

Axial and circular birefringence due to static electric and magnetic field combinations

M. W. Evans

Theory Center, Cornell University, Ithaca, New York 14853

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Axial and circular birefringence are derived for a combination of static electric field strength (\mathbf{E}_S) and static magnetic flux density (\mathbf{B}_S). For \mathbf{E}_S parallel to \mathbf{B}_S in the Z axis of the laboratory frame (X, Y, Z) the refractive index measured in a chiral ensemble with unpolarized light with wave vector \mathbf{K}_Z , propagating in Z , is different for \mathbf{K}_Z parallel and antiparallel to \mathbf{E}_{SZ} for fixed \mathbf{B}_{SZ} or vice versa. The effect is c times greater in magnitude than axial birefringence due to \mathbf{B}_{SZ} alone and is proportional to the product $\mathbf{B}_S \cdot \mathbf{E}_S$ and to the ensemble average $\langle A'_{1XXZZ} \rangle$, where \mathbf{A}_1 is an odd parity tensor mediating the effect of $\mathbf{B}_S \cdot \mathbf{E}_S$ on the molecular polarizability. Circular birefringence due to $\mathbf{E}_S \cdot \mathbf{B}_S$ also occurs in chiral ensembles only, but is c times smaller than axial birefringence. It is proportional to the ensemble average $\langle A''_{2XXZZ} \rangle$, where \mathbf{A}_2 is an even parity tensor mediating the effect of $\mathbf{E}_S \cdot \mathbf{B}_S$ on the molecular Rosenfeld tensor. There are no equivalent effects due to \mathbf{E}_S alone, $\mathbf{E}_S \cdot \mathbf{E}_S$ or $\mathbf{B}_S \cdot \mathbf{B}_S$, because they violate reversality. The $\mathbf{E}_S \cdot \mathbf{B}_S$ effects conserve reversality both in achiral and chiral ensembles, and provide information on new molecular property tensors. Their frequency dependencies provide novel molecular spectroscopies, and experimental configurations are suggested.

I. INTRODUCTION

In 1846 Faraday showed experimentally that the plane of polarization of a light beam is rotated by static magnetic flux density (\mathbf{B}_S) in lead borate glass. Subsequently, this well-known Faraday effect has been the basis for countless investigations of achiral and chiral molecular ensembles, and has become well known as "magnetic optical activity." The angle of rotation is proportional experimentally to \mathbf{B}_S through the well-known Verdet constant. On the other hand, optical activity induced by static electric field strength (\mathbf{E}_S) appears to have never been reported. Faraday's diary, reviewed by Bragg,¹ shows that he attempted the experiment and concluded that there was no effect. Barron has suggested^{2,3} that a careful distinction be maintained between the magnetic optical activity of the Faraday effect and natural optical activity, which is observed without \mathbf{B}_S in chiral ensembles only.

The reasons for the negative result with \mathbf{E}_S were obscure until symmetry arguments were developed by Buckingham, Graham, and Raab⁴ and by Barron⁵ based on the basic concepts by Wigner⁶ of complete experiment time-reversal symmetry (T) (reversality) and parity reversal (P). A good account is given in Ref. 3, where it is argued that circular birefringence due to \mathbf{E}_S violates reversality; the motion reversed complete experiment does not match the original, either in achiral or chiral molecular ensembles.

Nearly 140 years after Faraday's discovery, Wagnière and Meier⁷⁻⁹ deduced theoretically that \mathbf{B}_S also produces forward-backward (or axial) birefringence in chiral ensembles; the refractive index measured with unpolarized radiation parallel to \mathbf{B}_S is different from the antiparallel equivalent. This was named magnetochiral birefringence,¹⁰ but has not yet been observed experimentally, because it is a small effect and stretches contemporary instrumentation¹⁰ to the

limit. If observed, however, it would give interesting and novel information on frequency-dependent molecular property tensors. Several new axial and circular birefringence effects have been deduced recently¹¹⁻¹⁴ based on symmetry arguments¹⁵⁻¹⁸ and application of the Maxwell equations. Among these are circular and axial birefringence due to the electric part of optical rectification,¹¹ which appears to be several orders of magnitude larger than the magnetic field equivalents, and which conserve reversality.¹² The molecular dynamics of this effect have been investigated by computer simulation, using the appropriate torque between radiation and ensemble.¹⁹ The dynamics have also been animated on video.²⁰ Magnetochiral birefringence has been discussed by Wozniak²¹ in the context of laser fields, and applied to parity violation by Wagnière,²² a fundamental advance reviewed recently by Barron.^{2,23} Inverse magnetochiral birefringence has been reported recently by Wagnière²⁴ and several related effects are proposed in Refs. 11-14.

In this paper, it is shown that in chiral ensembles, there exist circular and axial birefringence due to a combination of \mathbf{E}_S and \mathbf{B}_S . In general, \mathbf{E}_S may be in any direction relative to \mathbf{B}_S . The particular case is considered for \mathbf{E}_S and \mathbf{B}_S in the Z axis of the laboratory frame (X, Y, Z), and it is shown that circular birefringence is induced in achiral and chiral ensembles in electromagnetic radiation propagating in Z with wave vectors \mathbf{K}_{RZ} or \mathbf{K}_{LZ} , denoting respectively right and left circularly polarized component wave vectors. The effect is proportional to the product of \mathbf{E}_S and \mathbf{B}_S . Axial and circular birefringence are induced by this product in chiral ensembles only. Both effects are mediated by new frequency-dependent molecular property tensors, providing novel and specific spectral information on the chiral molecular ensemble. Therefore, by adding magnetic flux density, the elusive electric field equivalent of the Faraday effect becomes visible in chiral ensemble. In Sec. II, the bulk polarization and mag-

netization due to $\mathbf{E}_S \cdot \mathbf{B}_S$ are defined in terms of Voigt-Born perturbations²⁵ of the molecular polarizability and optical activity tensors, which are, in general, complex and frequency dependent.³ Section III shows that circular and axial birefringence due to $\mathbf{E}_S \cdot \mathbf{B}_S$ conserve reversality both in achiral and chiral molecular ensembles. The circular birefringence conserves overall parity of the complete experiment in all ensembles, and the axial equivalent in chiral ensembles. Section IV solves the Maxwell equations for the new effects. Section V, finally, is a discussion and suggests experimental configurations, providing an order-of-magnitude estimate for each effect.

II. THE MOLECULAR PROPERTY TENSORS

The starting point of the derivation is a Taylor expansion²⁵ of the bulk polarization (P_i) and magnetization (M_i) in terms of the electric (\mathbf{E}) and magnetic (\mathbf{B}) field components of the probe electromagnetic radiation, and their gradients. Both P_i and M_i are proportional to the field terms through various molecular property tensors which are themselves perturbed by the static electric and magnetic fields through Voigt-Born²⁵ expansions. Thus, in standard tensor notation

$$\begin{aligned} \frac{P_i}{N} = & \alpha_{1ij} E_j + \alpha_{2ij} B_j + \frac{1}{3} (\alpha_{3ijk} \nabla_j E_k + \alpha_{4ijk} \nabla_j B_k) \\ & + \frac{1}{15} (\alpha_{5ijkl} \nabla_j \nabla_k E_l + \alpha_{6ijkl} \nabla_j \nabla_k B_l) \\ & + \dots + \text{cross terms} + \dots \end{aligned} \quad (1)$$

and

$$\begin{aligned} \frac{M_i}{N} = & \beta_{1ij} B_j + \beta_{2ij} E_j + \frac{1}{3} (\beta_{3ijk} \nabla_j B_k + \beta_{4ijk} \nabla_j E_k) \\ & + \frac{1}{15} (\beta_{5ijkl} \nabla_j \nabla_k B_l + \beta_{6ijkl} \nabla_j \nabla_k E_l) \\ & + \dots + \text{cross terms} + \dots \end{aligned} \quad (2)$$

Here $\alpha_{1ij}(\mathbf{B}_S, \mathbf{E}_S)$ is the molecular polarizability tensor; $\alpha_{2ij}(\mathbf{B}_S, \mathbf{E}_S)$ is the molecular Rosenfeld (optical activity) tensor; $\alpha_{3ijk}(\mathbf{B}_S, \mathbf{E}_S)$ is the electric dipole-electric quadrupole tensor, and so on. N is the number of molecules per meter.³ Similar tensors occur for the expansion of M_i in terms of \mathbf{E} and \mathbf{B} . Each of these tensors is also perturbed by \mathbf{E}_S and \mathbf{B}_S through the following double Voigt-Born expansions:

$$\begin{aligned} \alpha_{1ij}(\mathbf{B}_S, \mathbf{E}_S) = & \alpha_{1ij}(0,0) + a_{1ijk} E_{Sk} + a_{2ijk} B_{Sk} \\ & + \frac{1}{2!} (a_{3ijkl} E_{Sk} E_{Sl} + a_{4ijkl} E_{Sk} B_{Sl} \\ & + a_{5ijkl} B_{Sk} E_{Sl} + a_{6ijkl} B_{Sk} B_{Sl}) + \dots, \end{aligned} \quad (3)$$

$$\begin{aligned} \alpha_{2ij}(\mathbf{B}_S, \mathbf{E}_S) = & \alpha_{2ij}(0,0) + b_{1ijk} E_{Sk} + b_{2ijk} B_{Sk} \\ & + \frac{1}{2!} (b_{3ijkl} E_{Sk} E_{Sl} + b_{4ijkl} E_{Sk} B_{Sl} \\ & + b_{5ijkl} B_{Sk} E_{Sl} + b_{6ijkl} B_{Sk} B_{Sl}) + \dots, \end{aligned} \quad (4)$$

$$\begin{aligned} \alpha_{3ijk}(\mathbf{B}_S, \mathbf{E}_S) = & \alpha_{3ijk}(0,0) + c_{1ijkl} E_{Sk} \\ & + c_{2ijkl} B_{Sk} + \frac{1}{2!} (C_{3ijklm} E_{Sl} E_{Sm} \\ & + C_{4ijklm} E_{Sl} B_{Sm} + \dots) + \dots, \end{aligned} \quad (5)$$

and so on.

The perturbing three rank tensors a_{1ijk} , b_{2ijk} , and c_{1ijkl} , for example, are used in the standard treatment of the Faraday effect.³ In this paper we confine attention specifically to the tensors in Eqs. (3)–(5) which premultiply the products $E_{Si} B_{Sj}$, and solve the Maxwell equations for their specific influence on axial and circular birefringence.

III. CONSERVATION OF REVERSALITY AND PARITY IN THE COMPLETE EXPERIMENT

Symmetry diagram (1) illustrates the conservation of reversality and parity utilizing the three vectors \mathbf{E}_S , \mathbf{B}_S , and \mathbf{K}_Z in the Z axis of frame (X, Y, Z) . The panels also illustrate the effect of T and P on the circular birefringence variable, which is denoted by the symbol $(\theta_{11} - \theta_{11})$. The equivalent for axial birefringence is denoted by $n_{11} - n_{11}$. The effect of T and P on frame (X, Y, Z) itself is denoted by the next symbol. Finally, their effects are illustrated on a typical molecular achiral structure (water) and simple chiral structure (a molecular enantiomer). The panels therefore apply Wigner's principles to the variables of the complete experiment.³ This analysis is necessary before solving the Maxwell equations.

The effect of T is as follows (Fig. 1, right-hand panel). It reverses \mathbf{K}_Z and \mathbf{B}_S , but leaves \mathbf{E}_S unaffected. The T symmetry of the product $E_{Si} B_{Sj}$ is therefore negative. This is denoted in the right-hand panel of Fig. 1, which also illus-

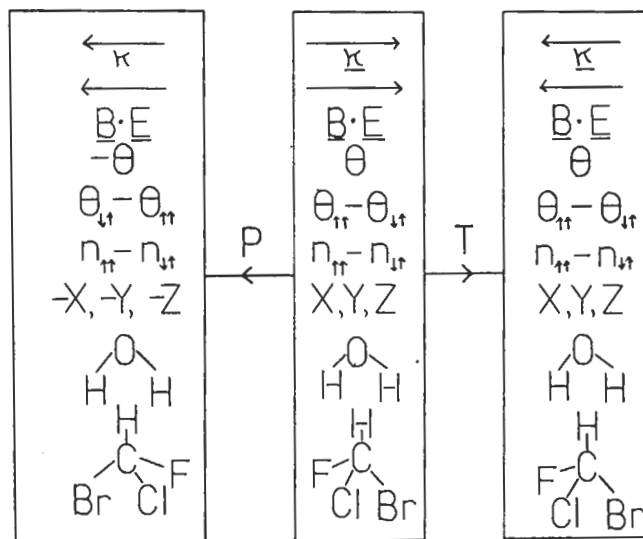


FIG. 1. Reversality and parity inversion symmetry of the variables in the complete experiment. From top to bottom in each panel: the propagation vector \mathbf{K} of the electromagnetic field; the product $\mathbf{E} \cdot \mathbf{B}$; the angle of rotation, θ , of plane polarized radiation; difference in this angle for \mathbf{E} parallel to \mathbf{B} both parallel to \mathbf{K} and both antiparallel with \mathbf{K} ; refractive index (n) of unpolarized radiation with \mathbf{E} parallel to \mathbf{B} and both antiparallel with \mathbf{K} ; the laboratory frame; water structure; a simple chiral molecular structure. Right-hand panel, variables in the motion-reversed experiment; left-hand panel, variables in the parity-inverted experiment.

trates the effect on the other observables. These bear the same relation to each other in the motion-reversed experiment, which therefore conserves reversality.³ The reversality symmetry is actually the same as that of the Faraday effect (\mathbf{B}_S alone). Circular and axial birefringence due to the product $E_{Si}B_{Sj}$ conserves T in all ensembles.

The left-hand panel of Fig. 1 illustrates the analogous effect of P . This reverses \mathbf{K}_S and \mathbf{E}_Z , leaving \mathbf{B}_S unaffected. The P symmetries of \mathbf{K}_Z and the product $E_{Si}B_{Sj}$ are therefore both negative. As in the motion-reversed experiment (right-hand panel of Fig. 1), the relative directions of \mathbf{K}_Z and $E_{Si}B_{Sj}$ are unchanged in the P -reversed experiment (right-hand panel of Fig. 1). However, the circular rotation variable is reversed in sign by P , but the axial variable is not. Consideration of parity reversal of the general experiment therefore implies that axial birefringence due to $E_{Si}B_{Sj}$ can exist in both chiral and achiral molecular ensembles, and the equivalent circular birefringence in chiral ensembles only. We shall see that symmetry restrictions on the mediating tensors further confine the existence of the axial effect to chiral ensembles only.

IV. SOLVING THE MAXWELL EQUATIONS

Having checked on the conservation of reversality in the complete experiment, it is reasonable to proceed to a solution of the Maxwell equations, which are written in tensor notation as

$$H_k = \frac{1}{\mu_0} (B_k - M_k), \quad D_i = \epsilon_0 E_i + P_i, \quad (6)$$

giving³

$$n_j \epsilon_{ijk} (B_k - M_k) = -\mu_0 c (\epsilon_0 E_i + P_i). \quad (7)$$

Here H_k is a component of the magnetic field strength, and D_i a component of the electric displacement. The symbol ϵ_{ijk} denotes the antisymmetric Levi-Civita tensor, whose non-vanishing components are

$$\begin{aligned} \epsilon_{XYZ} = \epsilon_{ZXY} = \epsilon_{YZX} = 1, \\ \epsilon_{XZY} = \epsilon_{YXZ} = \epsilon_{ZYX} = -1. \end{aligned} \quad (8)$$

In Eqs. (6) and (7), μ_0 and ϵ_0 are, respectively, the magnetic permeability and electric permittivity *in vacuo*. Finally, n_j is a component of the complex refractive index and c the velocity of light. Working out the tensor products for Z axis refractive index gives the Maxwell equation in the form

$$n_Z (B_X - M_X) = -\mu_0 c (\epsilon_0 E_Y + P_Y + P_Y^{(1)} n_Z), \quad (9)$$

where $P_Y^{(1)}$ comes from the dominant gradient term, involving the electric dipole-electric quadrupole tensor α_{3ijk} . Equation (9) gives the complex refractive index in the form

$$n_Z = \frac{-\mu_0 c}{B_X} (\epsilon_0 E_Y + P_Y) (1 - x)^{-1} \quad (10)$$

$$= \frac{-\mu_0 c}{B_X} (\epsilon_0 E_Y + P_Y) (1 + x + \dots), \quad (11)$$

where

$$x = \frac{M_X - c P_Y^{(1)}}{B_X}. \quad (12)$$

For $x \ll 1$ this reduces to the simple result

$$n_Z \doteq \frac{-\mu_0 c}{B_X} (\epsilon_0 E_Y + P_Y) \quad (13)$$

valid for dilute solutions of chiral molecules in achiral solvents. Splitting this equation into real and complex parts of the refractive index, defined by

$$n_Z \equiv n'_Z + i n''_Z, \quad (14)$$

and separating right (R) and left (L) circularly polarized components, gives the core equations¹⁴

$$(n'_{LZ} - n'_{RZ}) = 2\mu_0 c N (\alpha''_{1XY} c - \alpha''_{2XX}), \quad (15)$$

$$(n''_{LZ} - n''_{RZ}) = 2\mu_0 c N (\alpha'_{2XX} - \alpha'_{1XY} c) \quad (16)$$

for circular birefringence and dichroism, respectively. For axial birefringence we can take the average

$$n'_{avZ} = \frac{1}{2} (n'_{LZ} + n'_{RZ}), \quad (17)$$

giving the core equations

$$n'_{avZ} = \mu_0 c (\epsilon_0 c + N c \alpha'_{1XX} + N \alpha'_{2XY}), \quad (18)$$

$$n''_{avZ} = \mu_0 c N (\alpha''_{1XX} c + \alpha''_{2XY}), \quad (19)$$

and

$$A (\text{neper cm}^{-1}) = 2 \frac{\omega}{c} n''. \quad (20)$$

We now introduce the specific perturbations

$$\alpha''_{2XX} (\mathbf{E}_S, \mathbf{B}_S) = \alpha''_{2XX} (0,0) \pm E_{SZ} B_{SZ} A''_{2XXZZ} \quad (21)$$

and

$$\alpha'_{1XX} (\mathbf{E}_S, \mathbf{B}_S) = \alpha'_{1XX} (0,0) \pm E_{SZ} B_{SZ} A'_{1XXZZ} \quad (22)$$

where the plus sign denotes that the product $E_{SZ} B_{SZ}$ is parallel to the wave vector of the radiation, propagating in $+Z$. The minus sign means that the product is antiparallel to the wave vector. Introduction of the perturbations into the core equations gives the desired circular and axial birefringence (and dichroism). The circular birefringence is

$$\begin{aligned} \langle n'_{LZ} - n'_{RZ} \rangle_{11} - \langle n'_{LZ} - n'_{RZ} \rangle_{11} \\ = -4\mu_0 c N \langle A''_{2XXZZ} \rangle E_{SZ} B_{SZ}, \end{aligned} \quad (23)$$

and the axial birefringence is

$$\langle n_{av} \rangle_{11} - \langle n_{av} \rangle_{11} = 2\mu_0 c^2 N \langle A'_{1XXZZ} \rangle E_{SZ} B_{SZ}. \quad (24)$$

Both results are isotropic averages, in which the tensor components $\langle A''_{2XXZZ} \rangle$ and $\langle A'_{1XXZZ} \rangle$ are the only ones not to vanish. The former has even parity and the latter odd parity. We therefore reach the following interesting conclusions:

(1) Circular birefringence due to $E_{SZ} B_{SZ}$ exists in chiral ensembles only, because of complete experiment parity reversal symmetry considerations. This is despite the fact that its mediating component $\langle A''_{2XXZZ} \rangle$ has even parity.

(2) Axial birefringence due to $E_{SZ} B_{SZ}$ is allowed in all ensembles by complete experiment parity reversal symmetry, but is also restricted to chiral ensembles only due to the fact that its mediating component $\langle A'_{1XXZZ} \rangle$ has odd parity.

We have repeated this analysis with the method of Barrow and Vrbancich,¹⁰ and their Eqs. (3.7) and (3.8) lead to the same results, (23) and (24) of this paper, because the fifth-rank tensors mediating the effect of $E_{SZ} B_{SZ}$ on the elec-

tric dipole–electric quadrupole tensor vanish after isotropic averaging.²⁶

V. DISCUSSION

Equation (24) for axial birefringence has the interesting property of being c times greater in magnitude than magnetochiral birefringence, which in this notation is given by

$$\langle \langle n_{av} \rangle_{11} - \langle n_{av} \rangle_{1i} \rangle_{B_{SZ}} = 2\mu_0 c N \langle b'_{2XYZ} \rangle_{B_{SZ}} + \text{quadrupole terms}, \quad (25)$$

where $\langle b'_{2XYZ} \rangle$ is a rank-three antisymmetric component. To observe the axial birefringence experimentally, electrodes are added to the Rayleigh refractometer arms described in Ref. 10. Holes are drilled to allow for passage of the probe laser, and strong magnetic fields are applied parallel and antiparallel in each arm. The circular birefringence (23) is similarly observed by this electrode modification of standard Faraday effect apparatus. In both cases the effect should be proportional to the product of applied static electric field strength and magnetic flux density. This isolates it from the Faraday effect itself, proportional to B_{SZ} , or from magnetochiral birefringence, also proportional to B_{SZ} . There are no effects proportional to E_{SZ} , because they would violate reversality of the complete experiment. Similarly, there are no effects proportional to $E_{SZ}E_{SZ}$ or $B_{SZ}B_{SZ}$, for the same reason. The experimental task would therefore consist of isolating the new effects from those proportional to B_{SZ} only. For axial birefringence this appears to be straightforward because the second-order effect is c times greater. However, the relative magnitudes also depend on those of the mediating ensemble averaged scalar components, such as $\langle b'_{2XYZ} \rangle$ and $\langle A'_{1XXZZ} \rangle$. In this respect the latter is a Voigt–Born perturbation of the molecular polarizability, whereas the former derives from the Rosenfeld tensor. The polarizability tensor is usually several orders of magnitude greater¹⁰ in S.I. units, suggesting that the second-order effect introduced here will dominate axial birefringence, especially for electric field strengths approaching 10^7 V per meter, as used, for example, by Buckingham and Shatwell.²⁷ This can be combined with intense magnetic fields from superconducting devices.

If so, the axial birefringence and dichroism will be frequency dependent, providing specific and novel spectral information on the chiral molecular crystal, liquid crystal, molecular liquid, or gas, essentially a new kind of molecular spectroscopy.

The circular birefringence due to $\langle A'_{2XXZZ} \rangle$ appears to

be more difficult to see, because it is c times smaller than the accompanying Faraday effect, given in this notation by

$$\langle \langle n'_{LZ} - n'_{RZ} \rangle_{11} - \langle n'_{LZ} - n'_{RZ} \rangle_{1i} \rangle_{B_{SZ}} = 4\mu_0 c^2 N \langle a''_{1XYZ} \rangle_{B_{SZ}} + \text{quadrupole terms}, \quad (26)$$

and is mediated by a perturbation of the smaller Rosenfeld tensor. However, the great sensitivity of the contemporary Faraday effect apparatus should be easily adequate for its isolation in chiral molecular ensembles. This would also be a novel source of information on the fundamental properties of chiral molecules.

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