X-ray natural circular dichroism

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This paper discusses a theory of natural circular dichroism in the x-ray region. Integrated spectra are interpreted in terms of microscopic effective operators, which are derived in the framework of a localised (atomic) model. It is shown that the generators of a de Sitter group, such as that introduced by Goshen and Lipkin for nuclear structure, are suitable for describing electronic properties of non-centrosymmetric crystals.

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In recent years, near-edge dichroism in crystals, i.e. the dependence of x-ray absorption on crystal and/or magnetic orientations with respect to the polarisation of the photon, has been thoroughly investigated at synchrotron radiation sources. Particular attention has been given to x-ray magnetic circular dichroism (XMCD), namely the difference in absorption between right- and left-circularly polarised photons in a system with a net magnetisation. Various authors have demonstrated the effect [1–4], which requires the breaking of time-reversal symmetry and the presence of a spin-orbit interaction. Electric-dipole (E1) and, in some cases, electric-quadrupole (E2) transitions [3,4] account for the pertinent inner-shell excitations.

Theoretically, efforts have been made to identify crystalline microscopic properties revealed by the observed spectra; and, in this context, atomic theory has provided a number of results. Among these is a set of sum rules, which relate integrated dichroic intensities to the ground-state expectation value of effective one-electron operators [5,6]. In the case of XMCD these operators coincide with the spin and orbital contributions to the magnetic moment, thus providing experimentalists with a simple interpretative framework.

To cover the more realistic case of an atom in a solid, a formulation of the problem in terms of a minimal set of muffin-tin orbitals has also been reported [6]. In this case, corrections to the atomic results are found to be small in most cases.

More recently a novel phenomenon, termed x-ray natural circular dichroism (XNCD), was observed in an organic non-centrosymmetric single crystal [7] and in a stereogenic organometallic complex [8]. The effect stems from the interference between E1 and E2 transitions, thus requiring an ordered structure and the breaking of space inversion.

Aimed at deriving an XNCD sum rule, earlier theoretical work [11] has identified the relevant effective operator with a rank-two tensor. Its microscopic nature and symmetry properties were not, however, fully determined.

The current paper follows the program of Ref. [11] to its natural conclusion. Particular symmetry considerations are needed to complete the analysis; in virtue of them new effects, still to be probed experimentally, emerge.

It is worth reminding the reader that effective operators for x-ray dichroism are irreducible tensors constructed from the generators of the underlying symmetry group. In the case of pure electric multipole-transitions, it suffices to work within the rotation group, i.e. with the spherical components of the angular momentum. In this way, sum rules for CMXD and linear x-ray dichroism were obtained [7,8]. (Linear dichroism implies a difference in absorption between radiations with linear polarisation parallel or perpendicular to a local symmetry axis.) To study interference terms an extension of the symmetry group is required. As shown below, the extended symmetry is identified with a de Sitter group, O(3,2), a non-compact version of O(5). Its generators will serve to write out a sum rule for XNCD.

An aspect of symmetry relevant to XNCD is the absence/presence of mirror planes in the permitted point groups, with the ensuing difference between enantiomeric and non-enantiomeric systems. To properly elucidate this point, effective operators will be discussed for the E1 - magnetic dipole (M1) interference, which governs the natural dichroism in the optical range.

Central to our considerations is the integrated intensity

\[ \Sigma_{\text{XNCD}} = \int_{j_- + j_+} \frac{\sigma_{\text{XNCD}}(\omega)}{(\hbar \omega)^2} d(\hbar \omega), \]  

where \( \sigma_{\text{XNCD}}(\omega) = \sigma_X^\alpha(\omega) - \sigma_X^g(\omega) \) denotes the cross section for natural circular dichroism in the x-ray region (X), a macroscopically measurable quantity. Integration is over a finite photon-energy range in Eq. (1), corresponding to the two partners of a spin-orbit split inner shell. The partners are identified by \( j_\pm = c \pm \frac{1}{2} \).

\textit{E1-E2 interference.} The link between \( \Sigma_{\text{XNCD}} \) and a microscopic description is provided by the relation

\[ \sigma_X^\alpha(\omega) = 4\pi^2 \alpha \hbar \omega \left[ \frac{1}{2} \sum_f \sum_{nn'} \langle g | \epsilon^* \cdot r_n | f \rangle \right] \]  

\[ \langle f | \epsilon \cdot r_{n'k} \cdot r_{n'} | g \rangle + \text{c.c.} \delta(E_f - E_g - \hbar \omega), \]
picking out the E1–E2 interference in the absorption cross section. The notation is as follows: $\hbar \omega$, $\mathbf{k}$ and $\mathbf{e}$ 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 $n$ and $n'$; $\alpha = e^2/\hbar c$.

We consider the fermionic field

$$\Psi(r) = \sum_{l,\lambda,\sigma} a_{l\lambda\sigma} \psi_{l\lambda\sigma}(r) + \sum_{m} a_{jm} \psi_{jm}(r),$$

and go over to a second quantisation description. Here, $a_{jm}$ and $a_{l\lambda\sigma}$ $(a_{l\lambda\sigma}$) annihilate inner-shell and valence electrons, respectively.

The matrix element appearing in Eq. (2) can then be given the form

$$\sum_{n'n'} \langle g | \epsilon^* \cdot r_n | f \rangle \langle f | \epsilon \cdot r_n' \cdot k \cdot r_n' | g \rangle = \sum_{\lambda',\lambda',m'm'} \langle \psi_{jm'} \cdot \epsilon^* \cdot r | \psi_{l\lambda\sigma} \rangle \langle \psi_{l\lambda\sigma} | \epsilon \cdot r \cdot k \cdot r \psi_{jm} \rangle\langle f | \psi_{jm} \rangle \langle \psi_{jm'} \cdot \epsilon \cdot r_n' | g \rangle$$

The atomic basis set, which enters the definition of the fermionic field, is chosen as follows. Core electrons are identified by coupled atomic orbitals

$$\psi_{jm}(r) = \sum_{\gamma,\sigma} C_{lj\gamma,\sigma} \varphi_{\gamma \sigma}(r) \xi_{\sigma},$$

with $C_{lj\gamma,\sigma}$ a Clebsch-Gordan coefficient, $\varphi_{\gamma \sigma}(r) = \varphi_{\gamma}(r) Y_{\gamma \sigma}(\hat{r})$, and $\xi_{\sigma}$ a spinor. Valence states are described by uncoupled atomic wave functions,

$$\psi_{l\lambda\sigma}(r) = \varphi_{l}(r) Y_{\lambda \sigma}(\hat{r}) \xi_{\sigma},$$

and similarly for $l' \lambda' \sigma'$. The derivation then proceeds by applying the Wigner-Eckart theorem and simple recoupling transformations. (Algebraic details are omitted as they can be found in the work of Natoli et al. [14].) The result reads

$$\Sigma_{\text{INC}} = \frac{8\pi^2\alpha}{\hbar c} \sqrt{\frac{2\pi}{15}} \sqrt{2c + 1} \sum_{l''} R_{c1}^{(1)} R_{c2}^{(2)}$$

$$\sqrt{2l + 1} C_{l0;10}^{l'} C_{20;0}^{l''} \left\{ \begin{array}{ccc} l & l' & 2 \\ 2 & 1 & c \end{array} \right\} Y_{20}(\hat{k})$$

$$i \sum_{m'm'} \langle g | C_{l'm';lm}^{20} a_{lm}^\dagger a_{l'm'} \rangle - \text{h.c.} \langle g \rangle,$$

with the radial integrals defined by

$$R_{c1}^{(L)} = \int_{0}^{\infty} dr \varphi_{c}(r) r^{L+2} \varphi_{1}(r).$$

Also, $\hat{a}_{lm} = (-1)^{l-m} a_{lm}$, so that $\hat{a}_{lm}$ and $\hat{a}_{l'm'}$ transform as the components of irreducible tensors [2]. Equation (3), which is restricted to the case of full circular polarisation $(P_c = 1)$, is derived by neglecting relativistic corrections to the radial part of the atomic wave functions [3].

Our task is to identify the physical observable defined by the hermitian one-electron operator

$$i \sum_{m,m'} \left( C_{l'm';lm}^{20} a_{lm}^\dagger \hat{a}_{l'm'} - \text{h.c.} \right),$$

with $l' = l \pm 1$. To this end, we define

$$A = n f_1(N_0) + \nabla_{l} f_2(N_0),$$

with $n = r/r$ and $\nabla_{l} = -in \times l$; $l$ denotes the orbital angular momentum. Also,

$$f_1(N_0) = (N_0 - \frac{1}{2}) \sqrt{(N_0 - 1)/N_0}$$

and

$$f_2(N_0) = \sqrt{(N_0 - 1)/N_0},$$

with $N_0 |lm\rangle = (l + \frac{1}{2}) |lm\rangle$.

The action of $A$, $A^\dagger$, $l$ and $N_0$ on the spherical harmonics identifies a representation of $O_{3,2}$, a rank-two Lie algebra [15]. The corresponding de Sitter group, $O(3,2)$, has been used by Goshen and Lipkin to describe rotational and vibrational states of nucleons in a 2$d$ harmonic-oscillator potential [14,15]. In their work, the $O(3,2)$ generators are represented using Schwinger’s uncoupled-boson scheme [14]. Our considerations will be based on representation (8) from which, we believe, physical properties are easier to grasp. [The possibility of mapping our problem onto a two-dimensional harmonic oscillator reflects the fact that Eq. (6) depends only on two angular variables.]

The Wigner-Eckart theorem yields

$$\sum_{m} C_{l'm';lm}^{20} a_{lm}^\dagger a_{l't+1-m}$$

$$= c_l \sum_{m} \langle lm | (A.l)_{l0}^{(2)} | l+1m \rangle a_{lm}^\dagger a_{l't+1-m} ,$$

with $c_l = -\sqrt{\Omega/\sqrt{2l+1}(l+1)(l+2)(2l+3)}$ [7]. Setting

$$\sum_{n} \left[ (A.l)^{(2)}_{\rho} \right]_{n}^{l'l'} = \sum_{m,m'} \langle lm | (A.l)^{(2)}_{\rho} | l'm' \rangle a_{lm}^\dagger a_{l'm'},$$

extends the definition of coupled tensors [2] to $l,l'$ pairs. [The couplings are defined by $(U^{(s)} V^{(t)})_{\rho}^{(k)} = \sum_{\rho \alpha} C_{\sigma \tau \rho \alpha}^{kp} U^{(s)}_{\mu} V_{\nu}^{(t)}$, where $s,t$ and $k$ denote the ranks of the corresponding irreducible tensors; $s = t = 1$ and $k = 2$ in Eq. (10).] We thus have

$$i \sum_{m} \left( C_{l'm';lm}^{20} a_{lm}^\dagger a_{l't+1-m} - \text{h.c.} \right)$$

$$= i \sum_{n} \left[ (A.l)^{(2)}_{l0} - (A.l)^{(2)}_{0l} \right]_{n}^{l+l+1},$$

(11)
where the relation,
\[
[(A, l)_{\rho}^{(x)}]_{-\rho}^{(l)} = (-1)^{x-\rho}(l, A^1)_{-\rho}^{(x)},
\]
has been used. A similar result is obtained for the symmetry related pair \(l, l-1\). The rank-two tensor given by Eq. 13 is even under time reversal and odd under space inversion. Tensors with these symmetry properties are known as pseudodeviators. (We recall that the expectation value of inversion-odd operators vanishes in any state of definite parity.)

Writing out the the totally symmetric components, e.g. \((A, l)_{0}^{(2)} = [3A_0 l_0 - A \cdot l] / \sqrt{6}\), and using the orthogonality relations \(A \cdot l = l \cdot A^\dagger = 0\), the r.h.s. of Eq. (11) can be given the simpler form
\[
\sqrt{\frac{3}{2}} \sum_n \left[ (A_0 - A^\dagger_0) \right]_{n}^{l,l+1}.
\]
(12)
The symmetry group is thus restricted to the subgroup \(O(3, 2) \cap O(2, 1) \times O(2)\). \(O(2, 1)\) is a three dimensional Lorentz group with generators \(A_0, A^\dagger_0\) and \(N_0\); \(l_0\) commutes with all of them. \(O(2, 1)\)

A sum rule for XNCD, integrated over the two partners
\[
\Sigma_{XNCD} = \frac{2\pi^2 \alpha}{\hbar c} (3 \cos \theta^2 - 1) \cos \theta^2 + 1
\]
(13)
\[
\sum_{l=0}^{l} \sum_{n} \langle n | R_{11}^{(1)} R_{12}^{(2)} a^{\dagger}_{l} (c, l) \rangle \langle g \rangle \sum_{n} \left[ (A_0 - A^\dagger_0) \right]_{n}^{l,l+1} (g)
\]
where \(\cos \theta = \mathbf{k} \cdot \mathbf{\hat{z}}\), with \(\mathbf{\hat{z}}\) the quantisation axis, and
\[
a_{l-1}(c, l) = \frac{(2l+1)(2l+3)(4+3c(c+1)-l(3l+5))}{(c-l-3)(c+l+4)(c+l+2)^2(c+l+2)^2}.
\]
Equation (13) is consistent with Kuhn’s natural dichroism sum rule 13.

As x-ray linear dichroism experiments in non-centrosymmetric crystals are currently under work, it seems appropriate to extend our analysis of E1-E2 integrated spectra to the case of arbitrary polarisation. We obtain
\[
\int_{\eta_+}^{\eta_-} \sum_{x=1}^{3} \int_{x=1}^{2} \int_{x=1}^{1} T_0(x) (c, l) \sigma_{x}(\omega) \left(\frac{\hbar c}{\omega}\right)^2 d(\hbar c) \propto \left\{ \begin{array}{cc}
1 & l = \pm x \\
2 & l = 1 \\
1 & l = -1 \end{array} \right. T_0(\gamma)(c, l)
\]
(14)
\[
i \sum_{nmn'} \langle g | C_{mn'}^{0} a_{l_m}^{\dagger} a_{l_{m'}}^{\dagger} - \text{h.c.} | g \rangle,
\]
with the polarisation response given by
\[
T_0(\gamma)(c, l) = \sum_{\alpha \beta \delta \gamma} C_{10; 2c}^{0} Y_{\gamma}(\mathbf{e}^*) C_{10; 1\beta}^{2c} Y_{\gamma}(\mathbf{e}) Y_{\gamma}(\mathbf{k}).
\]
As observed, circular dichroism picks out the \(x = 2\) term. The remaining values, \(x = 1, 3\), are selected by linear dichroism. These contrabutions are associated with time-odd electronic properties of non-centrosymmetric crystals. For \(x = 1\), we find
\[
T_0^{(1)}(c, l) \sum_{nmn'} \left( C_{lm; m'}^{0} a_{l_m}^{\dagger} a_{l_{m'}}^{\dagger} - \text{h.c.} \right)
\]
\[
\propto \mathbf{k} \cdot (A \times l - l \times A^\dagger),
\]
(15)
providing a microscopic expression of the irreducible vector operator. A physical interpretation of the results (11) and (13) is provided below.

For simplicity, consider a single ion with a partially filled valence shell in configuration \(l_i\); all other shells filled. The effect 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 coupled tensors. As shown in previous work 13, linear and circular x-ray dichroism, from pure electric-multipole transitions, provide a measure of the ground-state expectation value of these tensors. As is well known, integrating over the two partners of a spin-orbit split inner shell singles out orbital moments, which can all be constructed by coupling the spherical components of \(l\).

Inclusion of hybridisation amounts to considering a valence shell given as a superposition of states with different \(l\) values. New electronic moments, stemming from \(l, l'\) pairs of states and probed by electric-multipole interferences, appear in this case. We will refer to them as intrinsic hybridisation moments. They are expressible by way of coupled tensors and the current work has shown how to write them out in terms of de Sitter generators, for the spinless case. The E1-E2 interference is sensitive to space-odd tensors. (The orbital pseudodeviator represents a space-odd intrinsic hybridisation moment of rank \(2\).) Space-even moments could be revealed by the E1-E3 interference, if ever observable.

The use of Eq. (8) leads to expressions for the hybridisation moments in terms of position and momentum operators, with \(r = n \frac{\partial}{\partial n} + \frac{\partial}{\partial n} \nabla \Omega \rightarrow \nabla \Omega\), since we are dealing with angular variables only.

**E1-M1 interference.** In the optical range (O), the absorption cross section is controlled by the E1-M1 interference and reads
\[
\sigma_{E}^{0}(\omega) = 4\pi^{2} c \hbar \omega \left\{ \int \frac{1}{2} \sum_{f, n} \langle g \mid e^* \cdot r_n \mid f \rangle \right\}
\]
(16)
\[
\langle f \mid e \times k \cdot l_{n'} \mid g \rangle + \text{c.c.} \delta (E_f - E_g - \hbar \omega).
\]
Proceeding as in the derivation of Eq. (7), effective operators of rank zero and two are obtained by coupling the
generators of $O(3,2)$. Notice that two-particle operators are found in this case, as we are considering intra-shell transitions. (Details of their derivation will be given elsewhere.) For the rank-zero tensor, we find

$$
\sum_{n \neq n'} \left[ i \left(A_n - A_{n'}^0\right) \cdot l_{n'}\right]^{l+l'},
$$

(17)

with $l' = l \pm 1$. (Its rank-two companion, i.e. the two-particle pseudodeviator will not be discussed.) Expression [17] defines an orbital pseudoscalar, an irreducible tensor able to distinguish between enantiomeric and non-enantiomeric systems. Indeed, it does not branch to the totally symmetric representation in the allowed point groups which contain a mirror plane. (These branchings can be obtained from Butler’s tables [19]; see also Table I in Jerphagnon and Chemla [20].)

In the $O(3,2)$ framework an exhaustive picture of one-electron effects accessible to x-ray dichroism is obtained. We distinguish four cases:

1. Time-odd electronic properties in centrosymmetric crystals. They are detected by XMCD. For E1 transitions, the spinless effective operator coincides with $l_0$ and we recover the familiar orbital sum rule [4].

2. Time-even electronic properties in centrosymmetric crystals. They are detected by x-ray linear dichroism. For E1 transitions, the spinless effective operator coincides with $3l^2 - l^2$ and the orbital-quadrupole sum rule is obtained [4].

3. Time-even electronic properties in non-centrosymmetric crystals. They are detected by x-ray circular dichroism. For E1-E2 interference, the spinless effective operator is given by Eq. (14), and we have the orbital-pseudodeviator sum rule. (If ferromagnetism is present, pure electric multipole transitions will also contribute yielding time-odd orbital tensors, usually detected by XMCD. These terms vanish when the magnetisation direction is perpendicular to the photon wave vector.)

4. Time-odd electronic properties in non-centrosymmetric crystals. They are detected by x-ray linear dichroism. For E1-E2 interference, two spinless effective operators contribute as shown by Eq. (14). (In the case of a magnetic crystal, pure electric transitions will also contribute yielding time-even tensors. These terms can be distinguished by full angular-dependence analysis.)

We note that integrating over a single partner ($j_\pm$) would provide spin-dependent intrinsic hybridisation moments. The generalisation of our results to x-ray resonant scattering would also be straightforward.

To summarise: We have discussed a theory for x-ray dichroism which is applicable to both centro- and non-centrosymmetric crystals. Our formalism is constructed from the generators of the $O(3,2)$ group. Previous theoretical work on integrated dichroic spectra [4] now appears as special case.

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