On the Natural Optical Activity in an Isotropic Medium: An Exactly Solvable Model

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Introduction

Although natural optical activity (rotation of the plane of polarization of electromagnetic waves propagating through a medium) is well-known classical effect, which is mentioned in almost every text books on optics, it is not so often that a particular simple model of an isotropic medium possessing this property is found. Therefore the aim of this note is to present such a model, providing an explicit demonstration of how optical rotation in an isotropic medium is intimately related to the chirality (handedness) of individual molecules.

In a framework of macroscopic electrodynamics all properties of a homogeneous medium are completely described by its dielectric permeability tensor $\in_{\alpha\beta}(\omega,\mathbf{k})$ (see, for example, Ref.1), where ω is the frequency and **k** is the wave vector of the electromagnetic field. The dependence of $\in_{\alpha\beta}$ on ω and **k** represents, respectively, temporal and spatial dispersion in a medium, and the latter effect is essential in the natural optical activity under discussion. Since the size *l* of an individual molecule must be small compared with the wavelength $\lambda = 2\pi/k$ by the very nature of a macroscopic description, the spatial dispersion is usually weak, and one can expand the dielectric tensor in powers of a small parameter k*l*. For an isotropic transparent medium the first two terms in this series take, in general, the following form:

$$\in_{\alpha\beta}(\omega,\mathbf{k}) = \in(\omega)\delta_{\alpha\beta} + if(\omega)e_{\alpha\beta\gamma}k_{\gamma} \tag{1}$$

Here $\delta_{\alpha\beta}$ and $e_{\alpha\beta\gamma}$ are unit invariant tensors of the second and third rank, respectively, while $\in$ and f are real constants (the latter follows from the requirements that tensor $\in_{\alpha\beta}$ must be Hermitian for a transparent medium. [1] Solving Maxwell's equations for a plane electromagnetic wave of frequency ω propagating in a medium with dielectric tensor (1), it can be shown that the left- and right-hand circularly polarized waves have slightly different refractive indices, n_+ and n_-, respectively, with

$$n_{\pm} \approx \sqrt{\in} \pm f\frac{\omega}{2c} \tag{2}$$

This difference leads to rotation of the polarization plane with the following rate per unit path length of the ray:

$$\frac{d\theta}{ds} = \frac{\omega}{2c}(n_+ - n_-) = f\frac{\omega^2}{2c^2} \tag{3}$$

To understand natural optical activity, knowledge of the inversion transformation $(\mathbf{r} \to -\mathbf{r})$ and inversion symmetry are essential (see Ref. 2 for detailed discussion on the relation between the symmetry and optical activity). From this point of view the unit tensor $\in_{\alpha\beta\gamma}$ is actually a pseudotensor (see, e.g.,Ref.3), and since the dielectric tensor $\in_{\alpha\beta\gamma}$ must be a true tensor, it follows from (1) that constant f has to be a pseudoscalar, and thus it changes sign under inversion. Therefore a nonzero value of f means that the corresponding medium is not inversionally symmetric. In other words, there two nonsuperposable mirror image forms of a substance (so-called enantiomorphic phases, or stereoisomers), which generate optical rotation of equal magnitude but opposite sense. It is worth noting that natural optical activity is but one manifestation of chirality of a medium- there are other manifestations, for example, different reflection of right and left circularly polarized light. [4]

Throughout the analysis given so far, it has been tacitly assumed that all physical forces involved are invariant under the inversion transformation, or in other words, the parity conservation law holds.[2] If this is not true, as actually occurs for the weak interaction, it becomes possible, in principle, to get optical activity even in an isotropic medium without enantiomorphism,[5] though the effect is extremely small. Nevertheless, during the last two decades successful experiments have been performed, aiming to observe optical rotation in vapours of free atoms in order to detect parity violating coupling between the nucleus and orbital electrons due to "weak neutral currents."[6,7] There are even speculations that the handedness of certain organic molecules of biological importance is related to parity nonconservation in atoms and molecules.[8]

However, the present note is devoted to "classical" optical activity due to chirality of a medium. Thus in what follows we will consider in detail a gas of double – helical molecules first suggested in Ref. 9. In fact, helices (both polarisable and conducting) have been widely used during the last decade as model molecules in constructing artificial chiral composites.[10,11] The aim was to make a direct measurement of the constitutive parameters of such a chiral medium microwave experiments , and compare the results with calculations of electromagnetic waves scattering by helical macromolecules. Since the latter inevitably require advanced theoretical methods, which now form a specialized branch of applied electrodynamics,[12] our objective is to investigate a much simplified model which allows one to derive the "activity" constant *f* [see Eq.(1)] starting from first principles.

MODEL AND CALCULATIONS

Let us assume a rarefied gas of randomly oriented right-handed "double helices" shown in Fig. 1- two rigid helical threads of radius *a* and pitch *h* with the charge ± ρ per unit length of each. Under the action of an electric field, the threads become displaced relative to each other along the joint helical by the distance Δ proportional to the net projection of the field on the helix.

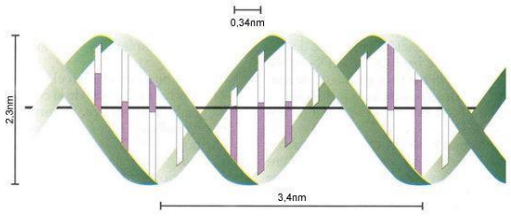

Fig. 1 The "double – helix" molecule.

$$\Delta = \beta \int_0^L \mathbf{E} \cdot d\mathbf{l} \tag{4}$$

with some coefficient β determined by the internal elasticity of a molecule.

To decide whether such a gas is optically active one needs to derive the gas dielectric tensor $\in_{\alpha\beta}$. In calculating the response of a molecule to the electromagnetic wave of frequency ω and wave vector **k** we assume that the size of a molecule is small compared with the wave length λ(i.e., ka, kh ≪ 1), so the electric field acting on a given molecule can be written approximately as

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \approx \mathbf{E}_0 e^{-i\omega t}(1 + i\mathbf{k}\cdot\mathbf{r}) \tag{5}$$

Where $\mathbf{E}_0 e^{-i\omega t}$ is the field at the origin of our coordinate system (point 0 in Fig.1). The orientation of a molecule is determined by two vectors: the unit vector **n** directed along the axis of a helix, and vector **a** denoting the tip of a molecule in the plane perpendicular to **n** (see Fig. 1). Then the position **R** of each molecular point along the helical line can be described by the parameter ϕ- the azimuthal angle in the projection on the plane orthogonal to **n**:

$$\mathbf{R}(\phi) = \frac{h}{2\pi}\varphi \, \mathbf{n} + \cos\phi \mathbf{a} + \sin\phi(\mathbf{n}\mathrm{x}\mathbf{a}) \tag{6}$$

So the integral in (4) is transformed to

$$\int_0^L \mathbf{E} \cdot d\mathbf{l} \approx \int_0^L \mathbf{E}_0 e^{-i\omega t}(1 + i\mathbf{k}\cdot\mathbf{R}) \cdot d\mathbf{R}$$

$$= \mathbf{E}_0 e^{-i\omega t} \int_0^{2\pi} \left\{ 1 + i\left[(\mathbf{k}\cdot\mathbf{n})h\frac{\varphi}{2\pi} + (\mathbf{k}\cdot\mathbf{a})\cos\varphi + \mathbf{k}\cdot(\mathbf{n}\mathrm{x}\mathbf{a})\sin\varphi \right] \right\}$$

$$\mathrm{x}\left[\frac{h}{2\pi}\mathbf{n} - \sin\varphi\mathbf{a} + \cos\varphi(\mathbf{n}\mathrm{x}\mathbf{a}) \right] d\phi \tag{7}$$

After straightforward integration of (7) the displacement of threads [Eq.(4)] takes the form

$$\Delta(n,a) = \beta e^{-i\omega t} \left\{ h(\mathbf{E}_0\cdot\mathbf{n}) + i\frac{h^2}{2}(\mathbf{E}_0\cdot\mathbf{n})(\mathbf{k}\cdot\mathbf{n}) + i(\mathbf{E}_0\cdot\mathbf{a})(\mathbf{k}\cdot\mathbf{n})h \right.$$

$$\left. -i\pi(\mathbf{E}_0\cdot\mathbf{a})\mathbf{k}\cdot(\mathbf{n}\mathrm{x}\mathbf{a}) + i\pi(\mathbf{k}\cdot\mathbf{a})\mathbf{E}_0\cdot(\mathbf{n}\mathrm{x}\mathbf{a}) \right\} \tag{8}$$

Since such displacement results in the appearance of electric charges ± q = ±ρΔ at the tips of the molecule, as well as in the electric current J = $\dot{\rho\Delta} = -i\omega\rho\Delta$ along the helix, the molecule gains electric (**d**) and magnetic (**m**) dipole moments equal to

$$\mathbf{d}=\mathbf{n}hq = \rho h\Delta\mathbf{n}, \quad \mathbf{m} = \frac{J}{c}\pi a^2\mathbf{n} = \frac{-i\omega\rho\Delta}{c}\pi a^2\mathbf{n} \tag{9}$$

Therefore the gas dielectric polarization **P** and magnetization **M** (the dielectric and magnetic dipole moments per unit volume, respectively) can be written as

$$\mathbf{P} = N\langle\mathbf{d}\rangle, \qquad \mathbf{M} = N\langle\mathbf{m}\rangle \tag{10}$$

where N is the number density of molecules and the symbol $\langle\ \rangle$ denotes an average over all possible orientations of molecules.

Knowing the polarization and magnetization of a medium it is possible to find the macroscopic (averaged) electric current, which relates to **P** and **M** in the following way (see, e.g., Ref 1):

$$\mathbf{j} = \frac{\partial\mathbf{P}}{\partial t} + c(\nabla x\mathbf{M}) = -i\omega\mathbf{P} + ic(\mathbf{k}x\mathbf{M}) \tag{11}$$

From this expression the conductivity tensor $\sigma_{\alpha\beta}$ can be derived, using its definition as $j_\alpha = \sigma_{\alpha\beta}E_\beta$. Finally, the dielectric permeability tensor is:

$$\in_{\alpha\beta} = \delta_{\alpha\beta} + \frac{4\pi i}{\omega}\sigma_{\alpha\beta} \tag{12}$$

The required macroscopic average in (10) can be perfomed in two steps. First, aasuming vector **n** fixed, one considers all possible directions of the vector **a** in the planr orthogonal to **n**. For example, using expression (8) for Δ in calculating vector $\langle\mathbf{d}\rangle$ from (9), the last term in the curly brackets of (8) results in the following contribution (written now in tensor notation):

$$i\pi\rho h\mathbf{n}(\mathbf{k}\cdot\mathbf{a})\mathbf{E}_0\cdot(\mathbf{n}x\mathbf{a}) = i\pi\rho h n_\alpha k_\beta a_\beta E_{0\gamma} e_{\gamma\delta\mu} n_\delta a_\mu \tag{13}$$

It can be easily checked that for a fixed vector **n**.

$$\langle a_\alpha\rangle = 0; \qquad \langle a_\beta a_\mu\rangle = \frac{a^2}{2}(\delta_{\beta\mu} - n_\beta n_\mu) \tag{14}$$

thus the first step average of (11) yields

$$i\pi\rho h\left\langle \mathbf{n}(\mathbf{k}\cdot\mathbf{a})\mathbf{E}_0\cdot(\mathbf{n}\mathrm{x}\mathbf{a})\right\rangle_a = i\pi\frac{a^2}{2}\rho h k_\beta E_{0\gamma} e_{\gamma\delta\beta} n_\alpha n_\delta \tag{15}$$

The fourth term in curly brackets of (8) gives the same contribution, while the thirds on tends to zero after the average.
In making now the second step (average over the randomly directed vector **n**) the following tensor relations are helpful:

$$\left\langle n_\alpha\right\rangle = 0; \qquad \left\langle n_\alpha n_\beta\right\rangle = 0; \qquad \left\langle n_\alpha n_\beta n_\gamma\right\rangle = 0 \tag{16}$$

thus yielding the gas polarization

$$P_\alpha = \tfrac{1}{3} N\beta\rho h e^{-i\omega t}\left[hE_{0\alpha} + i\pi a^2 e_{\alpha\gamma\delta} k_\gamma E_{0\delta}\right] \tag{17}$$

In calculating the gas magnetization **M** we first not that the corresponding contribution to the macroscopic current [the second term on the right –hand side of Eq. (11)] is already proportional to the wave vector **k**. Thus under the approximation adopted (weak spatial dispersion) it is sufficient to derive **M** with zeroth – order accuracy, retaining only the first term in right – hand side of (8). Then a simple average over **n** of expression (9) for **m** results in

$$\mathbf{M} = \frac{-i\omega\pi N\beta\rho a^2 h}{3c}\mathbf{E}_0 e^{-i\omega t} \tag{18}$$

Inserting now the above-obtained vectors **P** and **M** [Eqs.(17) and (18)] into (11), we get the macroscopic current

$$\mathbf{j} = -\frac{i\omega N\beta\rho}{3}\left[h^2\mathbf{E} + 2iha^2(\mathbf{k}\mathrm{x}\mathbf{E})\right] \tag{19}$$

and hence the conductivity tensor

$$\sigma_{\alpha\beta} = -\frac{-i\omega N h^2\beta\rho}{3}\delta_{\alpha\beta} - \frac{2\pi\omega N\beta\rho h^2}{3} e_{\alpha\beta\gamma} k_\gamma \tag{20}$$

Then according to (12), the dielectric permeability of such a gas is of the form (1) with

$$\in = 1 + \frac{4\pi N h^2\beta\rho}{3}$$

$$f = \frac{8\pi^2 N\beta\rho h a^2}{3} \tag{21}$$

Thus this gas of right – handed “double helices” indeed possesses the optical rotation effect determined by the constant *f* in (21). One can easily verify that for a gas of similar but left – handed molecules [formally the latter would be described by Eq. (6)with thr

opposite sign in the last term] the constant *f* simply changes its sign; therefore optical rotation would be equal magnitude but opposite sense. This two distinct forms are said to have opposite absolute configurations. Certainly, if a gas were a mixture of the two in equal proportions, from a macroscopic point of view this substance would not be enantiomorphic , and optical rotation would disappear.

It is also worth noting that the constant *f* tends to zero (and optical activity vanishes) under the limits $a \to 0$ or $h \to 0$. This is not surprising since in this limiting cases an initially helical molecule degenerates into a rod or a ring, respectively , thus losing its handedness. We conclude this section with two remarks. First, one can notice that the constants $\in$ y *f* in Eq. (21) do not depend on the frequency ω. This is a simple consequence of the model imposed: the response of a molecule (its displacement Δ) instantly adjusts to the electric field [Eq. (4)]; thus there is no temporal dispersion en such a gas. Second, it can be checked from Eqs. (11), (17), and (18) that polarization **P** and magnetization **M** generate equal contributions to the constant *f* [Eq. (21)], which is responsible for optical rotation. This is not by chance but is a manifestation of the intrinsic symmetry (reciprocity) of the constitutive equation in a isotropic chiral medium,[13] namely that

$$\mathbf{D} = \in \left[\mathbf{E} + \gamma(\nabla x \mathbf{E})\right]$$

$$\mathbf{B} = \mu\left[\mathbf{H} + \gamma(\nabla x \mathbf{H})\right] \qquad (22)$$

with the same constant γ in both the Eqs. (22).

APPENDIX

The above calculation of optical activity was based on the concept of polarization and magnetization of a medium. Though these notions have deep historical roots and are often very useful, in general one cannot uniquely separate polarization and magnetization electric currents in a medium with special dispersion. Therefore it might be instructive to get the same results in another way, namely by a straightforward average of the microscopic electric current $j^{(m)}$. To avoid singularities, let us introduce a very small but finite cross-sectional area S of a helical molecule. Then the microscopic current inside the molecule with fixed orientational vectors **n** and **a** is

$$\mathbf{j}^{(m)} = \dot{\rho}\Delta\mathbf{t}/s = -i\omega\rho\Delta(\mathbf{n},\mathbf{a},\mathbf{E}_0)\mathbf{t}/S \qquad (A1)$$

where

$$\mathbf{t} = \left[\mathbf{n}\frac{h}{2\pi} - \mathbf{a}\sin\varphi + (\mathbf{n}x\mathbf{a})\cos\varphi\right]/(a^2 + h^2/4\pi^2)^{1/2} \qquad (A2)$$

is the unit vector directed along the helical line of a molecule [see Eq. (6)]. Inserting expression (8) for the displacement Δ into (A1) one obtains the microscopic current at the point $\mathbf{R}(\phi)$ of a molecule in terms of $\mathbf{E}_0$- the electric field at the origin 0 (Fig. 1). However, to derive the macroscopic (averaged) conductivity tensor $\sigma_{\alpha\beta}$ we need to

know the relation between $\mathbf{j}^{(m)}(\mathbf{R})$ and $\mathbf{E}(\mathbf{R})$- the electric field at the same location. Thus with the required accuracy we can write now that

$$\mathbf{E}_0 = \mathbf{E}(\mathbf{R})e^{-i\mathbf{k}\cdot\mathbf{R}} \approx \mathbf{E}(\mathbf{R})(1 - i\mathbf{k}\cdot\mathbf{R}) \tag{A3}$$

Since all but the first term in (8) are already proportional to k, the difference between $\mathbf{E}_0$ and $\mathbf{E}(\mathbf{R})$ has to be taken into account only for this first term, putting $\mathbf{E}_0 = \mathbf{E}$ in all others. Then (8), (A1) and (A3) yield

$$\mathbf{j}^{(m)}(\mathbf{R}) = \frac{-i\omega\beta\rho}{S(a^2 + h^2/4\pi^2)^{1/2}}\left[\mathbf{n}\frac{h}{2\pi} - \mathbf{a}\sin\varphi + (\mathbf{n}\times\mathbf{a})\cos\varphi\right]\left\{h(\mathbf{E}\cdot\mathbf{n}) - ih(\mathbf{E}\cdot\mathbf{n})\left[(\mathbf{k}\cdot\mathbf{n})h\frac{\varphi}{2\pi} + (\mathbf{k}\cdot\mathbf{a})\cos\varphi + \right.\right.$$
$$\left.\left. + \mathbf{k}\cdot(\mathbf{n}\times\mathbf{a})\sin\varphi\right] + i\frac{h^2}{2}(\mathbf{E}\cdot\mathbf{n})(\mathbf{k}\cdot\mathbf{n}) + ih(\mathbf{E}\cdot\mathbf{a})(\mathbf{k}\cdot\mathbf{n}) - i\pi(\mathbf{E}\cdot\mathbf{a})\mathbf{k}\cdot(\mathbf{n}\times\mathbf{a}) + i\pi(\mathbf{k}\cdot\mathbf{a})\mathbf{E}(\mathbf{n}\times\mathbf{a})\right\}$$

(A4)

Thus the following microscopic conductivity tensor $\sigma_{\alpha\beta}^{(m)}$ can be deduced from (A4):

$$\sigma_{\alpha\beta}^{(m)} = \frac{-i\omega\beta\rho}{S(a^2 + h^2/4\pi^2)^{1/2}}\left[\frac{h}{2\pi}n_\alpha - a_\alpha\sin\varphi + e_{\alpha\beta\gamma}n_\beta a_\gamma\cos\varphi\right]\left\{hn_\beta\left[k_\gamma n_\gamma h\frac{\varphi}{2\pi} + k_\gamma a_\gamma\cos\varphi\right.\right.$$
$$\left.\left. + e_{\gamma\delta\nu}k_\gamma n_\delta a_\nu\sin\varphi\right] + i\frac{h^2}{2}n_\beta k_\gamma n_\gamma + iha_\beta k_\gamma n_\gamma - i\pi a_\beta k_\gamma e_{\gamma\delta\nu}n_\delta a_\nu + i\pi k_\gamma a_\gamma e_{\beta\delta\nu}n_\delta a_\nu\right\}$$

(A5)

To derive the macroscopic conductivity far this gas as a continuous medium one now needs to average $\sigma_{\alpha\beta}^{(m)}$ over a so-called "physically infinitesimal" volume, that is, a domain containing a large number of molecules but still small compared with the wavelength λ.Again, this type of average can be carried out in several steps. The first is to average (A5) over φ, i.e. different points of a molecule with fixed orientation vectors **n** and **a**. The second is to average over **a** and **n** using relations (14) and (16), similar to the method used above to obtain expressions (17) and (18). And finally, since the microscopic current (A4) is nonzero only inside molecules, the result of the average has to be multiplied by a factor equal to the proportion of the hole volume occupied by molecules, namely, by NSL, where $L = 2\pi(a^2 + h^2/4\pi^2)^{1/2}$ is the length of a molecule. We have omitted here straightforward calculation, which results in exactly the same macroscopic conductivity tensor as derived in (20).

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