Theory of apparent circular dichroism in a magnetic field

Robert P. Cameron*
SUPA and Department of Physics, University of Strathclyde, Glasgow, UK

Jessica Wade
Department of Materials, Imperial College London, London, UK

Matthew J. Fuchter
Centre for Processable Electronics, Imperial College London, South Kensington Campus, London, UK and Department of Chemistry and Molecular Sciences Research Hub, Imperial College London, White City Campus, London, UK

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We present a microscopic theory of apparent circular dichroism in chiral thin films, cast explicitly in terms of molecular property tensors. Our theory provides a general foundation for *ab initio* calculations and reveals that the films should exhibit an interesting magnetochiral apparent circular dichroism and other novel effects when subjected to a static magnetic field.

INTRODUCTION

Di Bari and collaborators have recently identified a novel form of apparent circular dichroism in thin films of chiral small organic molecules due to the interference of linear dichroism and linear birefringence with oblique principal axes [1–3]. This apparent circular dichroism enables strong discrimination between left- and right-handed circular polarisations of light and has the unusual property of changing sign upon sample flipping. It could find use in a variety of next-generation optoelectronic devices including photodetectors with intrinsic sensitivity to circular polarisation for chiral sensing [4]; high-efficiency CP-OLED displays that prolong battery life [5] and chiral optical microcavities with potential applications in spintronics, polaritonics and chiral lasing [6, 7].

In this paper we present a microscopic theory of apparent circular dichroism in chiral thin films, cast explicitly in terms of molecular property tensors. Our theory provides a general foundation for *ab initio* calculations and reveals that the films should exhibit an interesting magnetochiral apparent circular dichroism and other novel effects when subjected to a static magnetic field. We use Barron's theoretical formalism and notation throughout [4].

I. APPARENT CIRCULAR DICHROISM

Consider first a film of infinitesimal thickness $\mathrm{d}z$. Light of angular frequency ω propagating in the z direction through the film experiences changes in its Stokes parameters [8] given by

$$\begin{aligned}
S_0^{\mathrm{f}} - S_0 &\approx -(\overline{a}\, S_0 + \mathrm{ld}\, S_1 + \mathrm{ld}'\, S_2 - \mathrm{cd}\, S_3)\mathrm{d}z,\\
S_1^{\mathrm{f}} - S_1 &\approx -(\mathrm{ld}\, S_0 + \overline{a}\, S_1 + \mathrm{cb}\, S_2 + \mathrm{lb}'\, S_3)\mathrm{d}z,\\
S_2^{\mathrm{f}} - S_2 &\approx -(\mathrm{ld}'\, S_0 - \mathrm{cb}\, S_1 + \overline{a}\, S_2 - \mathrm{lb}\, S_3)\mathrm{d}z\\
S_3^{\mathrm{f}} - S_3 &\approx -(-\mathrm{cd}\, S_0 - \mathrm{lb}'\, S_1 + \mathrm{lb}\, S_2 + \overline{a}\, S_3)\mathrm{d}z
\end{aligned}$$

with

$$\begin{aligned}
\overline{\mathrm{a}} &= \frac{1}{2}N\omega\mu_0 c\mathfrak{I}(\tilde{a}^{\mathrm{f}}_{xx} + \tilde{a}^{\mathrm{f}}_{yy}),\\
\mathrm{ld} &= \frac{1}{2}N\omega\mu_0 c\mathfrak{I}(\tilde{a}^{\mathrm{f}}_{xx} - \tilde{a}^{\mathrm{f}}_{yy}),\\
\mathrm{ld}' &= -\frac{1}{2}N\omega\mu_0 c\mathfrak{I}(\tilde{a}^{\mathrm{f}}_{xy} + \tilde{a}^{\mathrm{f}}_{yx}),\\
\mathrm{cd} &= \frac{1}{2}N\omega\mu_0 c\mathfrak{R}(\tilde{a}^{\mathrm{f}}_{xy} - \tilde{a}^{\mathrm{f}}_{yx}),\\
\mathrm{lb} &= \frac{1}{2}N\omega\mu_0 c\mathfrak{R}(\tilde{a}^{\mathrm{f}}_{xx} - \tilde{a}^{\mathrm{f}}_{yy}),\\
\mathrm{lb}' &= -\frac{1}{2}N\omega\mu_0 c\mathfrak{R}(\tilde{a}^{\mathrm{f}}_{xy} + \tilde{a}^{\mathrm{f}}_{yx})\\
\mathrm{cb} &= -\frac{1}{2}N\omega\mu_0 c\mathfrak{I}(\tilde{a}^{\mathrm{f}}_{xy} - \tilde{a}^{\mathrm{f}}_{yx}),
\end{aligned}$$

where $\overline{\mathrm{a}}$, ld, ld$'$, cd, lb, lb$'$ and cb describe the average absorption, linear dichroism, circular dichroism, linear birefringence and circular birefringence of the film; N is the number density of molecules in the film and $\tilde{a}^{\mathrm{f}}_{\alpha\beta}$ is the forward molecular scattering tensor. Working to first order in the multipolar expansion parameter $\lambda = 1$, we take

$$\tilde{a}^{\mathrm{f}}_{\alpha\beta} \approx \tilde{\alpha}_{\alpha\beta} + \lambda\tilde{\zeta}_{\alpha\beta\gamma}n_\gamma,$$

where $\tilde{\alpha}_{\alpha\beta}$ is the complex molecular polarisability tensor, $\tilde{\zeta}_{\alpha\beta\gamma}$ is the complex molecular optical activity tensor and $\mathbf{n} = \hat{\mathbf{z}}$ is a unit vector in the direction of light propagation. It is helpful to partition these tensors into time-even,

* robert.p.cameron@strath.ac.uk

time-odd, dispersive and absorptive contributions as

$$\tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta}(f) + \mathrm{i}\alpha_{\alpha\beta}(g) - \mathrm{i}[\alpha'_{\alpha\beta}(f) + \mathrm{i}\alpha'_{\alpha\beta}(g)]$$
$$\tilde{\zeta}_{\alpha\beta\gamma} = \zeta_{\alpha\beta\gamma}(f) + \mathrm{i}\zeta_{\alpha\beta\gamma}(g) - \mathrm{i}[\zeta'_{\alpha\beta\gamma}(f) + \mathrm{i}\zeta'_{\alpha\beta\gamma}(g)],$$

where $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$ and $\zeta'_{\alpha\beta\gamma} = -\zeta'_{\beta\alpha\gamma}$ are time-even, $\alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha}$ and $\zeta_{\alpha\beta\gamma} = \zeta_{\beta\alpha\gamma}$ are time-odd, f is the dispersive lineshape function and g is the absorptive lineshape function.

Consider now a film of finite thickness l. The optical properties of the film can be described by the Mueller matrix [9]

$$M = \mathrm{e}^{-\overline{a}l}\mathrm{e}^{-fl}$$

with

$$f = \begin{bmatrix} 0 & \mathrm{ld} & \mathrm{ld}' & -\mathrm{cd} \\ \mathrm{ld} & 0 & \mathrm{cb} & \mathrm{lb}' \\ \mathrm{ld}' & -\mathrm{cb} & 0 & -\mathrm{lb} \\ -\mathrm{cd} & -\mathrm{lb}' & \mathrm{lb} & 0 \end{bmatrix}.$$

Assuming a *thin* film ($fl \ll 1$) and working to second order in fl, we have

$$M \approx \mathrm{e}^{-\overline{a}l}\left(1 - fl + \frac{1}{2}f^2l^2\right)$$

and thus

$$M_{03} \approx \mathrm{CD} + \mathrm{ACD}$$

with

$$\begin{aligned}
\mathrm{CD} &= \mathrm{cd}\, l \\
&\approx N\omega\mu_0 c\alpha'_{xy}(g)l + \lambda N\omega\mu_0 c\zeta'_{xyz}(g)l \\
\mathrm{ACD} &= \frac{1}{2}(\mathrm{ld}\,\mathrm{lb}' - \mathrm{ld}'\,\mathrm{lb})l^2 \\
&\approx \frac{1}{4}N^2\omega^2\mu_0^2c^2\{-[\alpha_{xx}(g) - \alpha_{yy}(g)]\alpha_{xy}(f) \\
&\quad + \alpha_{xy}(g)[\alpha_{xx}(f) - \alpha_{yy}(f)]\}l^2 \\
&\quad + \lambda\frac{1}{4}N^2\omega^2\mu_0^2c^2\{-[\alpha_{xx}(g) - \alpha_{yy}(g)]\zeta_{xyz}(f) \\
&\quad + \alpha_{xy}(g)[\zeta_{xxz}(f) - \zeta_{yyz}(f)] \\
&\quad - [\zeta_{xxz}(g) - \zeta_{yyz}(g)]\alpha_{xy}(f) \\
&\quad + \zeta_{xyz}(g)[\alpha_{xx}(f) - \alpha_{yy}(f)]\}l^2,
\end{aligned}$$

where CD describes the circular dichroism of the film and ACD describes the apparent circular dichroism. The λ^0 contribution to CD vanishes for a diamagnetic (time-even) film ($\alpha'_{\alpha\beta} = 0$), leaving only the λ^1 contribution as the natural circular dichroism. The λ^1 contribution to ACD also vanishes for a diamagnetic film ($\zeta_{\alpha\beta\gamma} = 0$), leaving only the λ^0 contribution as the natural apparent circular dichroism. Our expression for the latter is consistent with the detailed theoretical modelling presented recently by Salij, Goldsmith and Tempelaar [10].

To complete our theory we need to perform a suitable statistical average. Considering a classical Boltzmann average for a system in thermodynamic equilibrium at temperature T, we take

$$\mathrm{CD} \to \langle \mathrm{CD} \rangle$$
$$\mathrm{ACD} \to \langle \mathrm{ACD} \rangle$$

with

$$\langle X \rangle = \frac{\int X\mathrm{e}^{-V/k_BT}\mathrm{d}\Omega}{\int \mathrm{e}^{-V/k_BT}\mathrm{d}\Omega},$$

where V is the (unspecified) potential energy experienced by a molecule as a function of the molecule's orientation and Ω denotes Euler angles.

EFFECT OF A STATIC MAGNETIC FIELD

Let us specialise explicitly now to a diamagnetic film, subjected to a static magnetic field

$$\mathbf{B} = B_z\hat{\mathbf{z}}.$$

Assuming that the field is weak and working to second order in the magnetic perturbation parameter $\sigma = 1$, we take

$$\begin{aligned}
\alpha_{\alpha\beta}(\mathbf{B}) &\approx \alpha_{\alpha\beta} + \sigma^2\frac{1}{2}\alpha^{(mm,d)}_{\alpha\beta,\gamma\delta}B_\gamma B_\delta, \\
\alpha'_{\alpha\beta}(\mathbf{B}) &\approx \sigma\alpha'^{(m)}_{\alpha\beta,\gamma}B_\gamma, \\
\zeta_{\alpha\beta\gamma}(\mathbf{B}) &\approx \sigma\zeta^{(m)}_{\alpha\beta\gamma,\delta}B_\delta \\
\zeta'_{\alpha\beta\gamma}(\mathbf{B}) &\approx \zeta'_{\alpha\beta\gamma} + \sigma^2\frac{1}{2}\zeta'^{(mm,d)}_{\alpha\beta\gamma,\delta\epsilon}B_\delta B_\epsilon,
\end{aligned}$$

where a superscript m indicates linear magnetic perturbations and a superscript d indicates diamagnetic perturbations. It follows that

$$\mathrm{CD}(\mathbf{B}) \approx \mathrm{NCD} + \mathrm{MCD}\,B_z + \mathrm{NCD}^{(mm,d)}\,B_z^2$$
$$\mathrm{ACD}(\mathbf{B}) \approx \mathrm{NACD} + \mathrm{MChACD}\,B_z + \mathrm{NACD}^{(mm,d)}\,B_z^2$$

with

$$\mathrm{NCD} \approx \lambda N\omega\mu_0 c\zeta'_{xyz}(g)l,$$
$$\mathrm{MCD} \approx \sigma N\omega\mu_0 c\alpha'^{(m)}_{xy,z}(g)l$$
$$\mathrm{NCD}^{(mm,d)} \approx \lambda\sigma^2\frac{1}{2}N\omega\mu_0 c\zeta'^{(mm,d)}_{xyz,zz}(g)l$$

as well as

$$\begin{aligned}
\mathrm{NACD} &\approx \frac{1}{4}N^2\omega^2\mu_0^2c^2\{-[\alpha_{xx}(g)-\alpha_{yy}(g)]\alpha_{xy}(f)\\
&\quad+\alpha_{xy}(g)[\alpha_{xx}(f)-\alpha_{yy}(f)]\}l^2,\\
\mathrm{MChACD} &\approx \lambda\sigma\frac{1}{4}N^2\omega^2\mu_0^2c^2\{\\
&\quad-[\alpha_{xx}(g)-\alpha_{yy}(g)]\zeta^{(m)}_{xyz,z}(f)\\
&\quad+\alpha_{xy}(g)[\zeta^{(m)}_{xxz,z}(f)-\zeta^{(m)}_{yyz,z}(f)]\\
&\quad-[\zeta^{(m)}_{xxz,z}(g)-\zeta^{(m)}_{yyz,z}(g)]\alpha_{xy}(f)\\
&\quad+\zeta^{(m)}_{xyz,z}(g)[\alpha_{xx}(f)-\alpha_{yy}(f)]\}l^2\\
\mathrm{NACD}^{(mm,d)} &\approx \sigma^2\frac{1}{8}N^2\omega^2\mu_0^2c^2\{\\
&\quad-[\alpha^{(mm,d)}_{xx,zz}(g)-\alpha^{(mm,d)}_{yy,zz}(g)]\alpha_{xy}(f)\\
&\quad-[\alpha_{xx}(g)-\alpha_{yy}(g)]\alpha^{(mm,d)}_{xy,zz}(f)\\
&\quad+\alpha^{(mm,d)}_{xy,zz}(g)[\alpha_{xx}(f)-\alpha_{yy}(f)]\\
&\quad+\alpha_{xy}(g)[\alpha^{(mm,d)}_{xx,zz}(f)-\alpha^{(mm,d)}_{yy,zz}(f)]\\
&\quad-2[\alpha^{(m)}_{xx,z}(g)-\alpha^{(m)}_{yy,z}(g)]\alpha^{(m)}_{xy,z}(f)\\
&\quad+2\alpha^{(m)}_{xy,z}(g)[\alpha^{(m)}_{xx,z}(f)-\alpha^{(m)}_{yy,z}(f)]\}l^2,
\end{aligned}$$

where NCD describes the natural circular dichroism of the film, MCD describes the magnetic (Faraday) circular dichroism, $\mathrm{NCD}^{(mm,d)}$ describes the leading magnetic perturbation of the natural circular dichroism, NACD describes the natural apparent circular dichroism, MChACD describes an interesting magnetochiral apparent circular dichroism (discussed below) and $\mathrm{NACD}^{(mm,d)}$ describes the leading magnetic perturbation of the natural apparent circular dichroism. Crude estimates suggest that MCD $\sim (10^{-2}B_z\,\mathrm{T}^{-1})\,\mathrm{NCD}$, $\mathrm{NCD}^{(mm,d)} \sim (10^{-10}B_z^2\,\mathrm{T}^{-2})\,\mathrm{NCD}$, MChACD $\sim (10^{-8}B_z\,\mathrm{T}^{-1})\,\mathrm{NACD}$ and $\mathrm{NACD}^{(mm,d)} \sim (10^{-10}B_z^2\,\mathrm{T}^{-2})\,\mathrm{NACD}$ at visible wavelengths, although considerable variation is possible of course.

The magnetic field exerts a torque on the molecules, which reorientates them as

$$V(\mathbf{B}) \approx V - \sigma^2\frac{1}{2}\chi^{(d)}_{\alpha\beta}B_\alpha B_\beta,$$

where $\chi^{(d)}_{\alpha\beta}$ is the molecular diamagnetic susceptibility tensor. Incorporating this into our statistical average, we take

$$\begin{aligned}
\mathrm{NCD} &\to \langle\mathrm{NCD}\rangle,\\
\mathrm{MCD} &\to \langle\mathrm{MCD}\rangle,\\
\mathrm{NCD}^{(mm,d)} &\to \langle\mathrm{NCD}^{(mm,d)}\rangle\\
&\quad+\frac{1}{2k_BT}[\langle\mathrm{NCD}\,\chi^{(d)}_{zz}\rangle-\langle\mathrm{NCD}\rangle\langle\chi^{(d)}_{zz}\rangle]B_z^2,\\
\mathrm{NACD} &\to \langle\mathrm{NACD}\rangle,\\
\mathrm{MChACD} &\to \langle\mathrm{MChACD}\rangle\\
\mathrm{NACD}^{(mm,d)} &\to \langle\mathrm{NACD}^{(mm,d)}\rangle\\
&\quad+\frac{1}{2k_BT}[\langle\mathrm{NACD}\,\chi^{(d)}_{zz}\rangle\\
&\quad-\langle\mathrm{NACD}\rangle\langle\chi^{(d)}_{zz}\rangle]B_z^2,
\end{aligned}$$

where the angular brackets represent averages with respect to V only.

$\langle\mathrm{MChACD}\rangle$ is essentially an apparent circular dichroism due to the interference of linear dichroism and birefringence with (magnetically induced) gyrotropic dichroism and birefringence [11–13]. Historically there has been much confusion between natural optical activity and magnetic optical activity, which have fundamentally different origins [4]. Pasteur failed to appreciate the distinction, the phenomenon of magnetic optical rotation leading him in vain to try and induce chirality in crystal growth by applying a static magnetic field. Kelvin emphasised later that "the magnetic rotation has neither left-handed nor right-handed quality (that is to say, no chirality). This was perfectly understood by Faraday, and made clear in his writings, yet even to the present day we frequently find the chiral rotation and the magnetic rotation of the plane of polarized light classed together in a manner against which Faraday's original description of his discovery contains ample warning" [4, 14]. $\langle\mathrm{MChACD}\rangle$ is interesting in that it has characteristics in common with both $\langle\mathrm{NCD}\rangle$ and $\langle\mathrm{MCD}\rangle$, changing sign if either the chirality of the molecules or the direction of the magnetic field is inverted through a plane parallel to the film. Unlike $\langle\mathrm{NCD}\rangle$ and $\langle\mathrm{MCD}\rangle$, $\langle\mathrm{MChACD}\rangle$ also changes sign upon sample flipping and has a nonlinear dependence on the density and thickness of the film. A subtle point is that the molecules in Di Bari's films [1–3] are (preferentially [15]) oriented such that $\langle\mathrm{NACD}\rangle$ appears to have opposite signs for opposite enantiomers in films that face the same way relative to the incident light; $\langle\mathrm{MChACD}\rangle$ would then appear to have the same sign for opposite enantiomers.

The presence of both even and odd powers of B_z in $\langle\mathrm{CD}(\mathbf{B})\rangle$ and $\langle\mathrm{ACD}(\mathbf{B})\rangle$, together with the fact that $\langle\mathrm{CD}(\mathbf{B})\rangle$ retains its sign upon sample flipping whilst $\langle\mathrm{ACD}(\mathbf{B})\rangle$ changes sign, means that $M_{03}(\mathbf{B})$ can in principle have four different values for a given $|B_z|$ depending on whether B_z is positive or negative and on whether the film is facing forward or backward relative to the incident light.

OUTLOOK

There are many possible avenues for future work, including experimental and theoretical investigations.

We have considered a static magnetic field parallel to the incident light. Transverse configurations are also conceivable and might yield interesting new features.

Our predicted magnetochiral apparent circular dichroism and other novel effects will be weak in thin films of small diamagnetic molecules. It remains for us to investigate them in other systems where they might be enhanced [16].

We will return to these and related tasks elsewhere.

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