MULTIPOLE ELECTRO-MAGNETIC POLARIZABILITIES
IN OPTICAL CIRCULAR BIREFRINGENCE OF DENSE MEDIA *

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A semi-macroscopic theory of optical circular birefringence (OCB) in arbitrary dense optically active bodies is proposed, comprising in a concise tensorial formalism the electro-magnetic multipolar polarizabilities of all orders. Besides spatial dispersion of arbitrary order, frequency dispersion and absorption in OCB and the role of time and space fluctuations of the fields of electric and magnetic molecular multipoles in regions of short range ordering in liquids and solutions are discussed.

1. Introduction

Terwiel and Mazur [1], and Maaskant and Oosterhoff [2], independently formulated the molecular-statistical theory of optical activity in isotropic bodies with an accuracy to the electric quadrupole and magnetic dipole moments. Viewed generally, optical activity theory is based on Maxwell's equations, modified by de Groot and others [3] to include electric and magnetic multipoles. On this basis, Kielich introduced multipolar electric and magnetic tensorial molecular polarizabilities [4] and susceptibilities [5] of all orders for arbitrary dense media in linear as well as nonlinear approximations in the electric and magnetic fields.

Recently, various authors [6–10] performed anew analyses of multipolarity in optical activity by phenomenological as well as microscopic methods for various materials specifying widely ranging assumptions and restrictions. In this communication, we shall consider systematically, in addition to the electric and the magnetic multipolar polarizabilities, also cross electro-magnetic and magneto-electric multipolar polarizabilities. For simplicity, we shall omit retardation and relativistic effects [3,4]. To derive results applicable to the widest range of materials exhibiting spatial dispersion [11], we have recourse to the semi-macroscopic treatment proposed by Kirkwood [12] in his theory of dielectrics. Also, in order to formulate our rather complicated results concisely, we apply the general formalism of cartesian tensors of electric and magnetic multipole moments in a way to make them automatically translatable into that of spherical tensors. The results for OCB thus obtained are so highly general as to be applicable to molecular, macromolecular and biomolecular liquids and their mixtures, as well as molecular crystals.

2. Multipole expansion of electric and magnetic permittivity tensor

We consider generally an anisotropic medium with electric permittivity tensor ε and magnetic permittivity tensor μ in a volume V, immersed in an isotropic medium with the scalar permittivities ϵ_0 and μ_0. The electric field

of the light wave in the surrounding medium being $E_0(r, t)$, the mean macroscopic (maxwellian) field $E(r, t)$ existing in V will differ from $E_0(r, t)$. The two fields are related by the tensor R as follows [12]:

$$E_0(r, t) = \mathsf{R}_e \, E(r, t),$$ (1)

$$\mathsf{R}_e = \epsilon_0^{-1} [\epsilon_0 \, \mathsf{U} + \mathsf{L} \cdot (\boldsymbol{\varepsilon} - \epsilon_0 \mathsf{U})], \quad \text{for the ellipsoid};$$

$$= (3\epsilon_0)^{-1} (\boldsymbol{\varepsilon} + 2\epsilon_0 \mathsf{U}), \quad \text{for the sphere}.$$

$\mathsf{U} = xx + yy + zz$ is the rank 2 unit tensor in cartesian space XYZ with unit basis vectors x, y, z and L the depolarizing tensor. By analogy to (1) we define the relation between the magnetic vectors $H_0(r, t)$ and $H(r, t)$ of the wave.

The equations for the electric and magnetic permittivity tensors taking into account all multipolar contributions are [5]:

$$(\boldsymbol{\varepsilon} - \mathsf{U}) \cdot E(r, t) = 4\pi \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(2n-1)!!} \, \nabla^{n-1} \, [n-1] \, P_e^{(n)}(r, t),$$ (2)

$$(\boldsymbol{\mu} - \mathsf{U}) \cdot H(r, t) = 4\pi \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(2n-1)!!} \, \nabla^{n-1} \, [n-1] \, P_m^{(n)}(r, t),$$ (3)

where the brackets $[n-1]$ between the spatial derivation operators ∇^{n-1} and polarisation n-vectors denote $n-1$ fold contraction.

The operator of 2^n-pole electric polarisation $P_e^{(n)}(r, t)$ induced in the medium by the electric field at the space—time point (r, t) is generally a function of the vectors $E_0(r, t)$ and $H_0(r, t)$. On restricting ourself here to a linear approximation we have, in the semi-macroscopic treatment:

$$P_e^{(n)}(r, t) = V^{-1} \sum_{s=1}^{\infty} \frac{1}{(2s-1)!!} \, \{ {}_e^{(n)}\mathsf{A}_e^{(s)} \, [s] \, \nabla^{s-1} \, E_0(r, t) + {}_e^{(n)}\mathsf{A}_m^{(s)} [s] \nabla^{s-1} H_0(r, t) \},$$ (4)

where the tensor ${}_e^{(n)}\mathsf{A}_e^{(s)}$ of rank $n+s$ defines the electro-electric multipolar polarizability induced in the medium by the $(s-1)$th order spatial inhomogeneity of the linear electric field $E_0(r, t)$; similarly, the tensor ${}_e^{(n)}\mathsf{A}_m^{(s)}$ defines the respective electro-magnetic multipole polarizability of the medium.

By analogy to (4), we write the multipole expansion for the linear magnetic polarisation:

$$P_m^{(n)}(r, t) = V^{-1} \sum_{s=1}^{\infty} \frac{1}{(2s-1)!!} \, \{ {}_m^{(n)}\mathsf{A}_m^{(s)} [s] \nabla^{s-1} \, H_0(r, t) + {}_m^{(n)}\mathsf{A}_e^{(s)} [s] \nabla^{s-1} E_0(r, t) \},$$ (5)

where the $(n+s)$th rank tensors ${}_m^{(n)}\mathsf{A}_m^{(s)}$ and ${}_m^{(n)}\mathsf{A}_e^{(s)}$ define linear multipolar magneto-magnetic and magneto-electric polarizabilities of the medium.

The electric and magnetic vectors of a monochromatic light wave vibrating with the frequency ω and propagating in the direction S are, in Fourier representation:

$$E(r, t) = E(\omega, k) \exp\{i(k \cdot r - \omega t)\}, \quad H(r, t) = H(\omega, k) \exp\{i(k \cdot r - \omega t)\},$$ (6)

where, for a medium with refractive index n, we have $k = n(\omega/c)S$. By (6), the Maxwell equations for a nonconducting medium are:

$$k \times E(r, t) = (\omega/c) B(r, t), \quad k \times H(r, t) = -(\omega/c) D(r, t).$$ (7)

Applying these equations to wave propagation in the isotropic external medium of index $n_0 = (\epsilon_0 \mu_0)^{1/2}$, we can

eliminate the magnetic vector from the expansion (4) and the electric vector from (5), thus finally obtaining with regard to (2) and (3) the following multipole expansions for the tensors of electric and magnetic permittivities:

$$\varepsilon(\omega,k) - U = \frac{4\pi}{V} \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \frac{i^n(-i)^s}{(2n-1)!!(2s-1)!!} \{k^{n-1}[n-1]\,{}_{e}^{(n)}\Pi_{m}^{(s)}(\omega)[s-1]k^{s-1}\}\cdot R_{e}(\omega,k), \tag{8}$$

$$\mu(\omega,k) - U = \frac{4\pi}{V} \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \frac{i^n(-i)^s}{(2n-1)!!(2s-1)!!} \{k^{n-1}[n-1]\,{}_{m}^{(n)}\Pi_{e}^{(s)}(\omega)[s-1]\,k^{s-1}\}\cdot R_{m}(\omega,k). \tag{9}$$

Above, we have introduced the following tensors of multipolar total electro-magnetic and magneto-electric polarizabilities:

$$ {}_{e}^{(n)}\Pi_{m}^{(s)}(\omega) = {}_{e}^{(n)}A_{e}^{(s)}(\omega) + (\epsilon_0/\mu_0)^{1/2}\{{}_{e}^{(n)}A_{m}^{(s)}(\omega)\times S\}, \tag{10}$$

$$ {}_{m}^{(n)}\Pi_{e}^{(s)}(\omega) = {}_{m}^{(n)}A_{m}^{(s)}(\omega) - (\mu_0/\epsilon_0)^{1/2}\{{}_{m}^{(n)}A_{e}^{(s)}(\omega)\times S\}. \tag{11}$$

Eqs. (8)–(11) hold for arbitrary, isotropic as well as anisotropic bodies exhibiting spatial dispersion and frequency dispersion.

3. Multipole expansion of OCB

Assuming the wave to propagate along Z, the Maxwell equations (7) yield in a satisfactory approximation for the difference in refractive indices between right and left circular light polarisation:

$$n_+ - n_- = \tfrac{1}{2}(\epsilon\mu)^{-1/2}\{\epsilon_{xx}\mu_{yy} - \mu_{xx}\epsilon_{yy} + \epsilon_{xy}\mu_{xy} - \epsilon_{yx}\mu_{yx} - i(\epsilon_{xy}\mu_{yy} - \epsilon_{yx}\mu_{xx}) - i(\mu_{xy}\epsilon_{xx} - \mu_{yx}\epsilon_{yy}) + ...\}. \tag{12}$$

In particular, for isotropic bodies $\epsilon_{xx} = \epsilon_{yy} = \epsilon$ and $\mu_{xx} = \mu_{yy} = \mu$ (on neglecting the dependence of the diagonal components on spatial dispersion), and OCB is defined only by the non-diagonal components of the tensors (8) and (9). In this case, and if moreover the sample is spherical, we can assume that the tensor R_e is isotropic: approximately $R_e = \{(\epsilon + 2\epsilon_0)/3\epsilon_0\}U$ and, similarly, $R_m = \{(\mu + 2\mu_0)/3\mu_0\}U$. Taking this into account in conjunction with eqs. (8), (9) and (12), we obtain for OCB:

$$n_+(\omega,k) - n_-(\omega,k) = \frac{2\pi}{V} \sum_{n=0}^{\infty} \sum_{s=0}^{\infty} \frac{i^{n+1}(-i)^s}{(2n+1)!!(2s+1)!!} k^n[n]\,{}^{(n)}G_{em}^{(s)}(\omega)[s]k^s, \tag{13}$$

where we have introduced the multipolar gyration tensor of the medium

$$ {}^{(n)}G_{em}^{(s)}(\omega) = \left(\frac{\mu}{\epsilon}\right)^{1/2}\left(\frac{\epsilon+2\epsilon_0}{3\epsilon_0}\right)\langle\{x\cdot{}_{e}^{(n+1)}\Pi_{m}^{(s+1)}(\omega)\cdot y\} - \{y\cdot{}_{e}^{(n+1)}\Pi_{m}^{(s+1)}(\omega)\cdot x\}\rangle $$

$$ + \left(\frac{\epsilon}{\mu}\right)^{1/2}\left(\frac{\mu+2\mu_0}{3}\right)\langle\{x\cdot{}_{m}^{(n+1)}\Pi_{e}^{(s+1)}(\omega)\cdot y\} - \{y\cdot{}_{m}^{(n+1)}\Pi_{e}^{(s+1)}(\omega)\cdot x\}\rangle, \tag{14}$$

$\langle\ \rangle$ standing for statistical averaging.

Eqs. (13) and (14) define OCB of a dense isotropic medium including contributions of all orders from the multipolar electro-magnetic polarizabilities. If spatial dispersion is not excessively strong, we have by (13) with accuracy to octupolar polarizabilities:

$$n_+(\omega,k) - n_-(\omega,k) = -(2\pi/3V)\{ [k \cdot {}^{(1)}G_{em}^{(0)}(\omega) - {}^{(0)}G_{em}^{(1)}(\omega) \cdot k]$$

$$+ \tfrac{1}{15}i[3kk : {}^{(2)}G_{em}^{(0)}(\omega) - 5k \cdot {}^{(1)}G_{em}^{(1)}(\omega) \cdot k + 3 {}^{(0)}G_{em}^{(2)}(\omega) : kk]$$

$$- \tfrac{1}{105}[3kkk \vdots {}^{(3)}G_{em}^{(0)}(\omega) - 7kk : {}^{(2)}G_{em}^{(1)}(\omega) \cdot k + 7k \cdot {}^{(1)}G_{em}^{(2)}(\omega) : kk - 3 {}^{(0)}G_{em}^{(3)}(\omega) \vdots kkk] + ... \}, \quad (14a)$$

since for the isotropic body ${}^{(0)}G_{em}^{(0)}(\omega) = 0$.

4. Frequency dispersion and absorption of OCB

Considering a dielectric sphere of volume V in which N microsystems are present, we assume in a first approximation that neither statistical correlations nor molecular fields intervene. For this case, by having recourse to standard quantum-mechanical first-order perturbation calculus, we derive the electro-magnetic multipole polarizability tensor in the form [4, 5]:

$${}_e^{(n)}A_m^{(s)}(\omega) = \frac{N}{\hbar} \sum_{klr} \rho_{kl} \left[\frac{\langle k|M_e^{(n)}|r\rangle\langle r|M_m^{(s)}|l\rangle}{\omega_{rl} - \omega - i\Gamma_{rl}} + \frac{\langle k|M_m^{(s)}|r\rangle\langle r|M_e^{(n)}|l\rangle}{\omega_{rk} + \omega + i\Gamma_{rk}} \right], \quad (15)$$

where ρ_{kl} is the statistical matrix for quantum transitions $k \to l$ with Bohr frequency ω_{kl} and relaxation time Γ_{kl}^{-1}. Eq. (15) contains the electric and magnetic 2^n-pole moments of the microsystems defined by [4]:

$$M_e^{(n)} = \sum_i e_i r_i^n Y_i^{(n)}(r_i), \quad (16)$$

$$M_m^{(n)} = \frac{n}{(n+1)c} \sum_i e_i Y_i^{(n)}(r_i) \times \dot{r}_i, \quad (17)$$

where e_i is the ith electric charge of the microsystem with radius vector r_i, and $Y_i^{(n)}$ the nth order spherical function operator.

By (15), we get expressions for the remaining multipolar polarizabilities by interchanging the subscripts e and m. E.g., on replacing m by e, we get the tensor ${}_e^{(n)}A_e^{(s)}$, and so forth. On putting $k = l$ in (15), we can write the symmetric and antisymmetric parts:

$${}_e^{(n)}A_m^{(s)}(\omega)_S = \frac{N}{\hbar} \sum_{kr} \rho_{kk} \omega_{rk} (\langle k|M_e^{(n)}|r\rangle\langle r|M_m^{(s)}|k\rangle + \langle k|M_m^{(s)}|r\rangle\langle r|M_e^{(n)}|k\rangle) F_{rk}(\omega), \quad (18)$$

$${}_e^{(n)}A_m^{(s)}(\omega)_A = \frac{N}{\hbar} \sum_{kr} \rho_{kk} (\omega + i\Gamma_{rk}) (\langle k|M_e^{(n)}|r\rangle\langle r|M_m^{(s)}|k\rangle - \langle k|M_m^{(s)}|r\rangle\langle r|M_e^{(n)}|k\rangle) F_{rk}(\omega), \quad (19)$$

where we have introduced the complex function of frequency $F_{rk}(\omega) = F_{rk}'(\omega) + i F_{rk}''(\omega)$, with:

$$F_{rk}'(\omega) = \frac{\omega_{rk}^2 - \omega^2 + \Gamma_{rk}^2}{(\omega_{rk}^2 - \omega^2)^2 + 2(\omega_{rk}^2 + \omega^2)\Gamma_{rk}^2 + \Gamma_{rk}^4}, \quad (20a)$$

$$F_{rk}''(\omega) = \frac{2\omega\Gamma_{rk}}{(\omega_{rk}^2 - \omega^2)^2 + 2(\omega_{rk}^2 + \omega^2)\Gamma_{rk}^2 + \Gamma_{rk}^4}. \quad (20b)$$

Eqs. (18)–(20) define generally the frequency dispersion and absorption of OCB in a form separable into a real part and an imaginary part, i.e., circular dichroism.

5. Applications and discussion

For specified molecular models and approximations, our formulae go over into OCB results known from the literature. In particular, to take into account statistical correlations and molecular fields, one has to start from the following equation (the electric part only is adduced):

$$V P_e^{(n)}(r,t) = \sum_{p=1}^{N} \sum_{s=1}^{\infty} \frac{1}{(2s-1)!!} \, {}^{(n)}A_e^{(s)}(r_p)[s] \, \{\nabla^{s-1}E_0(r,t) + F_e^{(s)}(r_p,t)\}. \tag{21}$$

Here, the molecular electric field $F_e^{(s)}(r_p,t)$ of order s at the centre r_p of the molecule p and time t due to all the other $N-1$ molecules of the medium in the presence of $E_0(r,t)$ is [13,14]:

$$F_e^{(s)}(r_p,t) = \sum_{q \neq p}^{N} \sum_{m=1}^{\infty} \frac{(-1)^m}{(2m-1)!!} \, {}^{(s)}T_{pq}^{(m)} \, [m] \, M_e^{(m)}(r_q,t), \tag{22}$$

where the tensor of rank $s+m$:

$${}^{(s)}T_{pq}^{(m)} = \nabla_p^{s-1} \nabla_q^{m-1} (\nabla_p \nabla_q - k^2 U) r_{pq}^{-1} \exp(ik \cdot r_{pq}) \tag{23}$$

describes the 2^s-pole $-$ 2^m-pole interactions between electric multipoles of molecules p and q separated by a distance r_{pq}.

By (21), (22) and applying the method of successive substitutions we can express the multipole polarizability tensor ${}^{(n)}A_e^{(s)}$ of the medium as a whole in terms of the molecular polarizability tensors ${}^{(n)}A_e^{(s)}(r_p)$ and multipole interaction tensors (23). Likewise, we obtain expansions for the other multipole polarizability tensors, taking into account the Yvon–Kirkwood [12] statistical-translational fluctuations caused in short-range regions by time and space fluctuations of the electric and magnetic fields of molecular multipoles. Obviously, with the aim of obtaining results for isotropic bodies, one has to perform the indicated averaging in the gyration tensor (14). In a first approximation, one can perform an unweighted averaging of cartesian tensors of various ranks by applying the general formulae derived earlier for even and odd ranks [15,16] (see also refs. [8,9]). In particular, this leads to the results of Terwiel and Mazur [1] and Maaskant and Oosterhoff [2]. Other, new temperature-dependent expressions result for liquids and liquid mixtures from our formulae if multipole-interaction, dispersional, electrostatic and inductional energies [12,13,17–20] are taken into account when averaging the gyration tensor (14).

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