Parity-Odd Atomic Multipoles in X-ray Scattering and Absorption

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Scattering of x-rays enhanced by an electric dipole–electric quadrupole (E1–E2) event probe parity-odd atomic multipoles at the heart of many current theories of complex materials, e.g. Mott–Hubbard insulators and multiferroics. We achieve a complete decomposition of the E1–E2 scattering amplitude at spin–orbit split states in terms of atomic multipoles, albeit unfamiliar composite atomic operators built with electron position, spin and orbital variables. In consequence, one has clear insights to the physical makeup of quantities that determine structure factors for Bragg diffraction enhanced by resonant ions that occupy sites devoid of inversion symmetry.

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

Atomic multipoles are quantitative measures of electronic charge, spin and orbital degrees of freedom, and they are the tools of choice for the interpretation of experiments and simulations on complex materials.1–3) Parity-odd multipoles that enter x-ray scattering and absorption gained prominence in the science of materials in the past few years. Such multipoles are readily observed using beam-lines at x-ray synchrotron sources, and they are allowed by mixing of electron orbitals with opposing parties that drive a raft of material properties, electronic and magnetic. None more so than polar and magnetic properties of multiferroic materials, with potential applications in devices.4,5) Spaldin et al.6 review the toroidal moment, or anapole, in materials science and its relation to the magneto-electric effect. Use of resonant Bragg diffraction and magneto-chiral dichroism to observe the anapole, and other magneto-electric multipoles that include a magnetic charge,7 emulate parity-violation experiments in atomic physics to observe the nuclear anapole.8)

Resonant Bragg diffraction has been observed in many materials of current interest, e.g. chiral media, multiferroics and Mott–Hubbard insulators. By way of orientation to the field of research we may cite: direct observation of the enantiomorphic screw-axis in low quartz,9,10) anapoles in vanadium sesquioxide;11) quadrupole ordering in UPd2;12) magneto-electric monopoles and quadrupoles in multiferroic gallium ferrate;13) polar multipoles in potassium chromate;14) parity-even and parity-odd multipoles in the multiferroic modification of terbium manganate.15,16) There is a dearth of ab initio calculations of parity-odd properties of electrons using electronic structure codes. Observations of dichroic signals and resonant Bragg diffraction have motivated calculations for magnetite, germanium,17) vanadium sesquioxide,18) and multiferroic gallium ferrate.19–21)

Scattering and absorption are two sides of one coin for they are derived from one scattering amplitude. Our results for integrated, parity-odd dichroic signals — also known as sum-rules — are gathered in ref. 22. The sum-rules are analogues of the celebrated results for parity-even dichroic signals derived by Thole and collaborators.23,24) In this communication we investigate observable signals that originate from the electric dipole–electric quadrupole (E1–E2) event, and companion communications deal with the electric dipole–magnetic dipole, E1–M1, event.25,26) In §4 we display definitions of all relevant quantities and their respective relations. Our findings are collected in §5. A sum of intensities from the E1–E2 event gathered at spin–orbit split edges is related solely to orbital variables, while the difference of intensities is related to both spin and orbital variables. We provide a complete decomposition of the E1–E2 amplitude in terms of composite operator equivalents, a platform for analysis of simulations and data gathered by resonant Bragg diffraction. A précis of the decomposition is found in Table I, which lists all operators according to their rank and time-signature, with some explicit operator-equivalents gathered in Table II. Sections 2 and 3, respectively, summarize the resonant scattering length and the structure factor, from which we derive dichroic signals and the unit-cell structure factor for Bragg diffraction. Additional information about these various quantities, and the atomic framework employed, is found in refs. 25 and 27.

Table I. Operator-equivalents for polar (time-even) and magneto-electric (time-odd) multipole operators are listed by order of the tensor rank, K. Composite operators are constructed by the rule for tensor products and explicit examples are gathered in Table II. Operators prefaced by ± are contributed by $I_1(K, b)$ defined in eq. (4.8) and, equivalently, in (5.7), with total angular momentum of the intermediate state $I_e = I_1 ± 1/2$. These operators cancel in the sum of integrated dichroic signals gathered at spin–orbit split intermediate states. In particular, operators from $I_1(K, b)$ are absent for absorption at the K-edge, $I_e = 0$. Here we use a notation introduced in the main text, $D_1 = [I_1 ⊗ I_1]$, $D_3 = [I_1 ⊗ L_1] ⊗ R_1$, and $D_5 = [(I_1 ⊗ L_1) ⊗ L_1] ⊗ R_1$. Operators $A_K$ are the same as $D_K$ apart from $A_K$ in place of $R_K$.

<table>
<thead>
<tr>
<th>Polar multipoles in $U_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = 1$: $C(1) = R_1$, $±[S ⊗ R_1]_1$, $±[S ⊗ D_1]_1$</td>
</tr>
<tr>
<td>$K = 2$: $A_2$, $±[S ⊗ R_2]_2$, $±[S ⊗ A_2]_2$, $±[S ⊗ A_3]_2$</td>
</tr>
<tr>
<td>$K = 3$: $C(3)$, $±[S ⊗ D_3]_3$, $±[S ⊗ D_1]_3$, $±[S ⊗ D_3]_3$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Magneto-electric multipoles in $G_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = 1$: $A_1$, $±[S ⊗ A_1]_1$, $±[S ⊗ A_1]_1$</td>
</tr>
<tr>
<td>$K = 2$: $D_1$, $±[S ⊗ R_2]_2$, $±[S ⊗ D_1]_2$, $±[S ⊗ D_2]_2$</td>
</tr>
<tr>
<td>$K = 3$: $A_3$, $±[S ⊗ A_3]_3$, $±[S ⊗ A_3]_3$, $±[S ⊗ A_1]_3$</td>
</tr>
</tbody>
</table>
Table II. \( L^2 = L \cdot L \quad R \cdot R = 1 \) and \( L \cdot R = L \cdot \Omega = 0 \). Expressions given here are in terms of the position operator \( R = x, y, z \). Corresponding expressions with the orbital anapole, \( \Omega \), are obtained by the direct substitution \( R \rightarrow \Omega \).

\[
\begin{align*}
D_{12} &= [L \otimes R]^2 = \sqrt{3/2}L_z, \\
D_{12} &= [(L \otimes L)^2 \otimes R]^2, \\
D_{12} &= \left(1/\sqrt{10}\right)(2L_z^3 + 2R_z - 2L_z L_z^2)/2, \\
D_{12} &= \sqrt{3/2}L_z^3 + 2L_z^2 + 3L_z^2 + (L_z^2 + L_z^2)/2, \\
C_{L}(3) &= \{L_z^2 - 1/2, (S \otimes R)^2\} = \{S \otimes \mathbf{R}\}/\sqrt{2}, \\
[S \otimes D_{12}] &= -\sqrt{3/20}\{(S \otimes L)R + L(S \otimes R)\}, \\
[S \otimes R]^2 &= \sqrt{3/2}\{3S, -S \cdot \mathbf{R}\}, \\
[S \otimes D_{12}] &= \{1/2\}(S \times L_z) + (S \times R)(L_z) \\
&= \{1/2\}(S \times L_z) + (S \times R)(L_z).
\end{align*}
\]

2. Resonant Scattering Amplitude

Should the primary energy of the radiation, \( E \), be in close proximity to an atomic resonance with an energy \( \Delta \), the scattering amplitude for photons is of the form,

\[
f \simeq -\rho_0 F_{\mu'\nu} / (E - \Delta + i\eta/2),
\]

where \( \Gamma \) is the total width of the resonance, and the factor \( \rho_0 \) is defined later. In eq. (2.1), \( F_{\mu'\nu} \) is a structure factor for scattering in the channel with primary (secondary) polarization \( \nu(\mu') \). Since it may not be immediately obvious, we emphasize that the numerator of eq. (2.1) holds products of two matrix elements describing absorption and re-emission proceeding via intermediate states \( \Xi \) (see, for example, eq. (113) in ref. 27).

\[
Z(\text{E1--E2}) = \frac{1}{2} \sum_{\Xi} \langle (\epsilon' \cdot \mathbf{R})\langle\Xi| (\epsilon \cdot \mathbf{R})\langle q \cdot \mathbf{R}) \rangle - \langle (\epsilon' \cdot \mathbf{R})(q' \cdot \mathbf{R})\rangle \langle\Xi| (\epsilon \cdot \mathbf{R})\rangle). \tag{2.2}
\]

Here, \( Z(\text{E1--E2}) \) is proportional to \( \tilde{N}_{k,0} \), where the tilde denotes exchange of photon variables in the primary and secondary scattering channels, and values of these factors are listed in ref. 27, for all four polarization channels, \( \nu' \). With \( K = 1, 2, 3 \) and projections that satisfy \( -K \leq Q \leq K \), the unit-cell structure factor is,

\[
F_{\mu'\nu}(\text{E1--E2}) = \sum_{k} i^{k-1} \sum_{Q} (-1)^{Q} \times (-i)^{Q} \langle \epsilon_{k,0}(Q)\rangle \langle\tilde{N}_{k,-Q} + N_{k,-Q}\rangle_{\nu'}. \\
+ \langle \epsilon_{k,0}(Q)\rangle \langle\tilde{N}_{k,-Q} - N_{k,-Q}\rangle_{\nu'}. \tag{3.3}
\]

Here, \( \epsilon_{k,0}(Q) \) and \( \epsilon_{k,0}(u) \) are constructed according to eq. (3.2). Different combinations \( \tilde{N}_{k,0} + N_{k,0} \) and \( \tilde{N}_{k,-Q} - N_{k,-Q} \) accompany magneto-electric or polar multipoles. Crossing-symmetry in QED provides the rule for combining photon factors symmetric (anti-symmetric) with respect to exchange of primary and secondary photon states and magneto-electric (polar) atomic multipoles symmetric (anti-symmetric) with respect to inversion of the electron four-variable (space and time). Our formulation eq. (3.3) of the scattering amplitude enhanced by an E1--E2 event is the basis of universal forms of structure factors for Bragg diffraction that include dependence on the azimuthal angle.\( ^{16} \) Examples of the use of eq. (3.3) to the analysis of diffraction data gathered on non-magnetic and magnetic materials include terbium manganate,\( ^{16} \) low-quartz,\( ^{9,10} \) gallium ferrate,\( ^{13} \) potassium chromate,\( ^{14} \) and vanadium sesquioxide.\( ^{11} \)

Parity-odd absorption creates three dichroic signals, natural circular dichroism, magneto-chiral dichroism and non-reciprocal linear dichroism. These signals can occur with non-centrosymmetric media only, and isotropic media (fluids) that are chiral.\( ^{25,27,28} \) Expressions for integrated

\[
where the sum is over all resonant ions located at \( d \), and \( K = 1 \) (dipole), 2 (quadrupole), and 3 (octupole) for an E1--E2 event. Angular brackets \( \langle \cdots \rangle \) denote the expectation, or time-average, value of the enclosed quantum-mechanical operator.

Parity-odd events, like E1--E2 and E1--M1, are allowed when valence states at the site of the resonant ion are an admixture of orbitals with opposite 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 that a crystal structure must be non-centrosymmetric (see, for example, the discussion of the conundrum structure in ref. 27).

Multipoles \( (O_k) \) in eq. (3.2) have definite signatures for the discrete symmetries of time reversal and parity. Parity-odd, time-even multipoles, \( (U_k) \), are called polar, while parity-odd, time-odd multipoles, \( (G_k) \), are called magneto-electric.

For the E1--E2 event, \( I^k_{\mu'\nu} \) is proportional to \( \tilde{N}_{k,0} \), where the tilde denotes exchange of photon variables in the primary and secondary scattering channels, and values of these factors are listed in ref. 27, for all four polarization channels, \( \mu' \). With \( K = 1, 2, 3 \) and projections that satisfy \( -K \leq Q \leq K \), the unit-cell structure factor is,

\[
F_{\mu'\nu}(\text{E1--E2}) = \sum_{k} i^{k-1} \sum_{Q} (-1)^{Q} \times (-i)^{Q} \langle \epsilon_{k,0}(Q)\rangle \langle\tilde{N}_{k,-Q} + N_{k,-Q}\rangle_{\nu'}. \\
+ \langle \epsilon_{k,0}(Q)\rangle \langle\tilde{N}_{k,-Q} - N_{k,-Q}\rangle_{\nu'}. \tag{3.3}
\]

The structure factor \( \rho_0 \) in eq. (2.1) involves the product of two radial integrals. One is the familiar dipole radial integral from the E1-event, namely, \( \langle \Theta | (\mathbf{R} \cdot \Xi) | \Theta \rangle \), where \( \Theta \) is a valence state that carries orbital angular momentum \( l \), and \( \Xi \) is the intermediate state which accepts the photon and it carries orbital angular momentum \( l_c \). The second is the quadrupole radial integral, \( \langle \Theta' | (\mathbf{R}^2 \cdot \Xi) | \Theta' \rangle \), in which the valence state \( \Theta' \) carries orbital angular momentum \( f \). Sums \( l + l_c \) and \( f + l_c \) are odd and even, respectively, while \( l + f \) is odd.

With these definitions, the value of \( \rho_0 \) in eq. (2.1) is,

\[
\rho_0 = \frac{q}{\mathbf{R}} \langle \Theta | (\mathbf{R} \cdot \Xi) | \Theta \rangle \langle \Theta' | (\mathbf{R}^2 \cdot \Xi) | \Theta' \rangle. \tag{2.3}
\]

where \( q = E/\hbar c \) and \( a_0 \) is the Bohr radius.
dichroic signals are found in our original formulation of scattering enhanced by the E1–E2 event \(^{27}\) and, also, in an analysis of data gathered on gallium ferrate. \(^{28}\)

4. The Atomic Tensor \(\mathbf{\Upsilon}(K)\) and Its Relations with \(U_K\) and \(G_K\)

In the preceding \(\S 2\) and \(\S 3\) we have given a compact resumé of expressions derived in the treatment of X-ray resonance scattering. Although some details of the calculation have been published in ref. 27 and in several other places..., it is, perhaps, worthwhile to describe some steps and algebra involved in the approach to the key formula on which workings presented in \(\S 5\) are based.

From eqs. (2.1) and (2.2) we have seen that the scattering amplitude \(f\) contains the structure factor \(F_{\mu\nu}\), but, for the sake of simplicity, we concentrate on just a single atomic term from the sum over all ions in the unit cell. A rather involved series of steps employing graphical methods, covered in detail in Chapter 10 of ref. 29, complete the passage from eq. (2.2) to,

\[
Z(\text{E1–E2}) = \rho_0 \sum_{k,Q} (-1)^{Q} [N_{k,Q}(\mathbf{\Upsilon}^+_Q) + N_{k,Q}^*(\mathbf{\Upsilon}^+_Q)^*].
\]

(4.1)

Comparing eq. (2.2) with eq. (4.1), we note that products of two matrix elements in the former are now symbolized by expectation values of atomic tensors \(\mathbf{\Upsilon}^+_Q\). To be exact, the products convert into sums of multiples of rank \(K\) \((1 \leq K \leq 3)\). The sum over intermediate states \(z\) is now part of \(\mathbf{\Upsilon}^+_Q\). In the following, the quantity \(\mathbf{\Upsilon}^+_Q\) will be our main focus of interest. From the quantum theory of angular momentum\(^{30}\) we know that the reduced matrix element for a tensor operating on one part of a coupled system is characterized by a 6j-symbol. Matrix elements of the E1 and E2 operators in eq. (2.2) each contain a 6j-symbol while the algebra of recoupling to form a tensor of rank \(K\) contributes a third 6j-symbol, and the triple product of 6j-symbols we encounter below in eq. (4.4), which contains the reduced matrix element of \(\mathbf{\Upsilon}^+_Q\).

Two steps are missing to bring accordance with eq. (3.3); firstly, we need to introduce the sum over sites, eq. (3.2), and secondly, to rearrange the terms in eq. (4.1) to achieve such combinations of \(N_{k,Q}\) and \(N_{k,Q}^*\) that are time symmetric or anti-symmetric, with respect to an exchange of ingoing and outgoing scattering channel. We recall that, the tensors \(N_{k,Q},N_{k,Q}^*\) contain the phonon parameters describing polarization and momentum before (primary) and after (secondary channel) the scattering event. Concomitant rearrangements for the atomic tensors \(\mathbf{\Upsilon}^+_Q\) lead to the time-even \(U_K\) and time-odd \(G_K\). The notation used for the structure factors in eq. (3.3) indicates that \(\psi_{E,Q}(u)\) and \(\psi_{E,Q}(g)\) are constructed with \(U_K\) and \(G_K\), respectively.

In the following we study only reduced matrix elements and give our definitions for polar, \(U_K\), and magneto-electric, \(G_K\), multipoles which rest at the core of our presentation. Both, \(U_K\) and \(G_K\), derive from one quantity, \((j||\Upsilon(K)||f')\), and the corresponding expressions are,

\[
(j||U(K)||f') = \frac{(-1)^{f-1}}{2\rho_0} (j||\Upsilon(K)||f') - (-1)^{f-1+k} (j'||\Upsilon(K)||j'),
\]

(4.2)

and,

\[
(j||G(K)||f') = \frac{(-1)^K}{2\rho_0} [(j||\Upsilon(K)||f') - (-1)^{f+k} (j'||\Upsilon(K)||j')].
\]

(4.3)

The definition of \((j||\Upsilon(K)||f')\) is taken from the discussion in ref. 27, eq. (117), and the relevant parts considered here are

\[
(j||\Upsilon^k||f') = \sqrt{5/6}(-1)^{f+k+K+1} \times \left\{ \begin{array}{ccc} l & 1/2 & j \\ J_c & 1 & J_e \end{array} \right\} \left\{ \begin{array}{ccc} J_e & 1/2 & j' \\ J_c & 2 & J_e \end{array} \right\} \left\{ \begin{array}{ccc} 1 & 1 & K \\ 1 & j & K \end{array} \right\}.
\]

(4.4)

with some values appropriate for a rare-earth ion listed in Table III. As mentioned above, the expression for \((j||\Upsilon^k||f')\) is controlled by a product of three 6j-symbols. All of these contain the residual representative of the intermediate state \(z\), the angular momentum \(J_c\), because the sum over intermediate states referred only to the magnetic quantum numbers \(M_c\). Whence, one way to express the one approximation made in arriving at our starting point, eq. (2.1) with eq. (2.2), is to say that angular anisotropy in core states is negligible, which makes it a safe assumption to sum over \(M_c\). Corrections to this level of approximation have been derived for parity-even events and explored in the analysis of diffraction data, etc., low-quantz.\(^{30}\)

We want to demonstrate that it is possible to separate the dependence on \(J_c\) into a single 6j-symbol, if the product of three 6j-symbols is converted into a sum over an auxiliary variable \(a\), where the sum contains a 6j- and a 12j-symbol. In order to achieve this effective re-coupling for \(J_c\) one has to resort once more to graphical methods for treating and manipulating 3j-symbols as demonstrated, e.g., in ref. 29.

\[
\left\{ \begin{array}{ccc} j & 1/2 & j \\ J_c & 1/2 & J_e \end{array} \right\} \left\{ \begin{array}{ccc} J_e & 1/2 & j' \\ J_c & 2 & J_e \end{array} \right\} \left\{ \begin{array}{ccc} 1 & 1 & K \\ 1 & j & K \end{array} \right\}.
\]

Table III. Numerical values for \((j||\Upsilon(K)||f')\) are given for the special case \(l = 2\), \(l_c = 1\), and \(f = 3\) for the corresponding values of \(j = f = l = 1/2\), \(J_e = J_c = 1/2\), and \(f = f' = 1/2\). Zero entries result when a triangle rule is broken.

<table>
<thead>
<tr>
<th>(J_e = 1/2)</th>
<th>(K = 0)</th>
<th>(K = 1)</th>
<th>(K = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j = 3/2)</td>
<td>(f = 5/2)</td>
<td>(\sqrt{3})</td>
<td>(1/\sqrt{3})</td>
</tr>
<tr>
<td>(j = 3/2)</td>
<td>(f = 7/2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(j = 5/2)</td>
<td>(f = 5/2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(j = 5/2)</td>
<td>(f = 7/2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(J_c = 3/2)</td>
<td>(K = 0)</td>
<td>(K = 1)</td>
<td>(K = 2)</td>
</tr>
<tr>
<td>(j = 3/2)</td>
<td>(f = 5/2)</td>
<td>(1/\sqrt{3})</td>
<td>(1/\sqrt{3})</td>
</tr>
<tr>
<td>(j = 3/2)</td>
<td>(f = 7/2)</td>
<td>0</td>
<td>(1/\sqrt{3})</td>
</tr>
<tr>
<td>(j = 5/2)</td>
<td>(f = 5/2)</td>
<td>(-1/\sqrt{3})</td>
<td>(-1/\sqrt{3})</td>
</tr>
<tr>
<td>(j = 7/2)</td>
<td>(f = 7/2)</td>
<td>(1/\sqrt{3})</td>
<td>(1/\sqrt{3})</td>
</tr>
</tbody>
</table>
\[
\begin{aligned}
&= (-1)^{i+j+l+k} \sum_a (2a + 1)(-1)^a \\
&\times \left\{ \begin{array}{cccc}
\ell_e & a & \ell_e \\
\frac{1}{2} & \ell_e & \frac{1}{2}
\end{array} \right\} \\
&\times \left\{ \begin{array}{cccc}
- & a & \frac{1}{2} \\
K & -j & j \\
1 & \ell_e & -l
\end{array} \right\} \\
&\times \left\{ \begin{array}{cccc}
2 & \ell_e & l' - j
\end{array} \right\}.
\end{aligned}
\] (4.5)

Inspection of eq. (4.5) shows that the sum over \( a \) contains only two terms for either \( a = 0 \) or \( a = 1 \). The \( 12j(\Pi) \) symbols can, again by graphical methods or by using identities given in ref. 32, be transformed and from eq. (4.5) one obtains two parts resulting from \( a = 0 \) and \( a = 1 \).

\[
(j||T^k||l') = -(5/6)^{1/2} (l||C(1)||l_e||C(2)||l')
\times \left[ \begin{array}{cccc}
(2l_e + 1)/(2l + 1) & 1 & 1 & l_e \\
2 & l' & K & I_0(K)
\end{array} \right]
\pm \sqrt{6} (l_e(l_e + 1))^{-1/2} \sum_b (2b + 1)
\left[ \begin{array}{cccc}
l_e & 2 & l' \\
l & K & b
\end{array} \right] (I_0(K, b)),
\] (4.6)

where the \( \pm \) sign refers to the two cases \( J_e \pm 1/2 \). As expected, the term resulting from \( a = 0 \) is particularly simple, while the part for \( a = 1 \) leads to a sum over an auxiliary integer variable \( b \). Here we have introduced quantities, seemingly mere abbreviations, that are actually central to realization of physical entities in the scattering amplitude:

\[
I_0(K) = [(2j + 1)(2j' + 1)]^{1/2}
\times (-1)^{i+j+1/2+l}
\left[ \begin{array}{cccc}
- & j & \frac{1}{2} \\
j' & j' & K
\end{array} \right],
\] (4.7)

\[
I_1(K, b) = [(2j + 1)(2j' + 1)(2K + 1)]^{1/2}
\times (-1)^{i+j+1/2+l}
\left[ \begin{array}{cccc}
j & l & \frac{1}{2} \\
\frac{1}{2} & j & l
\end{array} \right]
\left[ \begin{array}{cccc}
1 & K & b
\end{array} \right].
\] (4.8)

The rationale behind these abbreviations is understood, when one notes that both \( I_0(K) \) and \( I_1(K, b) \) contain all the dependence on initial and final states represented by \( j \) and \( j' \). The corresponding \( 6j \)- and \( 9j \)-symbols can be interpreted as signatures of equivalent operators or rather their respective reduced matrix elements. Needless to say, another sea of algebra has to be crossed in the passage from these concepts to their realization in Tables I and II.

5. Principal Findings

5.1 Survey of findings

In §4 we have sketched the genesis of polar, \((U_K)\), and magneto-electric, \((G_K)\), multipoles and now proceed to re-express them as linear combinations of equivalent operators; some operators are independent of the particular absorption edge, with the remainder prefixed by the sign in the total angular momentum labelling the edge, \( J_e \pm 1/2 \) (see Table I). Specifically, multipole are constructed from composite tensor operators, \( I_0(K) \) and \( I_1(K, b) \), with results listed in Table I. Looking ahead, the algebraic definitions eqs. (4.7) and (4.8) for \( I_0(K) \) and \( I_1(K, b) \) are completely equivalent to the expressions in eqs. (5.1), (5.2), and (5.7). For now we only need note in regard to entries in Table I that, \( K \) is the tensor rank, and \( b = K - 1, K + 1 \) together with a triangle condition with angular momenta \( l \) and \( l' \) of initial and final states. One finds that \( b = 0 \) is forbidden, because \( l \neq l' \), and allowed values are \( b = 1, 2, 3, \) or \( 4 \), with \( l = l' \pm 1 \) and \( l = l' \mp 3 \). (Later we give explicit results for the most commonly occurring case \( l = l' \pm 1 \).)

Let us turn to the physical content of the foregoing results. Notable is the finding that \( I_0(K) \) corresponds to a purely orbital variable, and \( I_1(K, b) \) corresponds to a composite variable built from spin and orbital operators. (This property is not shared by the \( E_1-M_1 \) event.\(^{20} \)) Most importantly, physical properties established for \( I_0(K) \) and \( I_1(K, b) \) are also those of the polar and magneto-electric multipole, \((U_K)\) and \((G_K)\), respectively, observed in experiments. [This follows because use of eqs. (4.7) and (4.8), for \( I_0(K) \) and \( I_1(K, b) \), in eqs. (4.2) and (4.3) shows the latter possess the structure of the common element eq. (4.6), i.e., multipole are merely a linear combination of standard, reduced matrix-elements \( I_0(K) \) and \( I_1(K, b) \) with coefficients that do not depend on \( j \) and \( j' \).]

If the intermediate state angular momentum is zero, \( l = 0 \), \( I_1(K, b) \) does not contribute and multipoles are then proportional to \( I_0(K) \). Thus, with absorption at the \( K \)-edge multipoles are purely orbital and independent of electron spin. In this respect, polar and magneto-electric multipole are the same as parity-even multipoles encountered in \( E_1-E_2 \) and \( E_1-E_2 \) events.\(^{23,24,27} \)

We can go on yet further, exposing the physical content of multipole \((G_K)\) and \((U_K)\) with appropriate operator equivalents for them. Our findings for these operators are gathered in Tables I and II. Entries in Table I are a record of correlated electron variables revealed in x-ray absorption using the \( E_1-E_2 \) event, including dichroic signals and resonant Bragg diffraction. Simulations of Bragg intensities will yield estimates of the correlations while a direct path between observations and simulations is eqs. (4.6)-(4.8), our core results.

Inspection of the results in Table I reveals a remarkably simple and symmetric structure for multipole in the structure factor defined by eqs. (3.2) and (3.3). Unfortunately, there are many steps in the working by which results are derived, and there follows a summary of the principal ones.

5.2 Working for entries in Table I

We work with reduced, or double barred, matrix elements to be used in conjunction with the Wigner–Eckart theorem for atomic matrix elements.\(^{29-33} \) Starting from eq. (4.2) the questions we need answer for polar operators, \((U_K)\), are what operations have reduced matrix-elements equal to \((i) \times (i) I_0(K) \) and \((i) \times (i) I_1(K, b) \)? The corresponding questions for magneto-electric multipole, \((G_K)\), in eq. (4.3) involve reduced matrix-elements \((i) \times (i) I_0(K) \) and \((i) \times (i) I_1(K, b) \). By including with \( I_0(K) \) and \( I_1(K, b) \) factors \((i) \times (i) \) and \((i) \times (i) \), respectively, some reduced matrix-elements we handle purely real and some are purely imaginary. In this context, two parity-odd dipole operators merit consideration. The reduced matrix-element of the position operator, \( R \), is purely real with \((l' - l||R||l') = (l' - l||l||l') = -\sqrt{l}T \), while the reduced matrix-element of the orbital anapole, \( R_L = (L \times R - \)
R \times L), is purely imaginary with \((l' - 1)\|\Omega_k\|=2i(l')^{3/2}.
One reduced matrix-element is real and the other is imaginary because the two dipole operators differ in their time signatures, with R time-even and \(\Omega_k\) time-odd.\(^{29}\)

Operators that arise in representations of \((i)^{k-1}I_0(K)\) and \((i)^kI_0(K)\) and \((i)^{k+1}I_1(K,b)\) and \((i)^kI_1(K,b)\) have common features, but even so it pays to consider separately those involving \(I_0(K)\) and \(I_1(K,b)\). We begin with \(I_0(K)\) which has purely orbital character, with variables \(R\), \(L\), and \(\Omega_L\).

Polar multipoles of rank \(K = 1\) and \(K = 3\) have purely real reduced matrix-elements, and

\[
I_0(K) = (-1)^k \frac{(j_l(\|C(K)\|/l')}{\|C(K)\|/l')},
\]

where \(C(K)\) is a normalized spherical harmonic.\(^{30}\) (It is remarkable that \((j_l(\|C(K)\|/l')\) depends only on the \(j_s\) not on the \(l_s\) of the electrons.\(^{30,31}\)) Thus, purely orbital contributions to \(U_1\) and \(U_2\) are \(C(1) = R\) and \(C(3)\), and \(C(0)\) is found in Table II. The reduced matrix-element of the polar multipole \(U_2\) is purely imaginary, and proportional to \(i^l_0(2)\). One finds, for \(l = l' - 1\),

\[
i^l_0(2) = \frac{(j_l(\|L \otimes \Omega_L\|^2/\|l')}{\|L \otimes \Omega_L\|^2/l')} \cdot (2l' + 1) \frac{3}{4l + 3}.
\]

Here, the composite operator \((L \otimes \Omega_L)\) is a tensor product of rank 2 created with \(L\) and \(\Omega_L\), according to the rule,

\[
[a_{a}b_{b} \otimes a_{a}$ $b_{b}KQ] = \sum_{a,b} (aab\otimes bKQ)a_{a}b_{b}a\otimes b.l.
\]

where \(aab\otimes bKQ\) is a Clebsch-Gordan coefficient that is purely real.\(^{26,30}\) The result \((L \otimes \Omega_L) = \sqrt{3/2}1_{L}(\Omega_L)\) can be derived from expressions in Table II, and it is a Hermitian operator \((L \otimes \Omega_L)\) obey commutation rules obeyed by \(L\) and \(\Omega_L\). The denominator in eq. (5.2) is the reduced matrix-element \((j_l(\|L \otimes \Omega_L\|^2/\|l')\). For \(U_1\) the complete list of operators contributed by \((i)^{k-1}I_0(K)\) is \(R\), \((L \otimes \Omega_L)\), and \(C(3)\), and these are recorded in Table I.

A parallel discussion of the magneto-electric operator, \(G_K\), shows that operators contributed by \((i)^kI_0(K)\) are \(\Omega_L\), \((L \otimes R)\), and \((L \otimes L) \otimes \Omega_L\). Specific results are,

\[
i^l_0(1) = -\frac{(j_l(\|L \otimes L\|^2/\|l')}{\|L \otimes L\|^2/l')},
\]

and, with \(l = l' - 1\),

\[
i^l_0(2) = \frac{(j_l(\|L \otimes R\|^2/\|l')}{\|L \otimes R\|^2/\|l')},
\]

\[
i^l_0(3) = \frac{(j_l(\|L \otimes L\|^2 \otimes \Omega_L\|^2/\|l')}{\|L \otimes L\|^2 \otimes \Omega_L\|^2/l'}) = \frac{1}{2l' + 1} \frac{3}{2l' + 3}.
\]

In eq. (5.4) it is to be remembered that \((l \|\Omega_L\|^2)\) is purely imaginary with \((l' - 1)\|\Omega_L\|^2 \approx 2l(3/2)\). Expressions for \((L \otimes R)\) and \((L \otimes L) \otimes \Omega_L\) can be derived from results in Table II.

With our adopted definition a Hermitian operator, \(O_K\), satisfies \((O_K)^* = -iO_K\). where \(+\) denotes Hermitian conjugation, and the identity is satisfied by \(G_K\) and \(U_K\). The rule \((a_{a}b_{b}KQ) = (b_{b}a_{a}KQ)\) applies for two arbitrary operators.

Composite operators \((L \otimes R)^3\) and \((L \otimes L)^3 \otimes \Omega_L\) are Hermitian, even though constituent operators do not commute. This property arises because \((L \otimes R)^3\) and \((R \otimes L)^3\) have identical reduced matrix-elements, and the same is true of \((L \otimes R)^3 \otimes \Omega_L\) and \((\Omega_L \otimes (L \otimes R)^3)\). More generally, if \(O^k\) is a tensor product of \(r\) operators \(L\), tensor products \((O^k)^{\otimes r}\) and \((L \otimes O^k)^{\otimes r}\) have identical reduced matrix-elements, and the same holds when \(R\) is replaced by \(\Omega_L\). Operators of this type are used extensively and it is convenient to introduce a specific notation. If the operator contains \(R\), in addition to \(L\), it is labelled \(D_2\), while operators with \(\Omega_L\) in place of \(R\) are labelled \(D_3\). Examples encountered thus far are \(D_2 = (L \otimes R)^2\), \(D_3 = (L \otimes \Omega_L)^2\), \(\Omega_2 = (L \otimes \Omega_L)^3\), \(\Omega_3 = (L \otimes \Omega_L)^3 \otimes \Omega_L\), and a complete list is given in Table I.

The dependence on \(l\) associated with \(I_0(K)\) is obtained from eq. (4.6),

\[
\frac{(j_l(\|C(1)\|/l')}{\|C(2)\|/l')} = \frac{2l + 1}{2(2l + 1)} \left( \begin{array}{c} l' \ 1 \ 1 \\
2l + 1 \ 2 \ l' \ K \end{array} \right)
\]

For the special case \(l = 0\) this quantity reduces to

\[
\delta(l, l') = (2(-1)^{k+1}/\sqrt{15},
\]

and there is no contribution to \(U_K\) and \(G_K\).

We move ahead and consider contributions made by \((i)^kI_1(K,b)\) and \((i)^kI_1(K,b)\) to polar and magneto-electric multipoles, respectively. As mentioned above, the reduced matrix-element of a composite operator \((S \otimes B_0)^3\) is related to \(I_1(K,b)\), with \(B_0\) acting on orbital variables. For the orbital operator \(B_0\) we use a Hermitian operator with definite parity and time signatures \(a_{a}\) and \(a_{a}\), respectively.

Whence, the reduced matrix-element \((l' \|B_0\|)\) is \(((-1)^{k+1}a_{a}\sigma a_{a}b_{b}\|l' \|B_0\|)\). A short calculation reveals that \((S \otimes B_0)^{3} = ((-1)^{k+1}a_{a}\sigma a_{a}b_{b}\|l' \|B_0\|)\). The composite operator \((S \otimes B_0)^{3}\) is Hermitian (anti-Hermitian) for \(b + K\) odd (even). Reduced matrix-elements satisfy \((j_l(\|S \otimes B_0)^{3} \|j' \)\) is purely real and \((j_l(\|S \otimes B_0)^{3} \|j' \)\) is purely imaginary. Moreover, \((S \otimes R)^{1} = (S \otimes R)^{1}\). Spin operators are time-odd and satisfy \(S = S \times S\), which tells us that \(S\) is time-even, thus \((S \otimes R)^{1}\) is time-even. Similar reasoning shows that \((S \otimes \Omega_L)^{1}\) is time-odd. In general, the time-signature of a Hermitian composite operator \((S \otimes B_0)^{3}\) is \(-a_{a}\) and an anti-Hermitian composite operator has time signature \(+a_{a}\). The spin anapole \((S \times R)\) can be viewed as the spin analogue of the orbital anapole, \(\Omega_L\).\(^{29}\)

The generic form of \(I_1(K,b)\) is,

\[
I_1(K,b) = (j_l(\|S \otimes B_0)^{3} \|j' \)\}_{(1/2)\|S\|/2(1/2)\|B_0\|/l'),
\]

where the choice of orbital variable \(B_0\) depends on the case in hand, and \((1/2\|S\|/2(1/2)\|B_0\|/l') = \sqrt{7/2}l'= \sqrt{7/2}l'. Since I_1(K,b) is purely real the same must be true of \((j_l(\|S \otimes B_0)^{3} \|j' \)\).
Also, from the definition eq. (4.8), one gets the necessary condition
\[
(f'\| (S \otimes B_3)^k j) = (-1)^j - j + k + 1 \sigma_i \sigma_j (j'\| (S \otimes B_3)^k f')
\]

Let us consider the contribution \((i')^{K-1} I_1(K, b)\) to polar multipoles, \(U_K\). We start with Hermitian operators, \(b + K\) odd. For odd \(K\) and even \(b\) the composite operator is Hermitian, \(B_3\) is time-odd and constructed from \(R\) and odd numbers of \(L\). For example, with \(b = 2, D_2 = [L \otimes R]^2\) and for \(l = l' - 1\),
\[
([l]D_2^2 f') = ([l']2(l' - 1)(l' + 1))^{1/2}
\]

The result for \(I_1(1, 2)\) is listed in Table II, and it is explicitly time-even as required for all \(U_K\). The remaining term with odd \(K\) is \(I_1(3, 4)\) with \(D_4\) defined in Tables I and II, and for \(l = l' - 1\),
\[
([l]D_4^2 f') = -\frac{1}{2} ([l']2)2(2l' - 2)(2l' + 2) \times (l' - 1)(l' + 1)(2l' - 3)(2l' + 3))^{1/2}
\]

To complete Hermitian operators in the decomposition of \(U_K\) we need to consider \((i')^{K-1} I_1(K, b)\) with \(K = 2, b = 1\) and 3. Appropriate expressions are obtained from eq. (5.7) on taking \(B_3 = \Delta_1 = \Delta_2, B_3 = \Delta_3,\) and with \(l = l' - 1\),
\[
([l] \Delta_2^2 f') = 2i([l']2)^{1/2}
\]

It is to be noted that these reduced matrix-elements are purely imaginary, thus the contribution of \(I_1(2, b)\) to \(U_2\) is indeed directly related to time-even operators \([S \otimes \Delta_2]^2\) with \(b = 1\) and 3. An explicit expression for \([S \otimes \Delta_2]^2\) can be derived from results in Table II.

Non-Hermitian operators, with \(b + K\) even, are constructed with \(D_3\), and are nothing worse than Hermitian operators multiplied by \(i\). For odd \(K\) the two operators are \([S \otimes R]^1\) and \([S \otimes R]^3\), and the dipole is proportional to the spin anapole \((S \times R)\). The non-Hermitian quadrupole has \(b = 2\), and an expression for \([S \otimes D_2]^2\) is found in Table II.

The foregoing results are applied to the contribution from \((i')^{K-1} I_1(K, b)\) to magneto-electric operators, \(G_K\), involving the simple exchange \(R \rightarrow \Delta_L\), and results are gathered in Table I. Expressions for reduced matrix-elements \((|[B_3 f']\|)\) with \(l = l' - 1\) are obtained from eqs. (5.8)–(5.11), by multiplying matrix elements of \(R\) by \(2l'!\), e.g., \(([l] \Delta_2^2 f') = -2l'([l']2)!\).

We conclude with more remarks about reduced matrix-elements \((|[B_3 f']\|)\). One finds \((l'\|C(K))l' + 1\) = \(- l' + 1 \| C(K))l'\) with,
\[
l' - 1 \| C(1)l' = - \sqrt{f}, \]
\[
l' - 1 \| C(3)l' = \frac{3l'(l' - 1)(l' + 1)}{2(2l' - 3)(2l' + 3)}, \]

and, in the light of the foregoing identity, \((l' + 1 \| C(1)l'\) is derived from these specific results by the replacement of \(l'\) by \(l' + 1\) together with a change of sign, e.g., \((l' + 1 \| C(1)l'\) = \(- \sqrt{f} + f\). Additionally, \((l'\|C(1)l'\) = \(- l' + 1 \| C(1)l'\), thus \((l' + 1 \| C(1)l'\) is derived from \((l' - 1 \| C(1)l'\) = \(2i([l']2)^{1/2}\) by the replacement of \(l'\) by \(l' + 1\) and no change in sign. The rules to obtain \((|[B_3 f']\|)\) with \(l = l' + 1\) from the result with \(l = l' - 1\) is general. Looking at eqs. (5.8), (5.9), and (5.11) we see dependence on \(l'\) is a product of \(l'\) and factors \(n'\pm 1\) and \(n'\pm 3\) with \(n = 1\) and 2. We find this symmetric structure in all our results for \(l = l' - 1\), and it is also to be seen in results published by Racah.\(^{31}\)

6. Discussion
Our analysis has concentrated on parity-odd, \(E_1\)–\(E_2\), processes here. Parity-odd events, like \(E_1\)–\(E_2\) (and \(E_1\)–\(M_1\))\(^{26}\), are allowed when valence states at the site of the resonant ion are an admixture of orbitals with opposite parities, which can occur when the site is not a centre of inversion symmetry. The essential part of the resonance-enhanced scattering amplitude represents products of absorption and re-emission matrix elements by a set of single matrix elements of equivalent atomic tensors which are studied. Because the bare algebraic results, though useful for numerical calculations, are rather uninviting we have undertaken to find an equivalent representation by tensors constructed from basic tensor operators. Although these equivalent operators, especially for higher rank, may not seem simplicity itself, they display an intricate structure, and their reduced matrix elements are true representations of the original algebraic expressions. It is to be noted that the expression for the \(E_1\)–\(E_2\) amplitude published by Marri and Carra\(^{33}\) is flawed, i.e., the amplitude constructed from equation (4) and Table I in ref. 33 is not the same as eq. (3.3). Specifically, the amplitude provided by Marri and Carra\(^{33}\) does not satisfy crossing-symmetry while compliance with this necessary symmetry is explicit in our result.

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