X-ray Dichroism in Noncentrosymmetric Crystals

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In this paper the authors analyse near-edge absorption of x rays in noncentrosymmetric crystals. The work is motivated by recent observations of x-ray dichroic effects which stem from parity-nonconserving electron interactions. We provide a theoretical description of these experiments and show that they are sensitive to microscopic polar and magnetoelectric properties of the sample. Our derivation extends previous theoretical work on centrosymmetric systems and identifies new directions in the microscopic analysis of crystalline materials using x-ray absorption spectroscopy.

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I. INTRODUCTION

A. Pure electric transitions

Near-edge x-ray dichroism with synchrotron radiation is a powerful probe of electronic states in crystals. As is known, its effectiveness stems from two prominent features of inner-shell excitations

site selectivity, resulting from the tuning of the x-ray energy at a given inner-shell threshold;

electron angular momentum resolution, as enforced by the selection rules of pure electric multipole (E1, E=2, ...) transitions, which raise an inner-shell electron to empty valence orbitals.

Linear or circular polarisations are employed in experiments, leading to linear or circular x-ray dichroism, respectively. The former implies a difference between radiations with linear polarisations parallel or perpendicular to a local symmetry axis and is sensitive to charge anisotropies. The latter measures the difference in absorption between right and left circularly polarised radiations and reflects magnetic properties of crystals.

Following the pioneering work of Templeton and Templeton [1] and Schütz and coworkers [2], a number of authors have recorded x-ray dichroic signals in a variety of samples, ranging across the periodic table from 3d transition metals to actinides.

In parallel with this experimental activity, theory has aimed at identifying the microscopic origin of the observed spectra. Working within an atomic model [3, 4, 5] (a good approximation, as it was later demonstrated [6]) a set of sum rules was obtained, which relate integrated dichroic intensities to the ground-state expectation value of effective one-electron operators (irreducible tensors) [7]. Two classes of operators are obtained, which are identified by their transformation properties under space inversion (x → −x, I-transformation) and time reversal (t → −t, R-transformation). They correspond to charge (I-even, R-even) and magnetic (I-even, R-odd) order parameters of crystals. X-ray dichroism is thus sensitive to long-range crystalline orderings and these are distinguished by photon polarisation and by the nature (E1 or E2) of the inner-shell excitation. Undoubtedly, the most important result of this theoretical analysis has been to show that, in a ferromagnet (or ferrimagnet), x-ray circular dichroism provides a direct and independent determination of orbital and spin contributions to the magnetic moment [8].

It is important to observe that pure electric multipole transitions cannot probe electronic properties which stem from the breaking of space inversion: all order parameters revealed by pure E1 and E2 transitions are even under the transformation I.

B. Interference

In the x-ray region, other classes of dichroic phenomena have recently been investigated by Goulon et al. who reported the observation of three effects:

X-ray natural circular dichroism (XNCD), probed in Na3Nd(digly)3·2NaBF4·6H2O [9] and in α-LiIO3 [10]. (The effect was observed near the Nd L3 edge and near the iodine L edges.)

X-ray nonreciprocal linear dichroism (XNLD), detected near the vanadium K edge in the low-temperature insulating phase of a Cr-doped V2O3 crystal [11].

X-ray magnetochiral dichroism (XMCD), observed at the chromium K edge [12] in crystalline Cr2O3.

Here, inner-shell excitations are ascribed to the E1-E2 interference; detecting a nonvanishing signal thus requires an ordered structure and the breaking of space inversion.

In our view, the work of Goulon and his collaborators is of particular importance as it identifies new directions in the microscopic analysis of materials using x-ray absorption spectroscopy. In fact, symmetry considerations
indicate that XNCD, XNLD and XM\text DELD are sensitive to polar and \textit{magneto} electric (ME) properties of crystals.

It is immediately obvious that the microscopic theory of integrated spectra previously mentioned does not apply to the E1-E2 interference. Broader symmetry considerations are required to identify order parameters probed by x-ray natural and non-reciprocal dichroism. Such an analysis is outlined in the current work. Our discussion will be restricted to spectra integrated over the energy range corresponding to the two partners of a spin-orbit split inner shell: $j_\pm = l_c \pm \hbar \omega$, where $l_c$ denotes the angular momentum of the inner electron. Only orbital degrees of freedom (no spin) are observed in this case.

It will be shown that the E1-E2 interference is described by \textit{I}-odd microscopic operators, revealing the presence of parity nonconserving interactions. (We remind the reader that the expectation value of an \textit{I}-odd operator vanishes in any state of definite parity.) As in the case of pure electric multipole transitions, such operators are further distinguished by their behaviour under time reversal. Two classes of order parameters are therefore identified

\begin{itemize}
  \item \textit{R}-even and \textit{I}-odd operators corresponding to one-electron polar properties, which arise from a non-centrosymmetric distribution of charge.
  \item \textit{I}-odd and \textit{R}-odd operators, obviously invariant under the combined symmetry $RI$ and thus describing one-electron ME properties of crystals \cite{12}.
\end{itemize}

It is thus readily seen that E1-E2 x-ray dichroism is sensitive to additional charge and magnetic orderings, which manifest themselves when the crystal lacks space-inversion symmetry.

For convenience of the reader, a classification of order parameters as probed by various x-ray dichroisms is provided in Table I \cite{5}. [Notice that a class may contain more than one order parameter, as illustrated by the following example. Consider pure E2 absorption. Four irreducible tensors of rank $k = 0, 1, \ldots, 4$ contribute to the integrated spectrum, for arbitrary polarisation \cite{11}. In this case, magnetic circular dichroism selects two order parameters: a vector ($k = 1$) and an octapole ($k = 3$).]

\section{E1-E2 X-ray Dichroism}

This Section discusses general features of E1-E2 x-ray absorption. As we have anticipated, we will consider integrated spectra and express them as a linear combination of ground-state expectation values of one-electron irreducible tensors (order parameters). These order parameters are obtained by implementing Racah-Wigner recoupling techniques \cite{13}, a convenient framework for dealing with the angular part of matrix elements. The ensuing results will then be applied to x-ray natural and nonreciprocal dichroism. Our discussion focusses on the physical interpretation of dichroic spectra; algebraic details of the derivation will be given in an appendix.

\subsection{Space-odd Order Parameters}

Central to our considerations is the absorption cross section

\begin{equation}
\sigma^\epsilon(\omega) = 4\pi^2 \alpha \epsilon \omega \left[ \frac{i}{2} \sum_f \sum_{i,l, l'} \langle g | \epsilon^* \cdot r_i | f \rangle \langle f | \epsilon \cdot r_e k \cdot r_{l'} | g \rangle + \text{c.c.} \right] \delta(E_f - E_g - \hbar \omega),
\end{equation}

picking out the E1-E2 interference in the $p \cdot A$ interaction between x rays and electrons. The notation is as follows: $\hbar \omega$, $k$ and $\epsilon$ represent energy, wave vector and polarisation of the photon; $|g\rangle$ and $|f\rangle$ denote ground and final states of the electron system, with energies $E_g$ and $E_f$ respectively; electrons are labelled by $i$ and $i'$; $\alpha = e^2 / \hbar c$.

The integrated intensity \cite{4},

\begin{equation}
\int_{-\hbar \omega}^{\hbar \omega} \frac{\sigma^\epsilon(\omega)}{(\hbar \omega)^2} d(\hbar \omega),
\end{equation}

expands into a linear combinations of pairs of irreducible tensors of increasing rank, $\mu = 1, 2, 3$. Each pair is given by the scalar product between a wave-vector and polarisation response (geometrical factor) and the ground-state expectation value of an effective one-electron operator

\begin{equation}
\sum_q T_q^{(\mu, \pm)}(\epsilon, \hat{k}) \langle g | \mathcal{O}_q^{(\mu, \pm)}(l, l') | g \rangle.
\end{equation}

In the second quantisation formalism, the latter is defined by

\begin{equation}
\sum_i \langle l, l' \rangle \mathcal{O}_q^{(\mu, \pm)}(l, l') = \sum_{m m'} \langle l' m' | \mathcal{O}_q^{(\mu, \pm)} | l m \rangle a_{l m}^{m'} a_{l m} + \text{c.c.},
\end{equation}

where $l' = l \pm 1$ and $| lm \rangle$ stands for a spherical harmonic; $a_{l m}^{m'}$ and $a_{l m}^{m'}$ create and annihilate valence electrons. All $\mathcal{O}_q^{(\mu, \pm)}(l, l')$ are odd under space inversion; their behaviour (even or odd) under time reversal is denoted by the superscript $\pm$. 

\[\]
TABLE I: Order parameters and x-ray dichroic effects.

| Order Parameter | Space Inversion | Time Reversal | X-ray Dichroism | X-ray Transition |
|-----------------|-----------------|---------------|-----------------|-----------------|
| Charge          | even            | even          | Linear          | Pure E1 or E2   |
| Magnetic        | even            | odd           | Magnetic Circular | Pure E1 or E2   |
| Electric        | odd             | even          | Natural Circular | Interference E1-E2 |
| Magnetolectric  | odd             | odd           | Nonreciprocal    | Interference E1-E2 |

Four operators $O^{(\mu,\pm)}$ contribute to the E1-E2 absorption spectrum for arbitrary polarisation. They can all be written out in terms of three dimensionless order parameters: the familiar orbital angular momentum $L$, an electric dipole $n = r/r$, and $\Omega = (n \times L - L \times n)/2$, a ME vector.

By applying suitable recoupling transformations to Eq. (i), we obtain

$$O^{(1,-)} = \Omega, \quad O^{(2,+)} = [L, \Omega]^{(2)}, \quad O^{(2,-)} = [L, n]^{(2)} \quad \text{and} \quad O^{(3,-)} = [[L, L]^{(2)}, \Omega]^{(3)},$$

where the couplings are defined via Clebsch-Gordan coefficients

$$U^{(\mu)}(x)_{ij} = \sum_{\mu,\nu} C^{\mu q}_{\mu l \nu} U^{(p)}(x) \nu^\mu.$$

Equations (i) identify one-electron properties revealed by E1-E2 absorption in the x-ray domain. The corresponding geometrical factors are given in Table I. $T^{(1,+)}(\epsilon, k) = T^{(3,+)}(\epsilon, k) = 0$, the polar moments $O^{(1,+)} = n$ and $O^{(3,+)} = [[L, L]^{(2)}, n]^{(3)}$ do not contribute to expression (ii).

Our derivation is based on a localised model, which considers a single ion with a partially filled valence shell; all other shells filled. Inclusion of spin-orbit interactions and/or crystal fields results in a deformation of the electronic cloud. Its multipolar expansion will contain spin and orbital moments characteristic of the symmetry of the deformation and described by one-particle irreducible tensors. Valence states are hybridised in general, with the orbital part given as a superposition of two angular tensors. Valence states are hybridised in general, with the deformation and described by one-particle irreducible tensors. Only the off-diagonal part contributes to the ground-state matrix elements, in this case. Orbital angular momentum is not a good quantum number and electron states do not have definite parity. Hybridisation effects are now observable and described by the operators $O^{(\mu,\pm)}$.

TABLE II: Polarisation responses of the E1-E2 interference.

| Order Parameter | Space Inversion | Time Reversal | X-ray Dichroism | X-ray Transition |
|-----------------|-----------------|---------------|-----------------|-----------------|
| Charge          | even            | even          | Linear          | Pure E1 or E2   |
| Magnetic        | even            | odd           | Magnetic Circular | Pure E1 or E2   |
| Electric        | odd             | even          | Natural Circular | Interference E1-E2 |
| Magnetolectric  | odd             | odd           | Nonreciprocal    | Interference E1-E2 |

B. Interpretation of experiments

1. XNCD

In this case, a recoupling of Eq. (i) leads to the following integral relation

$$T^{(1,-)}(k)_{2} = -\frac{1}{2} \sqrt{\frac{1}{2}} k$$

$$T^{(2,+)}(\epsilon, k)_{2} = \sqrt{\epsilon} \left[ [\epsilon^{*}, \epsilon]^{(1)}, k_{2}^{(2)} \right]$$

$$T^{(2,-)}(\epsilon, k)_{2} = \frac{1}{2} \left[ [\epsilon^{*}, \epsilon]^{(2)}, k_{2}^{(3)} \right]$$

$$T^{(3,-)}(\epsilon, k)_{2} = \left[ [\epsilon^{*}, \epsilon]^{(2)}, k_{3}^{(2)} \right]$$
whose crystal structure (space group $P6_3/mmc$) is depicted in Fig. 1, with $\bullet = \text{Li}$, $\bullet = \text{O}$, and $\bullet = I$.

The XNCD experiment of Goulon et al. on $\alpha$-LiIO$_3$ is described in the manuscript. Their crystal structure (space group $P6_3/mmc$) is depicted in Fig. 1, and is readily interpreted with the help of Eq. 3.

In the case of XNLD, the integral relation reads

$$\int_{\gamma_{+-}, \gamma_{++}} \frac{\sigma_X^+(\omega) - \sigma_X^-(\omega)}{(h\omega)^2} d(h\omega) = \frac{8\pi^2\alpha}{3hc}(2l_c + 1) \sum_{i,l_i \pm 1} R_{(1)}^{(1)} R_{(2)}^{(2)} [l_i, l_i'] \sum_{q} \left\{ \sqrt{\frac{2}{3}} a_i^{(2, -)}(l_c, l) \left[ T_q^{(2, -)*}(\epsilon^\parallel, \hat{k}) - T_q^{(2, -)*}(\epsilon^\perp, \hat{k}) \right] \right\}$$

$$\langle g | \sum_l [L_i, n_{i q}^{(2)}(l, l')]|g \rangle - 2a_i^{(3, -)}(l_c, l) \left[ T_q^{(3, -)*}(\epsilon^\parallel, \hat{k}) - T_q^{(3, -)*}(\epsilon^\perp, \hat{k}) \right] \langle g | \sum_l [L_i, L_i]^{(2)} |l, l'\rangle |g \rangle ,$$

where $|\parallel$ and $|\perp$ denote two orthogonal linear-polarisation states. The expansion coefficients are given by

$$a_i^{(2, -)}(l_c, l) = \frac{a_i^{(2, +)}(l_c, l)}{6 + 3l_c(l_c + 1) - 2l(l + 1) - l'(l' + 1)}$$

and

$$a_i^{(2, +)}(l_c, l) = \frac{(l + l' + 1)(l' - l)}{2} a_i^{(2, +)}(l_c, l),$$

where $a_i^{(2, +)}(l_c, l)$ is defined by Eq. 3.

We focus on charge properties stemming from $sp$ hybridisation. (The 4$d$ shell of iodine is filled and the crystal displays no magnetism.) At the iodine sites the symmetry is $C_3$. Notice that $O^{(2, +)} = [L, \Omega]^{(2)}$, known as pseudodeviator or gyration tensor, is totally symmetric in this point group i.e., it is invariant under all $C_3$ transformations. It yields therefore a nonvanishing ground-state expectation value at each iodine site. The three-fold axes of all the iodate groups are parallel in the unit cell of $\alpha$-LiIO$_3$ ($P6_3$ is noncentrosymmetric). As a consequence, all the microscopic pseudodeviators add up upon absorption of circularly polarised x rays. This contribution to the E1-E2 absorption profile is selected by circular dichroism (see Table II) yielding the observed XNCD spectrum. The effect can thus be viewed as the $I$-odd analog of ferroquadrupolar ordering, which is probed by pure E1 x-ray linear dichroism.

The XNCD experiment of Goulon et al. on $\alpha$-LiIO$_3$ is described in the manuscript. Their crystal structure (space group $P6_3/mmc$) is depicted in Fig. 1, and is readily interpreted with the help of Eq. 3.
Equation (6) reveals the microscopic ME nature of XNLD. (Notice the peculiarity of this form of linear dichroism: it changes sign upon reversal of an external applied magnetic field[17]. The result implies that Goulon and his co-workers have probed ME properties of \((V_{1-x}Cr_x)_2O_3\).

\(V_2O_3\) is characterised by a strongly destructive first-order transition from a paramagnetic metallic phase (corundum structure) to an antiferromagnetic (AFM) insulating phase (monoclinic) at \(T_N \approx 150^\circ\text{K}\). The unit cells of pure \(V_2O_3\) are depicted in Fig. 2.

Substitution of \(Cr^{3+}\) in the \(V_2O_3\) lattice results in a Mott metal-to-insulator transition. At room temperature, charge properties of the compound can be deduced from structural studies, which have been reported by Dernier and Marezzo[18, 19]. These authors ascribe the Cr-induced metal-to-insulator transition to an increase in the nearest neighbour vanadium-vanadium distances, which is accompanied by an ‘umbrella-like’ distortion of the oxygen octahedra. Crystal-structure refinements indicate that at each vanadium site the point group is \(C_{3v}\) [19]. Formation of an electric-dipole moment is thus permitted by symmetry. Crystallography also suggests that nearest-neighbour pairs of vanadium atoms are antiferroelectrically ordered along the hexagonal \(c\) axis (the symmetry of a pair is \(D_{3h}\) [13]), as shown in Fig. 3. We can thus argue that, at about 300 °K in the insulating phase, \((V_{1-x}Cr_x)_2O_3\) is an antiferroelectric (AFE) crystal [20].

At \(T = T_N\), the crystal makes a nearly second-order transition to an AFM monoclinic phase [21]. The driving mechanism of this transition is not fully understood [22]. The lattice space group lowers to \(I2/a\), with magnetic point group \(C_{2h} \otimes R\) [23]. Notice that this symmetry is incompatible with the observation of XNLD. However, a reduction of magnetic symmetry leading to \(C_{2h}(C_{1h})\) or \(C_{2h}(C_2)\) might take place [24].

A lowering of magnetic symmetry could occur as follows. The structural change to the monoclinic phase eliminates the three-fold axis, which characterises the corundum structure. It probably involves a co-operative Jahn-Teller distortion, which tilts the electric moments.
A tilting with the pattern depicted in Fig. 3 would render \((V_{1-x}\text{Cr}_x)\text{O}_3\) an AFM, AFE, and ME crystal, thus explaining the observations of Goulon and his collaborators.

A physical interpretation of Eq. (9) is obtained by expanding the "energy" function \(W(n, L)\)\(^2\). The \(m\)th term in the MacLaurin formula reads: \(\frac{1}{m!} (n_c \partial_{n_c} + L_\beta \partial_{L_\beta})^m W(0, 0)\); here, greek letters denote cartesian components and repeated indexes are summed over. It is readily seen that \([L, n]^{(2)}\) stems from the \(m = 2\) term and describes a linear ME effect. The contribution \([\{L, L\}^2, \Omega]^{(3)}\) is found in the \(m = 4\) term and accounts for a trilinear ME effect.

\[
\int_{j^+} \frac{(\sigma^{+} + \sigma^{-})_{E1} d(h\omega)}{(h\omega)^2} = 4\pi^2 \alpha \sum_l \left[ \frac{2 n_h(l)}{3 (2l + 1)} + b^{(2,+)}(l, l) \langle g | \sum_i (3L^2_i - L^2) | g \rangle \right] [P_{l,l}^{(1)}]^2,
\]

where \(n_h(l) = 4l + 2 - \langle g | n | g \rangle\) denotes the number of holes in the valence \(l\) shell, and \(P_{l,l}^{(1)} = \langle c | \sqrt{4\pi/5} Y^{(1)} | l \rangle R_{l,l}^{(1)}\).

In the case of a magnetoelectric crystal, E1-E2 corrections to Eq. (10) need to be taken into account. They read

\[
\int_{j^+} \frac{(\sigma^{+} + \sigma^{-})_{E1-E2} d(h\omega)}{(h\omega)^2} = \frac{2\pi^2 \alpha}{\hbar c} (2l_c + 1) \sum_{l = l_c, l' = l \pm 1} \sum_{l' = l + 1} R_{l,l}^{(1)} R_{l',l'}^{(2)} \left[ \frac{2}{5} a^{(1,-)}_{l'}(l_c, l) k_z \langle g | \sum_i \Omega_i (l, l') | g \rangle \right] - \frac{16}{\sqrt{10}} a^{(3,-)}_{l'}(l_c, l) k_z \langle g | \sum_i [[L_i, L_i]^2, \Omega_{l,l'}^{(3)}] (l, l') | g \rangle
\]

with \(a^{(1,-)}_{l'}(l_c, l) = \frac{(l_c + l + 1)(l_c + l - 2l') h_1(l_c, l, l')}{(l_c + l)(l_c + l + 2)(l + l' + 1)^2}\), \(h_1(l_c, l, l') = l_c + 2l' - l + 1\) and \(l' = l \pm 1\). We have set \(k = \hat{z}\) in Eqs. (11-13).

Eqs. (11-13) indicate that XM\(\chi D\) is observed as follows. Record the \(\sigma^{+} + \sigma^{-}\) spectrum in a magnetoelectric crystal annealed in the parallel configuration. Ditto for antiparallel annealing. Subtract the two spectra.

### 3. XM\(\chi D\)

The third form of E1-E2 x-ray dichroism, namely XM\(\chi D\), was probed by Goulon and co-workers\(^{11}\) at the chromium K-edge in \(\text{Cr}_2\text{O}_3\) by implementing a new experimental technique: the dichroism of unpolarised x rays.

A microscopic description of this spectroscopy, which is readily obtained from our theory of integrated spectra, is reported in the current subsection.

As is known \(^{11}\), the following integral relationship holds for pure E1 transitions:

\[
\frac{2\pi^2 \alpha}{\hbar c} (2l_c + 1) \sum_{l = l_c, l' = l \pm 1} \sum_{l' = l + 1} R_{l,l}^{(1)} R_{l',l'}^{(2)} \left[ \frac{2}{5} a^{(1,-)}_{l'}(l_c, l) k_z \langle g | \sum_i \Omega_i (l, l') | g \rangle \right] - \frac{16}{\sqrt{10}} a^{(3,-)}_{l'}(l_c, l) k_z \langle g | \sum_i [[L_i, L_i]^2, \Omega_{l,l'}^{(3)}] (l, l') | g \rangle
\]

It goes without saying that such a dichroic spectrum, which is described by Eq. (12), reflects ME properties of crystals.

### III. DISCUSSION AND OUTLOOK

To provide a theoretical interpretation of recent x-ray experiments, which have detected XNCD, XNLD...
and XM\(_2\)D respectively in \(\alpha\)-LiIO\(_3\), \((V_{0.972\text{Cr}_{0.028}})\)\(_2\)O\(_3\) and Cr\(_2\)O\(_3\), the current paper has presented a theoretical analysis of near-edge absorption of polarised x rays in noncentrosymmetric crystals. Our work has centred on the derivation of integral relations for dichroic effects which stem from E1-E2 inner-shell excitations. Such relations are written out in terms of one-electron effective operators (order parameters), which identify crystalline microscopic properties revealed by the observed spectra. Two classes of parity-breaking order parameters have been found, which correspond to polar and magnetoelectric moments of valence electrons. Only orbital degrees of freedom have been considered in our derivation; inclusion of spin would be straightforward.

We remind the reader that two irreducible tensors, namely \(O^{(1,+)} = n\) and \(O^{(3,+)} = \{[L, L]|^{(2)} n\}^{(3)}\) (see Section II A), have not entered our discussion of integrated XNCD, XNLD and XM\(_2\)D spectra. As previously observed, \(O^{(1,+)}\) and \(O^{(3,+)}\) have vanishing geometrical factors and do not appear in our coupled expansion of expression (2). They do contribute however to x-ray resonant diffraction, as can be verified by extending the work of Luo et al. [26] to include E1-E2 processes. (Such a lengthy derivation will not be reported here.) The result is of interest as it indicates the possibility of detecting Bragg peaks from ferroelectric and AFE structures with x rays at resonance.

In conclusion, the pioneering experiments of Goulon and his collaborators appear to have paved the way for new investigations of electronic states in noncentrosymmetric crystals using x-ray absorption and resonant scattering. As shown by our work, a variety of one-electron properties, which result from parity-nonconserving electron interactions, can be measured, yielding valuable information in condensed matter physics and material science.

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APPENDIX: SYMMETRY ANALYSIS

Lie groups (or, alternatively, Lie algebras) furnish a powerful tool for interpreting x-ray dichroism in noncentrosymmetric crystals. In fact, effective microscopic operators, which express electronic properties revealed by the spectra, are readily deduced from the pertinent group generators. Our approach hinges therefore on spectrum-generating algebras, a concept originally introduced in nuclear [27] and particle physics [28, 29].

We follow Carra and Benoist [30] and consider the general framework of a de Sitter algebra: so(3,2) [27,31]. A realisation of such an algebra is provided by the operators:

\[
A^- = i(A-A^\dagger)/2, \quad A^+ = (A+A^\dagger)/2, \quad (A.1)
\]

\[
L \quad \text{and} \quad N_0, \quad (A.2)
\]

where \(L\) denotes the orbital angular momentum (in units of \(\hbar\)) and \(N_0|lm\rangle = (l+\frac{1}{2})|lm\rangle\), with \(|lm\rangle\) a spherical harmonic. Furthermore,

\[
A = n f_1(N_0) + \nabla_\Omega f_2(N_0), \quad (A.3)
\]

with \(n = r/r\), \(\nabla_\Omega = -in \times L\) and

\[
f_1(N_0) = (N_0 - 1/2)f_2(N_0), \quad (A.4)
\]

\[
f_2(N_0) = \sqrt{(N_0 - 1)/N_0}. \quad (A.5)
\]

\(A\) and \(A^\dagger\) are known as shift operators as their action on \(|lm\rangle\) changes \(l\) into \(l \pm 1\).

A physical interpretation of \(A^-\) is provided by the relation

\[
A^- = \sqrt{N_0} n \sqrt{N_0}. \quad (A.6)
\]

\(L, n\) and \(\Omega\) provide the building blocks of our derivation. They form a triad of mutually orthogonal dimensionless vectors. Their nature (magnetic, electric and magnetoelectric, respectively) is readily inferred from behaviour under space inversion and time reversal.

Notice that \(L\) (rotations) and \(\Omega\) (boosts) generate

\[
\Omega = (n \times L - L \times n)/2 = i[n, L^2]/2 = \frac{i}{2} \left[\nabla_\Omega - \nabla_\Omega^\dagger\right] = \frac{1}{2 \sqrt{N_0}} \left[N_0, A^-\right] + \frac{1}{\sqrt{N_0}}, \quad (A.6)
\]

where \([,...]\) denotes an anticommutator. Eq. (A.7) defines the (purely angular) orbital anapole [32,33,34].

A physical representation of the generator \(A^+\) is provided by

\[
A^+ = \sqrt{N_0} n \sqrt{N_0}. \quad (A.7)
\]
a homogeneous Lorentz group: SO(3,1). Also $L$ and $\sqrt{N_0} n_{\sqrt{N_0}}$, where $N_0 |lm\rangle = (l + \frac{3}{2}) |lm\rangle$, generate SO(3,1). The homogeneous Lorentz group enters our derivation of I-odd operators in a natural way, given its deep interweaving with chirality. Notice that $L$, $\Omega$ and $\sqrt{N_0} n_{\sqrt{N_0}}$ provide a realisation of the so(3,2) de Sitter algebra. This is the required symmetry extension, with respect to pure E1 or E2 transitions, that was mentioned in the Introduction.

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[16] In Eq. (4), the radial integrals are defined by $R^{(L)}_{l,m} = \int_0^{\infty} dr \varphi_l(r)r^{L+2} \varphi_l(r)$, where $\varphi_l(r)$ and $\varphi_l(r)$ denote inner-shell and valence radial wave functions, respectively. Our derivation neglects relativistic corrections to the radial part of the atomic wave functions.
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