1}, \dots \omega_{a_s}, \boldsymbol{k}_{a_1}, \dots \boldsymbol{k}_{a_s}) = \frac{1}{s!} \sum_{n_{a_1}=1}^{\infty} \dots \sum_{n_{a_s}=1}^{\infty} \frac{2^{n_{a_1}+\dots+n_{a_s}} n_{a_1}! \dots n_{a_s}!}{(2n_{a_1})! \dots (2n_{a_s})!} \times$$
$$\times {}^{(n)}_{e}\chi_e^{(n_{a_1}+\dots+n_{a_s})}(\omega_{a_1}, \dots \omega_{a_s}) [n_{a_1} + \dots + n_{a_s}] \boldsymbol{E}^{(n_{a_1})}(\omega_{a_1}, \boldsymbol{k}_{a_1}) \dots \boldsymbol{E}^{(n_{a_s})}(\omega_{a_s}, \boldsymbol{k}_{a_s}) \tag{6.2}$$

by consecutive interchange of the sign of the arguments $\omega_{a_1}, \dots \omega_{a_s}, \boldsymbol{k}_{a_1}, \dots \boldsymbol{k}_{a_s}$. The explicite quantum-mechanical form of the s-th-order multipole electric susceptibility tensor is (for comparison see [15] and [22]),

$${}^{(n)}_{e}\chi_e^{(n_{a_1}+\dots+n_{a_s})}(\omega_{a_1}, \dots \omega_{a_s}) = \frac{\varrho}{\hbar^s} S(a_1, \dots a_s) \sum_{k i_1 \dots i_s l} \varrho_{kl} \times$$
$$\frac{\langle k|\boldsymbol{M}_e^{(n_{a_1})}|i_1\rangle\langle i_1 \boldsymbol{M}_e^{(n_{a_2})}|i_2\rangle \dots \langle i_{t-1}|\boldsymbol{M}_e^{(n_{a_t})}|i_t\rangle\langle i_t|\boldsymbol{M}_e^{(n)}|i_{t+1}\rangle\langle i_{t+1}|\boldsymbol{M}_e^{(n_{a_{t+1}})}|i_{t+2}\rangle \dots \langle i_s|\boldsymbol{M}_e^{(n_{a_s})}|l\rangle}{\prod_{u=1}^{t}(\omega_{i_u k} - \omega_{a_1} - \omega_{a_2} - \dots - \omega_{a_u} + i\Gamma_{i_u k}) \prod_{u=t+1}^{s}(\omega_{i_u l} + \omega_{a_u} + \omega_{a_{u+1}} + \dots + \omega_{a_s} + i\Gamma_{i_u l})} \tag{6.3}$$

if only the purely electric part of the first-order perturbation Hamiltonian of (3.8) is used.

From Eq. (5.15) we obtain *e.g.* for the fourth-order multipole electric susceptibility tensor

$${}^{(n)}_{e}\chi_e^{(n_a+n_b+n_c+n_d)}(\omega_a, \omega_b, \omega_c, \omega_d) = \frac{\varrho}{\hbar^4} S(a, b, c, d) \sum_{klrstu} \varrho_{kl} \times$$
$$\times \left\{ \frac{\langle k|\boldsymbol{M}_e^{(n)}|r\rangle\langle r|\boldsymbol{M}_e^{(n_a)}|s\rangle\langle s|\boldsymbol{M}_e^{(n_b)}|t\rangle\langle t|\boldsymbol{M}_e^{(n_c)}|u\rangle\langle u|\boldsymbol{M}_e^{(n_d)}|l\rangle}{(\omega_{rl}+\omega_a+\omega_b+\omega_c+\omega_d+i\Gamma_{rl})(\omega_{sl}+\omega_b+\omega_c+\omega_d+i\Gamma_{sl})(\omega_{tl}+\omega_c+\omega_d+i\Gamma_{tl})(\omega_{ul}+\omega_d+i\Gamma_{ul})} + \right.$$
$$+ \frac{\langle k|\boldsymbol{M}_e^{(n_a)}|r\rangle\langle r|\boldsymbol{M}_e^{(n)}|s\rangle\langle s|\boldsymbol{M}_e^{(n_b)}|t\rangle\langle t|\boldsymbol{M}_e^{(n_c)}|u\rangle\langle u|\boldsymbol{M}_e^{(n_d)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sl}+\omega_b+\omega_c+\omega_d+i\Gamma_{sl})(\omega_{tl}+\omega_c+\omega_d+i\Gamma_{tl})(\omega_{ul}+\omega_d+i\Gamma_{ul})} +$$
$$+ \frac{\langle k|\boldsymbol{M}_e^{(n_a)}|r\rangle\langle r|\boldsymbol{M}_e^{(n_b)}|s\rangle\langle s|\boldsymbol{M}_e^{(n)}|t\rangle\langle t|\boldsymbol{M}_e^{(n_c)}|u\rangle\langle u|\boldsymbol{M}_e^{(n_d)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})(\omega_{tl}+\omega_c+\omega_d+i\Gamma_{tl})(\omega_{ul}+\omega_d+i\Gamma_{ul})} +$$
$$+ \frac{\langle k|\boldsymbol{M}_e^{(n_c)}|r\rangle\langle r|\boldsymbol{M}_e^{(n_b)}|s\rangle\langle s|\boldsymbol{M}_e^{(n_c)}|t\rangle\langle t|\boldsymbol{M}_e^{(n)}|u\rangle\langle u|\boldsymbol{M}_e^{(n_d)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{tk})(\omega_{sk}-\omega_a-\omega_b+i\Gamma_{sk})(\omega_{tk}-\omega_a-\omega_b-\omega_c+i\Gamma_{tk})(\omega_{ul}+\omega_d+i\Gamma_{ul})} +$$
$$\left. + \frac{\langle k|\boldsymbol{M}_e^{(n_a)}|r\rangle\langle r|\boldsymbol{M}_e^{(n_b)}|s\rangle\langle s|\boldsymbol{M}_e^{(n_c)}|t\rangle\langle t|\boldsymbol{M}_e^{(n_d)}|u\rangle\langle u|\boldsymbol{M}_e^{(n)}|l\rangle}{(\omega_{rk}-\omega_a+i\Gamma_{rk})(\omega_{sk}-\omega_a+i\Gamma_{sk})(\omega_{tk}-\omega_a-\omega_b-\omega_c+i\Gamma_{tk})(\omega_{ul}-\omega_a-\omega_b-\omega_c-\omega_d+i\Gamma_{uk})} \right\}. \tag{6.4}$$

In the special case when the spatial variation of the electric field can be ignored, Eq. (6.2) reduces to the following simpler form:

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\omega_{a_1},\dots\omega_{a_s})=\frac{1}{s!}\,{}^{(n)}\chi_e^{(s)}(\omega_{a_1},\dots\omega_{a_s})[s]\boldsymbol{E}(\omega_{a_1})\dots\boldsymbol{E}(\omega_{a_s}),\tag{6.5}$$

which corresponds to generation of the s-th mixed waves.

Consider, for instance, the case when a DC uniform electric field is applied to the medium; we obtain, instead of (6.5),

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\omega_{a_1},\dots\omega_{a_{s-1}},0_{a_s})=\frac{1}{(s-1)!}\,{}^{(n)}\chi_e^{(s)}(\omega_{a_1},\dots\omega_{a_{s-1}},0_{a_s})\times$$
$$\times[s]\boldsymbol{E}(\omega_{a_1})\dots\boldsymbol{E}(\omega_{a_{s-1}})\boldsymbol{E}(0_{a_s}),\tag{6.6}$$

for the linear DC electric field effect ($s\geqslant2$), and

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\omega_{a_1},\dots\omega_{a_{s-2}},0_{a_{s-1}},0_{a_s})=\frac{1}{2(s-2)!}\,{}^{(n)}\chi_e^{(s)}(\omega_{a_1},\dots\omega_{a_{s-2}},0_{a_{s-1}},0_{a_s})\times$$
$$\times[s]\boldsymbol{E}(\omega_{a_1})\dots\boldsymbol{E}(\omega_{a_{s-2}})\boldsymbol{E}(0_{a_{s-1}})\boldsymbol{E}(0_{a_s})\tag{6.7}$$

for the quadratic DC electric field effect ($s\geqslant3$).

If the frequencies of all interacting waves are the same $\omega_{a_1}=\omega_{a_2}=\dots\omega_{a_s}$, Eqs (6.6) and (6.7) reduce to the following simpler form:

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\omega_{s-1})=\frac{1}{(s-1)!}\,{}^{(n)}\chi_e^{(s)}(\omega_{s-1})[s]\boldsymbol{E}_\omega^{s-1}\boldsymbol{E}_{DC},\tag{6.8}$$

$$\overset{(s)}{\boldsymbol{P}}{}_e^{(n)}(\omega_{s-2})=\frac{1}{2(s-2)!}\,{}^{(n)}\chi_e^{(s)}(\omega_{s-2})[s]\boldsymbol{E}_\omega^{s-2}\boldsymbol{E}_{DC}^2.\tag{6.9}$$

Here, Eq. (6.8) describes linear DC electric field induced $(s-1)$-th-harmonic generation, $\omega_{s-1}=(s-1)\omega$, whereas Eq. (6.9) — quadratic DC electric field induced $(s-2)$-th-harmonic generation, $\omega_{s-2}=(s-2)\omega$.

For the case of an oscillating electric field as given by (1.4) the expression (6.8) yields ($s\geqslant1$)

$$\overset{(2s)}{\boldsymbol{P}}{}_e^{(n)}(\omega)=\frac{1}{2^{2s-2}(2s-1)!}\sum_{r=0}^{s-1}\binom{2s-1}{r}\,{}^{(n)}\chi_e^{(2s)}(\omega_{2s-2r-1})\times$$
$$\times[2s]\boldsymbol{E}_{DC}\boldsymbol{E}_0^{2s-1}\cos(2s-2r-1)\omega t,\tag{6.10}$$

$$\overset{(2s+1)}{\boldsymbol{P}}{}_e^{(n)}(\omega)=\frac{1}{2^{2s}(2s)!}\left\{\binom{2s}{s}\,{}^{(n)}\chi_e^{(2s+1)}(0)[2s+1]\boldsymbol{E}_{DC}\boldsymbol{E}_0^{2s}+\right.$$
$$\left.+\,2\sum_{r=0}^{s-1}\binom{2s}{r}\,{}^{(n)}\chi_e^{(2s+1)}(\omega_{2s-2r})[2s+1]\boldsymbol{E}_{DC}\boldsymbol{E}_0^{2s}\cos2(s-r)\omega t\right\}.\tag{6.11}$$

The preceding expressions show that on imposing a linear DC electric field the multipole electric polarization operators of even order are given by the odd harmonics ω, 3ω, 5ω *etc.*, whereas the multipole polarizations of odd order contain terms with the zeroth frequency and terms with the even harmonics 2ω, 4ω, and so forth. Thus, *e.g.*, by (6.10) and (6.11) we have for the polarization operators of respectively the second, third, fourth *etc.* orders

$$\overset{(2)}{\boldsymbol{P}}{}_e^{(n)}(\omega) = {}^{(n)}\chi_e^{(1+1)}(\omega) : \boldsymbol{E}_{DC}\boldsymbol{E}_0 \cos \omega t,$$

$$\overset{(3)}{\boldsymbol{P}}{}_e^{(n)}(\omega) = \frac{1}{4} \{{}^{(n)}\chi_e^{(1+2)}(0) \vdots \boldsymbol{E}_{DC}\boldsymbol{E}_0^2 + {}^{(n)}\chi_e^{(1+2)}(2\omega) \vdots \boldsymbol{E}_{DC}\boldsymbol{E}_0^2 \cos 2\omega t\},$$

$$\overset{(4)}{\boldsymbol{P}}{}_e^{(n)}(\omega) = \frac{1}{24} \{3\,{}^{(n)}\chi_e^{(1+3)}(\omega) :: \boldsymbol{E}_{DC}\boldsymbol{E}_0^3 \cos \omega t +$$

$$+ {}^{(n)}\chi_e^{(1+3)}(3\omega) :: \boldsymbol{E}_{DC}\boldsymbol{E}_0^3 \cos 3\omega t\}, \ldots \tag{6.12}$$

Similarly we obtain from (6.9)

$$\overset{(2s+2)}{\boldsymbol{P}}{}_e^{(n)}(\omega) = \frac{1}{2^{2s+1}(2s)!} \left\{ \binom{2s}{s} {}^{(n)}\chi_e^{(2s+2)}(0)\, [2s+2] \boldsymbol{E}_{DC}^2 \boldsymbol{E}_0^{2s} + \right.$$

$$\left. + 2 \sum_{r=0}^{s-1} \binom{2s}{r} {}^{(n)}\chi_e^{(2s+2)}(\omega_{2s}) [2s+2] \boldsymbol{E}_{DC}^2 \boldsymbol{E}_0^{2s} \cos 2(s-r)\omega t \right\}, \tag{6.13}$$

$$\overset{(2s+1)}{\boldsymbol{P}}{}_e^{(n)}(\omega) = \frac{1}{2^{2s-1}(2s-1)!} \sum_{r=0}^{s-1} \binom{2s-1}{r} {}^{(n)}\chi_e^{(2s+1)}(\omega_{2s-1}) \times$$

$$\times [2s+1] \boldsymbol{E}_{DC}^2 \boldsymbol{E}_0^{2s-1} \cos (2s-2r-1)\omega t \tag{6.14}$$

for the components of the multipole electric polarization operator of even and odd order $(s \geqslant 1)$ which in the third, fourth *etc.* approximation yield

$$\overset{(3)}{\boldsymbol{P}}{}_e^{(n)}(\omega) = \frac{1}{2} {}^{(n)}\chi_e^{(2+1)}(\omega) \vdots \boldsymbol{E}_{DC}^2 \boldsymbol{E}_0 \cos \omega t,$$

$$\overset{(4)}{\boldsymbol{P}}{}_e^{(n)}(\omega) = \frac{1}{8} \{{}^{(n)}\chi_e^{(2+2)}(0) :: \boldsymbol{E}_{DC}^2 \boldsymbol{E}_0^2 + {}^{(n)}\chi_e^{(2+2)}(2\omega) :: \boldsymbol{E}_{DC}^2 \boldsymbol{E}_0^2 \cos 2\omega t\}, \ldots . \tag{6.15}$$

In particular, the fourth-order multipole polarization includes the contribution

$$\overset{(4)}{\boldsymbol{P}}{}_e^{(n)}(2\omega) = \frac{1}{8} {}^{(n)}\chi_e^{(2+2)}(2\omega) :: \boldsymbol{E}_{DC}^2 \boldsymbol{E}_0^2 \cos 2\omega t, \tag{6.16}$$

which is responsible for quadratic DC electric field-induced second harmonic generation from non-centrosymmetric crystals, if the dipole approximation is made, or from centrosymmetric media, if the quadrupole approximation $(n = 2)$ is made.

In a similar manner we can examine the various contributions to higher-order electric multipole polarization from the magnetic field as well as the non-linear magnetic processes.

7. *Conclusion*

The general tensor formalism proposed here is adapted to the quantitative description of non-linear processes of arbitrary order, variable not only with regard to frequency but simultaneously spatially-variable. It is found that the formulation of a non-linear optics wherein beside frequency dispersion account is taken also of spatial dispersion of the operators of electric and magnetic polarization is by no means solely a matter of taking into consideration various corrections of the order of $ak \simeq a/\lambda$ (where a can denote the lattice constant or the radius of molecular interaction and λ — the wavelength in the medium) but is essentially a procedure whereby qualitatively quite new effects appear. Obviously, with regard to their order of magnitude, these novel effects (*e.g.* induced optical activity) are small as compared to known, experimentally investigated phenomena. By a judicious choice of experimental conditions, however, some of them may be measurable.

We have introduced tensors of the electric and magnetic multipolar susceptibilities of the first, second, third, *etc.* orders and determined their frequency-dependence by means of quantum-mechanical expressions. In order that the latter shall be valid within regions of resonance too, in deriving them we have recurred to the perturbation method based on excited-state wave functions with phenomenologically introduced damping constant [34]. The matrix elements of multipole transitions of the electric, magnetic or mixed type appearing in these expressions can be computed *e.g.* by means of a complete set of unperturbed Slater wave functions for the case of isolated atoms or, in considering the crystal state, with appropriate Bloch wave functions for the electrons. In the dipole and quadrupole approximations, one obtains results already derived by various authors [11—17, 20—23].

For the sake of simplicity, we have refrained from considering, in the present theory, stochastic properties of non-linear optical processes [35] and coherence properties of electromagnetic fields (see [36] and the papers cited there). It would be very useful to develop such a thoroughgoing theory, both in the classical and quantum approach. However, the mathematical expressions derived in this paper already raise some difficulties when we proceed to adapt them to numerical computations, which requires on the one hand various assumptions taking into account the specific micro-structure of the medium and, on the other, some degree of idealization involved by the inevitable simplifications of the model. These close studies will give us deeper insight into the mechanism and nature of various optical processes, thus yielding valuable information on the multipolar and non-linear properties of atoms and molecules in the presence of intense electromagnetic fields.

Since, in general, the statistical matrix ϱ_{kl} contains Boltzmann's factor $\exp\{-H_{kl}/kT\}$, additional contributions to the multipole operators $\boldsymbol{P}_e^{(n)}$ and $\boldsymbol{P}_m^{(n)}$ will appear resulting from the effects of optical molecular orientation (orientation of the optically anisotropic molecules in the optical field [37—39]). Therefore, in an isotropic medium such as a gas or liquid, the presence of the non-linear effect is due not only to *direct influence* of an intense electromagnetic field on an atom or molecule (the induced effect), but, moreover, to *statistical orientation* in this field of the optically anisotropic molecules. Which of these two processes will play the essential or sole part in any particular case will depend primarily on the structure and symmetry of the molecules, on the thermodynamical state at which the substance is investigated, on its frequency-dispersion, *etc.* The effect of intermolecular angular correlations upon measurable quantities can be calculated, as was done for other nonlinear phenomena in liquid dielectrics (see, *e.g.* [38—40]).

The formalism developed in this paper can be used with slight modifications for computing the nonlinear variations of static electric or magnetic permittivity tensors due to the strong electromagnetic field. Usually, in experimental investigations of these variations, the medium is acted on simultaneously by the weak measuring field, electric or magnetic, which varies slowly with frequency, and the strong *DC* electric or magnetic polarizing field, sufficing for producing nonlinear polarization of the medium [39]. Since, in general, the polarizing field may be electric or magnetic or else an optical field, we shall be dealing with several electric and magnetic saturation phenomena previously discussed for isotropic media, such as gases and liquids [38, 39].

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