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Atomic Theory of Parity-Odd (E1–M1) Photon Absorption Event

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Light scattering proceeding through electric and magnetic dipole absorption events (E1–M1) exhibits natural circular dichroism, widely used in the characterization of chiral media, and the magneto-chiral effect, which is under consideration as a mechanism for the homo-chirality of life. Additional manifestations of E1–M1 scattering are resonance enhanced Bragg diffraction and non-reciprocal linear dichroism. In spite of its established importance for a raft of significant phenomena, there has not been a complete treatment of E1–M1 light scattering by electrons. Starting from the interaction that includes both electron spin and angular momentum variables, we construct scattering that proceeds via a spin–orbit split intermediate state for the photo-ejected electron. Employing new relations for re-coupling angular momentum we give a theoretical basis for the derivation of sum-rules for integrated dichroic signals. In order to assist in the interpretation of the algebraic terms present for E1–M1 we construct a family of equivalent operators that include monopoles for chirality and magnetic charge. Worked examples of corresponding expectation values are given for two sample wave functions to demonstrate the flavour and support the use of specific equivalent tensor operators.

KEYWORDS: dichroism, sum-rules, resonant Bragg diffraction, magnetic charge, chirality
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1. Introduction

There is widespread use of natural circular dichroism experienced by light for the characterization of electrons in chiral media,[1–4] and the photon magneto-chiral effect is a serious candidate for the origin of the homo-chirality of life.[5–11] Notwithstanding the established importance of these two photo-electron absorption processes, alongside non-reciprocal linear dichroism and magneto-chiral dichroism, relatively little about their properties is established from quantum mechanics. Frequently ascribed to electric dipole (E1) and magnetic dipole (M1) absorption processes, inadequate calculations of the corresponding scattering amplitude lead to misunderstandings and false claims in the literature. For example, that natural circular dichroism (NCD) is forbidden for photon absorption by an intermediate s-like state that carries no orbital angular momentum,[12] or that E1–M1 absorption is absent unless two or more valence electrons participate.[13,14] Added to which there is no complete reduction of the E1–M1 amplitude for Bragg diffraction in terms of quantum mechanical operators, sometimes called equivalent or multipole operators, nor sum-rules that decompose integrated dichroic signals at spin–orbit split intermediate states conventionally labelled K-edge, L-edge, M-edge, etc.

We remedy all the mentioned shortcomings by (i) launching our calculation of the E1–M1 amplitude from quantum-electrodynamics in which electron spin is naturally included[15–17] and (ii) application of new angular-momentum identities in the scattering amplitude that allow electron charge, spin and orbital degrees of freedom to be reflected in atomic entities, possibly unfamiliar entities, that include, e.g., chirality and magnetic charge. From (ii) we derive sum-rules for E1–M1 dichroic signals, at an arbitrary absorption edge, that are analogues of the celebrated sum-rules derived by Thole and his collaborators for parity-even dichroic signals.[18,19] Tables I and II summarize our findings with the E1–M1 scattering amplitude resolved in to equivalent operators that form spherical tensors.

Our working appears in §5 while Appendix A contains much of the attendant algebra, including new relations for Racah symbols that enable decomposition of the scattering amplitude at spin–orbit split intermediate states. Notably, dependence of the E1–M1 amplitude on the total angular momentum of the intermediate state, $J_c = l_c \pm (1/2)$, is identical to the dependence of parity-even amplitudes on J_c. In consequence, sum-rules for parity-odd dichroic signals resemble those derived by Thole and collaborators.[18,19] However, the sum of E1–M1 amplitudes at the spin–orbit split absorption edges, labelled by $J_c = l_c \pm (1/2)$, depends explicitly on electron spin in contrast to the parity-even amplitudes, whose sum over the edges is purely orbital angular-momentum. We resolve electron degrees of freedom in the amplitude into equivalent, quantum–mechanical operators or atomic multipoles.

Some multipoles encountered in the E1–M1 amplitude do not arise in any other branch of chemistry or physics, to the best of our knowledge. One such multipole is a magnetic charge, or monopole, that can be observed in Bragg diffraction but not in a dichroic signal. The anapole, a dipole also odd with respect to both parity and time, is more familiar, perhaps. Use of resonant Bragg diffraction to observe an anapole, and other magneto-electric multipoles, emulates parity-violation experiments in atomic physics to observe the nuclear anapole[20] and it is the method of choice to observe enigmatic multipoles predicted in advanced simulations of complex materials.[21]

The Racah identities on which our achievements hinge, found in Appendix A, are of interest in their own right for they shed some insight on $12j$(I) and $12j$(II) Racah symbols which rarely arise in calculations. Familiar $3j$, $6j$, and $9j$ Racah symbols arise in the Wigner–Eckart theorem and reduced matrix-elements. We find that $12j$(I) and $12j$(II)

Table I. Operator equivalents derived from eq. (5.1) for the special case $l_c = 0$.

Tensor rank K	Polar multipoles $\mathbf{U}_K$	Magneto-electric multipoles $\mathbf{G}_K$
0	$\mathbf{S}\cdot\boldsymbol{\Omega}_S$	$\mathbf{S}\cdot\mathbf{R}$
1	$\mathrm{i}(\mathbf{R}\times\mathbf{S}) = \{\mathbf{S}(\mathbf{S}\cdot\mathbf{R}) - (\mathbf{S}\cdot\mathbf{R})\mathbf{S})\}$	$\boldsymbol{\Omega}_s$
2	$\{(\mathbf{S}\times\mathbf{S})\otimes\mathbf{R}\}^2$	$\{\mathbf{S}\otimes\mathbf{R}\}^2$

Table II. Operator equivalents derived from eq. (A·4) for the general case, $l_c > 0$, are listed by order of the tensor rank, K. Composite operators are constructed by the rule for tensor products. Operators prefaced by $\pm$ cancel in the sum of integrated dichroic signals gathered at spin–orbit split intermediate states, labelled by total angular momentum $J_c = l_c \pm 1/2$. Here, we use a $\mathbf{D}_2 = \{\mathbf{L}\otimes\mathbf{R}\}^2$ and $\mathbf{D}_3 = \{\{\mathbf{L}\otimes\mathbf{L}\}^2\otimes\mathbf{R}\}^3$. Operators $\boldsymbol{\Delta}_d$ are the same as $\mathbf{D}_d$ apart from $\boldsymbol{\Omega}_L$ in place of $\mathbf{R}$. The operator $\mathbf{W} = \{\mathbf{S}\otimes\mathbf{L}\}^0 = -\mathbf{S}\cdot\mathbf{L}/\sqrt{3}$.

	Polar multipoles $\mathbf{U}_K$
$K=0$	$\mathbf{S}\cdot\boldsymbol{\Omega}_S$
$K=1$	$\{\mathbf{R}\otimes(\mathbf{L}+2\mathbf{S})\}^1$, $\pm\{\mathbf{S}\otimes\mathbf{R}\}^1$, $\pm\{\mathbf{S}\otimes\mathbf{D}_2\}^1$, $\pm\{\mathbf{R}\otimes\mathbf{WS}\}^1$
$K=2$	$\{\boldsymbol{\Omega}_L\otimes(\mathbf{L}+2\mathbf{S})\}^2$, $\pm\{\mathbf{S}\otimes\boldsymbol{\Omega}_L\}^2$, $\pm\{\mathbf{S}\otimes\boldsymbol{\Delta}_2\}^2$, $\pm\{\mathbf{S}\otimes\boldsymbol{\Delta}_3\}^2$, $\pm\{\boldsymbol{\Omega}_L\otimes\mathbf{WS}\}^2$
	Magneto-electric multipoles $\mathbf{G}_K$
$K=0$	$\mathbf{S}\cdot\mathbf{R}$
$K=1$	$\{\boldsymbol{\Omega}_L\otimes(\mathbf{L}+2\mathbf{S})\}^1$, $\pm\{\mathbf{S}\otimes\boldsymbol{\Omega}_L\}^1$, $\pm\{\mathbf{S}\otimes\boldsymbol{\Delta}_2\}^1$, $\pm\{\boldsymbol{\Omega}_L\otimes\mathbf{WS}\}^1$
$K=2$	$\{\mathbf{R}\otimes(\mathbf{L}+2\mathbf{S})\}^2$, $\pm\{\mathbf{S}\otimes\mathbf{R}\}^2$, $\pm\{\mathbf{S}\otimes\mathbf{D}_2\}^2$, $\pm\{\mathbf{S}\otimes\mathbf{D}_3\}^2$, $\pm\{\mathbf{R}\otimes\mathbf{WS}\}^2$

Racah symbols are associated with spin and orbital variables, respectively.

The following section contains the definition of the resonant scattering amplitude and essential attendant information. Dichroic signals that arise from a parity-odd resonant event are quite well-known and briefly discussed in §3, mainly for the sake of completeness. Working presented in §5 are to be read in conjunction with Appendix A and Appendix B. Section 6 is a brief discussion of our work.

2. Resonant Scattering Amplitude

The scattering amplitude on which we base our work is calculated from quantum-electrodynamics.[15–17] A resonant processes may dominate all other contributions to the amplitude should the primary energy $|\mathbf{q}|\hbar c$ match an atomic resonance, where $\mathbf{q}$ ($\mathbf{q}'$) is the primary (secondary) photon wave-vector. In a development in powers of $\mathbf{q}$ and $\mathbf{q}'$, the zeroth-order amplitude describes an E1–E1 absorption event, and the next level E1–M1 and E1–E2 events. In this communication our interest is in the E1–M1 event, for which the amplitude is,

$$Z(\mathrm{E1\text{–}M1}) = \frac{1}{2}\sum_{\eta}\sum_{jj'}\langle\{\boldsymbol{\epsilon}'\cdot\mathbf{R}_j|\eta\rangle\langle\eta|(\mathbf{q}\times\boldsymbol{\epsilon})\cdot\boldsymbol{\mu}_{j'} + (\mathbf{q}'\times\boldsymbol{\epsilon}')\cdot\boldsymbol{\mu}_j|\eta\rangle\langle\eta|\boldsymbol{\epsilon}\cdot\mathbf{R}_{j'}\}\rangle, \quad (2.1)$$

where $\boldsymbol{\epsilon}$ ($\boldsymbol{\epsilon}'$) is the polarization vector of the primary (secondary) photon. In eq. (2.1), j labels an electron, and the magnetic moment $\boldsymbol{\mu} = (\mathbb{L} + 2\mathbb{S})$ with $\mathbb{R}$, $\mathbb{L}$, and $\mathbb{S}$ operators for position, orbital angular momentum and spin, respectively. Intermediate states visited in the resonant event are labelled η and angular brackets $\langle\cdots\rangle$ denote the expectation value, or time average, of the enclosed quantum–mechanical operator. Brouder[22] has derived the correct expression for the E1–M1 scattering amplitude using non-relativistic quantum mechanics [see eq. (3.15) in ref. 22]. However, Brouder limits applications to non-magnetic media and photon states with linear polarization, and neither limit applies in our work.

The presence of $\mathbb{S}$ in eq. (2.1) allows enhancement at a K-edge which would otherwise be forbidden on account of zero orbital angular momentum. To engage the M1 event in resonant scattering valence and intermediate states have common angular momentum, because matrix elements of $\mathbb{L}$ and $\mathbb{S}$ are diagonal with respect to orbital angular momentum. Thus absorption at a K-edge can engage $\boldsymbol{\mu}$ when s-like valence states are available. In addition, intermediate and valence states must not be orthogonal. Parity-odd events, like E1–M1 (and E1–E2), are allowed when valence states at the site of the resonant ion are an admixture of orbitals with different parities, which can occur when the site is not a centre of inversion symmetry. This requirement, on the resonant site for non-zero contributions to scattering from parity-odd events, does not mean in Bragg diffraction that the crystal structure must be non-centrosymmetric (see, for example, a discussion of the corundum structure in ref. 23).

Electron wave-functions in eq. (2.1) can be obtained from a simulation of states in the medium using, say, a cluster or band-structure code. Thereafter the expression can be estimated by a purely numerical method. This programme has already been followed in investigations of both E1–M1 and E1–E2 events (see, for example, refs. 24–27). However, numerical evaluation does not give much insight or a handle on properties of the valence electrons that contribute to a resonant event. Thole and his collaborators for a parity-even (E1–E1) dichroic signal[18,19] provided insight by writing the corresponding amplitude in terms of equivalent electron operators built from $\mathbb{R}$, $\mathbb{S}$, and $\mathbb{L}$. In this communication we pursue a parallel development for the E1–M1 event which is parity-odd. To this end, we exploit fundamental properties of the scattering amplitude and reach conclusions independent of estimates and assumptions.

The amplitude is a scalar quantity and as such it can be written as a scalar product of two quantities, one for the photons and one for the electrons. Application of the triangle rule to a pair of vector quantities, E1 and M1, shows that the scalar product is a sum of spherical tensors with rank $K = 0$ (scalar or charge), $K = 1$ (dipole), and $K = 2$ (quadrupole). Inspection of eq. (2.1) tells us that it consists basically of two terms, each a product of two matrix elements with a sum over intermediate states η. A lengthy algebraic calculation reveals the fundamental structure obtained from eq. (2.1) by separating the photon- and electron-related quantities into tensors forming scalar products for each rank K. Tensors $\langle\boldsymbol{\Upsilon}_K\rangle$ describe the electronic properties including the influence of the sum over intermediate states. One finds,

$$Z(\mathrm{E1\text{–}M1}) = \sum_K[\tilde{\mathbf{N}}_K\cdot\langle\boldsymbol{\Upsilon}_K\rangle + (\mathbf{N}_K\cdot\langle\boldsymbol{\Upsilon}_K\rangle)^*], \quad (2.2)$$

where $\mathbf{N}_K$ is constructed from $\mathbf{q}'\times\boldsymbol{\epsilon}'$, $\boldsymbol{\epsilon}$ and $\tilde{\mathbf{N}}_K$ is constructed from $\mathbf{q}\times\boldsymbol{\epsilon}$, $\boldsymbol{\epsilon}'$, i.e., $\mathbf{N}_K$ and $\tilde{\mathbf{N}}_K$ are related by interchange of un-primed and primed photon variables.

Values of $\mathbf{N}_K$ and $\tilde{\mathbf{N}}_K$ are found in ref. 28. The spherical tensor $\langle \Upsilon_K \rangle$ is the physical quantity of interest, for it describes ground-state properties of valence electrons that participate in the resonant event. In §5, we will write $\langle \Upsilon_K \rangle$ in terms of expectation values of electron operators **R**, **S**, and **L**. Before that we exploit a fundamental property of the scattering amplitude to re-write (2.2) in perspicacious form because $\langle \Upsilon_K \rangle$, though parity-odd, does not exhibit specific symmetry properties with respect to time reversal.

The property of QED we invoke is called the crossing transformation,[29] with the interchange of un-primed and primed photon variables conjugate to the product of time-reversal and inversion of electron variables. Pairing symmetric and anti-symmetric combinations of photon variables $\tilde{\mathbf{N}}_K \pm \mathbf{N}_K$ with two types of atomic variables that are parity-odd, by the very nature of the event, and time-odd or time-even, respectively, imposes on Z(E1–M1) a structure manifestly consistent with the crossing transformation.

Whence it is wise to construct two types of atomic multipoles from $\langle \Upsilon_K \rangle$ that have definite time signatures. Parity-odd, time-even multipoles $\langle \mathbf{U}_K \rangle$ are called polar. Polar multipoles with rank 0 and 1 have an immediate physical significance, for chirality = $\langle \mathbf{U}_0 \rangle$ and displacement = $\langle \mathbf{U}_1 \rangle$. Parity-odd, time-odd multipoles, $\langle \mathbf{G}_K \rangle$, are called magneto-electric by analogy with a necessary condition for the magneto-electric effect that the inversion is accompanied by time reversal. The magneto-electric monopole, $\langle \mathbf{G}_0 \rangle$, is a magnetic charge while the dipole, $\langle \mathbf{G}_1 \rangle$, is usually called an anapole, or toroidal moment.

The link between $\langle \Upsilon_K \rangle$ and polar and magneto-electric atomic multipoles is found to be,

$$\langle \Upsilon_K \rangle = \rho_0 \{ \mathrm{i}^{K-1} \langle \mathbf{U}_K \rangle - \mathrm{i}^K \langle \mathbf{G}_K \rangle \}, \tag{2.3}$$

where the dimensionless factor ρ_0 is defined later. Lastly, we combine eqs. (2.3) and (2.2). In doing so we take the opportunity to spell out states of polarization in the primary and secondary beams, and introduce a structure factor, $F = Z(\text{E1–M1})/\rho_0$, that proves useful in expressions for both integrated dichroic signals and the Bragg diffraction amplitude. With $K = 0, 1, 2$ and projections Q that satisfy $-K \le Q \le K$, the structure factor is,

$$\begin{aligned} F_{\mu'\nu}(\text{E1–M1}) = \sum_K \mathrm{i}^{K-1} \sum_Q (-1)^Q \\ \times \{ -\mathrm{i}\Psi_{K,Q}(g)[\tilde{N}_{K,-Q} + N_{K,-Q}]_{\mu'\nu} \\ + \Psi_{K,Q}(u)[\tilde{N}_{K,-Q} - N_{K,-Q}]_{\mu'\nu} \}. \end{aligned} \tag{2.4}$$

Subscripts on the structure factor label polarization in the channel with primary (secondary) polarization ν (μ'). In eq. (2.4), Ψ_K is a sum of atomic multipoles $\langle \mathbf{O}_K \rangle$ that are either of type $\langle \mathbf{G}_K \rangle$ or $\langle \mathbf{U}_K \rangle$,

$$\Psi_K = \sum_{\mathbf{d}} \langle \mathbf{O}_K \rangle_{\mathbf{d}} \exp\{\mathrm{i}\mathbf{d} \cdot (\mathbf{q} - \mathbf{q}')\}, \tag{2.5}$$

where the sum is over all resonant ions located at **d**. Integrated dichroic signals are proportional to the structure factor (2.4) evaluated at forward scattering, i.e., the trivial Bragg wave-vector is 0.

For Bragg diffraction the sum in eq. (2.5) is restricted to resonant ions in the unit-cell of the crystal lattice, and the Bragg condition for diffraction is met when the wave-vector $(\mathbf{q} - \mathbf{q}')$ coincides with a vector in the crystal reciprocal-lattice. Resonant Bragg diffraction by non-magnetic and magnetic crystals is discussed at length in refs. 23, 28, and 30. Already, it has been demonstrated that the E1–M1 event contributes in Bragg diffraction observed from the multi-ferroic modification of gallium ferrate.[31,32]

The factor ρ_0 in eq. (2.3) is dimensionless for the E1–M1 event, and purely real. It involves the product of two radial integrals. One is the familiar dipole radial integral from the E1-event, namely, $(\Theta|R|\Xi)$ where Θ is a valence state that carries orbital angular momentum l, and Ξ is the intermediate state which accepts the photon and it carries orbital angular momentum l_c; the two angular momenta differ by unity, of course. The second radial integral, $(\Theta'|\Xi)$, is the radial part of the matrix element of the magnetic moment and the valence state Θ' carries orbital angular momentum $l' = l_c$. With these definitions, the value of ρ_0 in eq. (2.3) is,

$$\rho_0 = \frac{q(\Theta|R|\Xi)(\Theta'|\Xi)}{2}, \tag{2.6}$$

where $q = E/\hbar c$.

3. Dichroic Signals

Parity-odd absorption creates three dichroic signals, natural circular dichroism (NCD), magneto-chiral dichroism (MχD) and non-reciprocal linear dichroism (NRLD). These signals can occur with non-centrosymmetric media only, and isotropic media (fluids) which contain chiral molecules.[33] In eqs. (2.4) and (2.5) set $(\mathbf{q} - \mathbf{q}') = 0$, and the corresponding sums are now $\Psi_{K,Q}(u)$ and $\Psi_{K,Q}(g)$ where the projection Q satisfies $-K \le Q \le K$. Polarization of the light is in terms of Stokes parameters;[17,23] P_2 is helicity (a pseudo-scalar) and P_3 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 σ-polarization) parallel to the x-axis. For the E1–M1 event,[33,34]

$$\text{NCD} = \rho_0 P_2 \{ \sqrt{2}\Psi_{0,0}(u) - \Psi_{2,0}(u) \}, \tag{3.1}$$

$$\text{M}\chi\text{D} = \rho_0 \eta \Psi_{1,0}(g), \tag{3.2}$$

$$\text{NRLD} = \mathrm{i}\rho_0 \eta P_3 \{ \Psi_{2,-2}(g) - \Psi_{2,+2}(g) \}, \tag{3.3}$$

where $\eta = q_z/|\mathbf{q}|$. Crystals not belonging to an enantiomorphic crystal class show no NCD signal. NCD has cylindrical symmetry and it does not change with rotation of the media about the beam. This property of NCD is required by its dependence on circular polarization, which has cylindrical symmetry about the beam. Anapoles contribute MχD and the signal is independent of Stokes parameters. A motif of parity-odd and time-odd quadrupoles generates NRLD.

4. Electron Operators

Basic electron operators are **R**, **L**, and **S**. Angular momentum operators **L**, **S**, and also $\mathbf{J} = \mathbf{L} + \mathbf{S}$, satisfy identities (commutation relations) of the form $(\mathbf{L} \times \mathbf{L}) = \mathrm{i}\mathbf{L}$. Operators **R** and **L** do not commute; $[L_x, R_y] = \mathrm{i}R_z$, say, with $[L_\alpha, R_\beta] = \mathrm{i}\varepsilon_{\alpha\beta\gamma}R_\gamma$ the general case. Angular momentum operators are parity-even (axial vectors) and time-odd, whereas **R** is parity-odd (polar vector) and time-even. Not surprisingly, our theoretical development in §5 demands a fourth basic operator that is parity-odd and time-odd (magneto-electric) and an anapole $\mathbf{\Omega}_L = (\mathbf{L} \times \mathbf{R} - \mathbf{R} \times \mathbf{L})$ possesses these properties.

Cartesian components of the four operators are Hermitian. Spherical components of a vector (dipole, $K = 1$), labelled by the projection $Q = \pm 1, 0$, and Cartesian components, labelled x, y, z, are related by $\mathbf{A}_{\pm 1} = \mp(A_x \pm \mathrm{i}A_y)/\sqrt{2}$ and $A_0 = A_z$, for an arbitrary vector $\mathbf{A}$. One finds $A_Q = (-1)^Q (A_{-Q})^*$. It can be shown that $\mathbf{L} \cdot \mathbf{R} = \mathbf{L} \cdot \boldsymbol{\Omega}_L = 0$. It proves useful in §5 to use a spin anapole $\boldsymbol{\Omega}_S = (\mathbf{S} \times \mathbf{R})$. Anapole operators are Hermitian.

Since $\boldsymbol{\Omega}_L$ and $\mathbf{R}$ are (polar) vectors with opposite time signatures their matrix elements are proportional and the coefficient of proportionality contains i. This relation is manifest in their reduced matrix elements, namely, $(l' \| \mathbf{R} \| l' + 1) = -(l' + 1 \| \mathbf{R} \| l')$ with $(l' - 1 \| \mathbf{R} \| l') = -\sqrt{l'}$ while $(l' \| \boldsymbol{\Omega}_L \| l' + 1) = (l' + 1 \| \boldsymbol{\Omega}_L \| l')$ and $(l' - 1 \| \boldsymbol{\Omega}_L \| l') = -2\mathrm{i}l'(l' - 1 \| \mathbf{R} \| l')$. In consequence, $\mathrm{i}\mathbf{R}$ and $\boldsymbol{\Omega}_L$ have matching physical properties. Note that $\mathbf{R}$ and $\boldsymbol{\Omega}_L$ are not orthogonal, with $\mathbf{R} \cdot \boldsymbol{\Omega}_L = -\boldsymbol{\Omega}_L \cdot \mathbf{R} = 2\mathrm{i}\mathbf{R} \cdot \mathbf{R}$ and $\mathbf{R} \cdot \mathbf{R} = 1$.

5. Decomposition of the E1–M1 Structure Factor

In this section we report a rewarding representation of electron variables in the E1–M1 structure factor that (i) exposes its dependence on the total angular-momentum used to label the intermediate state, $J_c = l_c \pm (1/2)$, and (ii) provides a reduction in terms of operator equivalents. The beauty of accomplishment (ii) is that electron degrees of freedom are neatly represented as quantum mechanical operators which provide both physical insight to observed quantities and, at the same time, a framework in which to interpret observable quantities derived in simulation calculations, e.g., by using cluster calculation or density-functional method. An outcome of the decomposition is a set of sum-rules for dichroic signals whereby electron degrees of freedom can be estimated from integrated signals at spin–orbit split intermediate states. Much of the detailed formalism of the actual decomposition is relegated to two Appendices in the hope that doing so will allow us to high-light our essential accomplishments in this section without detailed analysis of the algebra behind.

Parity-odd multipoles can be different from zero when the electron ground-state is a mixture of states with different angular momentum. Examples of a state that allows the E1–M1 event are eqs. (B·6) and (C·1); eq. (B·6) contains two components, one with angular momentum $l_c (j' = l_c \pm 1/2)$ and the other $l = l_c \pm 1 (j = l \pm 1/2)$. Equivalent operators suitable for $\mathbf{U}_K$ and $\mathbf{G}_K$ are defined in accord with eqs. (B·8) and (B·9) that relate the two parity-odd operators directly to one operator, $\boldsymbol{\Upsilon}_K$, introduced in eq. (2.2) and the subject of Appendix A. By and large, we give results for $\boldsymbol{\Upsilon}_K$ because it is common to both $\mathbf{U}_K$ and $\mathbf{G}_K$. Tables I and II contain our results for operator equivalents and our working is set out below.

5.1 *Special case $l_c = 0$*

We start with the simple case of absorption by an intermediate s-state, for which $l_c = 0$. The operator equivalents are gathered in Table I.

With $l_c = 0$, there are no orbital contributions to the structure factor. The spin contribution scales with $(2J_c + 1) = 2$ because there is just one absorption edge, i.e., two spin–orbit split edges collapse and form a single edge. Directly from eq. (A·4) we have,

$$(jl \| \boldsymbol{\Upsilon}_K \| j' l_c) = 2\rho_0 (-1)^K (jl \| \{\mathbf{S} \otimes \mathbf{R}\}^K \| j' l_c), \quad (5.1)$$

with ρ_0 defined in eq. (2.6). In eq. (5.1), the tensor product of rank K formed with spin, S, and unit vector, R, has three values; $\{\mathbf{S} \otimes \mathbf{R}\}^0 = -(\mathbf{S} \cdot \mathbf{R})/\sqrt{3}$, $\{\mathbf{S} \otimes \mathbf{R}\}^1 = \mathrm{i}(\mathbf{S} \times \mathbf{R})/\sqrt{2}$ with spin anapole $\boldsymbol{\Omega}_S = (\mathbf{S} \times \mathbf{R}) = -(\mathbf{R} \times \mathbf{S})$, while the diagonal part (projection $Q = 0$) of the quadrupole tensor-product $\{\mathbf{S} \otimes \mathbf{R}\}^2_Q$ is,

$$\{\mathbf{S} \otimes \mathbf{R}\}^2_0 = \frac{3S_z R_z - \mathbf{S} \cdot \mathbf{R}}{\sqrt{6}}. \quad (5.2)$$

Note that $\{\mathbf{S} \otimes \mathbf{R}\}^0$ and $\{\mathbf{S} \otimes \mathbf{R}\}^2$ are time-odd, while $\{\mathbf{S} \otimes \mathbf{R}\}^1$ is time-even. In the latter case, the time signature is deduced from the identity $\mathrm{i}\mathbf{S} = (\mathbf{S} \times \mathbf{S})$ in which the spin operator, S, is time-odd.

Let us consider the polar and magneto-electric monopoles. Setting $K = 0$ in eqs. (B·4) and (B·5) and using eq. (5.1),

$$\begin{aligned}(jl \| \mathbf{U}_0 \| j' l') = \mathrm{i}\delta_{j,j'} \{ &(jl \| \{\mathbf{S} \otimes \mathbf{R}\}^0 \| j' l') \delta_{l_c,l'} \\ &- (jl' \| \{\mathbf{S} \otimes \mathbf{R}\}^0 \| j' l) \delta_{l_c,l} \}, \\ (jl \| \mathbf{G}_0 \| j' l') = -\delta_{j,j'} \{ &(jl \| \{\mathbf{S} \otimes \mathbf{R}\}^0 \| j' l') \delta_{l_c,l'} \\ &+ (jl' \| \{\mathbf{S} \otimes \mathbf{R}\}^0 \| j' l) \delta_{l_c,l} \}.\end{aligned}$$

These two expressions satisfy eq. (B·2) for the reduced matrix-element of a Hermitian operator. We may immediately identify the Hermitian operator $\{\mathbf{S} \otimes \mathbf{R}\}^0 = -\mathbf{S} \cdot \mathbf{R}/\sqrt{3}$ as an operator equivalent for magnetic charge, $\mathbf{G}_0$. For the polar monopole, chirality, we must instead utilize an anti-Hermitian operator $\mathrm{i}\{\mathbf{S} \otimes \mathbf{R}\}^0 = -\mathrm{i}\mathbf{S} \cdot \mathbf{R}/\sqrt{3}$, with $\mathrm{i}\mathbf{S} \cdot \mathbf{R} = \mathbf{S} \cdot \boldsymbol{\Omega}_S$.

Proceeding to dipole and quadrupole operators, $\mathbf{G}_1$ and $\mathbf{G}_2$ are identified with Hermitian operators $\boldsymbol{\Omega}_S$ and $\{\mathbf{S} \otimes \mathbf{R}\}^2$, respectively. Corresponding results for polar multipoles are anti-Hermitian operators $\mathrm{i}(\mathbf{S} \times \mathbf{R}) = \{(\mathbf{S} \cdot \mathbf{R})\mathbf{S} - \mathbf{S}(\mathbf{S} \cdot \mathbf{R})\}$ and $\mathrm{i}\{\mathbf{S} \otimes \mathbf{R}\}^2_0 = (3z(\mathbf{S} \times \mathbf{S})_z - \mathbf{S} \cdot \boldsymbol{\Omega}_S)/\sqrt{6}$. All these findings are gathered in Table I, and they illustrate use of eqs. (B·8) and (B·9).

5.2 *General case $l_c > 0$*

$K = 0$

For the general case $l_c > 0$, let us continue to list findings by the rank of the atomic multipole. Setting $K = 0$ in eq. (A·4) reduces all but one term to zero. The term that survives stems from $a = 0$ and it is $\{\mathbf{S} \otimes \mathbf{R}\}^0$. The other term in eq. (A·4) with $K = 0$, $a = 0$ vanishes because $l \neq l' = l_c$, as can be seen immediately in eq. (A·3), while proof that all terms with $K = 0$, $a = 1$ add to zero requires some algebra. With $K = 0$ one must have $j = j'$ and,

$$(jl \| \boldsymbol{\Upsilon}_0 \| j l_c) = -\frac{\rho_0 (2J_c + 1)(jl \| \mathbf{S} \cdot \mathbf{R} \| j l_c)}{2\sqrt{3}(2l_c + 1)}. \quad (5.3)$$

Operator equivalents for the polar and magneto-electric monopoles derived from eq. (5.3) are listed in Table II, and they coincide with results for the special case $l_c = 0$ listed in Table I.

$K = 1$

With $K = 1$ in eq. (A·4) all operators are time-even, e.g., $\{\mathbf{S} \otimes \mathbf{R}\}^1 = \mathrm{i}(\mathbf{S} \times \mathbf{R})/\sqrt{2}$ already encountered in our account of the special case $l_c = 0$. In consequence, from eq. (A·4) we may immediately read off operator equivalents suitable for the polar dipole, and these are listed in Table II. There

we use a notation $\mathbf{D}_2 = \{\mathbf{L} \otimes \mathbf{R}\}^2$. One finds $\{\mathbf{S} \otimes \mathbf{D}_2\}^1 = -\sqrt{(3/20)}\{(\mathbf{S}\cdot\mathbf{L})\mathbf{R} + \mathbf{L}(\mathbf{S}\cdot\mathbf{R})\}$ which is explicitly time-even, for $\{\mathbf{S} \otimes \mathbf{D}_2\}^1$ is a component of a polar multipole.

Corresponding results for the magneto-electric dipole follow by substituting the orbital anapole, $\mathbf{\Omega}_L$, for $\mathbf{R}$; results are listed in Table II.

K = 2

All operators in eq. (A·4) are explicitly time-odd and thus give a decomposition of the magneto-electric quadrupole, with results listed in Table II. For example, it is easy to show that $\{\mathbf{S} \otimes \mathbf{R}\}^2_0 = \sqrt{(1/6)}\{3z\mathbf{S}_z - \mathbf{S}\cdot\mathbf{R}\}$ and,

$$\{\mathbf{S} \otimes \mathbf{D}_2\}^2_0 = \frac{\mathrm{i}}{2}\{z(\mathbf{S}\times\mathbf{L})_z + (\mathbf{S}\times\mathbf{R})_z\mathbf{L}_z\}$$
$$= \frac{\mathrm{i}}{2}\{(\mathbf{S}\times\mathbf{L})_z z + \mathbf{L}_z(\mathbf{S}\times\mathbf{R})_z\}.$$

For $\mathbf{D}_2$ we find $\mathbf{D}_2 = \sqrt{(2/3)}z\mathbf{L}_z$ because $\mathbf{L}$ and $\mathbf{R} = (x, y, z)$ are orthogonal variables.

Corresponding results for the polar quadrupole follow by substituting $\mathbf{\Omega}_L$ for $\mathbf{R}$.

6. Summary

We have demonstrated similarity between sum-rules for integrated dichroic signals at spin–orbit split absorption edges due to parity-odd and parity-even absorption events. The demonstration is but one outcome of a decomposition of the E1–M1 scattering amplitude in terms of equivalent operators.

For the case in which the intermediate state into which photons are absorbed has no orbital angular momentum, an s-like state, equivalent operators are related to a composite operator formed with spin, $\mathbf{S}$, and unit vector, $\mathbf{R}$. Specifically, monopole operators for magnetic charge and chirality of the resonant ion can be represented by $\mathbf{S}\cdot\mathbf{R}$ and $\mathrm{i}\mathbf{S}\cdot\mathbf{R} = \mathbf{S}\cdot\mathbf{\Omega}_S$, respectively, where the spin anapole $\mathbf{\Omega}_S = \mathbf{S}\times\mathbf{R}$. For parity-even events, E1–E1 and E2–E2, the monopole is related to electric charge in the ground state of the resonant ion. Magnetic charge is known not to contribute to parity-odd dichroic signals but it may contribute in resonant Bragg diffraction.[32] Dipole and quadrupole operators observed with an s-like intermediate state are listed in Table I.

In the general case, in which the intermediate state possesses angular momentum, addition of integrated intensities collected at the two spin–orbit split edges is proportional to ground-state expectation values of composite operators built from spin and orbital variables. This contrasts with parity-even absorption where the corresponding sum-rule relates intensity to purely orbital expectation values. For the E1–M1 event, atomic multipoles have rank $K = 0$ (monopole), 1 (dipole), and 2 (quadrupole) and we provide explicit expressions, in Table II, for all equivalent operators that control dichroic signals and, also, intensities observed in Bragg diffraction. With this achievement we identify electron degrees of freedom that participate in the multipoles, and a framework for their simulation.

Appendix A: Re-Coupling with 12*j*(I)- and 12*j*(II)-Symbols

It has become clear in §5 that the operators Υ_K are central quantities in our considerations and we select the parts constituting the reduced matrix element $(jl\|\Upsilon(K)\|j'l')$ from eq. (B.1) in ref. 33.

Table A·I. Reduced matrix elements calculated from eq. (A·1) or (A·2), for example, with $l = 2$ and $l' = 1$, all j, j' and rank, K.

$(jl\|\Upsilon(K)\|j'l')$				
$J_c = \frac{1}{2}$		$K = 0$	$K = 1$	$K = 2$
$j = \frac{3}{2}$	$j' = \frac{1}{2}$	0	$\frac{1}{3}\sqrt{\frac{2}{3}}$	$\frac{1}{3}\sqrt{\frac{10}{3}}$
$j = \frac{3}{2}$	$j' = \frac{3}{2}$	$-\frac{2}{3}\sqrt{\frac{1}{3}}$	$-\frac{1}{3}\sqrt{\frac{10}{3}}$	$-\frac{1}{3}\sqrt{\frac{10}{3}}$
$j = \frac{5}{2}$	$j' = \frac{1}{2}$	0	0	0
$j = \frac{5}{2}$	$j' = \frac{3}{2}$	0	0	0
$J_c = \frac{3}{2}$		$K = 0$	$K = 1$	$K = 2$
$j = \frac{3}{2}$	$j' = \frac{1}{2}$	0	$-\frac{1}{3}\sqrt{\frac{2}{3}}$	$\frac{1}{3}\sqrt{\frac{2}{15}}$
$j = \frac{3}{2}$	$j' = \frac{3}{2}$	$-\frac{4}{3}\sqrt{\frac{1}{3}}$	$-\frac{4}{3}\sqrt{\frac{2}{15}}$	$\frac{8}{3}\sqrt{\frac{2}{15}}$
$j = \frac{5}{2}$	$j' = \frac{1}{2}$	0	0	$2\sqrt{\frac{1}{5}}$
$j = \frac{5}{2}$	$j' = \frac{3}{2}$	0	$2\sqrt{\frac{6}{5}}$	$2\sqrt{\frac{14}{5}}$

$$(jl\|\Upsilon(K)\|j'l') = \rho_0(l\|\mathbf{C}(1)\|l')$$
$$\times \delta_{l_c,l'}(-1)^{1+J_c-j'}(2J_c+1)$$
$$\times [(2j+1)(2j'+1)]^{1/2}(-1)^K(2K+1)^{1/2}$$
$$\times \left((l'\|\mathbf{L}\|l') \begin{Bmatrix} l' & J_c & \frac{1}{2} \\ j' & l' & 1 \end{Bmatrix} \right.$$
$$\left. + (-1)^{j'-J_c} 2\left(\tfrac{1}{2}\|\mathbf{S}\|\tfrac{1}{2}\right) \begin{Bmatrix} \frac{1}{2} & J_c & l' \\ j' & \frac{1}{2} & 1 \end{Bmatrix} \right)$$
$$\times \begin{Bmatrix} j' & 1 & J_c \\ 1 & j & K \end{Bmatrix} \begin{Bmatrix} l & j & \frac{1}{2} \\ J_c & l' & 1 \end{Bmatrix}.$$

Representative values of the reduced matrix-element are found in Table A·I. Orbital angular momenta, l' and l, are appropriate for p- and d-like orbitals.

Both contributions, orbital and spin marked by their respective reduced matrix elements $(l'\|\mathbf{L}\|l') = [l'(l'+1)(2l'+1)]^{1/2}$ and $(\frac{1}{2}\|\mathbf{S}\|\frac{1}{2}) = \sqrt{3/2}$,[36,37] are controlled by a product of three 6*j*-symbols. Although all of these contain the intermediate angular momentum J_c it is possible to separate the dependence on J_c into a single 6*j*-symbol common to orbital and spin part. The new identities used for the separation employ a 12*j*-symbol (second kind) for the orbital part,

$$\begin{Bmatrix} l' & J_c & \frac{1}{2} \\ j' & l' & 1 \end{Bmatrix} \begin{Bmatrix} j' & 1 & J_c \\ 1 & j & K \end{Bmatrix} \begin{Bmatrix} l & j & \frac{1}{2} \\ J_c & l' & 1 \end{Bmatrix}$$
$$= \sum_a (2a+1)(-1)^{a+K+l+l'}$$
$$\times \begin{Bmatrix} \frac{1}{2} & a & \frac{1}{2} \\ l' & J_c & l' \end{Bmatrix} \begin{Bmatrix} - & a & \frac{1}{2} & \frac{1}{2} \\ K & - & j' & j \\ 1 & l' & - & l \\ 1 & l' & l' & - \end{Bmatrix},$$

and a 12*j*-symbol (first kind) for the spin part,

$$\begin{Bmatrix} \frac{1}{2} & J_c & l' \\ j & \frac{1}{2} & 1 \end{Bmatrix} \begin{Bmatrix} j' & 1 & J_c \\ 1 & j & K \end{Bmatrix} \begin{Bmatrix} l & j & \frac{1}{2} \\ J_c & l' & 1 \end{Bmatrix}$$
$$= \sum_a (2a+1)(-1)^{a+K+j+l+j'+J_c+1/2}$$
$$\times \begin{Bmatrix} \frac{1}{2} & a & \frac{1}{2} \\ l' & J_c & l' \end{Bmatrix} \begin{Bmatrix} 1 & & \frac{1}{2} & & \frac{1}{2} & & j \\ & \frac{1}{2} & & a & & l & & K \\ j' & & l' & & l' & & 1 & \end{Bmatrix}.$$

In order to achieve this effective re-coupling for J_c one has to resort to graphical methods for treating and manipulating $3nj$-symbols as demonstrated in ref. 35 and outlined in refs. 38 and 39.

The $12j$-symbols can, again by graphical methods or by using identities given in ref. 39, be transformed into sums on j_x,

$$\langle jl\|\mathbf{T}(K)\|j'l'\rangle = \rho_0(l\|\mathbf{C}(1)\|l')\delta_{l_c,l'}(-1)^{1+J_c-j'}[(2j+1)(2j'+1)]^{1/2}(2J_c+1)(-1)^K(2K+1)^{1/2}\sum_a(2a+1)\begin{Bmatrix}\frac{1}{2} & a & \frac{1}{2}\\ l' & J_c & l'\end{Bmatrix}$$
$$\times\sum_{j_x}(2j_x+1)\begin{Bmatrix}\frac{1}{2} & 1 & j_x\\ \frac{1}{2} & l & j\\ a & l' & l'\end{Bmatrix}\left(\langle l'\|\mathbf{L}\|l'\rangle\begin{Bmatrix}j_x & l' & j\\ 1 & 1 & K\\ \frac{1}{2} & l' & j'\end{Bmatrix}+(-1)^{j_x+j+l+K}2\langle\tfrac{1}{2}\|\mathbf{S}\|\tfrac{1}{2}\rangle\begin{Bmatrix}j & j' & K\\ \frac{1}{2} & j_x & l'\end{Bmatrix}\begin{Bmatrix}K & 1 & 1\\ \frac{1}{2} & j_x & \frac{1}{2}\end{Bmatrix}\right). \tag{A·1}$$

Note all quantities in eq. (A·1) are purely real. The reduced matrix-element of $C(1)$ is different from zero for $l = l' \pm 1$.[36,37]

Result (A·1) is usefully contrasted with its analogue for parity-even event which is found in eq. (73) of ref. 23. Notably, the $6j$-symbol that carries all dependence on J_c is exactly the same for both parity-even and parity-odd events. In consequence, the dependence on J_c exposed by writing out the two terms in eq. (A·1) with $a = 0$ and 1 is the same for both types of event. However, in the case of E1–M1 the two terms $a = 0$ and 1 contribute multipoles that depend on electron spin, whereas $a = 0$ is pure orbital for parity-even events. Applied to dichroic signals, what we find for the dependence on J_c of eq. (A·1) means that the structure of sum-rules for integrated dichroic signals is the same for parity-even and parity-odd events.

Whence, for all K, the sum of the two integrated signals at the spin–orbit split states labelled $J_c = l_c \pm 1/2$ is proportional to contributions defined by $a = 0$, which scale with $(2J_c + 1)$, and the difference of the two integrated signals is proportional to contributions defined by $a = 1$.

In eq. (A·1) the sum over a consists of two terms, namely for $a = 0$ and 1, and these are simplified and collected in the bottom line of eq. (A·2),

$$\langle jl\|\mathbf{T}(K)\|j'l'\rangle = \rho_0(l\|\mathbf{C}(1)\|l')\delta_{l_c,l'}[(2j+1)(2j'+1)]^{1/2}(-1)^K(2K+1)^{1/2}\sum_{j_x=1/2,3/2}(-1)^{j_x+j'+l}(2j_x+1)$$
$$\times\left(\frac{(2J_c+1)}{2(2l'+1)}\begin{Bmatrix}j & l & \frac{1}{2}\\ 1 & j_x & l'\end{Bmatrix}\pm(-1)^{1/2-j_x}\left[\frac{6l'(l'+1)}{(2l'+1)}\right]^{1/2}\begin{Bmatrix}\frac{1}{2} & 1 & j_x\\ \frac{1}{2} & l & j\\ 1 & l' & l'\end{Bmatrix}\right)$$
$$\times\left(\langle l'\|\mathbf{L}\|l'\rangle\begin{Bmatrix}j_x & l' & j\\ 1 & 1 & K\\ \frac{1}{2} & l' & j'\end{Bmatrix}-2\langle\tfrac{1}{2}\|\mathbf{S}\|\tfrac{1}{2}\rangle(-1)^{j_x+j+l'+K}\begin{Bmatrix}j & j' & K\\ \frac{1}{2} & j_x & l'\end{Bmatrix}\begin{Bmatrix}K & 1 & 1\\ \frac{1}{2} & j_x & \frac{1}{2}\end{Bmatrix}\right). \tag{A·2}$$

Result (A·2) includes explicit proof of the foregoing statements about the structure of $\langle jl\|\mathbf{T}(K)\|j'l'\rangle$ as a function of $J_c = l_c \pm 1/2$.

For the $a = 0$ term the sum on j_x in eq. (A·2) collapses to nj-symbols. For $a = 1$ no such collapse occurs. However, the two sums are usefully re-arranged. The orbital contribution is converted to a sum over integer b and as such it is a sum of reduced matrix-elements of equivalent operators with rank b discussed in §5. The spin contribution arising from the $12j$(I)-symbol, by contrast, is a single reduced matrix-element. Thus we arrive at the foundation of our analysis of the E1–M1 event, namely,

$$\langle jl\|\mathbf{T}(K)\|j'l'\rangle = \rho_0(l\|\mathbf{C}(1)\|l')\delta_{l_c,l'}[(2j+1)(2j'+1)]^{1/2}(2K+1)^{1/2}$$
$$\times\left(\frac{(2J_c+1)}{2(2l'+1)}\left[\langle l'\|\mathbf{L}\|l'\rangle(-1)^{j+l+1/2}\begin{Bmatrix}l' & K & l\\ 1 & l' & 1\end{Bmatrix}\begin{Bmatrix}l' & j' & \frac{1}{2}\\ j & l & K\end{Bmatrix}+2\langle\tfrac{1}{2}\|\mathbf{S}\|\tfrac{1}{2}\rangle(-1)^{j+j'}\begin{Bmatrix}j & K & j'\\ \frac{1}{2} & 1 & \frac{1}{2}\\ l & 1 & l'\end{Bmatrix}\right]\right.$$
$$\pm\sqrt{6}l'(l'+1)\left[\sum_b(2b+1)(-1)^{j+j'}\begin{Bmatrix}l' & 1 & l\\ l' & 1 & l'\\ 1 & K & b\end{Bmatrix}\begin{Bmatrix}\frac{1}{2} & j & l\\ \frac{1}{2} & j' & l'\\ 1 & K & b\end{Bmatrix}\right.$$
$$\left.\left.+\frac{2\langle\frac{1}{2}\|\mathbf{S}\|\frac{1}{2}\rangle}{\langle l'\|\mathbf{L}\|l'\rangle}\sum_{j_x}(2j_x+1)(-1)^{j_x}(-1)^{l+1/2+K}\begin{Bmatrix}\frac{1}{2} & j_x & l'\\ j' & \frac{1}{2} & 1\end{Bmatrix}\begin{Bmatrix}l & j & \frac{1}{2}\\ j_x & l' & 1\end{Bmatrix}\begin{Bmatrix}j & K & j'\\ 1 & j_x & 1\end{Bmatrix}\begin{Bmatrix}\frac{1}{2} & l' & j_x\\ l' & \frac{1}{2} & 1\end{Bmatrix}\right]\right). \tag{A·3}$$

Although this result, as well as the preceding ones, can be used for numerical calculations we find it instructive to replace nj-symbols that depend on j, j' in eq. (A·3) by reduced matrix elements of basic operators. Essential identities that enable us to do this are in Edmonds,[36] §7. For the $a = 1$ spin contribution in the last line of eq. (A·3) one may use an equivalent operator $\{\mathbf{R}\otimes\mathbf{WS}\}^K$ with $\mathbf{W} = \{\mathbf{S}\otimes\mathbf{L}\}^0 = -(\mathbf{S}\cdot\mathbf{L})/\sqrt{3}$. We then find

$$\langle jl\|\Upsilon(K)\|j'l'\rangle = \rho_0\delta_{l_c,l'}\left\{\frac{(2J_c+1)}{2(2l_c+1)}\langle jl\|\{\mathbf{R}\otimes(\mathbf{L}+2\mathbf{S})\}^K\|j'l_c\rangle\right.$$
$$\left.\mp\sqrt{6}l_c(l_c+1)\left(\langle l\|\mathbf{C}(1)\|l_c\rangle\sum_b(2b+1)\begin{Bmatrix}1 & K & 1\\ l & b & l_c\\ l_c & 1 & l_c\end{Bmatrix}I(K,b)+\frac{2\sqrt{2}}{\langle l_c\|\mathbf{L}\|l_c\rangle}\langle jl\|\{\mathbf{R}\otimes\mathbf{WS}\}^K\|j'l_c\rangle\right)\right\}, \quad (A\cdot4)$$

where $I(K,b)$ is defined by

$$I(K,b) = [(2j+1)(2j'+1)(2K+1)]^{1/2}\begin{Bmatrix}\frac{1}{2} & j' & l'\\ \frac{1}{2} & j & l\\ 1 & K & b\end{Bmatrix}.$$

Expression (A·4) is responsible for results in §5. The choice of equivalent operators appearing in eq. (A·4) might not be unique but any arbitrariness will not affect observable quantities cited in §5.

Appendix B: Reduced Matrix-Elements

Observed multipoles are defined by reference to the numerator of the resonant scattering length (2.1). Let $\Upsilon_{K,Q}$ denote the one-electron operator appearing in the parity-odd amplitude.[23,33] It is defined by the expression (A·1). The relation between $\Upsilon_{K,Q}$ and our polar and magneto-electric operators is,

$$\Upsilon_{K,Q} = \rho_0\{\mathrm{i}^{K-1}\mathbf{U}_{K,Q} - \mathrm{i}^K\mathbf{G}_{K,Q}\}, \quad (B\cdot1)$$

where ρ_0 for the E1–M1 event is defined in eq. (2.6). Unlike $\Upsilon_{K,Q}$, polar and magneto-electric operators possess, by design, definite parity and definite time-reversal signatures, ±1, that we denote by m_π and m_θ, respectively. Reduced matrix-elements of such operators, $\mathbf{B}(K)$, say, required in the Wigner-Eckart theorem for atomic matrix elements[35–37] satisfy,

$$\langle j'l'\|\mathbf{B}(K)\|jl\rangle = (-1)^{j-j'}\langle jl\|\mathbf{B}(K)\|j'l'\rangle^*, \quad (B\cdot2)$$
$$\langle j'l'\|\mathbf{B}(K)\|jl\rangle = (-1)^{j-j'}(-1)^K m_\pi m_\theta\langle jl\|\mathbf{B}(K)\|j'l'\rangle. \quad (B\cdot3)$$

In eq. (B·3), $m_\pi m_\theta = +1$ for a magneto-electric (Gerade) multipole, while $m_\pi m_\theta = -1$ for a polar (Ungerade) multipole. Results (B·1) and (B·3) enable us to calculate matrix elements of observable polar and magneto-electric operators from our knowledge of $\langle jl\|\Upsilon(K)\|j'l'\rangle$, which is purely real and the subject of Appendix A. The general expressions,

$$\langle jl\|\mathbf{U}(K)\|j'l'\rangle = \frac{(-\mathrm{i})^{K-1}}{2\rho_0}\{\langle jl\|\Upsilon(K)\|j'l'\rangle - (-1)^{j-j'}(-1)^K\langle j'l'\|\Upsilon(K)\|jl\rangle\}, \quad (B\cdot4)$$

$$\langle jl\|\mathbf{G}(K)\|j'l'\rangle = -\frac{(-\mathrm{i})^K}{2\rho_0}\{\langle jl\|\Upsilon(K)\|j'l'\rangle + (-1)^{j-j'}(-1)^K\langle j'l'\|\Upsilon(K)\|jl\rangle\}, \quad (B\cdot5)$$

follow immediately from eqs. (B·1) and (B·3).

By way of orientation to the impact of these identities consider a ground state that can give a non-zero expectation value of a parity-odd multipole. We choose for this exercise,

$$\mathcal{N}^{1/2}\{|jlm\rangle + f|j'l_cm'\rangle\}, \quad (B\cdot6)$$

where the mixing parameter f can be complex, and the normalization $\mathcal{N}$ is determined by $\mathcal{N}(1+|f|^2) = 1$. Values of l are $l = l_c \pm 1$ where l_c is the angular momentum of the intermediate state. For $\mathbf{G}_{K,Q}$ and eq. (B·6) one finds,

$$\langle\mathbf{G}_{K,Q}\rangle = \mathcal{N}\{f\langle jlm|\mathbf{G}_{K,Q}|j'l_cm'\rangle + f^*\langle j'l_cm'|\mathbf{G}_{K,Q}|jlm\rangle\}, \quad (B\cdot7)$$

with a similar expression for $\langle\mathbf{U}_{K,Q}\rangle$. The two reduced matrix-elements in this expression are related by eq. (B·3), and $\langle\mathbf{G}_{K,Q}\rangle$ can be taken to be proportional to $\langle jl\|\mathbf{G}(K)\|j'l_c\rangle$, say. The Hermitian property $\langle\mathbf{G}_{K,Q}\rangle^* = (-1)^Q\langle\mathbf{G}_{K,-Q}\rangle$ is guaranteed by eq. (B·2). Returning to eqs. (B·4) and (B·5) and expression (A·1) for $\langle jl\|\Upsilon(K)\|j'l'\rangle$ we see that the latter vanishes unless $l' = l_c$. In consequence, we may work exclusively with reduced matrix-elements $\langle jl\|\mathbf{U}(K)\|j'l'\rangle$ and $\langle jl\|\mathbf{G}(K)\|j'l'\rangle$ derived from $\langle jl\|\Upsilon(K)\|j'l'\rangle$ using eqs. (B·4) and (B·5) in which $l' = l_c$.

Whence we elect equivalent operators for $\mathbf{U}_{K,Q}$ and $\mathbf{G}_{K,Q}$, defined in accord with reduced matrix-elements with $l' = l_c$. Using this value of l' in eqs. (B·4) and (B·5) we arrive at expressions for our elected equivalent operators, namely,

$$\langle jl\|\mathbf{U}(K)\|j'l_c\rangle = \frac{(-\mathrm{i})^{K-1}}{(2\rho_0)}\langle jl\|\Upsilon(K)\|j'l_c\rangle, \quad (B\cdot8)$$

$$\langle jl\|\mathbf{G}(K)\|j'l_c\rangle = -\frac{(-\mathrm{i})^K}{(2\rho_0)}\langle jl\|\Upsilon(K)\|j'l_c\rangle. \quad (B\cdot9)$$

Equivalent operators for $\mathbf{U}_{K,Q}$ and $\mathbf{G}_{K,Q}$ so defined have correct symmetry with respect to parity (both odd) and time reversal (even and odd, respectively). Used in the context described here, equivalent operators generate expectation values $\langle\mathbf{U}_{K,Q}\rangle$ and $\langle\mathbf{G}_{K,Q}\rangle$ with all desired properties.

Appendix C: Model Calculation of Parity-Odd Multipoles

The wave function chosen for our exercise is an admixture of p- and d-like single-particle, atomic states. Mixing parameters may originate from several sources, including, odd-order contributions to the crystal electric field, configuration interaction and covalency.[27] There are two d-states, with angular symmetry yz plus z^2, chosen so that a parity-even quadrupole, that may appear in the E1–E1 structure factor, is different from zero while the orbital angular momentum is zero. (The parity-even quadrupole contributes Templeton and Templeton scattering.) For a p-state we choose $|l',0\rangle$ with angular momentum $l' = 1$ which has z-like angular symmetry and no orbital angular momentum because the projection $m' = 0$. Mixture of the states $|l,m\rangle$ and $|l',0\rangle$ with $l = 2$ and $l' = 1$ in the wave-function allow parity-odd multipoles to be different from zero. Electron spin is saturated with a wave-function $|s = 1/2, m_s = 1/2\rangle$.

The complete wave-function for the resonant ion is a product state,

$$\mathcal{N}^{1/2}|s = 1/2, m_s = 1/2\rangle\{|l,0\rangle + \mathrm{i}b(|l,+1\rangle + |l,-1\rangle)/\sqrt{2} + f|l',0\rangle\}, \quad (C\cdot1)$$

with the normalization $\mathcal{N}$ determined by $\mathcal{N}(1+b^2+|f|^2)=1$. In eq. (C·1), the parameter f is allowed to be a complex number, $f=f'+\mathrm{i}f''$, and it measures mixing of the two states with opposite parity.

The parameter b in eq. (C·1) is chosen to be purely real and consequently expectation values of the orbital angular momentum are zero, i.e., $\langle \mathbf{L}_\beta \rangle = 0$ for $\beta = x$, y, or z, leading to $\mu_\beta = 0$ for $\beta = x$ or y and $\mu_z = 1$ where μ is the magnetic moment.

We cite expectation values of some polar and magneto-electric multipoles at the L_2 and L_3 edges to illustrate the outcome of our working in §5.

Using our model wave-function (C·1), the polar monopole (chirality) and dipole in the E1–M1 structure factor are,

$$\langle \mathbf{U}_{0,0} \rangle = \begin{cases} \frac{1}{9}\sqrt{\frac{1}{5}}\mathcal{N}f'' & \mathrm{L}_2\text{-edge}, \\ \frac{2}{9}\sqrt{\frac{1}{5}}\mathcal{N}f'' & \mathrm{L}_3\text{-edge}, \end{cases} \tag{C·2}$$

and

$$\langle \mathbf{U}_{1,0} \rangle = \begin{cases} 0 & \mathrm{L}_2\text{-edge}, \\ \sqrt{\frac{1}{30}}\mathcal{N}f' & \mathrm{L}_3\text{-edge}. \end{cases} \tag{C·3}$$

In §5 it is shown that, the contribution to a structure factor from a monopole is proportional to $(2J_c+1)$. This result is illustrated in eq. (C·2) by values for $\langle \mathbf{U}_{0,0} \rangle$ at the L_2 edge ($J_c = 1/2$) and the L_3 edge ($J_c = 3/2$). Notable is the null value of $\langle \mathbf{U}_{1,0} \rangle$ at the L_2 edge, whereas $\langle \mathbf{U}_{1,0} \rangle$ at the L_3 edge and $\langle \mathbf{R}_0 \rangle$ may be different from zero.

Magnetic charge that can be observed in the state (C·1) is found to be,

$$\langle \mathbf{G}_{0,0} \rangle = \begin{cases} \frac{1}{9}\sqrt{\frac{1}{5}}\mathcal{N}f' & \mathrm{L}_2\text{-edge}, \\ \frac{2}{9}\sqrt{\frac{1}{5}}\mathcal{N}f' & \mathrm{L}_3\text{-edge}. \end{cases} \tag{C·4}$$

Note that chirality and magnetic charge are related, respectively, to the imaginary and real parts of the mixing parameter, f. For magneto-electric quadrupoles we find,

$$\langle \mathbf{G}_{2,0} \rangle = \begin{cases} \frac{1}{9}\sqrt{\frac{2}{5}}\mathcal{N}f' & \mathrm{L}_2\text{-edge}, \\ \frac{2}{5}\sqrt{\frac{2}{5}}\mathcal{N}f' & \mathrm{L}_3\text{-edge}. \end{cases} \tag{C·5}$$

Results (C·4) and (C·5) demonstrate that monopoles and quadruples can have similar magnitudes.

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