

# Quantum theory of natural circular, magneto-chiral and non-reciprocal linear dichroism

Stephen W Lovesey<sup>1,2</sup> and Ewald Balcar<sup>3</sup>

<sup>1</sup> ISIS Facility, Harwell Science and Innovation Campus, Oxfordshire OX11 0QX, UK

<sup>2</sup> Diamond Light Source Ltd, Oxfordshire OX11 0DE, UK

<sup>3</sup> Vienna University of Technology, A-1020 Vienna, Austria

E-mail: Stephen.Lovesey@stfc.ac.uk

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## Abstract

For dichroic signals produced by parity-odd absorption events, we expose, in correct and concise form, electron degrees of freedom that participate in correlations between spin and orbital variables. Additionally, and for the first time, we prove sum rules for integrated dichroic signals, analogous to the celebrated work by Thole *et al* (1992 *Phys. Rev. Lett.* 68 1943) for parity-even events. Natural circular dichroism is a standard method for characterizing chiral materials, and the photon magneto-chiral effect is an important candidate for the origin of the homo-chirality of life.

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Natural circular, magneto-chiral and non-reciprocal linear dichroic signals are allowed when the sites occupied by resonant ions lack inversion symmetry. (This requirement on the resonant site for nonzero contributions to parity-odd dichroic signals does not mean that the structure of the material must be non-centrosymmetric.) For magneto-chiral ( $M\chi D$ ) and non-reciprocal linear (NRLD) dichroic signals to be different from zero, the properties of the material must lack symmetry with respect to the inversion of time, by supporting magnetic order. The condition for nonzero  $M\chi D$  and NRLD, namely violation of space and time inversion symmetry, mirrors a necessary condition for the appearance of the magneto-electric effect. Materials that allow natural circular dichroism (NCD) possess an enantiomorphic structure, and there is widespread use of NCD to characterize chiral media [1–4]. The photon magneto-chiral effect is a serious candidate for the origin of the homo-chirality of life [5].

We outline a quantum theory of the three dichroic signals. While we use the language of atomic theory, our findings are robust against limitations of the theory because our work exploits selection rules and symmetry embedded in the quantum theory of absorption of light. Our starting point is the standard expression for photon absorption by electrons with interactions created by events using the electric-dipole

(E1) and magnetic-dipole (M1) and the electric-dipole and electric-quadrupole (E2) [6–8]. The principal outcome of our work is a decomposition of dichroic signals in terms of operators, listed in appendices A and B, which portray the spin and orbital degrees of freedom of electrons in the ground state of the material under investigation. To this extent, we achieve for parity-odd dichroic signals the celebrated sum rules of Thole *et al* for parity-even, E1–E1 and E2–E2, dichroic signals [9, 10].

Dichroic signals can be expressed in terms atomic multipoles,  $\langle O_K \rangle$ , where angular brackets denote the time average of the enclosed operator taken in the ground state of electrons in the material. Central to expressions for integrated dichroic signals are electron structure factors of the form [7, 8]

$$\Psi_K = \sum_d \langle O_K \rangle_d, \quad (1)$$

where the sum is over all resonant ions, and the positive integer  $K$  is the rank of the multipole. With an E1–M1 event,  $K = 0$  (monopole), 1 (dipole) and 2 (quadrupole) and for an E1–E2 event  $K = 1, 2$  and 3 (octupole).

For parity-odd absorption events, there are two types of atomic multipoles. Polar multipoles,  $\langle U_K \rangle$ , are parity-odd and time-even. The polar monopole,  $\langle U_0 \rangle$ , is a pseudo-scalar and a measure of the chirality of electrons in the material. Magneto-electric multipoles,  $\langle G_K \rangle$ , are parity-odd and

time-odd. The dipole operator,  $\mathbf{G}_1$ , is related to either the spin anapole,  $\Omega_S = (\mathbf{S} \times \mathbf{R})$ , or the orbital anapole,  $\Omega_L = \mathbf{L} \times \mathbf{R} - \mathbf{R} \times \mathbf{L}$ , formed with the electron variables the position,  $\mathbf{R}$ , the spin,  $\mathbf{S}$ , and the orbital angular momentum,  $\mathbf{L}$ . The corresponding structure factors are  $\Psi_{K,Q}(u)$  and  $\Psi_{K,Q}(g)$ , where the projection  $Q$  satisfies  $-K \leq Q \leq K$ .

Two of the three dichroic signals depend on photon polarization. Polarization of light is expressed in terms of Stokes parameters [7, 8];  $P_2$  is helicity (a pseudo-scalar) and  $P_3$  is linear polarization. The coordinate system  $(x, y, z)$  for the experiment has the photon wave vector,  $\mathbf{q}$ , parallel to the  $z$ -axis and linear polarization  $P_3 = +1$  (often labelled  $\sigma$ -polarization) parallel to the  $x$ -axis. For the E1–M1 event, integrated dichroic signals are

$$\text{NCD} = P_2 \{ \sqrt{2} \Psi_{0,0}(u) - \Psi_{2,0}(u) \}, \quad (2)$$

$$\text{M}\chi\text{D} = \eta \Psi_{1,0}(g), \quad (3)$$

and

$$\text{NRLD} = i\eta P_3 \{ \Psi_{2,-2}(g) - \Psi_{2,+2}(g) \}, \quad (4)$$

where  $\eta = q_z/|\mathbf{q}|$ . Applications of (2)–(4) to analysis of the data gathered on copper metaborate and gallium ferrate are found in [11, 12]. The quantities (2)–(4) are purely real. Rotation of the material about the light beam by an angle  $\varphi$  results in a change to  $\Psi_{K,Q}$ , namely  $\Psi_{K,Q} \rightarrow \exp(i\varphi Q) \Psi_{K,Q}$ . NCD has cylindrical symmetry and does not change with rotation of the material about the beam. This property of NCD is required by its dependence on circular polarization, which has matching cylindrical symmetry about the beam. Anapoles contribute M $\chi$ D and the signal is independent of Stokes parameters. A motif of parity-odd and time-odd quadrupoles generates NRLD. Rotation of the medium by  $90^\circ$  changes the sign of NRLD, and this change of sign matches the change in sign of  $P_3$  on exchanging  $\sigma$ -polarization by  $\pi$ -polarization. Integrated dichroic signals created by the E1–E2 event are the same as (2)–(4) apart from additional contributions proportional to  $\Psi_{3,0}(g)$  and  $\Psi_{3,\pm 2}(g)$  to M $\chi$ D and NRLD, respectively [7].

Operators  $\mathbf{U}_K$  and  $\mathbf{G}_K$  used in  $\Psi_K(u)$  and  $\Psi_K(g)$ , which appear in the integrated dichroic signals (2)–(4), can be written in terms of composite operators showing the relevant degrees of freedom of the electrons. The operators for E1–M1 and E1–E2 events are listed in appendices A and B. Operators prefaced by  $\pm$  cancel in the sum of integrated dichroic signals gathered at spin–orbit split intermediate states, labelled by total angular momentum  $J_c = c \pm 1/2$ , where  $c$  is the angular momentum of the intermediate state. The division of intensity at the spin–orbit split states is analogous to the finding by Thole *et al* [9] for parity-even dichroism [10]. For the E1–E2 event there is complete analogy with E1–E1 and E2–E2 dichroic signals, in the sense that a sum of integrated signals exposes purely orbital degrees of freedom, while a difference in signals exposes correlations between spin and orbital degrees of freedom in the electrons. The situation is very different for E1–M1, because M1 is the magnetic moment  $\mathbf{L} + 2\mathbf{S}$ . The presence of spin,  $\mathbf{S}$ , in the interaction means the event is allowed for an intermediate state with zero angular momentum, an s-state [13]. The results for the special case  $c = 0$  are listed in appendix A, and inspection shows the pivotal role of electron spin. In the general case, the sum and

difference of integrated dichroic signals depend on spin and orbital electron degrees of freedom.

A composite operator is made from two arbitrary operators  $\mathbf{A}_a$  and  $\mathbf{B}_b$  by the rule

$$\{\mathbf{A}_a \otimes \mathbf{B}_b\}_Q^K = \sum_{\alpha\beta} (a\alpha b\beta | K Q) A_{a,\alpha} B_{b,\beta}, \quad (5)$$

where  $(a\alpha b\beta | K Q)$  is a Clebsch–Gordan coefficient that is purely real [14–16]. Some explicit expressions relevant to our work are found in appendix C.

Our method of working for the results in appendices A and B starts by considering a matrix element in the expectation values  $\langle \mathbf{U}_K \rangle$  and  $\langle \mathbf{G}_K \rangle$ . Consider a matrix element  $\langle j\uparrow m | \mathbf{O}_{K,Q} | j'\uparrow m' \rangle$ , where  $j = \pm 1/2$ , and  $\mathbf{O}_K$  is either a polar or magneto-electric operator. The matrix element is proportional to  $(jmj'm' | K Q) \langle j\uparrow | \mathbf{O}_K | j'\uparrow \rangle$  where the double-barred matrix element, called a reduced matrix element, is independent of the projections  $m$  and  $m'$ . This geometric information within the matrix element is factored out in the Clebsch–Gordan coefficient, a powerful result called the Wigner–Eckart theorem [14–16]. Advanced methods of re-coupling angular momentum have been used by us to expose the dependence of  $\langle j\uparrow | \mathbf{O}_K | j'\uparrow \rangle$  on the total angular momentum  $J_c = c \pm 1/2$  of the intermediate electron state engaged in absorption [16], and details of the algebra used in executing the re-coupling are given in [17].

Let us here illustrate the process by which we establish entries in appendix A. With  $c = 0$  and an E1–M1 event one finds

$$\begin{aligned} \langle j\uparrow | \mathbf{U}_K | j'\uparrow \rangle &= -(i)^{K-1} \{ \langle j\uparrow | \{\mathbf{S} \otimes \mathbf{R}\}^K | j'\uparrow \rangle \delta(c, \uparrow) \\ &\quad - (-1)^{K+j-j'} \langle j'\uparrow | \{\mathbf{S} \otimes \mathbf{R}\}^K | j\uparrow \rangle \delta(c, \downarrow) \}, \end{aligned} \quad (6)$$

and

$$\begin{aligned} \langle j\uparrow | \mathbf{G}_K | j'\uparrow \rangle &= (i)^K \{ \langle j\uparrow | \{\mathbf{S} \otimes \mathbf{R}\}^K | j'\uparrow \rangle \delta(c, \uparrow) \\ &\quad + (-1)^{K+j-j'} \langle j'\uparrow | \{\mathbf{S} \otimes \mathbf{R}\}^K | j\uparrow \rangle \delta(c, \downarrow) \}. \end{aligned} \quad (7)$$

Reduced matrix elements  $\langle j\uparrow | \mathbf{U}_K | j'\uparrow \rangle$  and  $\langle j\uparrow | \mathbf{G}_K | j'\uparrow \rangle$  satisfy conditions for Hermitian operators and expectation values satisfy the identity  $\langle \mathbf{O}_{K,Q} \rangle = (-1)^Q \langle \mathbf{O}_{K,-Q} \rangle^*$ , where  $*$  denotes complex conjugation [14–16]. The Kronecker delta-functions appear in (6) and (7) because the magnetic moment operator, M1, does not change orbital angular momentum. For the magneto-electric quadrupole,  $K = 2$ , the result (7) immediately tells us that  $\{\mathbf{S} \otimes \mathbf{R}\}^2$  is a suitable equivalent operator for  $\mathbf{G}_2$ . With all other cases there are factors of  $i$  on the right-hand side that need interpretation. The case for  $\mathbf{G}_1$  is relatively straightforward because  $i\{\mathbf{S} \otimes \mathbf{R}\}^1 = -(\mathbf{S} \times \mathbf{R})/\sqrt{2} = -\Omega_S/\sqrt{2}$ . Consider next  $\mathbf{U}_0$  obtained from (6) and  $\{\mathbf{S} \otimes \mathbf{R}\}^0 = -\mathbf{S} \cdot \mathbf{R}/\sqrt{3}$ . Since angular momentum obeys  $i\mathbf{S} = (\mathbf{S} \times \mathbf{S})$  one finds  $i\mathbf{S} \cdot \mathbf{R} = \mathbf{S} \cdot \Omega_S$ , which is the operator for chirality,  $\mathbf{U}_0$ , entered in appendix A. Calculations confirm that chirality,  $\langle \mathbf{U}_0 \rangle$ , is related to the imaginary part of parameters that mix electron orbitals with opposing parity, while magnetic charge,  $\langle \mathbf{G}_0 \rangle$ , is proportional to the real part of mixing parameters [17].

In conclusion, we report a quantum-mechanical treatment of the photon absorption processes that underpin NCD and the magneto-chiral effect. Previous treatments of the E1–M1

event [18, 19] omit spin in the M1 operator, which leads to the false conclusions that NCD, for example, is absent for absorption by an s-state ( $K$ -edge) and, for other states, it proceeds only by two-electron processes.

For integrated, parity-odd, natural circular, magneto-chiral and non-reciprocal linear dichroism, we perform a programme of analysis accomplished by Thole *et al* for parity-even dichroic signals [9, 10]. A principal result is that integrated signals for the two cases, parity-even and parity-odd, possess the same structure, and contributions can be sorted by adding and subtracting data at spin-orbit split absorption edges. For the E1–E2 event, the parallel between the two cases goes further, since adding intensities exposes electron orbital variables, and taking the difference of intensities exposes the correlations between spin and orbital variables. Not so for the E1–M1 event. Because the M1 operator depends on electron spin, intensities are pregnant with information about electron spin correlations. This is particularly marked in the analysis of photon absorption by an intermediate state with zero angular momentum, for the signal would vanish were it not for the spin interaction in M1 [13]. Yet another instance is provided by the sum of integrated magneto-chiral signals from E1–M1, which exposes correlations between the orbital anapole,  $\Omega_L$ , and the magnetic moment,  $L + 2S$ .

### Appendix A

Operator equivalents for E1–M1 for the special case  $c = 0$ . The spin anapole  $\Omega_S = (S \times R)$  where  $S$  and  $R$  are, respectively, spin and position operators of an electron [13].

E1–M1 Polar multipoles  $U_K$

$$\begin{aligned} K = 0: & S \cdot \Omega_S, \\ K = 2: & \{(S \times S) \otimes R\}^2. \end{aligned}$$

E1–M1 Magneto-electric multipoles  $G_K$

$$\begin{aligned} K = 1: & \Omega_S, \\ K = 2: & \{S \otimes R\}^2. \end{aligned}$$

### Appendix B

Operator equivalents for the general case,  $c > 0$ , are listed by order of the tensor rank,  $K$ . Electron operators for position, spin and orbital angular momentum are  $R$ ,  $S$  and  $L$ , respectively, and the orbital anapole  $\Omega_L = L \times R - R \times L$ . Operators prefaced by  $\pm$  cancel in the sum of integrated dichroic signals gathered at spin-orbit split intermediate states, labelled by total angular momentum  $J_c = c \pm 1/2$ . We use  $\Delta_2 = \{L \otimes \Omega_L\}^2$ ,  $\Delta_3 = \{\{L \otimes L\}^2 \otimes \Omega_L\}^3$  and  $\Delta_4 = \{\{\{L \otimes L\}^2 \otimes L\}^3 \otimes \Omega_L\}^4$ . Operators  $D_b$  are derived from  $\Delta_b$  with the substitution  $\Omega_L \rightarrow R$ . The operator  $W = \{S \otimes L\}^0 = -S \cdot L / \sqrt{3}$ .

E1–M1 Polar multipoles  $U_K$

$$\begin{aligned} K = 0: & S \cdot \Omega_S, \\ K = 2: & \{\Omega_L \otimes (L + 2S)\}^2, \pm\{S \otimes \Omega_L\}^2, \pm\{S \otimes \Delta_2\}^2, \\ & \pm\{S \otimes \Delta_3\}^2, \pm\{\Omega_L \otimes WS\}^2. \end{aligned}$$

E1–M1 Magneto-electric multipoles  $G_K$

$$\begin{aligned} K = 1: & \{\Omega_L \otimes (L + 2S)\}^1, \pm\{S \otimes \Omega_L\}^1, \pm\{S \otimes \Delta_2\}^1, \\ & \pm\{\Omega_L \otimes WS\}^1, \\ K = 2: & \{R \otimes (L + 2S)\}^2, \pm\{S \otimes R\}^2, \pm\{S \otimes D_2\}^2, \\ & \pm\{S \otimes D_3\}^2, \pm\{R \otimes WS\}^2. \end{aligned}$$

E1–E2 Polar multipoles  $U_K$

$$K = 2: \Delta_2, \pm\{S \otimes \Omega_L\}^2, \pm\{S \otimes \Delta_2\}^2, \pm\{S \otimes \Delta_3\}^2.$$

E1–E2 Magneto-electric multipoles  $G_K$

$$\begin{aligned} K = 1: & \Omega_L, \pm\{S \otimes \Omega_L\}^1, \pm\{S \otimes \Delta_2\}^1, \\ K = 2: & D_2, \pm\{S \otimes R\}^2, \pm\{S \otimes D_2\}^2, \pm\{S \otimes D_3\}^2, \\ K = 3: & \Delta_3, \pm\{S \otimes \Delta_2\}^3, \pm\{S \otimes \Delta_3\}^3, \pm\{S \otimes \Delta_4\}^3. \end{aligned}$$

### Appendix C

Equation (5) is the rule for building composite operators.  $\Delta_b$  is defined in appendix B. Results use  $L^2 = L \cdot L$ ,  $R \cdot R = 1$  and  $L \cdot \Omega_L = 0$ .

$$\Delta_{2,0} = \sqrt{(3/2)}(\Omega_L)_z L_z,$$

$$\begin{aligned} \Delta_{3,0} = & (1/\sqrt{10})[(5(L_z)^2 + 1)(\Omega_L)_z \\ & - ((\Omega_L)_z L^2 + L^2(\Omega_L)_z)/2], \end{aligned}$$

$$\begin{aligned} \Delta_{4,0} = & \sqrt{(5/56)}[(7(L_z)^2 + 5)(\Omega_L)_z \\ & - 3((\Omega_L)_z L^2 + L^2(\Omega_L)_z)/2]L_z, \end{aligned}$$

$$\begin{aligned} \{S \otimes \Omega_L\}^1 = & i(S \times \Omega_L)/\sqrt{2}, \{S \otimes \Delta_2\}^1 \\ = & -\sqrt{(3/20)}\{(S \cdot L)\Omega_L + L(S \cdot \Omega_L)\}, \end{aligned}$$

$$\{S \otimes \Omega_L\}_0^2 = \sqrt{(1/6)}\{3(\Omega_L)_z S_z - S \cdot \Omega_L\},$$

$$\{S \otimes \Delta_2\}_0^2 = (i/2)\{(\Omega_L)_z(S \times L)_z + (S \times \Omega_L)_z L_z\}.$$

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