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Nonlinear optical rotatory dispersion: application of group theoretical statistical mechanics

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Abstract. The third principle of group theoretical statistical mechanics is used to define the existence of many new nonlinear optical rotatory phenomena caused by the interaction of intense electromagnetic radiation with molecular ensembles. This treatment removes the necessity of having to distinguish between 'natural' and 'magnetic' optical activity; both processes emerge consistently from the analysis, which is based on an application of the Hellman–Feynman theorem and a double Taylor expansion of the induced electric and magnetic dipole moments.

1. Introduction

The application of the well developed theory of point groups to statistical mechanics has resulted recently in three principles of group theoretical statistical mechanics (GTSM) [1–5]. The first of these is the Neumann–Curie principle; written in the language of group theory, the second applies principle one to the molecule fixed frame (x, y, z) and the third is a powerful cause/effect principle dealing with the response of ensembles to externally applied fields. These three principles have been used recently to draw some useful new conclusions about microrheology [6–8], shear-induced depolarised light scattering [9] thermal conductivity due to combined elongation and shear [10] the nature of c.c.f.s in liquid crystals [11, 12] and to molecular dynamics [13–16].

These methods allow a precise definition of ensemble averages in terms of symmetry operators and irreducible representations of the point group of the ensemble. They are used in this communication to analyse the nonlinear interaction of electromagnetic fields with ensembles for optical rotation and circular dichroism [17–21]. The analysis extends to third order in **E** and **B**, the electric and magnetic components of the electromagnetic field, and results in a new method of classification of possible rotatory and dichroic phenomena in terms of basic symmetry properties of the ensemble.

2. The Hamiltonian: field induced electric and magnetic dipoles

The change in the Hamiltonian due to the interaction of an electromagnetic field and the ensemble is assumed to be

$$H = -\boldsymbol{\mu}\cdot\mathbf{E} - \mathbf{m}\cdot\mathbf{B} + \ldots, \tag{1}$$

where $\boldsymbol{\mu}$ is the total molecular electric dipole moment and $\mathbf{m}$ the total molecular magnetic dipole moment. The field components **E** and **B** are complex, right (R), or left (L) polarised and sum (+) or difference (−) frequencies:

$$\mathbf{E}_{-}^{(L)} = E_0(\mathbf{i}+\mathrm{i}\mathbf{j})\exp(-\mathrm{i}\theta_L), \qquad \mathbf{E}_{-}^{(R)} = E_0(\mathbf{i}-\mathrm{i}\mathbf{j})\exp(-\mathrm{i}\theta_R),$$
$$\mathbf{E}_{+}^{(L)} = E_0(\mathbf{i}-\mathrm{i}\mathbf{j})\exp(\mathrm{i}\theta_L), \qquad \mathbf{E}_{+}^{(R)} = E_0(\mathbf{i}+\mathrm{i}\mathbf{j})\exp(\mathrm{i}\theta_R),$$
$$\mathbf{B}_{-}^{(L)} = B_0(\mathbf{j}-\mathrm{i}\mathbf{i})\exp(-\mathrm{i}\theta_L), \qquad \mathbf{B}_{-}^{(R)} = B_0(\mathbf{j}+\mathrm{i}\mathbf{i})\exp(-\mathrm{i}\theta_R),$$
$$\mathbf{B}_{+}^{(L)} = B_0(\mathbf{j}+\mathrm{i}\mathbf{i})\exp(\mathrm{i}\theta_L), \qquad \mathbf{B}_{+}^{(R)} = B_0(\mathbf{j}-\mathrm{i}\mathbf{i})\exp(\mathrm{i}\theta_R),$$
$$\theta_L = \omega t - \mathbf{k}_L\cdot\mathbf{r}, \qquad \theta_R = \omega t - \mathbf{k}_R\cdot\mathbf{r}.$$

For each molecule of the ensemble the Hellman–Feynman theorem gives

$$\frac{\partial E_n}{\partial \mathbf{E}} = \left\langle \frac{\partial H}{\partial \mathbf{E}} \right\rangle_e = -\langle \boldsymbol{\mu} \rangle_e \qquad \frac{\partial E_n}{\partial \mathbf{B}} = \left\langle \frac{\partial H}{\partial \mathbf{B}} \right\rangle_e = -\langle \mathbf{m} \rangle_e \tag{2}$$

from the Hamiltonian (1). Here $\langle\ \rangle_e$ denotes an 'expectation value'. A double Taylor expansion of the energy gives

$$\begin{aligned} E_n(\mathbf{E},\mathbf{B}) &= E_{n_{0,0}} + \boldsymbol{\mu}_0\mathbf{E} + \mathbf{m}_0\mathbf{B} \\ &+ (1/2!)(\boldsymbol{\alpha}_1\mathbf{EE} + \boldsymbol{\alpha}_2\mathbf{EB} + \mathbf{a}_2\mathbf{BE} + \mathbf{a}_1\mathbf{BB}) \\ &+ (1/3!)(\boldsymbol{\beta}_1\mathbf{EEE} + \boldsymbol{\beta}_2\mathbf{EEB} + \ldots) \\ &+ \ldots, \end{aligned} \tag{3}$$

a sum of scalar components of complete tensor products of field- and molecular-property tensors defined as follows:

$$\boldsymbol{\mu}_0 \equiv -\left(\frac{\partial E_n}{\partial \mathbf{E}}\right)_{00}, \qquad \mathbf{m}_0 \equiv -\left(\frac{\partial E_n}{\partial \mathbf{B}}\right)_{00}, \qquad \boldsymbol{\alpha}_1 \equiv -\left(\frac{\partial^2 E_n}{\partial \mathbf{E}\,\partial \mathbf{E}}\right)_{00},$$
$$\boldsymbol{\alpha}_2 \equiv -\left(\frac{\partial^2 E_n}{\partial \mathbf{E}\,\partial \mathbf{B}}\right)_{00}, \qquad \mathbf{a}_2 \equiv -\left(\frac{\partial^2 E_n}{\partial \mathbf{B}\,\partial \mathbf{E}}\right)_{00}, \qquad \mathbf{a}_1 \equiv -\left(\frac{\partial^2 E_n}{\partial \mathbf{B}\,\partial \mathbf{B}}\right)_{00},$$
$$\boldsymbol{\beta}_1 \equiv -\left(\frac{\partial^3 E_n}{\partial \mathbf{E}\,\partial \mathbf{E}\,\partial \mathbf{E}}\right)_{00}, \qquad \boldsymbol{\beta}_2 \equiv -\left(\frac{\partial^3 E_n}{\partial \mathbf{E}\,\partial \mathbf{E}\,\partial \mathbf{B}}\right)_{00},$$
$$\mathbf{b}_1 \equiv -\left(\frac{\partial^3 E_n}{\partial \mathbf{B}\,\partial \mathbf{B}\,\partial \mathbf{B}}\right)_{00}, \qquad \mathbf{b}_2 \equiv -\left(\frac{\partial^3 E_n}{\partial \mathbf{B}\,\partial \mathbf{B}\,\partial \mathbf{E}}\right)_{00}, \ldots,$$
$$\boldsymbol{\gamma}_1 \equiv -\left(\frac{\partial^4 E_n}{\partial \mathbf{E}\,\partial \mathbf{E}\,\partial \mathbf{E}\,\partial \mathbf{E}}\right)_{00}, \qquad \boldsymbol{\gamma}_2 \equiv -\left(\frac{\partial^4 E_n}{\partial \mathbf{E}\,\partial \mathbf{E}\,\partial \mathbf{E}\,\partial \mathbf{B}}\right)_{00}, \ldots,$$
$$\mathbf{g}_1 \equiv -\left(\frac{\partial^4 E_n}{\partial \mathbf{B}\,\partial \mathbf{B}\,\partial \mathbf{B}\,\partial \mathbf{B}}\right)_{00}, \qquad \mathbf{g}_2 = -\left(\frac{\partial^4 E_n}{\partial \mathbf{B}\,\partial \mathbf{B}\,\partial \mathbf{B}\,\partial \mathbf{E}}\right)_{00}, \ldots,$$

The total electric dipole moment is therefore the series sum

$$\begin{aligned} \boldsymbol{\mu} &= \boldsymbol{\mu}_0 + \boldsymbol{\alpha}_1\mathbf{E} + \boldsymbol{\alpha}_2\mathbf{B} + (1/2!)(\boldsymbol{\beta}_1\mathbf{EE} + \boldsymbol{\beta}_2\mathbf{EB} + \boldsymbol{\beta}_3\mathbf{BE} + \boldsymbol{\beta}_4\mathbf{BB}) \\ &+ (1/3!)(\boldsymbol{\gamma}_1\mathbf{EEE} + \boldsymbol{\gamma}_2\mathbf{EEB} + \boldsymbol{\gamma}_3\mathbf{EBE} + \boldsymbol{\gamma}_4\mathbf{EBB} \\ &+ \boldsymbol{\gamma}_5\mathbf{BEE} + \boldsymbol{\gamma}_6\mathbf{BEB} + \boldsymbol{\gamma}_7\mathbf{BBE} + \boldsymbol{\gamma}_8\mathbf{BBB}) \\ &+ (1/4!)(\ldots) \\ &+ \ldots \end{aligned} \tag{4}$$

and the total magnetic dipole moment

$$\begin{aligned}\mathbf{m} = \mathbf{m}_0 &+ \mathbf{a}_1\mathbf{B} + \mathbf{a}_2\mathbf{E} + (1/2!)(\mathbf{b}_1\mathbf{BB} + \mathbf{b}_2\mathbf{BE} + \mathbf{b}_3\mathbf{EB} + \mathbf{b}_4\mathbf{EE}) \\ &+ (1/3!)(\mathbf{g}_1\mathbf{BBB} + \mathbf{g}_2\mathbf{BBE} + \mathbf{g}_3\mathbf{BEB} + \mathbf{g}_4\mathbf{BEE} \\ &+ \mathbf{g}_5\mathbf{EBB} + \mathbf{g}_6\mathbf{EBE} + \mathbf{g}_7\mathbf{EEB} + \mathbf{g}_8\mathbf{EEE}) \\ &+ (1/4!)(\ldots) \\ &+ \ldots \end{aligned} \tag{5}$$

3. Symmetry analysis

The irreducible representations of each molecular property (MP) and field tensor can be defined [1–5] in two point groups of interest: $R_h(3)$ for ensembles of structurally achiral molecules and R(3) for ensembles of chiral molecules. These are respectively the group of all rotations and reflections; and the group of all rotations. The irreducible representations of both are the well known D symbols [1–5], which are related to the spherical harmonics. For $R_h(3)$, superscripts 0, 1, 2, ..., n denote tensor order, and subscripts u or g denote $-$ or $+$ to the parity inversion operator P [1–5]. In R(3), the subscripts vanish, because P produces the opposite enantiomer.

The field- and MP-tensors also have $+$ or $-$ signatures under T, the time reversal operator. The overall P and T symmetries are built up from the fundamental definitions of **E** and **B** in terms of the scalar (ϕ) and vector (**A**) potentials

$$\mathbf{E} = -\partial\mathbf{A}/\partial t - \nabla\phi, \qquad \mathbf{B} = \nabla \times \mathbf{A} \tag{6}$$

from which **E** is $-$ to P and $+$ to T and **B** is $+$ to P and $-$ to T.

With these definitions the third principle of GTSM can be applied to define the new ensemble averages created by the Hamiltonian (1). The ensemble responds to the field through the MP tensors, and in consequence the third principle [1–5] asserts that the symmetry of any ensemble average at field-on equilibrium is part of the complete products on the right-hand sides of equations (3), (4), and (5). The symmetry of energy (equation (3)) in $R_h(3)$ is the totally symmetric $D_g^{(0)}(+)$, where T symmetry is denoted in brackets; that of the electric dipole (equation (4)) is $D_u^{(1)}(+)$ and of **m** (equation (5)) $D_g^{(1)}(-)$. According to the third principle these are generated, term by term, as parts of the appropriate sums of complete tensor products on the right-hand sides of equations (3), (4) and (5).

4. Symmetry of optical rotation

The accepted definition of rotational strength (R) is the Rosenfeld equation [22], which makes R proportional to the pseudoscalar product of $\boldsymbol{\mu}$ and **m**, having $D_u^{(0)}(-)$ symmetry. Rosenfeld's signature is one part of the MP tensor $\boldsymbol{\alpha}_2$, which appears to first order in **B** in the expansion (4) of the total electric dipole moment, and thus contributes at first order to the electromagnetically induced molecular electric dipole moment through the complete tensor product $\boldsymbol{\alpha}_2\mathbf{B}$.

The third principle therefore asserts in this context that the symmetry of the induced electric dipole moment is generated through the $D_u^{(1)}(+)$ parts of the complete product of that of the magnetic component **B** of the electromagnetic field with the MP tensor $\boldsymbol{\alpha}_2$. This tensor may be defined through the relation (equation (3)):

$$\boldsymbol{\alpha}_2 = -\partial^2 E_n/(\partial\mathbf{E}\,\partial\mathbf{B}) \tag{7}$$

i.e. it is the partial differential of the energy with respect to the complete product **EB**.

Table 1. D-symmetries of molecular properties and field tensors for optical rotation: $R_h(3)$†

Molecular property	Field		Part of dipole moment	$D_u^{(0)}$	Order
α_2, $\mathbf{a}_2$ — $D_u^{(0)}+D_u^{(1)}+D_u^{(2)}(-)$	**B**	$D_g^{(1)}(-)$	μ	1	1
	E	$D_u^{(1)}(+)$	**m**	1	1
β_1	**EE**	$D_g^{(0)}+D_g^{(1)}+D_g^{(2)}(+)$	μ	1	2
β_4, $\mathbf{b}_2$, $\mathbf{b}_3$ — $D_u^{(0)}+3D_u^{(1)}+2D_u^{(2)}+D_u^{(3)}(+)$	**BB**	$D_g^{(0)}+D_g^{(1)}+D_g^{(2)}(+)$	μ	1	2
	BE	$D_u^{(0)}+D_u^{(1)}+D_u^{(2)}(-)$	**m**	1	2
	EB	$D_u^{(0)}+D_u^{(1)}+D_u^{(2)}(-)$	**m**	1	2
γ_2, γ_3, γ_5, γ_8 — $3D_u^{(0)}+6D_u^{(1)}+6D_u^{(2)}+3D_u^{(3)}+D_u^{(4)}(-)$	**EEB**	$D_g^{(0)}+3D_g^{(1)}+2D_g^{(2)}+D_g^{(3)}(-)$	μ	3	3
	EBE		μ	3	3
	BEE		μ	3	3
	BBB		μ	3	3
$\mathbf{g}_2$, $\mathbf{g}_3$, $\mathbf{g}_5$ — $D_u^{(0)}+3D_u^{(1)}+2D_u^{(2)}+D_u^{(3)}(+)$	**BBE**	$D_u^{(0)}+3D_u^{(1)}+2D_u^{(2)}+D_u^{(3)}(+)$	**m**	3	3
	BEB		**m**	3	3
	EBB		**m**	3	3

† For R(3) remove *g* or *u* subscripts.

Table 2. Known and new optical-rotation effects to third order with suggested nomenclature.

Effect	Origin		Accompanies	Reference	Status
'Rosenfeld' optical rotation ('First order **B** rotation')	α_2 **B** part of	μ	polarization	[22]	known
'first order **E** rotation'	$\mathbf{a}_2$**E**	**m**	magnetization	—	new
'second order **EE** rotation'	β_1**EE**	μ	polarization	—	new
magneto-chiral birefringence ('second order **BB** rotation')	β_4**BB**	μ	polarization	[24]	known
Inverse magneto-chiral birefringence ('second order **BE** and **EB** rotations')	$\mathbf{b}_2$**BE**, $\mathbf{b}_3$**EB**	**m**	magnetization	[25]	known
'third order **EEB** rotation'	γ_2**EEB**	μ	polarization	—	new
'third order **EBE** rotation'	γ_3**EBE**	μ	polarization		
'third order **BEE** rotation'	γ_5**BEE**	μ	polarization		
'third order **BBB** rotation'	γ_8**BBB**	μ	polarization		
'third order **BBE** rotation'	$\mathbf{g}_2$**BBE**	**m**	magnetization		
'third order **BEB** rotation'	$\mathbf{g}_3$**BEB**	**m**	magnetization		
'third order **EBB** rotation'	$\mathbf{g}_5$**EBB**	**m**	magnetization		
'third order **EEE** rotation'	$\mathbf{g}_8$**EEE**	**m**	magnetization		

Proceeding analogously we can define other optical-rotatory effects which are not recorded in the literature. In so doing, we will develop a definition of the symmetry signature of optical rotation, which is based on the occurrence of the signatures $D_u^{(0)}(+)$ or $D_u^{(0)}(-)$ in the MP tensors, some of which are summarized in table 1.

5. Some new optical rotatory effects

These are classified as 'linear' if they accompany the induction of an electric- or magnetic-dipole moment through a field–MP product which is linear in either **E** or **B**. Thus Rosenfeld's equation is classified as linear. Otherwise, the optical rotatory effect is 'nonlinear'.

An optical rotatory effect occurs whenever an MP tensor contains $D_u^{(0)}$, with either + or − T symmetry. They are summarized in table (2), and referred there to any known documented effects.

6. Discussion

The literature contains some references to definitions of 'natural' and 'magnetic' optical rotation [23]. 'Natural' or 'true' optical rotation is defined by Barron [23] as always being $D_u^{(0)}(+)$ and 'magnetic' optical rotation as $D_g^{(1)}(-)$, the symmetry of **B**. One of the problems with this type of classification is that it appears to treat rotatory effects in an *ad hoc* manner, with no unifying framework. Thus magneto-chiral optical rotation (table 2) is classified [23] as $D_u^{(1)}(-)$. In light of the definition in section 5, different classifications for the same observable (optical rotation) become superfluous, we need only look to see if the relevant MP tensor contains $D_u^{(0)}$. Expansions (3) to (5) provide the framework for a unified treatment of all the various nonlinear optical effects. Only a tiny minority of these are named (table 2) in the literature, implying that there are many left unexplored, even at low order in the field components. Within this framework, the magneto-chiral effect [24] is treated through the molecular property tensor $\boldsymbol{\beta}_4$, which contains $D_u^{(0)}(+)$: it is an electric dipole moment induced by $(1/2!)\boldsymbol{\beta}_4\mathbf{BB}$. The molecular property tensor $\boldsymbol{\beta}_4$ contains $D_u^{(0)}(+)$, signifying that optical rotation is possible. To observe this rotation we can use intense plane-polarised laser radiation in R(3), an ensemble of chiral molecules. This powerful plane-polarised laser has equal (R) and (L) circularly polarised components, as usual, and the chirality of R(3) means that rotation of the (L) component is not balanced by that of the (R). The magneto-chiral effect can be thought of as the second-order (nonlinear) equivalent of Rosenfeld optical rotation, which is generated through $\boldsymbol{\alpha}_2\mathbf{B}$. The third-order effect in this sequence is generated through $(1/3!)\boldsymbol{\gamma}_8\mathbf{BBB}$, whose $\boldsymbol{\gamma}_8$ contains $D_u^{(0)}$ three times, signifying three independent third-order optical-rotatory effects. Note that the T symmetry of the MP tensor alternates, being $(-1)^n$, where n is the order of the effect. This is simply due to the fact that magnetic components $\mathbf{B}^n$ are inducing an electric-dipole moment through the appropriate MP tensor. Clearly, **B** may be a magnetic component of an electromagnetic field, as in tables (1) and (2), or a separate magnetic field. The latter is the case discussed by Barron [23] and Wagnière and Meier [24].

This treatment can be repeated for other series of effects, as in tables (1) and (2), for example the inverse magneto-chiral effect, recently proposed by Wagnière [25].

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