X-Ray Absorption and Resonant Scattering in Noncentrosymmetric Crystals

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XV ciclo
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Introduction

Near-edge x-ray dichroism with synchrotron radiation is a powerful probe of electronic states in crystals. 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, E2, ...) transitions, which raise an inner-shell electron to empty valence orbitals.

Linear or circular polarizations are employed in experiments, leading to linear or circular x-ray dichroism, respectively. The former implies a difference between radiations with linear polarizations 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 polarized 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 the 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 one-electron operators (irreducible tensors). Two classes of operators are obtained, which are identified by their transformation properties under space inversion \((x \rightarrow -x, \hat{I}\text{-transformation})\) and time reversal \((t \rightarrow -t, \hat{T}\text{-transformation})\). They correspond to charge \((\hat{I}\text{-even, } \hat{T}\text{-even})\) and magnetic \((\hat{I}\text{-even, } \hat{T}\text{-odd})\) order parameters of crystals. X-ray dichroism is thus sensitive to long-range crystalline orderings and these are distinguished by photon polarization and by the nature \((E1 \text{ or } E2)\) 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 contribution to the magnetic moment [4, 5].

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

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

- **X-ray natural circular dichroism** (XNCD), probed in \(Na_3Nd\text{(digly)}_3 \cdot 2NaBF_4 \cdot 6H_2O\) [9] and in \(\alpha - LiIO_3\) [10]. (The effect was observed near the \(Nd L_3\) 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 \(V_2O_3\) crystal [11].

- **X-ray magnetochaliral dichroism** (XMD), observed at the chromium \(K\) edge [12] in crystalline \(Cr_2O_3\).

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.

\(^1\)X-ray dichroism implies excitations from inner shells, which are filled in the ground state and can therefore be ‘integrated out’. As a result, one electron properties of valence states are probed in the x-ray region.
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 $XNCD$, $XNLD$, $XM\chi D$ are sensitive to polar and magnetolectric (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: $j_\pm = l_c \pm \frac{1}{2}$, 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 $\hat{I}$-odd microscopic operators, revealing the presence of parity nonconserving interactions. (We remind the reader that the expectation value of an $\hat{I}$-odd operator vanishes in any state of definite parity.) As in the case of pure electronic multipole transitions, such operators are further distinguished by their behaviour under time reversal. Two classes of order parameters are therefore identified:

- $\hat{T}$-even and $\hat{I}$-odd operators corresponding to one-electron polar properties, which arise from a noncentrosymmetric distribution of charge.
- $\hat{T}$-odd and $\hat{I}$-odd operators, obviously invariant under the combined symmetry $\hat{T}\hat{I}$ and thus describing one-electron ME properties of crystals [13].

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.

The current manuscript, which represent the continuation of the work of Ref. [14], arise to investigate the microscopic properties of noncentrosymmetric crystals.

In chapter one, starting from the $E1-E2$ absorption cross section [15], using the
Wigner-Racah algebra and a single-ion model with hybridized valence orbitals we will obtain an integral relation for arbitrary polarization. In this case we will discuss the possibility to connect the x-ray absorption spectra with one-electron operators evaluated on the ground state. The form of these operators will be obtained by using Wigner-Racah irreducible tensor algebra.

In chapter two a set of experimental results obtained by Goulon and co-workers [10, 11, 12] will be illustrated and, through the formulation of specific integral relations, a microscopic interpretation of these will be provided.

In chapter three the Luo et al. [16] approach to the scattering amplitude will be generalized to the case of E1-E2 transitions. Applying the “fast collision” approximation, the latter will be expressed as a linear combination of scalar products between irreducible tensors (called geometrical factors) depending on light properties (polarization and wave vector) and on one electron operators evaluated on the ground state.

The analytic developments presented in this thesis are the results of two-year work under the supervision of Paolo Carra. They aim at extending to complex physical systems the range of application of x-ray spectroscopies, that has been successful in the last decade to describe the simpler magnetic systems. This work would also point out the critical aspects that must be carefully considered in the interpretation of the new class of experiments that can be performed today.
Chapter 1

E1-E2 X-Ray Absorption Integral Relation
1.1 Natural Optical Activity

"Optical Activity" indicates the ability of a system to rotate the polarization plane of a linearly polarized light beam. These systems are called 'Optically Active'. When this effect occurs in the absence of external "influences" (generally in the absence of an external magnetic field) or in non-magnetic systems we have "Natural Optical Activity" (more precisely we say that the system exhibits “Natural Optical Activity”).

The "Natural Optical Activity" is closely connected to geometrical proprieties of the system; only chiral or low symmetry structures are able to rotate the linear polarization plane of the light in absence of a net magnetization^1.

Initially, the general opinion was that only the systems exhibiting what Pasteur called "dissymmetry" (the impossibility to superpose an object to its mirror image) could show Optical Natural Activity. Dissymmetric figures are not necessary "asymmetric", that means absence of all symmetry elements, since they may have one or more proper rotation axes (the finite cylindrical helix, the archetype of this object, has a two-fold rotation axes $C_2$ thought the mid point of the coil, perpendicular to the long helix axis). However dissymmetry exclude the presence of improper rotation axes, of a center of inversion, of reflection planes or rotation-reflection axis. Indeed, while the absence of a center of inversion, of reflection planes and rotation-reflection axes in individual molecules, is mandatory if an isotropic ensemble is to show Natural Optical Activity, some crystals and oriented molecules, which lack a center of inversion but have reflection planes or rotation-reflection axis (so that they are superposable to their mirror images) ^2, can show Natural Optical Activity for some directions of propagation of the light beam thus the only really peculiarity that mark these systems is the absence of an inversion-center. In this case the systems are said noncentrosymmetric.

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^1These systems present always hybridized valence shells with no-definite parity.

^2We remind that systems which exist in 2 non-superposable mirror image forms are said to exhibit "enantiomorphism".
Theoretical studies on the "Natural Optical Activity" have been performed by Condon [17], Burckingham [18, 19] and Barron [20, 21]. These authors analyzed the deformation of the molecular electronic cloud in presence of an external field variable in time. Among the results obtained, two have a great relevance for our aim:

- In the optical region (characterized by a wavelength $\lambda$ in the range between 400nm and 800nm), the spectrum recorded in a circular dichroism experiment performed on an optically-active system is described by the cross section

$$
\sigma_O(\omega) = \frac{2\pi^2 \alpha \hbar}{m} \left[ \sum_f \sum_{i,i'} \langle g \mid \vec{e}^* \cdot r_i \mid f \rangle \langle f \mid \vec{e} \times k_{\nu'} \cdot l_{\nu'} \mid g \rangle + c.c. \right] \delta(E_f - E_g - \hbar\omega)
$$

where $i, i'$ are electron labels and $\vec{e}$ is the polarization of the light. In this case we say that the excitation process is determined by the $E1-M1$ interference.

- If we achieve a circular dichroism experiment in the x-ray region in a system that show Natural Optical Activity, the signal obtained is reproducible assuming an absorption cross section given by:

$$
\sigma_X(\omega) = 2\pi^2 \alpha \hbar \omega \left[ \sum_{i,i'} \langle g \mid \vec{e}^* \cdot r_i \mid f \rangle \langle f \mid (\vec{e} \cdot r_{\nu'}) (k \cdot r_{\nu'}) \mid g \rangle + c.c. \right] \delta(E_f - E_g - \hbar\omega)
$$

that is, only excitation mechanisms involving $E1-E2$ transition matrix elements give a non zero contribution to the x-ray dichroic spectra. [$\vec{e} \cdot r$ and $(\vec{e} \cdot r)(k \cdot r)$ are respectively the electric dipole and the electric quadrupole transition operators.]

Starting from these considerations Goulon et al. [10, 22] performed the first experiment of x-ray natural circular dichroism ($XNCD$) working on an uniaxial non-magnetic gy-
rotropic crystal of $\alpha - LiIO_3$ that is known to crystallize with space group $P6_3$ and to exhibit a very strong nonlinear susceptibility. The $L_I$, $L_{II}$, $L_{III}$ edge of iodine observed in this experiment were reproduced by Natoli et al. [23] which confirmed the origin of the signals, i.e. the $E1-E2$ interference.

### 1.2 XMCD and relative sum rules

In the last two decades, near-edge x-ray dichroism in crystals has been thoughtfully investigated at synchrotron radiation sources. Particular attention has been paid to x-ray magnetic circular dichroism (XMCD), namely the difference in absorption between right and left circularly polarized photons, in a system with a net magnetization. Various authors have demonstrated the effect [24, 25] which requires the breaking of the time-reversal symmetry and the presence of a spin-orbit interaction. Electric dipole $E1$ and, in the same case, electric quadrupole $E2$ transitions [26, 27] account for the pertinent inner-shell excitation. Starting from these considerations, T. Thole and P. Carra [3, 4] developed, in the early nineties, an important theoretical method for the study of the fundamental properties of magnetic systems. Analyzing near-edge x-ray circular dichroism, using a single ion model with the valence shell only partially filled, they obtained an important set of sum-rules, which relate the XMCD signal, integrated over both or over a single partner of a spin-split core level energy, to the ground state expectation value of effective one-electron operators.

Starting from the absorption cross section for $E1$ pure transitions [15]

$$
\sigma_X(\omega) = 4\pi^2 \alpha \hbar \omega \sum_{f,i} |\langle f | \hat{\mathbf{e}} \cdot \mathbf{r}_i | g \rangle|^2 \delta(E_f - E_g - \hbar \omega)
$$

(1.1)

(\text{where } \hbar \omega \text{ and } \mathbf{e} \text{ represent energy and polarization of the photon, } \alpha = \frac{e^2}{4\hbar c} \text{ ; } | g \rangle \text{ and } | f \rangle \text{ denote ground state and final state of the electron system with energy } E_g \text{ and } E_f)

\footnote{A more general work that analyzes the x-ray linear dichroism and extend the analysis to the quadrupole transition is given in reference [5].}
respectively, \( i \) is the electron coordinate label), integrating over the photon energy and applying the Wigner-Racah coupling techniques [28, 29, 30, 31, 32, 33] they obtained the following integral relation:

\[
\int_{j_+ + j_-} (\mu^+ - \mu^-)d\omega \propto a_1(l_c, l)\langle g \mid L_z \mid g \rangle, \tag{1.2}
\]

\[
\int_{j_\pm} (\mu^+ - \mu^-)d\omega \propto a_2(l_c, l)\langle g \mid L_z \mid g \rangle \pm a_3(l_c, l)\langle g \mid S_z \mid g \rangle \pm a_4(l_c, l)\langle g \mid T_z \mid g \rangle. \tag{1.3}
\]

The meaning of the symbols, of common use in this work, is the following:

\( l_c \) represent the core hole orbital quantum number, \( l \) the valence orbital number and \( j_\pm = l_c \pm \frac{1}{2} \) the quantum number of two partners of the spin-orbit split inner shell; \( L_z \) and \( S_z \) are the traditional orbital and spin magnetic moment operators while \( T_z = [\sum_i s_i - 3\mathbf{r}_i \cdot \mathbf{s}_i]_z \) is the magnetic dipole operator. The first integral (1.2) is evaluated over a complete spin-orbit split core level \( (j_+ + j_-) \), the second (1.3) over a single partner \( j_\pm; \mu_+ - \mu_- \) represents the difference between the absorption coefficients for the right- and left-circularly polarized x-rays; \( a_k(l_c, l) \) (with \( k = 1, 2, 3, 4 \)) denotes a set of coefficients which depend on \( l_c \) and \( l \). The importance of these relations lies in the fact that left-hand-side (l.h.s.) of expression (1.2) and (1.3) can be obtained experimentally, thus providing direct informations about magnetic properties of system \(^6\).

Despite the wide field of applications of these sum rules, they are not applicable to \( XNCD \) experiments which are determined by \( E1-E2 \) excitations. For example, relation (1.2) implies that that \( \mu_+ = \mu_- \) in a non-magnetic system, i.e. \( < L_z > = 0 \). Such results is in disagreement with the observation of \( XNCD \) in \( \alpha - LiIO_3 \) by Goulon et al. [10, 22]. Starting from these considerations P. Carra has obtained new integral relations for \( E1-E2 \) excitation [14]. These relations provided a microscopic interpretation of \( XNCD \) in terms of new class of effective one-electron operators.

Ref. [14] represents the starting point of the current work, which will generalize the

\(^6\)When \( T_z \) is negligible the relations (1.2) and (1.3) offer a direct evaluation of \( \langle g \mid L_z \mid g \rangle \) and \( \langle g \mid S_z \mid g \rangle \), the ground state expectation value of the operators \( L_z \) and \( S_z \).
approach to cover other important experiments recently performed at the ESRF and aimed at broadening our understanding of noncentrosymmetric crystals.

1.3 Integral Relation for E1-E2 transitions

Central to our considerations is the absorption cross section

$$\sigma_X^s(\omega) = 4\pi^2\alpha\hbar\omega\left[\frac{i}{2}\sum_f \sum_{i,i'} \langle g | \vec{e}^* \cdot \vec{r}_i | f \rangle \langle f | (\vec{e} \cdot \vec{r}_f)(\vec{k} \cdot \vec{r}_f) | g \rangle + c.c. \right] \delta(E_f - E_g - \hbar\omega)$$

(1.4)

picking out the E1-E2 interference in the p \cdot A interaction between x rays and electrons. The notation is as follows: $\hbar\omega$, $\vec{k}$ and $\vec{e}$ represent energy, wave vector and polarization of the photon; $| g \rangle$ and $| f \rangle$ denote ground and final state 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 $^7$

$$\int_{j_++j_-} \frac{\sigma_X^s(\omega)}{(\hbar\omega)^2} d\hbar\omega$$

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

$$\sum_{i,i'} T_p^{(x,\pm)}(\vec{e}, \vec{k}) \langle g | \sum_i \mathbf{O}_p^{(x,\pm)}(l, l') | g \rangle.$$

In the second quantization formalism, the latter is defined by [14]

$$\mathbf{O}_p^{(x,\pm)}(l, l') = \sum_i \mathbf{O}_p^{(x,\pm)}(l, l')_i = \sum_{m,m'} \langle l' m' | \mathbf{O}_p^{(x,\pm)}(l, l') | l m \rangle a_{l'm'}^\dagger a_{lm} +$$

$$+ \langle l m | \mathbf{O}_p^{(x,\pm)}(l, l') | l' m' \rangle a_{l'm'}^\dagger a_{lm}.$$  

$^7$Integration is over a finite energy interval, which correspond to the two partners of a spin-orbit split inner shell.
where \( a^\dagger_{l'm'} \) and \( a_{lm} \) create and annihilate valence electrons, \( |lm\rangle \) stands for a spherical harmonics, and \( l' = l \pm 1 \). All \( O^{\pm}(l, l') \) are odd under space inversion; their behavior (even or odd) under time reversal is denoted by the superscript \( \pm \). Going over to a second-quantization description, we consider the fermionic field

\[
\Psi(\mathbf{r}) = \sum_{l\lambda\sigma} a_{l\lambda\sigma}\psi_{l\lambda\sigma}(\mathbf{r}) + \sum_{jm} a_{jm}\psi_{jm}(\mathbf{r})
\]

(1.5)

where \( a_{jm} \) and \( a_{l\lambda\sigma} \) annihilate inner shell and valence electron respectively. The atomic basis set, which enters in the definition (1.5) is chosen as follows [34]. Core electrons are identified by coupled atomic orbitals

\[
\psi_{jm}(\mathbf{r}) = \sum_{\gamma} C^{jm}_{\mu l_{c}\gamma;\frac{1}{2}\sigma}\rho_{\mu l_{c}}(\mathbf{r})\chi_{\sigma},
\]

(1.6)

with \( C^{jm}_{\mu l_{c}\gamma;\frac{1}{2}\sigma} \) a Clebsch-Gordan coefficient, \( \rho_{\mu l_{c}}(\mathbf{r}) = \varphi_{\mu l_{c}}(\mathbf{r})Y_{l_{c}\gamma}(r) \) \(^8\) and \( \chi_{\sigma} \) a spinor. Valence states are described by uncoupled wave functions [34] \(^9\)

\[
\psi_{l\lambda\sigma}(\mathbf{r}) = \varphi_l(\mathbf{r})Y_{l\lambda}(r)\chi_{\sigma}.
\]

(1.7)

Equation (1.4) can thus be written in the form

\[
\mathbf{\sigma}^\hat{e}(\omega) = 4\pi^2\alpha\hbar\omega \left[ \frac{i}{2} \sum_{jl\lambda\sigma} \sum_{j'm'} \sum_{jm} \langle \psi_{j'm'} | \mathbf{\hat{e}} \cdot \mathbf{r} | \psi_{l\lambda\sigma} \rangle \langle \psi_{l\lambda\sigma} | \psi_{j'l'\lambda'\sigma'} \rangle \langle \mathbf{\hat{e}} \cdot \mathbf{r} | \mathbf{k} \cdot \mathbf{r} | \psi_{jm} \rangle \times \langle \mathbf{k} | a^\dagger_{j'm',l\lambda\sigma} | \mathbf{f} \rangle \langle \mathbf{f} | a^\dagger_{j'l'\lambda'\sigma'} a_{jm} | \mathbf{g} \rangle + c.c. \right] \delta(E_f - E_g - \hbar\omega).
\]

(1.8)

Introducing covariant spherical components, we have

\[
\mathbf{\hat{e}} \cdot \mathbf{r} = \frac{4\pi}{3}r \sum_{\delta} (-)^\delta Y_{1\delta}(\mathbf{\hat{e}})Y_{1-\delta}(\mathbf{\hat{r}})
\]

\[
\mathbf{\hat{e}}^* \cdot \mathbf{r} = \frac{4\pi}{3}r \sum_{\delta} (-)^\delta Y_{1\delta}(\mathbf{\hat{e}}^*)Y_{1-\delta}(\mathbf{\hat{r}})
\]

\[
\mathbf{k} \cdot \mathbf{r} = \frac{4\pi}{3}kr \sum_{\mu} (-)^\mu Y_{1\mu}(\mathbf{k})Y_{1-\mu}(\mathbf{\hat{r}}).
\]

\(^8\)\( \varphi_{\mu l_{c}}(\mathbf{r}) \) is the radial part of \( \rho_{\mu l_{c}}(\mathbf{r}) \), \( Y_{l_{c}\gamma}(r) \) is a spherical harmonic identified by the quantum numbers \( l_{c} \) and \( \gamma \).

\(^9\)\( \sigma \) and \( \bar{\sigma} \) are respectively the spin components of the valence and core electron.
A similar expression is obtained for the electric-quadrupole transition operator (Ref. [35] p. 156); it reads

\[(\mathbf{e} \cdot \mathbf{r})(\mathbf{k} \cdot \mathbf{r}) = \left(\frac{4\pi}{3}\right)^2 k r^2 \sqrt{\frac{3}{10\pi}} \sum_{\zeta} Y^*_{2\zeta}(\mathbf{r}) \sum_{\alpha\beta} C^{2\zeta}_{1\alpha,1\beta} Y_{1\alpha}(\mathbf{e}) Y_{1\beta}(\mathbf{k}).\]

Collecting terms together, Eq. (1.8) can be rewritten as

\[
\sigma^\xi_X(\omega) = 4\pi^2 \alpha \hbar \omega k \left[\frac{i}{2} \left(\frac{4\pi}{3}\right)^3 \sqrt{\frac{3}{10\pi}} \sum_{l,l'} R^l_{l,l'} R^{l'2} \sum_{\alpha\beta\zeta} \sum_{\chi\gamma} C^{j\prime m}_{l_0\gamma',1/2\sigma} \sum_{\delta} (-)^\delta Y_{1\delta}(\mathbf{e}^*) \times \\
\times \langle l_c\gamma' | Y_{1-\delta}(\mathbf{r}) | l\lambda\rangle C^{j\prime m}_{l_0\gamma,1/2\sigma} Y_{1\alpha}(\mathbf{e}) Y_{1\beta}(\mathbf{k}) C^{2\zeta}_{1\alpha1\beta} \langle l'\lambda' | Y^*_{2\zeta}(\mathbf{r}) | l_c\gamma \rangle (\chi_\sigma \cdot \chi_\sigma') (\chi_{\sigma'} \cdot \chi_\sigma) \times \\
\times \sum_f \langle g | a_{j_0} a_{l\lambda_\sigma} | f \rangle \langle f | a_{l'\chi_{\lambda'}} a_{j_0} | g \rangle + c.c. \rangle \delta(E_f - E_g - \hbar\omega), \tag{1.9}
\]

where

\[
R^l_{l,l} = \int_0^\infty \varphi_{l_0}(r) r^{l+2} \varphi_l(r)dr
\]
define the radial integral. As can be readily inferred from Eq. (1.9), the orbital principal quantum numbers \(l\) and \(l'\) identify valence states, which are reached by \(E1\) and \(E2\) transitions, respectively. From \((\chi_\sigma \cdot \chi_{\sigma'}) = \delta_{\sigma\sigma'}\) and \((\chi_{\sigma'} \cdot \chi_\sigma) = \delta_{\sigma'\sigma}\), Eq. (1.9) becomes

\[
\sigma^\xi_X(\omega) = \frac{4\pi^2 \alpha (\hbar \omega)^2}{\hbar c} \left[\frac{i}{2} \left(\frac{4\pi}{3}\right)^3 \sqrt{\frac{3}{10\pi}} \sum_{l,l'} R^l_{l,l'} R^{l'2} \sum_{\alpha\beta\zeta} \sum_{\chi\gamma} C^{j\prime m}_{l_0\gamma,1/2\sigma} \sum_{\delta} (-)^\delta Y_{1\delta}(\mathbf{e}^*) \times \\
\times \langle l_c\gamma' | Y_{1-\delta}(\mathbf{r}) | l\lambda\rangle C^{j\prime m}_{l_0\gamma,1/2\sigma} Y_{1\alpha}(\mathbf{e}) Y_{1\beta}(\mathbf{k}) C^{2\zeta}_{1\alpha1\beta} \langle l'\lambda' | Y^*_{2\zeta}(\mathbf{r}) | l_c\gamma \rangle \times \\
\times \sum_f \langle g | a_{j_0} a_{l\lambda_\sigma} | f \rangle \langle f | a_{l'\chi_{\lambda'}} a_{j_0} | g \rangle + c.c. \rangle \delta(E_f - E_g - \hbar\omega) \tag{1.10}
\]

where \(k = (\hbar\omega)/hc\) has been used.

The next step toward the derivation of a sum rule is the dropping of the energy dependent terms [obtained by dividing the absorption cross section by \((\hbar \omega)^2\)] and by performing the
integration over the photon energy in order to eliminate the delta function, leaving\(^{10}\)

\[
\sum_f |f\rangle \langle f| = 1.
\]

In other words we have to evaluate the integral

\[
\Sigma_{E_1-E_2} = \int_{j_+ + j_-} \frac{\sigma_X^I(\omega)}{(h\omega)^2} d(h\omega), \tag{1.11}
\]

that is conveniently rewritten as

\[
\Sigma_{E_1-E_2} = \Sigma_{E_1-E_2}^I + (\Sigma_{E_1-E_2}^I)^* = \Sigma_{E_1-E_2}^I + \Sigma_{E_1-E_2}^{II}
\]

where:

\[
\Sigma_{E_1-E_2}^I = \int_{j_+ + j_-} \frac{\sigma_X^I(\omega)}{(h\omega)^2} d(h\omega)
\]

and

\[
\Sigma_{E_1-E_2}^{II} = (\Sigma_{E_1-E_2}^I)^* = \int_{j_+ + j_-} \frac{(\sigma_X^I)^*(\omega)}{(h\omega)^2} d(h\omega) = \int_{j_+ + j_-} \frac{\sigma_X^{II}(\omega)}{(h\omega)^2} d(h\omega).
\]

For \(E1-E2\) transitions

\[
\sigma^I = 2\pi^2 \alpha h\omega \left[ i \sum_f \sum_{i,i'} \langle g | \bar{\epsilon}^* \cdot \mathbf{r}_i | f \rangle \langle f | \bar{\epsilon} \cdot \mathbf{r}_{i'} | (\mathbf{k} \cdot \mathbf{r}_i) | g \rangle \right] \delta(E_f - E_g - h\omega).
\]

In the following sections, using the Wigner-Racah coupling techniques, the integral \(\Sigma_{E_1-E_2}^I\) will be expressed as a linear combination of scalar products between irreducible tensors. This approach, easily extendible to the \(\Sigma_{E_1-E_2}^{II}\) integral, allows to write \(\Sigma_{E_1-E_2}\) separating the geometrical factor terms (containing the informations about the wave-vector and the polarization state of the photon) and the ground state properties of the matter.

\(^{10}\)The elimination of the final states \(|f\rangle\),

\[
\sum_f \langle g | a_{j'm'}^{\dagger} a_{i\lambda\sigma} | f \rangle \langle f | a_{i'\lambda'\sigma'}^{\dagger} a_{jm} | g \rangle = \langle g | a_{j'm'}^{\dagger} a_{i\lambda\sigma} a_{i'\lambda'\sigma'}^{\dagger} a_{jm} | g \rangle = \delta_{jj'} \delta_{mm'} \delta_{\lambda\sigma} \delta_{\lambda'\sigma'} \langle g | a_{i\lambda\sigma} a_{i'\lambda'\sigma'} | g \rangle
\]

produces the physically evident conditions \(j = j'\) and \(m = m'\).
1.3.1 Algebraic details

In this subsection the integral

\[ \Sigma_{E_1-E_2}^I = \int_{j_+}^{j_-} \frac{\sigma^I_X(\omega)}{(\hbar \omega)^2} d(\hbar \omega). \]

will be analyzed. Recalling the form of the absorption cross section (Eq. 1.10), using the relation \( \sum_{jj'} \sum_{mm'} \delta_{jj'} \delta_{mm'} C_{jj',1/2\sigma}^{1/2\sigma} = \delta_{\gamma\gamma'} \delta_{\sigma\sigma'} \) and removing the spin contribution\(^{11}\) we have

\[ \Sigma_{E_1-E_2}^I = \int_{j_+}^{j_-} \frac{\sigma^I_X(\omega)}{(\hbar \omega)^2} d(\hbar \omega) = \frac{8\pi^2\alpha^I_l}{\hbar c} \frac{i}{2} \frac{(4\pi)}{3} \sqrt{\frac{3}{10\pi}} \sum_{l'l''} R_{l'l''}^1 R_{l'l''}^2 \sum_{\lambda\gamma} \sum_{\gamma\delta} (-)^\delta Y_{1\delta}(e^*) \times \]

\[ \times \langle l_c | Y_{1-\delta}(\vec{r}) | l\lambda \rangle \sum_{\alpha\beta\zeta} Y_{1\delta}(\vec{e}^*) Y_{1\alpha}(\vec{e}) (-)^\delta \langle Y_{1\beta}(\vec{k}) C_{1\alpha,1\beta}^{2\zeta} | l_c \gamma | Y_{1-\delta}(\vec{r}) | l\lambda \rangle \langle l'\lambda' | Y_{2\zeta'}(\vec{r}) | l_c \gamma \rangle. \] (1.12)

For our purposes, it is convenient to re-write the term

\[ \sum_{\alpha\beta\zeta} Y_{1\delta}(\vec{e}^*) Y_{1\alpha}(\vec{e}) (-)^\delta \langle Y_{1\beta}(\vec{k}) C_{1\alpha,1\beta}^{2\zeta} | l_c \gamma | Y_{1-\delta}(\vec{r}) | l\lambda \rangle \langle l'\lambda' | Y_{2\zeta'}(\vec{r}) | l_c \gamma \rangle \]

in the following form

\[ \sum_{\alpha\beta\zeta} \delta_{\delta',\delta} \delta_{\zeta',\zeta} Y_{1\delta}(\vec{e}^*) Y_{1\alpha}(\vec{e}) (-)^{(\delta' + \zeta')} \langle Y_{1\beta}(\vec{k}) C_{1\alpha,1\beta}^{2\zeta} | l_c \gamma | Y_{1\delta'}(\vec{r}) | l\lambda \rangle \langle l'\lambda' | Y_{2\zeta'}(\vec{r}) | l_c \gamma \rangle = \]

\[ = \sum_{\alpha\beta\zeta} C_{1\alpha,1\beta}^{2\zeta} C_{1\alpha,1\beta}^{2\zeta} Y_{1\delta}(\vec{e}^*) Y_{1\alpha}(\vec{e}) Y_{1\beta}(\vec{k}) \sum_{\delta\zeta'} \sum_{\delta'\zeta'} C_{1\delta,1\delta'}^{2\zeta} (-)^{(\delta' + \zeta')} \langle l_c \gamma | Y_{1\delta'}(\vec{r}) | l\lambda \rangle \langle l'\lambda' | Y_{2\zeta'}(\vec{r}) | l_c \gamma \rangle = \]

\[ = \sum_{\alpha\beta\zeta} C_{1\alpha,1\beta}^{2\zeta} C_{1\alpha,1\beta}^{2\zeta} Y_{1\delta}(\vec{e}^*) Y_{1\alpha}(\vec{e}) Y_{1\beta}(\vec{k}) \sum_{\delta\zeta'} \sum_{\delta'\zeta'} C_{1\delta,1\delta'}^{2\zeta} (-)^{(\delta' + \zeta')} \langle l_c \gamma | Y_{1\delta'}(\vec{r}) | l\lambda \rangle \langle l'\lambda' | Y_{2\zeta'}(\vec{r}) | l_c \gamma \rangle \]

where the relation \( \sum_{xp} C_{1\alpha,1\beta}^{2\zeta} C_{1\alpha,1\beta}^{2\zeta} = \delta_{\delta',\delta} \delta_{\zeta',\zeta} \) and \( C_{1\delta,1\delta'}^{2\zeta} = (-)^{1-x} C_{1\delta,1\delta'}^{2\zeta} \) has been used. By applying the Wigner-Eckart theorem, we obtain

\[ \langle l_c \gamma | Y_{1\delta'}(\vec{r}) | l\lambda \rangle = C_{1\alpha,1\beta}^{l_c \gamma} \frac{\langle l_c | Y_{1}(\vec{r}) | l \rangle}{\sqrt{2l_c + 1}} \] (1.13)

\(^{11}\)This operation consist to replace \( \sum_{\sigma\sigma'} \delta_{\sigma\sigma'} a_{l \lambda \sigma} a_{l \lambda' \sigma'}^\dagger \) with \( 2a_{l \lambda} a_{l \lambda'}^\dagger \).
and
\[
\langle l' \ell' \mid Y_{2 \ell} \langle \mathbf{r} \mid l_c \rangle \rangle = C^{\ell', \ell'}_{\ell_c, 2 \ell} \frac{\langle l' \mid Y_2 \langle \mathbf{r} \mid l_c \rangle \rangle}{\sqrt{2l' + 1}},
\]
where \( \langle l_c \mid Y_1 \langle \mathbf{r} \mid l \rangle \rangle \) and \( \langle l' \mid Y_2 \langle \mathbf{r} \mid l_c \rangle \rangle \) are the reduced matrix elements of the spherical harmonics \( Y_1(\theta, \psi) \) and \( Y_2(\theta, \psi) \). By inserting these expressions in equation (1.12) we get
\[
\Sigma^{\ell \ell} = \int_{j^+} \int_{j^-} \frac{\sigma_{\text{X}}(\omega)}{(\hbar \omega)^2} d\hbar \omega = i \frac{4\pi^2 \alpha}{\hbar c} \left( \frac{4\pi}{3} \right)^3 \sqrt{\frac{3}{10\pi}} \sum_{l'} \sum_{l''} R_{l_1, l_2} R_{l_2, l_3} \left( \sum_{\lambda, \gamma} C^{\ell \lambda}_{\gamma, 2 \lambda} C_{\ell, \gamma, 2 \lambda} \right) \times
\]
\[
\times \sum_{\alpha \beta} C^{\ell \beta}_{1 \alpha, 1 \beta} Y_{1 \alpha}(\mathbf{r}) Y_{1 \beta}(\mathbf{k}))(\gamma)^{x+\rho+1} C^{\ell \eta, \lambda}_{1 \alpha, 1 \beta} C^{\ell \lambda}_{1 \alpha, 1 \beta} \langle l_c \mid Y_1 \langle \mathbf{r} \mid l \rangle \rangle C^{\ell \lambda}_{\ell_c, 2 \lambda} \langle l' \mid Y_2 \langle \mathbf{r} \mid l_c \rangle \rangle \times
\]
\[
\times \langle g \mid a_{\lambda} a_{\ell', \lambda} \rangle | g \rangle.
\]

Using the recoupling transformation
\[
\sum_{\gamma, \delta, \zeta} C^{\ell \rho, \lambda}_{\gamma \delta, 2 \lambda} C^{\ell \lambda, \lambda}_{1 \alpha, 1 \beta} C^{\ell \lambda, \lambda}_{1 \alpha, 1 \beta} C^{\ell \lambda, \lambda}_{1 \alpha, 1 \beta} = (-)^{l - x - l} \sqrt{(2l_c + 1)(2x + 1)} C^{l \lambda}_{x - \rho, \lambda} \left\{ \begin{array}{ccc} l & l' & x \\ 2 & 1 & l_c \end{array} \right\}.
\]

Eq. (1.15) can be given the form
\[
\Sigma^{\ell \ell} = -\frac{4\pi^2 \alpha}{\hbar c} \left( \frac{4\pi}{3} \right)^3 \sqrt{\frac{3}{10\pi}} \sum_{l'} \sum_{l''} R_{l_1, l_2} R_{l_2, l_3} \left( \frac{3}{4\pi} \right)^{\frac{3}{2}} \sum_{\lambda} \sum_{\alpha \beta} \left[ C^{\ell \rho, \lambda}_{\delta \gamma, 1 \beta} C^{\ell \lambda, \lambda}_{1 \alpha, 1 \beta} \mathbf{\hat{e}}_{\alpha} \mathbf{\hat{e}}_{\beta} \right] (-)^{\rho} \times
\]
\[
\times \sqrt{\frac{2x + 1}{2l + 1}} C^{\ell \lambda}_{x - \rho, \lambda} \left\{ \begin{array}{ccc} l & l' & x \\ 2 & 1 & l_c \end{array} \right\} \langle l_c \mid Y_1 \langle \mathbf{r} \mid l \rangle \rangle \langle l' \mid Y_2 \langle \mathbf{r} \mid l_c \rangle \rangle \langle g \mid a_{\lambda} a_{\ell', \lambda} \rangle | g \rangle.
\]

The geometrical factor
\[
T^x_{\rho}(\mathbf{\hat{e}}_x, \mathbf{\hat{e}}_y, \mathbf{\hat{k}}) = \sum_{\delta} \sum_{\alpha \beta} C^{\rho \rho}_{1 \delta, 2 \delta} C^{\ell \lambda}_{1 \alpha, 1 \beta} \mathbf{\hat{e}}_{\alpha} \mathbf{\hat{e}}_{\beta}
\]
\[
(1.17)
\]
describes properties of the ingoing photon as already stated. The coupling scheme provided by Eq. (1.17) is not well suited to analyze x-ray absorption experiments. A more convenient form is obtained from the recoupling transformation
\[
\sum_{\zeta} C^{\ell \lambda}_{1 \alpha, 1 \beta} C^{\ell \lambda}_{1 \alpha, 1 \beta} = \sum_{\nu \nu'} (-)^{1 + x} \sqrt{5(2\nu + 1)} \left\{ \begin{array}{ccc} l & l' & \nu \\ 1 & 2 & \nu \end{array} \right\} C^{\ell \lambda}_{1 \alpha, 1 \beta} C^{\ell \lambda}_{1 \alpha, 1 \beta},
\]
\[
11
\]
which gives
\[
T_{\rho}^{x}(\epsilon^{*}, \hat{\epsilon}, \hat{k}) = \sum_{\delta \zeta} \sum_{\alpha \beta} C_{\alpha \beta}^{\nu \rho} C_{\delta \zeta}^{\nu \rho} \epsilon_{\alpha} \hat{\epsilon}_{\beta} = \sum_{\nu \nu'} \sum_{\delta \alpha \beta} (-1)^{1+x} \sqrt{5(2\nu + 1)} \left\{ \begin{array}{ccc} 1 & 1 & \nu \\ 1 & x & 2 \end{array} \right\} \times C_{\delta \alpha \beta}^{\nu \nu'} C_{\nu \nu', \delta \alpha \beta}^{\nu \nu'} \epsilon_{\alpha} \hat{\epsilon}_{\alpha} \hat{k}_{\beta},
\]
(1.18)

thus providing a direct coupling between \(\hat{\epsilon}\) and \(\epsilon^{*}\).

From the general relation
\[
\langle l' \parallel Y_{L} \parallel l \rangle = \sqrt{\frac{(2L + 1)(2l + 1)}{4\pi} C_{l_{0}, l_{0}}^{L_{0}}}
\]
we have
\[
\langle l_{c} \parallel Y_{L} \parallel l \rangle = \sqrt{\frac{3(2l + 1)}{4\pi} C_{l_{0}, l_{0}}^{L_{0}}}
\]
and
\[
\langle l' \parallel Y_{L} \parallel l_{c} \rangle = \sqrt{\frac{5(2l_{c} + 1)}{4\pi} C_{l_{0}, l_{0}}^{L_{0}}}
\]

Therefore
\[
\Sigma_{E_{1} - E_{2}}^{I} = -i \left[ \frac{4\pi^{2} \alpha}{\hbar c} \right]^{3} \frac{3}{10\pi} \sum_{l'} R_{l_{0}, l_{0}}^{1} R_{l_{0}, l_{0}}^{2} \left( \frac{3}{4\pi} \right)^{\frac{3}{2}} \left( -\right)^{x+l-l'} \sum_{x_{\rho}} \langle \epsilon^{*} \parallel \epsilon_{\alpha} \hat{\epsilon}_{\alpha} \hat{k}_{\beta} \parallel \epsilon_{\alpha} \hat{\epsilon}_{\alpha} \hat{k}_{\beta} \rangle \times
\]
\[
\left\{ \begin{array}{ccc} l & l' & x \\ 2 & 1 & l_{c} \end{array} \right\} \sqrt{\frac{15(2l + 1)(2l_{c} + 1)}{4\pi}} C_{l_{0}, l_{0}}^{L_{0}} C_{l_{0}, l_{0}}^{L_{0}} \sum_{\lambda \lambda'} \langle g \parallel C_{\lambda_{0}, l_{0}}^{\lambda_{0}} \hat{a}_{\lambda_{0}}^{+} a_{\lambda_{0}} \parallel g \rangle \]
(1.19)

where the identity \(C_{x_{0}, l_{0}}^{\lambda_{0}, \lambda_{0}} = (-)^{x+l-l'} C_{\lambda_{0}, x_{0}}^{\lambda_{0}, \lambda_{0}}\) has been used.

A similar expression is readily obtained for
\[
\Sigma_{E_{1} - E_{2}}^{II} = \int_{j_{+}+j_{-}} \frac{(\sigma_{X})^{s}}{\hbar \omega} d\hbar \omega = \int_{j_{+}+j_{-}} \frac{\sigma_{X}^{II}}{\hbar \omega} d\hbar \omega,
\]
where
\[
\sigma_{X}^{II} = -4\pi^{2} \alpha \hbar \omega \left[ \frac{i}{2} \sum_{f, f, f'} \langle g \parallel (\epsilon^{*} \cdot r_{n}) (k \cdot r_{n'}) \parallel f \rangle \langle f \parallel \epsilon \cdot r_{n} \parallel g \rangle \right] \delta(E_{f} - E_{g} - \hbar \omega).
\]
(1.20)
In this case we have

\[
\Sigma_{E_1-E_2}^{II} = -i \left[ \frac{4\pi^2\alpha}{hc} \frac{4\pi}{3} \right]^3 \sqrt{\frac{3}{10\pi}} \sum_{l' \nu} (-)^{x+l'-\nu} R_{l'l}^1 R_{l'l'}^2 \left( \frac{3}{4\pi} \right)^{3/2} \sum_{xp} (-)^p \sqrt{\frac{15(2l+1)(2l_c+1)}{(4\pi)^2}} \times \]

\[
\times \sqrt{2x+1} \left\{ \begin{array}{ccc}
 l & l' & x \\
 2 & 1 & l_c
\end{array} \right\} C_{l_0,0}^{l',0} C_{l_0,0}^{d',0} \tilde{T}_p^{\nu}(\vec{\epsilon}, \vec{\kappa}) \langle g | \sum_{\lambda X} \frac{C_{l_0,0}^{\nu\lambda, x-\rho}}{\sqrt{2l'+1}} a_{l \lambda}^\rho a_{l' \lambda}^\nu | g \rangle
\]

(1.21)

where

\[
\tilde{T}_p^{\nu}(\vec{\epsilon}, \vec{\kappa}) = \sum_{\alpha \beta \delta} C_{1,0,0}^{2\alpha} C_{2,0,0}^{\nu \delta} \tilde{\epsilon}_\alpha \tilde{\epsilon}_\beta \tilde{\epsilon}_\delta = \sum_{\nu' \delta \alpha} (-)^{\nu'} \sqrt{5(2\nu+1)} \left\{ \begin{array}{ccc}
 1 & 1 & \nu' \\
 1 & x & 2
\end{array} \right\} C_{1,0,0}^{\nu \delta} C_{1,0,0}^{\nu' \delta} \tilde{\epsilon}_\alpha \tilde{\epsilon}_\beta \tilde{\epsilon}_\delta.
\]

Putting equations (1.19) and (1.21) together, we obtain:

\[
\Sigma_{E_1-E_2} = \Sigma_{E_1-E_2}^{I} + \Sigma_{E_1-E_2}^{II} = -i \left[ \frac{4\pi^2\alpha}{hc} \frac{4\pi}{3} \right]^3 \sqrt{\frac{3}{10\pi}} \sum_{l' \nu} (-)^{x+l'-\nu} R_{l'l}^1 R_{l'l'}^2 \times \]

\[
\times \left\{ \begin{array}{ccc}
 l & l' & x \\
 2 & 1 & l_c
\end{array} \right\} C_{l_0,0}^{l',0} C_{l_0,0}^{d',0} \tilde{T}_p^{\nu}(\vec{\epsilon}, \vec{\kappa}) \langle g | \sum_{\lambda X} \frac{C_{l_0,0}^{\nu\lambda, x-\rho}}{\sqrt{2l'+1}} a_{l \lambda}^\rho a_{l' \lambda}^\nu | g \rangle + \tilde{T}_p^{\nu}(\vec{\epsilon}, \vec{\kappa}) \langle g | \frac{C_{l_0,0}^{\nu\lambda, x-\rho}}{\sqrt{2l'+1}} a_{l \lambda}^\rho a_{l' \lambda}^\nu | g \rangle
\]

(1.22)

i.e. a general integral relation for E1-E2 x-ray absorption, in the case of arbitrary photon polarization \( \vec{\epsilon} \). It is appropriate to redefine the annihilator operators as follows: \( \tilde{a}_{l \lambda} = (-)^{l-\lambda} a_{l-\lambda} \) so that \( a_{l \lambda}^\dagger \) and \( \tilde{a}_{l \lambda} \) transform as the components of irreducible tensors [28].

Eq. (1.23) takes then the form:

\[
\Sigma_{E_1-E_2} = \Sigma_{E_1-E_2}^{I} + \Sigma_{E_1-E_2}^{II} = -i \left[ \frac{4\pi^2\alpha}{hc} \frac{4\pi}{3} \right]^3 \sqrt{\frac{3}{10\pi}} \sum_{l' \nu} (-)^{x+l'-\nu} R_{l'l}^1 R_{l'l'}^2 \times \]

\[
\times \left\{ \begin{array}{ccc}
 l & l' & x \\
 2 & 1 & l_c
\end{array} \right\} C_{l_0,0}^{l',0} C_{l_0,0}^{d',0} \tilde{T}_p^{\nu}(\vec{\epsilon}, \vec{\kappa}) \langle g | \sum_{\lambda X} \frac{C_{l_0,0}^{\nu\lambda, x-\rho}}{\sqrt{2l'+1}} a_{l \lambda}^\rho a_{l' \lambda}^\nu | g \rangle
\]

(1.23)
In general $l$ and $l'$ must be of opposite parities.

Our derivation will be restricted to the case $l' = l \pm 1$, which hold for $l_c = l \pm 1$. (more details on this point will be given below.) Eq. (1.24) provides a suitable form for the expansion of pairs of irreducible tensors, which has been mentioned previously. We remind the reader that $x = 1, 2, 3$. These contributions will be separately discussed in the remaining part of the current chapter.

\[
\times \sum_{\lambda} \left[ T^x_{\rho}(\vec{e}', \vec{e}, \vec{k}) \langle g \mid C^{x-\rho}_{\lambda'; \lambda} a_{\lambda'}^\dagger \tilde{a}_{\lambda} \mid g \rangle + \tilde{T}^x_{\rho}(\vec{e}', \vec{e}, \vec{k}) \langle g \mid C^{x-\rho}_{\lambda; \lambda'} a_{\lambda}^\dagger \tilde{a}_{\lambda'} \mid g \rangle \right].
\]
1.4 The $x = 1$ term.

1.4.1 Geometrical factor

Consider $T^1_\rho(\vec{e}^*, \hat{\vec{e}}, \hat{\vec{k}})$ and $\tilde{T}^1_\rho(\vec{e}^*, \hat{\vec{e}}, \hat{\vec{k}})$ as defined by:

$$T^1_\rho(\vec{e}^*, \hat{\vec{e}}, \hat{\vec{k}}) = \sum_{\nu \nu'} \sum_{\delta \alpha \beta} \sqrt{5(2\nu + 1)} \begin{pmatrix} 1 & 1 & \nu \\ 1 & 1 & 2 \end{pmatrix} C^{\nu \nu'}_{10,10} C^{1\rho}_{10,10} \hat{\vec{e}}_\alpha \hat{\vec{e}}_\beta \hat{\vec{k}}_\beta$$ (1.25)

and

$$\tilde{T}^1_\rho(\vec{e}^*, \hat{\vec{e}}, \hat{\vec{k}}) = \sum_{\nu \nu'} \sum_{\delta \alpha \beta} (-)^\nu \sqrt{5(2\nu + 1)} \begin{pmatrix} 1 & 1 & \nu \\ 1 & 1 & 2 \end{pmatrix} C^{\nu \nu'}_{10,10} C^{1\rho}_{10,10} \hat{\vec{e}}_\alpha \hat{\vec{e}}_\beta \hat{\vec{k}}_\beta,$$ (1.26)

respectively. Only the value $\nu = 0, 2$ need to be considered, thus $T^1_\rho(\vec{e}^*, \hat{\vec{e}}, \hat{\vec{k}})$ can be written as:

$$T^1_\rho(\vec{e}^*, \hat{\vec{e}}, \hat{\vec{k}}) = \sum_{\delta \alpha \beta} \sqrt{5} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 2 \end{pmatrix} C^{00}_{10,10} C^{1\rho}_{00,00} \hat{\vec{e}}_\alpha \hat{\vec{e}}_\beta \hat{\vec{k}}_\beta + \sum_{\delta \alpha \nu} \sum_{\beta \nu} \begin{pmatrix} 1 & 1 & 2 \\ 1 & 1 & 2 \end{pmatrix} C^{2\nu'}_{1\nu,1\nu} C^{1\rho}_{2\nu',1\nu} \hat{\vec{e}}_\alpha \hat{\vec{e}}_\beta \hat{\vec{k}}_\beta$$ (1.27)

with

$$\begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 2 \end{pmatrix} = \frac{1}{3} \quad \text{and} \quad \begin{pmatrix} 1 & 1 & 2 \\ 1 & 1 & 2 \end{pmatrix} = \frac{1}{30}.$$ (1.27)

Introducing coupled tensors, usually defined via Clebsch-Gordan coefficients,

$$(U^s, V^t)^k_q = \sum_{\nu \mu} C^{s \mu}_{\nu \mu} U^s_{\nu} V^t_{\mu},$$ we have

$$T^1_\rho(\vec{e}^*, \hat{\vec{e}}, \hat{\vec{k}}) = \frac{\sqrt{5}}{3} ((\vec{e}^*, \vec{e})^0, \hat{\vec{k}})^1_\rho + \frac{1}{6} ((\vec{e}^*, \vec{e})^2, \hat{\vec{k}})^1_\rho.$$ (1.28)

Noticing that

$$((\vec{e}^*, \vec{e})^2, \hat{\vec{k}})^1_\rho = \sqrt{\frac{3}{5}} \left[ \frac{1}{3} \hat{\vec{k}} (\vec{e}^* \cdot \vec{e}) - \frac{1}{2} \vec{e} (\vec{e}^* \cdot \hat{\vec{k}}) - \frac{1}{2} \vec{e}^* (\vec{e} \cdot \hat{\vec{k}}) \right]_\rho = \frac{1}{3} \sqrt{\frac{3}{5}} \hat{k}_\rho,$$

12The term corresponding to $\nu = 1$ is proportional to $(\vec{e}^* \times \vec{e}) \times \hat{\vec{k}}$ that is zero for transversal wave.
and
\[
(\mathbf{e}^*, \mathbf{e})^0 = -\frac{1}{\sqrt{3}}(\mathbf{e}^* \cdot \mathbf{e}) = -\frac{1}{\sqrt{3}},
\]
we finally have
\[
T_\rho^1(\mathbf{e}^*, \mathbf{e}, \mathbf{k}) = -\frac{1}{2} \sqrt{\frac{3}{5}} \mathbf{k}_\rho.
\]
(1.29)
A similar derivation for \(\tilde{T}_\rho^1(\mathbf{e}^*, \mathbf{e}, \mathbf{k})\) lead to the identity
\[
\tilde{T}_\rho^1(\mathbf{e}^*, \mathbf{e}, \mathbf{k}) = T_\rho^1(\mathbf{e}^*, \mathbf{e}, \mathbf{k}) = -\frac{1}{2} \sqrt{\frac{3}{5}} \mathbf{k}_\rho.
\]

The term corresponding to \(x = 1\) of Eq. (1.23) takes therefore the form
\[
\sum_{E_1-E_2=1} \frac{-4\pi^2 \alpha}{\hbar c} \left(\frac{4\pi}{3}\right)^3 \frac{3}{\sqrt{10\pi}} \sum \frac{1}{2l} R_{l_1}^1 R_{l_1}^2 \left(\frac{3}{4\pi}\right)^{3/2} \sum (-)^{\rho} \sqrt{\frac{15(2l+1)(2l_c+1)}{(4\pi)^2}} 
\times
\begin{pmatrix}
  l & l' & 1 \\
  2 & 1 & l_c 
\end{pmatrix}
C_{l_0,10}^{l l_0} C_{l_0,020}^{l_0 l_0} \left[T_\rho^1(\mathbf{e}^*, \mathbf{e}, \mathbf{k}) \cdot \sum \langle g | \frac{C_{l_\lambda l,1-\rho}^{l_\lambda l,1-\rho}}{\sqrt{2l+1}} a_{l_\lambda l}^\dagger a_{l_\lambda l} | g \rangle \right].
\]
(1.30)

1.4.2 One electron effective operator: orbital anapole

The current section aims at identifying the one-electron properties described by the operator
\[
\sum_{\lambda\lambda'} i \left[ \frac{C_{l_\lambda l,1-\rho}^{l_\lambda l,1-\rho}}{\sqrt{2l+1}} a_{l_\lambda l}^\dagger a_{l_\lambda l} + \frac{C_{l_\lambda l,1-\rho}^{l_\lambda l,1-\rho}}{\sqrt{2l+1}} a_{l_\lambda l}^\dagger a_{l_\lambda l'} \right].
\]
(1.31)
We proceed as follows. In expression (1.31), the Clebsch-Gordan coefficients are formally replaced using Wigner-Eckart theorem
\[
C_{l_0 m_0}^{l' m'_0} = \frac{\langle l' m' | \widehat{M}_1 \cdot | l m \rangle}{\sqrt{2l' + 1}} \cdot \langle l' || \widehat{M}_1 \cdot | l \rangle.
\]
with \(\widehat{M}_1\) a rank one irreducible tensor. Notice that \(\widehat{M}_1\) change \(l\) into \(l \pm 1\). To determine \(\widehat{M}_1\) we thus consider the pair of operator \(\mathbf{A}\) and \(\mathbf{A}^\dagger\) with [36]
\[ A = n f_1(N_0) + \nabla_\Omega f_2(N_0) \]  

where \( n = \frac{r}{\rho} \), \( \nabla_\Omega = -i n \times L \) (\( L \) denotes the orbital angular momentum operator), furthermore

\[ f_1(N_0) = \left(N_0 - \frac{1}{2}\right) \sqrt{\frac{(N_0 - 1)}{N_0}} \]  

and

\[ f_2(N_0) = \sqrt{\frac{(N_0 - 1)}{N_0}}. \]  

with \( N_0 / lm = (l + \frac{1}{2}) / lm \).

\( A \) and \( A^\dagger \) are known as shift operators as their action on \( | lm \rangle \) changes \( l \) in \( l - 1 \) and \( l + 1 \), respectively. Explicitly, we have\(^{13} \)

\[
\begin{align*}
A_0 Y_{lm} &= \sqrt{(l^2 - m^2)} Y_{l-1m} \\
A_{\pm} Y_{lm} &= \sqrt{(l \mp m)(l \mp m - 1)} Y_{l-1m_{\pm 1}} \\
A_0^\dagger Y_{lm} &= \sqrt{(l + 1 + m)(l + 1 - m)} Y_{l+1m} \\
A_{\pm}^\dagger Y_{lm} &= \sqrt{(l \pm m + 1)(l \pm m + 2)} Y_{l+1m_{\pm 1}}.
\end{align*}
\]  

We note that \( A^- = i(A - A^\dagger) \), \( A^+ = (A + A^\dagger) \), \( L \) and \( N_0 \) provide a realization of \( so(3, 2) \), a de Sitter algebra. The cases \( l' = l + 1 \) and \( l' = l - 1 \) will be treated separately and then unified in a single relation that will provide the “desired” sum rule. In order not to overburden the reader, unless otherwise provided, the demonstrations will be given only for the case \( l' = l + 1 \) while for \( l' = l - 1 \) only the final result will be provided.

Expressing the Clebsch-Gordan coefficients in term of \( A \) and \( A^\dagger \) matrix elements

\[ C_{l'\lambda',1-\rho}^{l\lambda} = \sqrt{2l + 1} \frac{\langle l\lambda | A_{-\rho} | l'\lambda' \rangle}{\langle l || A || l' \rangle} \]

\(^{13}\)We remember that

\[
\begin{align*}
l_0 Y_{lm} &= m Y_{lm} \\
l_{\pm} Y_{lm} &= \sqrt{(l \mp m)(l \pm m + 1)} Y_{lm_{\pm 1}}.
\end{align*}
\]
and
\[ C_{\lambda \lambda', \lambda' - 1} = \sqrt{2l' + 1} \frac{\langle l' \lambda' \mid A_{\lambda', \lambda} \mid l \lambda \rangle}{\langle l' \mid A \mid l \rangle}, \]
and recalling that \( \langle l' \mid A \mid l \rangle = -\langle l' \mid A^\dagger \mid l \rangle \)
we can write Eq. (1.31) as
\[
\sum_{\lambda \lambda'} i \langle g \mid \frac{C_{\lambda \lambda', \lambda' - 1}}{\sqrt{2l' + 1}} a_{l' \lambda'} a_{l \lambda} + \frac{C_{\lambda' \lambda, \lambda - 1}}{\sqrt{2l + 1}} a_{l \lambda} a_{l' \lambda'} \mid g \rangle = i \sum_{\lambda \lambda'} \langle g \mid \frac{\langle l' \lambda' \mid A_{\lambda', \lambda} \mid l \lambda \rangle}{\langle l' \mid A \mid l \rangle} a_{l' \lambda'} a_{l \lambda} + \frac{\langle l \lambda \mid A_{\lambda', \lambda} \mid l' \lambda' \rangle a_{l \lambda} a_{l' \lambda'} - \langle l' \lambda' \mid A_{\lambda', \lambda} \mid l \lambda \rangle a_{l' \lambda'} a_{l \lambda} \mid g \rangle.
\]
Setting now
\[
\sum_i \left[ A_{-\rho} \right]_{l' i} = \sum_{\lambda \lambda'} \langle l \lambda \mid A_{-\rho} \mid l' \lambda' \rangle a_{l' \lambda'} a_{l \lambda} + \sum_{\lambda \lambda'} \langle l' \lambda' \mid A_{-\rho} \mid l \lambda \rangle a_{l \lambda} a_{l' \lambda'}
\]
and
\[
\sum_i \left[ A_{-\rho}^\dagger \right]_{l' i} = \sum_{\lambda \lambda'} \langle l' \lambda' \mid A_{-\rho}^\dagger \mid l \lambda \rangle a_{l \lambda} a_{l' \lambda'} + \langle l \lambda \mid A_{-\rho}^\dagger \mid l' \lambda' \rangle a_{l' \lambda'} a_{l \lambda},
\]
equation (1.31) becomes
\[
i \sum_{\lambda \lambda'} \langle g \mid \frac{C_{\lambda \lambda', \lambda' - 1}}{\sqrt{2l' + 1}} a_{l' \lambda'} a_{l \lambda} + \frac{C_{\lambda' \lambda, \lambda - 1}}{\sqrt{2l + 1}} a_{l \lambda} a_{l' \lambda'} \mid g \rangle = i \sum_{\lambda \lambda'} \langle g \mid \left[ A_{-\rho} \right]_{l' i} \mid g \rangle \tag{1.36}
\]
where \( A^- \) is a space-inversion odd and time-reversal odd operator.

The physical interpretation of \( A^- \) is provided by the relation (see Refs. [37] [38])

\[
\Omega = \frac{(n \times L - L \times n)}{2} = i \frac{[n, L]^2}{2} = i \left( \nabla \Omega - \nabla \Omega^\dagger \right) = \frac{1}{2 \sqrt{N_0}} \frac{1}{\sqrt{N_0}} \left[ N_0, A^- \right] + \frac{1}{\sqrt{N_0}} \tag{1.37}
\]
where \([...]_+\) denotes an anticommutator. \( \Omega \) defines a (purely angular) orbital anapole.

The possibility of express the (1.31) in function of the orbital anapole is given by the

\begin{footnotesize}
\footnote{This relation will be demonstrated in the following section.}
\footnote{These relations extend the definition of one electron operator to l-l’ pairs.}
\footnote{The link between the operators \( i(A - A^\dagger) \) and the orbital anapole \( \Omega \) is also provided in reference [39], where it is proved that:}
\end{footnotesize}
relations 73 and 74, p. 493, Ref. [40]

\[ \langle l' \lambda' | (\mathbf{n}, \mathbf{L})_{\kappa}^{K} | l \lambda \rangle = (-)^{l+l'+K} C_{\lambda KL}^{\lambda'} \sqrt{\frac{(2K+1)(l+1)(2l'+1)}{2l+1}} C_{l010}^{l0} \begin{pmatrix} 1 & 1 & K \\ l' & l & l \end{pmatrix}, \]

(1.38)

\[ \langle l' \lambda' | (\mathbf{L}, \mathbf{n})_{\kappa}^{K} | l \lambda \rangle = (-)^{l+l'+K} C_{\lambda KL}^{\lambda'} \sqrt{\frac{(2K+1)(l+1)(2l'+1)}{2l+1}} C_{l010}^{l0} \begin{pmatrix} 1 & 1 & K \\ l' & l & l \end{pmatrix}, \]

(1.39)

\[ \langle l \lambda | (\mathbf{n}, \mathbf{L})_{\kappa}^{K} | l' \lambda' \rangle = (-)^{l+l'+K} C_{\lambda KL}^{\lambda'} \sqrt{\frac{(2K+1)(l+1)(2l'+1)}{2l+1}} C_{l010}^{l0} \begin{pmatrix} 1 & 1 & K \\ l & l' & l' \end{pmatrix}, \]

(1.40)

\[ \langle l \lambda | (\mathbf{L}, \mathbf{n})_{\kappa}^{K} | l' \lambda' \rangle = (-)^{l+l'+K} C_{\lambda KL}^{\lambda'} \sqrt{\frac{(2K+1)(l+1)(2l'+1)}{2l+1}} C_{l010}^{l0} \begin{pmatrix} 1 & 1 & K \\ l & l' & l \end{pmatrix}. \]

(1.41)

that, for \( l' = l + 1 \) and \((K, \kappa) = (1, -\rho)\) assume the form

\[ \langle l' \lambda' | (\mathbf{n}, \mathbf{L})^{-1}_{-\rho} | l \lambda \rangle = C_{\lambda KL}^{\lambda'} \frac{l \sqrt{l+1}}{\sqrt{2(2l+3)}}, \]

(1.42)

\[ \langle l' \lambda' | (\mathbf{L}, \mathbf{n})^{-1}_{-\rho} | l \lambda \rangle = -C_{\lambda KL}^{\lambda'} \frac{(l+2) \sqrt{l+1}}{\sqrt{2(2l+3)}}, \]

(1.43)

\[ \langle l \lambda | (\mathbf{n}, \mathbf{L})^{-1}_{-\rho} | l' \lambda' \rangle = C_{\lambda KL}^{\lambda'} \frac{l+2 \sqrt{l+1}}{\sqrt{2(2l+1)}}, \]

(1.44)

\[ \langle l \lambda | (\mathbf{L}, \mathbf{n})^{-1}_{-\rho} | l' \lambda' \rangle = -C_{\lambda KL}^{\lambda'} \frac{l \sqrt{l+1}}{\sqrt{2(2l+1)}}, \]

(1.45)
Subtracting (1.43) to (1.42) and (1.45) to (1.44) and isolating the Clebsch-Gordan coefficients we obtain

\[
\frac{C_{\lambda,1-\rho}^{\mu\nu}}{\sqrt{2l'+1}} = \frac{\sqrt{2l'+3}}{\sqrt{2(l+1)\sqrt{(l+1)(2l'+1)}}} (l'\lambda' \mid (n, L)^{1}_{1-\rho} - (L, n)^{1}_{1-\rho} \mid l\lambda) = \\
\frac{i\sqrt{2l'+3}}{(l+1)\sqrt{(l+1)(2l'+1)}} (l'\lambda' \mid (n \times L - L \times n)^{1}_{-\rho} \mid l\lambda) \tag{1.46}
\]

and

\[
\frac{C_{\mu\nu,1-\rho}^{\lambda}}{\sqrt{2l+1}} = \frac{\sqrt{2l+3}}{\sqrt{2(l+1)\sqrt{(l+1)(2l'+1)}}} (l\lambda \mid (n, L)^{1}_{1-\rho} - (L, n)^{1}_{1-\rho} \mid l'\lambda') = \\
\frac{i\sqrt{2l+3}}{(l+1)\sqrt{(l+1)(2l'+1)}} (l\lambda \mid (n \times L - L \times n)^{1}_{-\rho} \mid l'\lambda') \tag{1.47}
\]

relations that connect the orbital anapole with the Clebsch-Gordan coefficients of relation (1.31). The evaluation of the term

\[
S(l, l' = l + 1, l_c)_{x=1} = \sqrt{15(2l+1)(2l_c+1)} \frac{(4\pi)^2}{2(l+1)\sqrt{(l+1)(2l'+1)}} \left\{ \begin{array}{ccc} l & l+1 & 1 \\ 2 & 1 & l_c \end{array} \right\} C_{l,0}^{l,10} C_{l+10,0}^{l,10} = \\
(-)^{1-l_c-l(l_c+1)(l_c-l-2)(1+l_c+l)(3+l_c+l)} \tag{1.48}
\]

and the relations (1.46) and (1.47) allow to write the Eq. (1.30) as

\[
\sum_{l+1}^{x=1} \frac{\alpha\pi^2}{3hc} \sum_{ll'} R_{l,l'}^{l+1} R_{l',l}^{l+1} a^{(1-)}_{l+1}(l, l_c) \sqrt{\frac{3}{5}} \sum_{\rho} (-)^{\rho} T^l_{\rho}(\epsilon^*, \epsilon, \nu) \langle g \mid \sum_i \left[ \frac{(n \times L - L \times n)^{1}_{-\rho}}{2} \right]^{ll'}_{i} \mid g \rangle \tag{1.49}
\]

where the one electron operator \( [n \times L - L \times n]^{ll'}_{i} \) satisfy the relation

\[
\sum_i [n \times L - L \times n]^{ll'}_{i} = \sum_{\lambda\lambda'} \langle l'\lambda' \mid (n \times L - L \times n) \mid \lambda \rangle a^\dagger_{\lambda\mu} a_{l\lambda} + \langle l'\lambda' \mid (n \times L - L \times n) \mid l\lambda \rangle a^\dagger_{l\lambda} a_{l'\lambda'} \]

and

\[
a^{(1-)}_{1+l}(l, l_c) = \frac{(2l_c + 1)(l_c - 2 - l)(1 + l_c + l)(3 + l_c + l)}{(l_c + l)(l + 1)^2(2 + l_c + l)} \tag{1.50}
\]

These considerations can be extended to the case \( l' = l - 1 \); the integral relation form does not change but the numerical coefficient becomes

\[
a^{(1-)}_{l-1}(l, l_c) = \frac{(2l_c + 1)(2 + l_c - l)(l_c + l + 1)(1 + l_c + l)}{l^2(l_c + l)(2 + l_c + l)} \tag{1.51}
\]
A more compact form for Eq. (1.30) is obtained by getting the coefficients (1.50) and (1.51) together in a single term including both the cases \( l' = l + 1 \) and \( l' = l - 1 \); in this case we have

\[
\Sigma_{E1-E2}^{x=1} = \frac{\alpha \pi^2}{3 \hbar c} \sum_{l'} R_{l,l'} R_{l',l} a_{l'}^{(-)}(l, l_c) \sqrt{\frac{3}{5}} \sum_{\rho} (-)^{\rho} T_{\rho}^{31}(\vec{e}^*, \vec{e}, \vec{k}) \langle g | \sum_{i} \left[ \frac{(n \times L - L \times n)_{-\rho}}{2} \right]_{i}^{u'} | g \rangle
\]

with \( a_{l'}^{(-)}(l, l_c) \)

\[
a_{l'}^{(-)}(l, l_c) = \frac{4(2l_c + 1)(1 + l_c + l)(l_c + l - 2l')(l_c + 2l' - l + 1)}{(l_c + l)(2 + l_c + l)(l + l' + 1)^2}
\]

and \( l' = l \pm 1 \). The superscript (-) denote the \( \Omega \) behaviour under time reversal transformation (it is time-reversal odd).

1.4.3 Appendix: reduced matrix element of \( A \) and \( A^\dagger \)

In this appendix, we show that the reduced matrix elements of \( A \) and \( A^\dagger \) are connected by the relations

\[
\langle l' | A | l \rangle = -\langle l | A^\dagger | l' \rangle, \quad \text{for } l' = l - 1 \tag{1.54}
\]

and

\[
\langle l' | A^\dagger | l \rangle = -\langle l | A | l' \rangle, \quad \text{for } l' = l + 1. \tag{1.55}
\]

Consider Eq. (1.54) (case \( l' = l - 1 \)).

Applying the Wigner-Eckart theorem and using the definition (1.32), (1.33) and (1.34), we obtain

\[
\langle l' \lambda' | A_{\rho} | l \lambda \rangle = C_{l\lambda,1\rho}^{\nu' \sigma} \langle l' | A | l \rangle = \sqrt{\frac{2l - 1}{2l + 1}} \langle l' \lambda' | n_{\rho} | l \lambda \rangle + \sqrt{\frac{2l - 1}{2l + 1}} \langle l' \lambda' | \nabla n_{\rho} | l \lambda \rangle.
\]

Given that

\[
\langle l' | n | l \rangle = \sqrt{2l + 1} C_{l0,10}^{\nu 0}
\]

and

\[
\langle l' | \nabla_{\Omega} | l \rangle = -\{l \sqrt{l + 1} \delta_{l,l+1} + (l + 1) \sqrt{l} \delta_{l,l-1} \},
\]

21
(see, for example, p. 484 and p. 487 of Ref. [40]) we have
\[
\langle l' \lambda' | n_{\rho} | l \lambda \rangle = \frac{\langle l' \parallel n \parallel l \rangle}{\sqrt{2l'+1}} C_{l,\lambda,1\rho}^{l',\lambda'} = \sqrt{\frac{2l+1}{2l+1}} C_{l,0,0}^{l',0} C_{l,\lambda,1\rho}^{l',\lambda'} = -\sqrt{\frac{l}{2l-1}} C_{l,\lambda,1\rho}^{l',\lambda'}
\]
and
\[
\langle l' \lambda' | \nabla n_{\rho} | l \lambda \rangle = -(l + 1) \sqrt{\frac{l}{2l-1}} C_{l,\lambda,1\rho}^{l',\lambda'} = -(l + 1) \sqrt{\frac{l}{2l-1}} C_{l,\lambda,1\rho}^{l',\lambda'}.
\]
Eq. (1.56) takes the form
\[
\langle l' \lambda' | A_{\rho} \parallel l \lambda \rangle = l \sqrt{\frac{2l-1}{2l+1}} \langle l' \lambda' | n_{\rho} \parallel l \lambda \rangle + \sqrt{\frac{2l-1}{2l+1}} \langle l' \lambda' | \nabla n_{\rho} \parallel l \lambda \rangle = -\sqrt{\frac{l(2l+1)(2l-1)}{2l-1}} C_{l,\lambda,1\rho}^{l',\lambda'},
\]
yielding
\[
\langle l' \parallel \parallel l \rangle = -\sqrt{l(2l+1)(2l-1)}.
\]
The matrix element \( \langle l \lambda | A_{\rho}^{\dagger} | l' \lambda' \rangle \), where
\[
A_{\rho}^{\dagger} = f_{1}(N_{0})n + if_{2}(N_{0})(n \times L)^{\dagger} = f_{1}(N_{0})n - if_{2}(N_{0})(L \times n),
\]
can be written as
\[
\langle l \lambda | A_{\rho}^{\dagger} | l' \lambda' \rangle = \langle l \lambda | f_{1}(N_{0})n_{\rho} | l' \lambda' \rangle - i\langle l \lambda | f_{2}(N_{0})(L \times n)_{\rho} | l' \lambda' \rangle =
\]
\[
= l \sqrt{\frac{2l-1}{2l+1}} \langle l \lambda | n_{\rho} | l' \lambda' \rangle - \sqrt{2} \sqrt{\frac{2l-1}{2l+1}} \langle l \lambda | (L, n)_{\rho}^{\dagger} | l' \lambda' \rangle = C_{l,\lambda,1\rho}^{l,\lambda} \frac{l(l-1)(2l+1)}{\sqrt{2l+1}}.
\]
(1.57)
Using
\[
\langle l \lambda | n_{\rho} | l' \lambda' \rangle = \sqrt{\frac{l}{2l+1}} C_{l,\lambda,1\rho}^{l,\lambda}
\]
and
\[
\langle l \lambda | (L, n)_{\rho}^{\dagger} | l' \lambda' \rangle = -iC_{l,\lambda,1\rho}^{l,\lambda} \frac{\sqrt{l(l+1)}}{\sqrt{2l+1}}
\]
we obtain:
\[
\langle l \parallel A_{\rho}^{\dagger} \parallel l' \rangle = \sqrt{l(2l-1)(2l+1)},
\]
that is:
\[
\langle l \parallel A_{\rho}^{\dagger} \parallel l' \rangle = -\langle l' \parallel A_{\rho} \parallel l \rangle.
\]
Eq. (1.55) is derived in a similar way.
1.5 The $x = 2$ terms

1.5.1 Geometrical factor

Consider $T^2(\vec{e}^*, \vec{\epsilon}, \vec{k})$ and $\tilde{T}^2(\vec{e}^*, \vec{\epsilon}, \vec{k})$.

From expressions (1.18) and (1.22) we have

$$T^2_{\rho}(\vec{e}^*, \vec{\epsilon}, \vec{k}) = -\sum_{\nu} \sqrt{5(2\nu + 1)} \begin{pmatrix} 1 & 1 & \nu \\ 1 & 2 & 2 \end{pmatrix} (\vec{e}^*, \vec{\epsilon})^\nu, \vec{k})^2$$

(1.58)

and

$$\tilde{T}^2_{\rho}(\vec{e}^*, \vec{\epsilon}, \vec{k}) = \sum_{\nu} (-)^\nu \sqrt{5(2\nu + 1)} \begin{pmatrix} 1 & 1 & \nu \\ 1 & 2 & 2 \end{pmatrix} (\vec{e}^*, \vec{\epsilon})^\nu, \vec{k})^2$$

(1.59)

with $\nu = 0, 1, 2$.

From

$$\begin{pmatrix} 1 & 1 & 0 \\ 1 & 2 & 2 \end{pmatrix} = 0 \quad \begin{pmatrix} 1 & 1 & 1 \\ 1 & 2 & 2 \end{pmatrix} = -\frac{1}{2\sqrt{5}} \quad \begin{pmatrix} 1 & 1 & 2 \\ 1 & 2 & 2 \end{pmatrix} = -\frac{1}{10}$$

we obtain

$$T^2_{\rho}(\vec{e}^*, \vec{\epsilon}, \vec{k}) = \frac{\sqrt{3}}{2} (\vec{e}^*, \vec{\epsilon})^1, \vec{k})^2 + \frac{1}{2} (\vec{e}^*, \vec{\epsilon})^2, \vec{k})^2$$

and

$$\tilde{T}^2_{\rho}(\vec{e}^*, \vec{\epsilon}, \vec{k}) = \frac{\sqrt{3}}{2} (\vec{e}^*, \vec{\epsilon})^1, \vec{k})^2 - \frac{1}{2} (\vec{e}^*, \vec{\epsilon})^2, \vec{k})^2$$

The $x = 2$ contribution to Eq. (1.23) takes therefore the form

$$\Sigma_{E1-E2}^{x=2} = \frac{4\pi^2\alpha}{\hbar c} \left( \frac{4\pi}{3} \right)^3 \sqrt{\frac{15}{10\pi}} \sum_{l,l'} R_{l,l'}^1 R_{l,l'}^2 \left( \frac{3}{4\pi} \right)^{3/2} \sum_{\rho} (-)^\rho \sqrt{\frac{15(2l + 1)(2l' + 1)}{(4\pi)^2}} \times$$

\[ 17 \text{We remember that an irreducible tensor of rank } p \, K^p \text{ given by} \]

$$K_\xi^p = (A^a, B^b)^p$$

is obtained by the coupling scheme $K_\xi^p = \sum_{a,b} A^a_{\alpha} B^b_{\beta} C_{\alpha\beta}^{p\xi}$ where $A^a$ and $B^b$ are irreducible tensor of rank $a$ and $b$ and $C_{\alpha\beta}^{p\xi}$ is a Clebsch-Gordan coefficient.
\[ \times \left\{ \begin{array}{ccc} l & l' & 2 \\ 2 & 1 & l_c \end{array} \right\} C_{l_0,0}^{l_0} C_{l_0,0}^{l_0} \left\{ \begin{array}{c} i \sqrt{3} \\ 2 \end{array} \right\} \left( (\tilde{e}^*, \tilde{e})^1, \tilde{\kappa} \right)^{k^2} \left[ \langle g \mid C^{l_0,0}_{l_0,0} a^{\dagger}_{l_0} a_{l_0} + C^{l_0,0}_{l_0,0} a_{l_0} a^{\dagger}_{l_0} \mid g \rangle \right] + \right. \\
\left. + \frac{i}{2} (\tilde{e}^*, \tilde{e})^2, \tilde{\kappa} \right)^{k^2} \left[ \langle g \mid C^{l_0,0}_{l_0,0} a^{\dagger}_{l_0} a_{l_0} - C^{l_0,0}_{l_0,0} a_{l_0} a^{\dagger}_{l_0} \mid g \rangle \right] \right\}. \tag{1.60} \\

### 1.5.2 One-electron effective operators: orbital pseudodeviator and magnetic quadrupole

Eq. (1.60) contains two rank-2 one-electron effective operators. To determine them we proceed as follows. The cases \( l' = l + 1 \) and \( l' = l - 1 \) will be treated separately.

For \( l' = l + 1 \), we have

\[ C^{l_0,0}_{l_0,0} = \frac{\langle l' \lambda' \mid (A^\dagger, L)^{k^2} \mid l \lambda \rangle}{\langle l' \mid (A^\dagger, L)^{k^2} \mid l \rangle} \sqrt{2l' + 1} \tag{1.61} \]

and

\[ C^{l_0,0}_{l_0,0} = \frac{\langle l \lambda \mid (A, L)^{k^2} \mid l' \lambda' \rangle}{\langle l \mid (A, L)^{k^2} \mid l' \rangle} \sqrt{2l + 1}. \tag{1.62} \]

We have \( \langle l \mid (A, L)^2 \mid l' \rangle = -\langle l' \mid (A^\dagger, L)^{k^2} \mid l \rangle \). \(^{18}\)

Yielding

\[ i \left[ \langle g \mid C^{l_0,0}_{l_0,0} a^{\dagger}_{l_0} a_{l_0} + C^{l_0,0}_{l_0,0} a_{l_0} a^{\dagger}_{l_0} \mid g \rangle \right] = i \frac{\langle g \mid \sum_i [(A - A^\dagger, L)^{k^2}]_{l_0} \mid g \rangle}{\langle l \mid (A, L)^{k^2} \mid l' \rangle} \tag{1.63} \]

and

\[ i \left[ \langle g \mid C^{l_0,0}_{l_0,0} a^{\dagger}_{l_0} a_{l_0} - C^{l_0,0}_{l_0,0} a_{l_0} a^{\dagger}_{l_0} \mid g \rangle \right] = i \frac{\langle g \mid \sum_i [(A + A^\dagger, L)^{k^2}]_{l_0} \mid g \rangle}{\langle l' \mid (A^\dagger, L)^{k^2} \mid l \rangle}, \tag{1.64} \]

where we have used the definitions

\[ \sum_i [(A^\dagger, L)^{k^2}]_{l_0} = \sum_{\lambda \lambda'} \langle l' \lambda' \mid (A^\dagger, L)^{k^2} \mid l \lambda \rangle a^{\dagger}_{l' \lambda} a_{l \lambda} + \langle l \lambda \mid (A^\dagger, L)^{k^2} \mid l' \lambda' \rangle a^{\dagger}_{l \lambda} a_{l' \lambda}, \]

\[ \sum_i [(A, L)^{k^2}]_{l_0} = \sum_{\lambda \lambda'} \langle l' \lambda' \mid (A, L)^{k^2} \mid l \lambda \rangle a^{\dagger}_{l' \lambda} a_{l \lambda} + \langle l \lambda \mid (A, L)^{k^2} \mid l' \lambda' \rangle a^{\dagger}_{l \lambda} a_{l' \lambda}. \]

\(^{18}\)As a consequence of the relation \( \langle l \mid A \mid l' \rangle = -\langle l' \mid A^\dagger \mid l \rangle. \)
and

\[
\sum_i [(A \pm A^\dagger, L)^2]_{i}^{ll'} = \sum_{\lambda\lambda'} \langle l'l' | (A \pm A^\dagger, L)^2 | l\lambda \rangle a_{l\lambda}^\dagger a_{l\lambda} + \langle l\lambda | (A \pm A^\dagger, L)^2 | l'l' \rangle a_{l'l'}^\dagger a_{l'l'}.
\]

In the previous section we have provided the physical representation of the operator \( A^- = i(A - A^\dagger) \) introducing the orbital anapole. Similarly we can connect the generator \( A^+ = (A + A^\dagger)/2 \) with \( n \) by the relation

\[
A^+ = (A + A^\dagger)/2 = \sqrt{N_n} n \sqrt{N_0}.
\]  

(1.65)

The link between \( A^- \) and \( \Omega \) and between \( A^+ \) and \( n \) allow to express equations (1.63) and (1.64) in term of the effective operators \([(\Omega, L)^2]_i^{ll'} \) (orbital pseudodeviator) and \([(n, L)^2]_i^{ll'} \) (magnetic quadrupole) obtaining that

\[
i \left[ \langle g | \frac{C_{\lambda \lambda'}^{l'l'}}{\sqrt{2l'+1}} a_{l'l'}^\dagger a_{l\lambda} + \frac{C_{\lambda \lambda'}^{l'l'}}{\sqrt{2l'+1}} a_{l\lambda}^\dagger a_{l'l'} | g \rangle \right] = C_1(g | \sum_i [(\Omega, L)^2]_{-\rho}^{ll'} | g) \]  

(1.66)

and

\[
i \left[ \langle g | \frac{C_{\lambda \lambda'}^{l'l'}}{\sqrt{2l'+1}} a_{l'l'}^\dagger a_{l\lambda} - \frac{C_{\lambda \lambda'}^{l'l'}}{\sqrt{2l'+1}} a_{l\lambda}^\dagger a_{l'l'} | g \rangle \right] = iC_2(g | \sum_i [(n, L)^2]_{-\rho}^{ll'} | g) \]  

(1.67)

with \( C_1 \) and \( C_2 \) numerical coefficients to be evaluated. We have

\[
\sum_i [(\Omega, L)^2]_{-\rho}^{ll'} = \sum_{\lambda\lambda'} \langle l'l' | (\Omega, L)^2 | l\lambda \rangle a_{l\lambda}^\dagger a_{l\lambda} + \langle l\lambda | (\Omega, L)^2 | l'l' \rangle a_{l'l'}^\dagger a_{l'l'}
\]

(1.68)

and

\[
\sum_i [(n, L)^2]_{-\rho}^{ll'} = \sum_{\lambda\lambda'} \langle l'l' | (n, L)^2 | l\lambda \rangle a_{l\lambda}^\dagger a_{l\lambda} + \langle l\lambda | (n, L)^2 | l'l' \rangle a_{l'l'}^\dagger a_{l'l'}
\]

(1.69)

Defining \( T^{(2)}(\vec{e}, \vec{e}, \hat{k}) = \frac{\sqrt{2}}{2} ((\vec{e}, \vec{e})^1, \hat{k})^2 \) and \( T^{(2)}(\vec{e}, \vec{e}, \hat{k}) = \frac{i}{2} ((\vec{e}, \vec{e})^2, \hat{k})^2 \), evaluating the numerical coefficient

\[
S(l, l + 1, l_c)_{x=2} = \frac{\sqrt{15(2l + 1)(2l_c + 1)}}{4\pi} \left\{ \begin{array}{ccc} l & l + 1 & 2 \\ 2 & 1 & l_c \end{array} \right\} C_{l,0}^{l_c,0} C_{l_c,0}^{l_c + 1} = \frac{(2l + 3)(-4 + 5l + 3l^2 - 3l_c - 3l_c^2)(2l + 1)(2l_c + 1)\sqrt{6l(l + 1)(l + 2)}}{8\pi(3 + l - l_c)(l + l_c)^2(2 + l + l_c)(4 + l + l_c)}.
\]  

(1.70)
and calculating $^{19}$ $C_1$ and $C_2$ we can write $\Sigma_{E1-E2}^2$ as

$$\Sigma_{E1-E2}^2 = -\frac{8\pi^2\alpha\sqrt{2}}{3hc\sqrt{2}} \sum_{\ell'} R_{i,l}^1 R_{i',l'} a_{i+1}^{(2+)}(l_c, l) \sum_{\rho} (-)^{\rho} \eta^{(2+)}(\epsilon^*, \epsilon, \bar{k}) \times$$

$$\times \langle g | \sum_i [(\Omega, L)^2\gamma_i]_{\ell'} | g \rangle + \frac{4\pi^2\alpha\sqrt{6}}{3hc} \sum_{\ell'} R_{i,l}^1 R_{i',l'} a_{i+1}^{(2-)}(l_c, l) \times$$

$$\times \sum_{\rho} (-)^{\rho} \eta^{(2-)}(\epsilon^*, \epsilon, \bar{k}) \langle g | \sum_i [(\Omega, L)^2\gamma_i]_{\ell'} | g \rangle \quad (1.71)$$

where

$$a_{i+1}^{(2+)}(l_c, l) = \frac{(2l_c + 1)(2l + 1)(2l + 3)(4 + 3l_c(l_c + 1) - l(3l + 5))}{(3 + l - l_c)(l + l_c)^2(2 + l + l_c)(4 + l + l_c)(l + 1)}$$

(1.72)

$$a_{i+1}^{(2-)}(l_c, l) = \frac{(2l_c + 1)(2l + 1)(2l + 3)(4 + 3l_c(l_c + 1) - l(3l + 5))}{(3 + l - l_c)(l + l_c)^2(2 + l + l_c)(4 + l + l_c)}$$

(1.73)

$^{19}$The coefficients $C_1$ and $C_2$ of relations (1.66) and (1.67) can be obtained using the Rel. 10 p. 476 Ref. [40]

$$\langle n'j'm' | (P^a, Q^b)^c \gamma | njm \rangle = (-)^{j'+c} \frac{\Pi_c}{\Pi_{j'}} C_{j'm'}^{j'm'} \sum_{n, l_1} \left\{ \begin{array}{ccc} a & b & c \\ j & j' & j_1 \end{array} \right\} \langle n'j' || P^a || n_1j_1 \rangle \langle n_1j_1 || Q^b || nj \rangle$$

that allow to express a generic Clebsch-Gordan coefficient $C_{j'm'}^{j'm'}$ in function of an effective rank $c$ tensor obtained coupling two irreducible operators of rank $a$ and $b$ (we recall that $\Pi_{a,b,...,c} = \sqrt{(2a + 1)(2b + 1)...(2c + 1)}$). In our case the Clebsch-Gordan coefficient is $C_{\lambda, \lambda, \rho}^{\lambda', \lambda', \rho}$ (or $C_{\lambda, \lambda, \rho}^{\lambda', \lambda', \rho}$) and the operators $P^a$ and $Q^b$ are respectively $-\sqrt{2}(n, L)^{-1} - (L, n)^{1}$ and $L$ for the relation (1.66), $n$ and $L$ for the (1.67). Applying this formula we obtain, for $l' = l + 1$

$$\left[ \frac{C_{\lambda, \lambda, \rho}^{\lambda', \lambda', \rho}}{\sqrt{2l' + 1}} a_{i, \lambda}^{\dagger} a_{i, \lambda} + \frac{C_{\lambda', \lambda', \rho}^{\lambda, \lambda, \rho}}{\sqrt{2l' + 1}} a_{i, \lambda}^{\dagger} a_{i, \lambda} \right] = \frac{1}{(l + 1)\sqrt{2l(l + 1)(l + 2)}} \left[ \langle l' \lambda' \mid \langle n \times L - L \times n, L \rangle^2 \rho \mid l \lambda \rangle a_{i, \lambda}^{\dagger} a_{i, \lambda} + \\
+ \langle l \lambda \mid \langle n \times L - L \times n, L \rangle^2 \rho \mid l' \lambda' \rangle a_{i, \lambda}^{\dagger} a_{i, \lambda} \right]$$

and

$$\left[ \frac{C_{\lambda, \lambda, \rho}^{\lambda', \lambda', \rho}}{\sqrt{2l' + 1}} a_{i, \lambda}^{\dagger} a_{i, \lambda} - \frac{C_{\lambda', \lambda', \rho}^{\lambda, \lambda, \rho}}{\sqrt{2l' + 1}} a_{i, \lambda}^{\dagger} a_{i, \lambda} \right] = \sqrt{\frac{2}{l(l + 1)(l + 2)}} \left[ \langle l' \lambda' \mid \langle n, L \rangle^2 \rho \mid l \lambda \rangle a_{i, \lambda}^{\dagger} a_{i, \lambda} + \\
+ \langle l \lambda \mid \langle n, L \rangle^2 \rho \mid l' \lambda' \rangle a_{i, \lambda}^{\dagger} a_{i, \lambda} \right]$$

26
The result obtained can be extended to the case \( l' = l - 1 \); the integral relation form does not change but the numerical coefficients become

\[
a_{l-1}^{2+} = \frac{(2l_e + 1)(2l + 1)(2l - 1)(6 + 3l_e(l_e + 1) - l(3l + 1))}{l(l - l_e - 3)(-2 + l + l_e)(l + l_e)^2(2 + l + l_e)^2} \tag{1.74}
\]

and

\[
a_{l-1}^{(2-)} = \frac{(6 + 3l_e(l_e + 1) - l(3l + 1))(2l_e + 1)(2l + 1)(2l - 1)}{(-3 + l - l_e)(-2 + l + l_e)(l + l_e)^2(2 + l + l_e)^2}. \tag{1.75}
\]

A more compact form is obtained putting the coefficients (1.72) and (1.74) and the coefficients (1.73) and (1.75) together; in this case the integral \( \Sigma_{E_1-E_2}^2 \) will assume the form

\[
\Sigma_{E_1-E_2}^2 = -8\pi^2\alpha\sqrt{3} \sum_{l''} R_{l_e,l}^1 R_{l_e,l'}^2 a_{l'}^{(2+)}(l_e, l) \sum \rho \langle - \phi \rangle^{(2+)}(\mathbf{e}, \mathbf{\hat{e}}) \times
\]

\[
\langle g | \sum_i \left[ (\Omega, \mathbf{L})_{\rho}^{2} \mid \frac{\mathbf{L}_i}{i} \right] g \rangle + \frac{4\pi^2\alpha\sqrt{3}}{3\hbar c} \sum_{l''} R_{l_e,l}^1 R_{l_e,l'}^2 a_{l'}^{(2-)}(l_e, l) \times
\]

\[
\sum \rho \langle - \phi \rangle^{(2-)}(\mathbf{\hat{e}}, \mathbf{\hat{e}}) \langle g | \sum_i \left[ (\mathbf{n}, \mathbf{L})_{\rho}^{2} \mid \frac{\mathbf{L}_i}{i} \right] g \rangle \tag{1.76}
\]

where

\[
a_{l'}^{(2+)} = \frac{2(2l_e + 1)(2l + 1)(2l' + 1)(6 + 3l_e(l_e + 1) - 2l(l + 1) - l'(l' + 1))}{(l + l_e + 2)^2(l + l' + 1)(l_e - 3l' + 2l)(l_e + 3l' - 2l + 1)(l + l_e)^2}
\]

and

\[
a_{l'}^{(2-)} = \frac{(l + l' + 1)(l' - l)a_{l'}^{(2+)}(l, l_c)}{4}
\]

with \( l' = l \pm 1 \).

### 1.6 The \( \Sigma_{E_1-E_2}^3 \) rank three tensor

In this section we will complete the study of relation (1.23) discussing the contribution \( x = 3 \).
1.6.1 Geometrical factor

From expressions (1.18) and (1.22) we have

\[ T^3_{\rho}(\tilde{\epsilon}^*, \tilde{\epsilon}, \tilde{k}) = \sum_{\nu\nu'} \sum_{\alpha\beta\gamma} \sqrt{5(2\nu + 1)} \left\{ \begin{array}{ccc} 1 & 1 & \nu \\ 1 & 3 & 2 \end{array} \right\} C_{\nu\nu',1\alpha}^{\nu\nu'} C_{\nu\nu',1\beta}^{3\beta} \tilde{\epsilon}_\alpha \tilde{k}_\beta \] (1.77)

and

\[ \tilde{T}^3_{\rho}(\tilde{\epsilon}^*, \tilde{\epsilon}, \tilde{k}) = \sum_{\nu\nu'} \sum_{\alpha\beta\gamma} (-)^\nu \sqrt{5(2\nu + 1)} \left\{ \begin{array}{ccc} 1 & 1 & \nu \\ 1 & 3 & 2 \end{array} \right\} C_{\nu\nu',1\alpha}^{\nu\nu'} C_{\nu\nu',1\beta}^{3\beta} \tilde{\epsilon}_\alpha \tilde{\epsilon}_\beta \tilde{k}_\beta \] (1.78)

Only \( \nu = 2 \) is allowed\(^{20}\).

From

\[ \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ 1 & 3 & 2 \end{array} \right\} = \frac{1}{5} \]

we obtain

\[ T^3_{\rho}(\tilde{\epsilon}^*, \tilde{\epsilon}, \tilde{k}) = ((\tilde{\epsilon}^*, \tilde{\epsilon})^2, \tilde{k})^3_{\rho} \] (1.79)

and

\[ \tilde{T}^3_{\rho}(\tilde{\epsilon}^*, \tilde{\epsilon}, \tilde{k}) = ((\tilde{\epsilon}^*, \tilde{\epsilon})^2, \tilde{k})^3_{\rho}. \] (1.80)

The \( x = 3 \) contribute of Eq. (1.23) takes therefore the form

\[ \Sigma_{E1-E2}^{x=3} = -i \frac{4\pi^2 \alpha}{\hbar c} \left( \frac{4\pi}{3} \right)^3 21^{\frac{3}{2}} \sum_{l_l,l_l',l_{c}} R_{l_l,l_l'} R_{l_{c}}^2 \left( \frac{3}{4\pi} \right)^{3/2} \sum_{\rho} (-)^\rho \sqrt{\frac{15(2l + 1)(2l_{c} + 1)}{(4\pi)^2}} \times \]

\[ \times \left\{ \begin{array}{ccc} l & l' & 3 \\ 2 & 1 & l_{c} \end{array} \right\} C_{l_l,0}^{l_l} C_{l_l',0}^{l_l'} \left[ T^{(3-)}_{\rho}(\tilde{\epsilon}^*, \tilde{\epsilon}, \tilde{k}) \cdot \sum_{\lambda \lambda'} \langle g | \frac{C_{l_l l_{c} 3-} \alpha_{l_{c}}}{\sqrt{2l_{c} + 1}} a_{l_{c}}^{\dagger} a_{l_{c} \lambda} + \frac{C_{l_l l_{c} 3-} \alpha_{l_{c}}}{\sqrt{2l_{c} + 1}} a_{l_{c} \lambda}^{\dagger} a_{l_{c}} \lambda \lambda' | g \rangle \right] \] (1.81)

where we have defined \( T^{(3-)}_{\rho}(\tilde{\epsilon}^*, \tilde{\epsilon}, \tilde{k}) = ((\tilde{\epsilon}^*, \tilde{\epsilon})^2, \tilde{k})^3_{\rho}. \)

\(^{20}\)In other cases \( C_{\nu\nu',1\beta}^{3\beta} \) does not fulfill the triangular relations [34].
1.6.2 One electron effective operator: the rank three operator

Eq. (1.81) contains a rank-three one-electron effective operator. It will be determined as follows. The cases \( l' = l + 1 \) and \( l' = l - 1 \) will be separately treated.

For \( l' = l + 1 \) we have

\[
\frac{C_{l\lambda,3-\rho}^{l',\lambda'}}{\sqrt{2l' + 1}} = \frac{\langle l\lambda' | (A^\dagger, (L, L)^2)^3_{-\rho} | l\lambda \rangle}{\langle l' | (A^\dagger, (L, L)^2)^3 || l \rangle}
\]

and

\[
\frac{C_{l\lambda,3-\rho}^{l',\lambda'}}{\sqrt{2l' + 1}} = \frac{\langle l\lambda | (A, (L, L)^2)^3_{-\rho} | l\lambda' \rangle}{\langle l | (A, (L, L)^2)^3 || l' \rangle}
\]

where \( \langle l' | (A, (L, L)^2)^3 || l \rangle = -\langle l | (A^\dagger, (L, L)^2)^3 || l' \rangle \).

Yielding

\[
i \sum_{\lambda\lambda'} \frac{C_{l\lambda,3-\rho}^{l',\lambda'}}{\sqrt{2l' + 1}} a_{l\lambda}^\dagger a_{l\lambda'} = i \sum_{\lambda\lambda'} \frac{\langle l\lambda | (A, (L, L)^2)^3_{-\rho} | l\lambda' \rangle}{\langle l | (A, (L, L)^2)^3 || l' \rangle} \quad (1.82)
\]

where we have used the definitions

\[
\sum_i [(A^\dagger, (L, L)^2)^3]_{l\lambda}^{l'} = \sum_{\lambda\lambda'} \langle l\lambda' | (A^\dagger, (L, L)^2)^3 | l\lambda \rangle a_{l\lambda}^\dagger a_{l\lambda'} + \langle l\lambda | (A^\dagger, (L, L)^2)^3 | l\lambda' \rangle a_{l\lambda'}^\dagger a_{l\lambda}
\]

\[
\sum_i [(A, (L, L)^2)^3]_{l\lambda}^{l'} = \sum_{\lambda\lambda'} \langle l\lambda' | (A, (L, L)^2)^3 | l\lambda \rangle a_{l\lambda}^\dagger a_{l\lambda'} + \langle l\lambda' | (A, (L, L)^2)^3 | l\lambda \rangle a_{l\lambda}^\dagger a_{l\lambda'}
\]

and

\[
\sum_i [(A - A^\dagger, (L, L)^2)^3]_{l\lambda}^{l'} = \sum_{\lambda\lambda'} \langle l\lambda | (A - A^\dagger, (L, L)^2)^3 | l\lambda' \rangle a_{l\lambda}^\dagger a_{l\lambda'} + \\
+ \langle l\lambda' | (A - A^\dagger, (L, L)^2)^3 | l\lambda \rangle a_{l\lambda'}^\dagger a_{l\lambda} \quad (1.83)
\]

The link between \( A^- \) and \( \Omega \) allows to express Eq. (1.82) in term of the effective rank-3 operator \( (\Omega, (L, L)^2)^3 \) obtaining that \(^{21}\)

\[
\sum_{\lambda\lambda'} \frac{C_{l\lambda,3-\rho}^{l',\lambda'}}{\sqrt{2l' + 1}} a_{l\lambda}^\dagger a_{l\lambda'} + \frac{C_{l\lambda,3-\rho}^{l',\lambda'}}{\sqrt{2l' + 1}} a_{l\lambda'}^\dagger a_{l\lambda'} = \frac{i \sqrt{15}}{(l + 1) \sqrt{(l(1 + l)(l + 2)(2l - 1)(2l + 5)}}
\]

\(^{21}\)We use relation 18 p. 478 Ref. [40].
\[
\times \sum_{\lambda \lambda'} \left[ \langle l' \lambda' \mid (\Omega, (\mathbf{L}, \mathbf{L})^2)_{-\rho} \mid l \lambda \rangle a_{l \lambda}^\dagger a_{l' \lambda'} + \langle l \lambda \mid (\Omega, (\mathbf{L}, \mathbf{L})^2)_{-\rho} \mid l' \lambda' \rangle a_{l' \lambda'}^\dagger a_{l \lambda} \right] = \\
= \frac{i \sqrt{15}}{(l + 1) \sqrt{l(l + 1)(l + 2)(2l - 1)(2l + 5)}} \sum_i [\Omega, (\mathbf{L}, \mathbf{L})^2]_{i l}^{(3)}].\]

Evaluating the numerical coefficient
\[
\sqrt{\frac{15(2l_c + 1)(2l + 1)}{4\pi}} \left\{ \begin{array}{ccc}
  l & l + 1 & 3 \\
  2 & 1 & l_c
\end{array} \right\} C_{l_0 l,0}^{l_0,0} C_{l,0,0}^{l+10} = \sqrt{\frac{6(2l_c + 1)(2l + 1)(2l + 3)}{2\pi(l_c - 3 - l)(l_c + l)^2(2 + l_c + l)^2(4 + l_c + l)}}
\]

we can write \(\Sigma_{E1-E2}^3\) as
\[
\Sigma_{E1-E2}^3 = \frac{16\pi^2 \alpha}{hc} \sum_{l' l} R_{l,l} R_{l',l'} a_{l l+1}^{(-3)}(l, l_c) \sum_{\rho} (-\rho) T_{\rho}^{(3)}(\mathbf{\epsilon}, \mathbf{\epsilon}, \mathbf{k}) \times \\
\times \langle g \mid \sum_i [(\Omega, (\mathbf{L}, \mathbf{L})^2)_{-\rho}]_{i l}^{(3)} l' \rangle \mid g \rangle. \quad (1.86)
\]

where
\[
a_{l l+1}^{(-3)} = \frac{(2l_c + 1)(2l + 1)(2l + 3)}{(l + 1)(l_c - 3 - l)(c + l)^2(2 + l_c + l)^2(4 + l_c + l)}. \quad (1.87)
\]

Extending the result to the case \(l' = l - 1\) we obtain that the integral relation form does not change and that the numerical coefficient becomes
\[
a_{l l-1}^{(-3)} = \frac{(2l - 1)(2l_c + 1)(2l + 1)}{l(3 + l_c - l)(l_c + l - 2)(l_c + l)^2(2 + l_c + l)^2}. \quad (1.88)
\]

A more compact form for Eq. (1.86) is obtained by putting the coefficients (1.87) and (1.88) together including the cases \(l' = l + 1\) and \(l' = l - 1\). In this case we have:
\[
\Sigma_{E1-E2}^3 = \frac{16\pi^2 \alpha}{hc} \sum_{l' l} R_{l,l} R_{l',l'} a_{l l+1}^{(-3)}(l, l_c) \sum_{\rho} (-\rho) T_{\rho}^{(3)}(\mathbf{\epsilon}, \mathbf{\epsilon}, \mathbf{k}) \times \\
\times \langle g \mid \sum_i [(\Omega, (\mathbf{L}, \mathbf{L})^2)_{-\rho}]_{i l}^{(3)} l' \rangle \mid g \rangle. \quad (1.89)
\]

where
\[
a_{l l}^{(-3)}(l, l) = \frac{a_{l l}^{(2+)}(l, l)}{6 + 3l(l + 1) - 2l(l + 1) - l'(l' + 1)}.
\]

and \(l' = l \pm 1\).
The Magnetoelectricity

The magnetoelectric effect (ME) is characterized by the appearance of an electric polarization upon applying an external magnetic field or of a magnetization upon applying an electric field. Already in 1894 P. Curie suggested the existence of ME effect on symmetry arguments [41]. In 1932, because of several unsuccessful experimental attempts to establish the existence of the effect, Van Vleck argued that the ME effect could not exist [42]. Only in 1957 Landau and Lifschitz realized that the time reversal transformation was not an independent symmetry operation of magnetically order crystals. On the basis of these considerations they predicted the existence of the ME effect in magnetically ordered crystals [42].

The first prediction of the ME effect in a specific case is due to Dzyaloshinskii, in 1959; on the basis of symmetry arguments, he concluded that the effect could be observed in \( \text{Cr}_2\text{O}_3 \).

Magnetoelectricity of \( \text{Cr}_2\text{O}_3 \) was measured in 1960 [43].

The (linear) magnetoelectric effect is due to the presence of terms of type \( (\alpha_{ij}E_iH_j) \) in the thermodynamic potential \( F \), which is the Legendre transform of the Helmoltz free energy, where the magnetization \( \mathbf{M} \) and the electric polarization \( \mathbf{P} \) has been substituted as independent variables by \( \mathbf{E} \) and \( \mathbf{H} \); developing the latter in term of these variable we have:

\[
F(\mathbf{H}, \mathbf{E}) = F_0 + \sum_i \psi_i \mathbf{E}_i + \sigma_i \mathbf{H}_i + \sum_{ij} \frac{1}{2} k_{ij} \mathbf{E}_i \mathbf{E}_j + \frac{1}{2} \chi_{ij} \mathbf{H}_i \mathbf{H}_j + \alpha_{ij} \mathbf{E}_i \mathbf{H}_j + \ldots
\]  

(1.90)

where \( F_0 \) is independent of the components of \( \mathbf{H} \) and \( \mathbf{E} \). The coefficients on the right hand side are respectively the pyroelectric and the pyromagnetic coefficients (\( \psi \) and \( \sigma \)), the electric susceptibility (\( k_{ij} \)), the magnetic susceptibility (\( \chi_{ij} \)) and the magnetoelectric susceptibility (\( \alpha_{ij} \)) (the subscript \( ij \) denote any of the cartesian coordinates \( x, y, z \)). Only crystals with magnetic point group that allow the occurrence of \( \mathbf{E}_i \mathbf{H}_j \)-type terms show (linear) magnetoelectric effect.
The electric polarization and/or the magnetization generated in crystal by applying an external magnetic or electric field can be obtained by Maxwell equations:

\[ P_i = -\frac{dF}{dE_i}, \quad M_i = -\frac{dF}{dH_i} \] (1.91)

or better, substituting in relation (1.91) the thermodynamic potential expression (1.90), we get

\[ P_i = \psi_i + \kappa_{ij} E_j + \alpha_{ij} H_j + ... \]

\[ M_i = \sigma_i + \chi_{ij} H_j + \alpha_{ij} E_j + ... \]

where

\[ \alpha_{ij} = \frac{\partial F^2}{\partial E_i \partial H_j} = \frac{\partial P_i}{\partial H_j}. \]

Expanding (1.90) to third order, terms of the form \( \frac{1}{2} B_{ijk} E_i H_j H_K \) and \( \frac{1}{2} \gamma_{ijk} E_i E_j H_K \) are obtained, giving a non-linear ME effect.

Having demonstrated the (macroscopic) existence of the ME effect, its microscopic origin remained to be understood.

The link between the crystal properties and the crystal symmetry is provided by the Neumann’s principle, which stresses the importance of group theory in the determination of physical properties of a system. The principle states that the symmetry elements of any physical properties of a crystal must include all the symmetry elements of the point group of the crystal. This implies that any given physical properties may have a higher symmetry than the one owned by the crystal but cannot be of a lower symmetry than that of the crystal.

The situation becomes slightly more complicated if we consider a magnetic crystal. A magnetic crystal has not only a three dimensional arrangement of atoms but there is also a magnetic moment associated with some or all atoms. These magnetic moments are themselves ordered in a three dimensional pattern. As soon as a crystal becomes magnetically ordered it exhibits a periodic structure in space and time. The time inversion operators \( I' \), the effect of which consists of reversing the direction of all magnetic moments,
becomes an additional transformation of the point group. In this way, it is possible to construct 1651 magnetic space groups and to find 90 magnetic point group [44]. The ME effect is closely related to the magnetic point group of the crystal. Due to the different transformation properties of the polar vector $E$ and the axial vector $H$ under time reversal ($t \to -t$)

$$E \to E \quad H \to -H$$

and space inversion ($x \to -x$)

$$E \to -E \quad H \to H,$$

it’s clear that the ME effect can only occur in crystals where the time and the space inversion are simultaneously broken. Of the 90 magnetic point groups only 58 are compatible with the ME effect. The symmetry operations of these point groups further reduce the number of nonzero components of the ME susceptibility tensor, $\alpha_{ij}$, and define its form. In Ref. [45] are listened a set of systems (and their magnetic group) in which this effect is observable. We will return on these considerations in next chapter when an important set of experiment will be discussed.

To identify the microscopic origin of the ME effect, models were developed by Rado [46, 47, 48] and by Hornreich and Shtrikman [49]. In both approaches the ME effect arises because the application of an electric field introduce an inequivalence between those sites occupied by up spins and those occupied by down spins\textsuperscript{22}.

However, we think, it is possible to provide a different interpretation on the microscopic origin of the magnetoelectric effect assuming the presence, in some or in all crystal ions of ME tensors (e.g. $\Omega$, $(\mathbf{n}, \mathbf{L})^2$ and $(\Omega, (\mathbf{L}, \mathbf{L})^2)^3$) that are invariant under the combined symmetry operations $\hat{T} \hat{I}$ and so able to describe one-electron ME properties of the crystal. An example of magnetoelectricity will be illustrated in next chapter when the

\textsuperscript{22}Rado (1962), in deriving the temperature dependence of the ME tensor for $Cr_2O_3$, considered the induced change in the single-ione anisotropy. Hornreich and Shtrikman (1967) extend the theory for $Cr_2O_3$ to include Dzyaloshinkii antisymmetric exchange interaction.
Figure 1.1: Figure taken from reference [12]. a) No external fields are applied and the electric distribution is uniform in the anular orbit b) because of an external magnetic field the electrons $e_1$ and $e_2$ have different energies, condition that produce a not uniform electric distribution and so an electric polarization is induced.

An intuitive picture of the anapole [12] can be obtained by considering a toroidal solenoid that generate an anular magnetic field $H_a(r)$ and, along the torus axis, a current $J_z(r)$ which has the peculiarity to be odd with respect to both parity and time reversal [50, 51, 52]. The (toroid) anapole moment is directed along $J_z(r)$. In solid-state physics, anular magnetic fields result from either spin or orbital currents. An easy explication of the magnetoelectric character of a spin anapole ($H_a(r) = S_i$) is illustrated in Figure 1.1. The interaction of an external magnetic field, $H$, with the spin carriers (electrons $e_i$), which are constrained on a circular orbit, will induce a non-uniform electron distribution, thus inducing an electric polarization $P$.

### 1.8 The orbital current

In this section we will prove that the effective operators $\Omega_i (n, L)^2...$ previously introduced are present in the orbital current [53]

$$\sum_i p_i e^{ikr_i} + e^{ikr_i} p_i = \sum_i 2mi \frac{\hbar}{\hbar} [H, r(ik \cdot r)^{-1}(e^{ikr} - 1)]_i - i\hbar \times [\frac{1}{2} L f(k \cdot r) + f(k \cdot r) \frac{1}{2} L]_i, \tag{1.92}$$
where \( m \) is the electron mass, \( H \) the hamiltonian for atomic electrons and \( f(k \cdot r) \) is given by
\[
f(k \cdot r) = 2 \sum_{n} \frac{(i k \cdot r)^n}{(n + 2)n!} = 4\pi \sum_{lm} i^l g_l(kr) Y_{lm}(n) Y_{lm}^*(k) = g_0(kr) + 3i g_1(kr)(n \cdot k) + \ldots,
\]
with \( n = r/r \) and
\[
g_l(x) = \frac{2}{x^2} \int_{0}^{\infty} \zeta j_l(\zeta) d\zeta.
\]
\((j_l(\zeta) \text{ denotes a spherical Bessel function.})\)

We consider now the component of the term
\[
\frac{1}{2}[Lf(k \cdot r) + f(k \cdot r)L]
\]
that we write as
\[
\mathbf{L}(k \cdot r)_\gamma = \frac{1}{2}[L_\gamma f(k \cdot r) + f(k \cdot r)L_\gamma] = g_0(kr)L_\gamma + \frac{3i g_1(kr)}{2}[L_\gamma (n \cdot k) + (n \cdot k)L_\gamma] + \ldots \quad (1.93)
\]
where \( n \cdot k = -\sqrt{3} \sum_{\alpha \beta} C^{00}_{1\alpha,1\beta} n_\alpha k_\beta \), that means that the term \( L_\gamma (n \cdot k) \) of relation (1.93) can be written as
\[
L_\gamma (n \cdot k) = -\sqrt{3} L_\gamma \sum_{\alpha \beta} C^{00}_{1\alpha,1\beta} n_\alpha k_\beta = -\sqrt{3} \sum_{\alpha \beta} C^{11}_{1\gamma,00} C^{00}_{1\alpha,1\beta} L_\rho n_\alpha k_\beta. \quad (1.94)
\]
Recalling that
\[
C^{a\xi}_{b\beta,d\delta} C^{c\psi}_{a\alpha,f\psi} = \sum_{x \epsilon} \Pi_{x d} C^{x \xi}_{a a,b \beta} C^{c \psi}_{f \psi,x \epsilon} \left\{ \begin{array}{ccc} a & b & c \\ e & f & d \end{array} \right\}
\]
we recouple the Clebsch-Gordan coefficients \( C^{11}_{1\gamma,00} C^{00}_{1\alpha,1\beta} \) as
\[
C^{11}_{1\gamma,00} C^{00}_{1\alpha,1\beta} = \sum_{x \epsilon} \sqrt{2x + 1} C^{x \epsilon}_{1\alpha,1\beta} C^{11}_{1\gamma,00} \left\{ \begin{array}{ccc} 1 & 1 & x \\ 1 & 1 & 0 \end{array} \right\}, \quad (1.95)
\]
and we write the (1.94) as
\[
L_\gamma (n \cdot k) = -\sqrt{3} \sum_{\alpha \beta} \sqrt{2x + 1} C^{x \epsilon}_{1\alpha,1\beta} C^{11}_{1\gamma,00} \left\{ \begin{array}{ccc} 1 & 1 & x \\ 1 & 1 & 0 \end{array} \right\} L_\rho n_\alpha k_\beta = \ldots
\]

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\[ \left\{ \frac{1}{2} \text{ for } n \geq 0 \right\} \]

where

\[ \left\{ \frac{1}{2} \right\} \]

Repeating the same operations for the term \((k \cdot n)L\) and substituting in equation (1.93) we obtain

\[ \tilde{L}(k \cdot r)_\gamma = g_0(kr)L_\gamma + \frac{3i g_1(kr)}{2} (\Omega \times k) - \frac{1}{2}((L \times n) \times k) - \frac{\sqrt{15}}{3}((L, n)^2, k)_1 + \ldots \]

relation that prove that the orbital current contain the terms \(\Omega, (n, L)^2\) ...

1.9 Conclusions

In the current chapter the \(E1-E2\) x-ray absorption spectroscopy has been studied. Employing a single-ion model and implementing the methods offered by the Wigner-Racah calculus \([28, 29, 30, 31, 32, 34]\), the integral

\[ \Sigma_{E1-E2} = \int_{E_1}^{E_2} \sigma_x(\omega) d(\omega) \]

has been expanded into a linear combination of irreducible tensors, obtaining the relation

\[ \Sigma_{E1-E2} = \sum_{x=1}^{3} C^{(x,\pm)} \sum_{l,l'_{\pm=1}} R_{l,l'}^{x} a_{\ell'}^{(x\pm)}(l_{c}, l) \sum_{\rho} T^{(x\pm)}_{\rho}(\hat{\epsilon}, \hat{k}) \langle g | \sum_{i} (O(l, l'))_{\rho}(x\pm) | g \rangle, \]

(1.96)

where the operators \(T^{(x\pm)}_{\rho}(\hat{\epsilon}, \hat{k})\) and \(O^{x\pm}_{\rho} = O(l, l')^{x\pm}_{\rho}\) and the numerical coefficients \(C^{(x,\pm)}\) and \(a_{\ell'}^{(x\pm)}(l_{c}, l)\) are depicted in Tables 1.1 and 1.2.

We have studied only the cases\(^{23} l' = l \pm 1.\) (Our derivation neglects also the relativistic...
Table 1.1: The irreducible tensors present in the relation (1.96) are reported.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_{\rho}^{(x+)}(\epsilon, \hat{\epsilon}, \hat{k})$</th>
<th>$T_{\rho}^{(x-)}(\epsilon, \hat{\epsilon}, \hat{k})$</th>
<th>$O_{\rho}^{(x+)}$</th>
<th>$O_{\rho}^{(x-)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>/</td>
<td>$-\frac{1}{2} \sqrt{\frac{3}{2}} \hat{k}_{\rho}$</td>
<td>/</td>
<td>$\Omega_{\rho}$</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{\sqrt{3}}{2} (\epsilon^*, \hat{\epsilon})^2_{\rho}$</td>
<td>$\frac{i}{2} (\epsilon^*, \hat{\epsilon})^2_{\rho}$</td>
<td>$(\Omega, L)^2_{\rho}$</td>
<td>$(\Omega, (L, L)^2)^3_{\rho}$</td>
</tr>
<tr>
<td>3</td>
<td>/</td>
<td>$(\epsilon^*, \hat{\epsilon})^3$</td>
<td>/</td>
<td>$(\Omega, (L, L)^2)^3_{\rho}$</td>
</tr>
</tbody>
</table>

Table 1.2: In this Table the coefficients present in the relation (1.96) are reported.

Notice that Eq. (1.96) is important because the l.h.s. can be obtained experimentally, thus proving direct information about polar and magnetic properties of the system. Moreover, we have discuss the possibility to describe $ME$ properties of crystals through the tensors $\Omega$, $(n, L)^2$ and $(\Omega, (L, L)^2)^3$ that are invariant under the combined symmetry operations $\hat{T}\hat{I}$. Finally we have proved that these tensors operators are contained in the orbital current.

---

23The relation $l' = l \pm 1$ holds for $l_c = 0, 1$. In general $l$ and $l'$ must be of opposite parities. As pointed out by C. Brouder (private communication) the valence $l' = l \pm 1$ and $l' = l \pm 3$ are permitted in the matrix elements $\langle \ell'm' | O^{3+}_q | \ell m \rangle$ for $l_c = 2$. A re-definition of $O^{3\pm}$ to include $l' = l \pm 3$ hybridization is required in this case.
Chapter 2

Theoretical interpretation of $XNCD$, $XNLD$ and $XM\chi D$ experiments.
2.1 Introduction

A set of experiments performed by Goulon et al. [10, 11, 12] at the European Synchrotron Radiation Facility (ESRF) of Grenoble will be discussed in this chapter. They provide the first experimental evidence of XNCD (observed in a uniaxial gyrotropic crystal of $\alpha$–LiIO$_3$), of XNLD (observed in a crystal of $(V_{1-x}Cr_x)2O_3$ with $x = 0.028$) and of XM$\chi$D (observed in a $Cr_2O_3$ crystal).

A theoretical interpretation of these experiments will be provided by deriving integral relations for the observed spectra. Particular attention will be given to the analysis of XNLD and XM$\chi$D experiments, which represent successful attempts to detect magnetoelectric properties of crystals using x-ray absorption spectroscopy.

As shown below, magnetoelectric properties are accounted for by a set of irreducible tensor, which are selected by crystal symmetry. For convenience of the reader, the 58 magnetoelectric Shubnikov point groups are listed in Table 2.1.

<table>
<thead>
<tr>
<th>AFM</th>
<th>AFE</th>
<th>$\Omega \neq 0$</th>
<th>$\Omega = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>FE</td>
<td>$mm2, 3m, 4mm, 6mm, (2mm)\dagger, (m2m)\dagger$</td>
<td>222, $m'm'm', 4'/m', 4'/m'm'm'$, $4'm'm', \bar{4}2m, \bar{4}2m, 32, 3'm'$, $4/m'm'm'$, 422, $\bar{4}'2m'$, $\bar{4}'m'2$, 622, $\bar{6}'2m'$, $\bar{4}'m'2$</td>
</tr>
<tr>
<td>FM</td>
<td>AFE</td>
<td>$32', 42'2', 62'2'$</td>
<td>\bar{4}</td>
</tr>
<tr>
<td>FM</td>
<td>FE</td>
<td>3, 4, 6</td>
<td>$4m'm', 6m'm', m'm'2, 3m'$</td>
</tr>
<tr>
<td>weak FM</td>
<td>AFE</td>
<td>$22'2', (2'22')\dagger, (2'2'2)\dagger$</td>
<td></td>
</tr>
<tr>
<td>weak FM</td>
<td>FE</td>
<td>1, 2, $m$, $2'$, $m'$, $mm'2'$, $m'm2'$</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: The 58 ME groups; $\dagger$ stand for non-standard group.
The compatibility with ferro-/antiferromagnetic and ferro-/antiferroelectrics orders is explicitly indicated. Notice that only 36 groups are compatible with the existence of the anapole toroidal moment \[52\].

### 2.1.1 \(XNCD\) integral relation

We define \(left\ (+\) and \(right\) \(-\)) circularly polarization as \[54, 55\]

\[
\epsilon^\pm = \pm \frac{i}{\sqrt{2}}(\epsilon_x \pm i\epsilon_y). \quad (2.1)
\]

An integral relation for \(XNCD\) will be obtained by analysing the term

\[
\Sigma_{E_1-E_2}^{XNCD} = \int_{j_+}^{j_-} \frac{\sigma_{XNCD}}{(h\omega)^2} d(h\omega), \quad (2.2)
\]

where \(\sigma_{XNCD} = \sigma^+_{X}(\omega) - \sigma^-_{X}(\omega)\) is the \(XNCD\) cross section.

Using Eq. (1.96), Eq. (2.2) can be written as

\[
\Sigma_{E_1-E_2}^{XNCD} = \int_{j_+}^{j_-} \frac{\sigma_{XNCD}}{(h\omega)^2} d(h\omega) = \sum_x C^{(x\pm)} \sum_{l=l_0}^{l_{c+1}} R_{l+l} R_{l+l'} a_{l'}^{(x\pm)}(l, l) \times
\]

\[
\times \sum_{\rho} (-)^\rho \left( T_{\rho}^{(x\pm)}(\epsilon^-, \epsilon^+, \hat{k}) - T_{\rho}^{(x\pm)}(\epsilon^+, \epsilon^-, \hat{k}) \right) \langle g | \sum_i [O(l, l')^{(x\pm)}]_i | g \rangle \quad (2.3)
\]

where \(\left( T_{\rho}^{(x\pm)}(\epsilon^-, \epsilon^+, \hat{k}) - T_{\rho}^{(x\pm)}(\epsilon^+, \epsilon^-, \hat{k}) \right)\) does not vanish only for \((x\pm) = (2+)\).

Therefore

\[
\sum_x T_{\rho}^{(x\pm)}(\epsilon^-, \epsilon^+, \hat{k}) - T_{\rho}^{(x\pm)}(\epsilon^+, \epsilon^-, \hat{k}) = T_{\rho}^{(2+)}(\epsilon^-, \epsilon^+, \hat{k}) - T_{\rho}^{(2+)}(\epsilon^+, \epsilon^-, \hat{k}) = 2T_{\rho}^{(2+)}(\epsilon^-, \epsilon^+, \hat{k}) = \sqrt{3}(\epsilon^*, \epsilon^1, \hat{k})_{\rho}^2. \quad (2.4)
\]

Eq. (2.2) takes the form

\[
\Sigma_{E_1-E_2}^{XNCD} = 2C^{2+} \sum_{l=l_0}^{l_{c+1}} R_{l+l} R_{l+l'} a_{l'}^{(2+)}(l, l) \sum_{\rho} (-)^\rho T_{\rho}^{(2+)}(\epsilon^-, \epsilon^+, \hat{k}) \langle g | \sum_i [O(L)^{(2+)}]_{i} | g \rangle, \quad (2.5)
\]

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where
\[ C^{2+} = -\frac{8\pi^2 \alpha \sqrt{3}}{3hc\sqrt{2}} \]
and
\[ a^{(2+)}_{l'}(l_c, l) = \frac{2(2l_c + 1)(2l + 1)(2l' + 1)(6 + 3l_c(l_c + 1) - 2l(l + 1) - l'(l' + 1))}{(l + l_c)^2(l + l_c + 2)^2(l + l' + 1)(l - 3l' + 2l)(l_c + 3l' - 2l - 1)} \]

Eq. (2.5) provides a microscopic interpretation of XNCD by relating this form of dichroism to the presence of an effective rank-two \( \hat{l} \)-odd one-electron operator, which is known as gyration tensor or pseudodeviator.

XNCD is observed when \( (\Omega, L)^{(2+)} \) is totally symmetric with respect to the crystal site point-group and when its mean value over the unit cell does not vanish.

### 2.2 XNCD experimental work

As mentioned in the introduction, the first observations of XNCD were performed by Alagna et al. at the Nd L\(_3\) edge in a stereogenic organometallic complex \((Na_3Nd(digly)_3 \cdot 2NaBF_46H_2O)\) and by Goulon et al. at the \(L_1\), \(L_{1I}\) and \(L_{1II}\) edges of \(\alpha - LiO_3\), a noncentrosymmetric crystal. Given its relatively simple structure and for the presence of numerical calculations, we have chosen to describe the experiment on \(\alpha - LiO_3\).

#### 2.2.1 \(\alpha - LiO_3\)

A theoretical analysis indicates that Natural Optical Activity is described by a cartesian (reducible) rank three tensor: the Optical Activity Tensor. This object can be decomposed in three irreducible parts:

- A pseudoscalar
- A vector
- A rank 2 pseudodeviator
Only the pseudoscalar and the pseudodeviator contribute to the so-called gyration tensor which determines the rotatory power and the *Natural Optical Activity*.

*Buckingham* and *Barron* have pointed out that both \( E1-E2 \) and \( E1-M1 \) interference contribute to the pseudodeviator, whereas the pseudoscalar is controlled by \( E1-M1 \) only. Crystallography states that only 13 point groups are compatible with a non-vanishing pseudodeviator. These are: \( C_1, C_{1h}, C_2, C_{2v}, D_2, D_{2d}, C_3, D_3, C_4, D_4, S_4, C_6, D_6 \).

It is also important to note that experimental works have related the pseudodeviator to the presence of a large nonlinear susceptibility at optical wavelengths.

These considerations have guided *Goulon et al.* [10] in selecting a non-magnetic uniaxial non-centrosymmetric crystal to observe XNCD. \( \alpha \text{LiIO}_3 \) turned out to be a good candidate.

This compound exhibits a large specific rotatory power [56, 57, 58] together with a strong nonlinear susceptibility in the visible range [58, 59, 60, 61, 62].

\( \alpha - \text{LiIO}_3 \) crystallizes with space group \( P6_3 \) (group 173) [63] with two molecules per unit cell (Fig. 2.1: lattice parameters: \( a = 5.481 \text{ Å}, b = 5.172 \text{ Å} \)).

As noted by Templeton and Templeton [64], this is a suitable material for the observation

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure}
\caption{Structure of hexagonal \( \alpha - \text{LiIO}_3 \) along \( a_1 \) axis (left panel) and projections on (001) of a left-handed helical structure (a) and a right-handed helical structure (b) (right panel). Small circle: \( \text{Li} \); medium-sized circles: \( \text{I} \); large circles: \( \text{O} \).}
\end{figure}
of dichroism because the 3-fold axis of the two achiral iodine are parallel. It is the relative disposition of the $IO_3$ groups which generate chiral helical structures with alternating iodine and oxygen atoms. $XNCD$ experiments were performed at the ESRF beam line ID12. The group $P6_3$ [65] is compatible with enantiomorphism. It is thus possible to grow crystals with opposite chiralities, i.e., to select one of the two configurations displayed in Fig. (2.1)$^1$. $\alpha - LiIO_3$ is a polar molecule, which shows piezo- and pyroelectric behavior.

The $L_{II}, L_{III}, L_{III}$ iodine edge were studied. Figures 2.2 (top-left panels) displays results obtained from $XANES$ experiments. In this case (as for the $XNCD$ signal) the spectra are normalized with respect to the edge jump.

The $XANES$ spectrum at the $L_I$ edge shows a strong white-line behavior, with respect to the $L_{II,III}$ edges. In Figures 2.2 (top-right and bottom panels), $XNCD$ spectra at the $L_I, L_{II}, L_{III}$ edges $^2$ are shown. Two important considerations are in order

- The iodine ions are in a non-magnetic configuration $[K\tau]4d^{10}5s^2$, therefore the observed signals are not interpretable with the sum rules of Thole and Carra [3].

- The $L_{II}$ and $L_{III}$ edges are very similar and present the same shape. This should be in contrast to x-ray magnetic circular dichroism ($XMCD$) spectra, which usually exhibits opposite signs at the $L_{II}$ and $L_{III}$ edges [66, 67].

On the basis of these considerations, Goulon et al. excluded the presence of pure $E1$ contributions in the observed spectra. This fact was confirmed by Natoli et al. [23], who numerically reproduced the spectra of Fig. 2.3 by considering $E1-E2$ transitions only. Other numerical calculations, which correctly reproduce the local $p,d$ and $f$ projected density of the states in the iodine Wigner-Seitz sphere, pointed out the presence of $(p,d)$ and $(d,f)$ hybridized orbitals [23].

Therefore to identify the microscopic origin of $XNCD$ in $\alpha - LiIO_3$, we will focus on

$^1$Obviously the sample used by Goulon had a well define chirality.

$^2$The signal is assumed positive when $\sigma^- > \sigma^+$. 

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charge properties stemming from \((p,d)\) hybridization\(^3\).

At the iodine sites the symmetry is \(C_3\) (see Fig. 2.4, right panel). Notice that \((\Omega, L)^{(2+)}\) is totally symmetric in this point group. It yields therefore a nonvanish ground state expectation value at each iodine site. The three-fold axes of all the iodine groups are parallel in the unit cell of \(\alpha-LiIO_3\). As a consequence, all the microscopic pseudodeviators add up upon adsorption of circularly polarized x rays. This contribution to the \(E1-E2\)

\(^3\)The hybridized orbital \((d, f)\) is empty.
absorption profile is selected by circular dichroism yielding the observed XNCD spectra. The effect can thus be viewed as the \(^{\hat{1} - odd}\) analog of the ferroquadrupolar ordering, which is probed by pure \(E1\) x-ray linear dichroism \([5]\).

\section*{2.3 XNLD: Theoretical interpretation}

In this section we will derive an integral relation for nonreciprocal x-ray linear dichroism. We remind the reader that linear-dichroism experiments detect the difference in absorption between radiations with linear polarization parallel or perpendicular to a local symmetry axis as denoted by \(\epsilon^\parallel\) or \(\epsilon^\perp\).

Specializing Eq. (1.96) to linear dichroism, we have

\[
\Sigma_{E1-E2}^{XNLD} = \int \frac{\sigma^\parallel - \sigma^\perp}{(h\omega)^2} d(h\omega) = \sum_x C^{(x\pm)} \sum_{l=l_c, l\pm} R^{1}_{l\epsilon} R^{2}_{l\epsilon^\perp} a_{l'}^{(x\pm)}(l_c, l) \times \\
\times \sum_{\rho} (-)^\rho \left( T^{(x\pm)}(\epsilon^\parallel, \hat{k}) - T^{(x\pm)}(\epsilon^\perp, \hat{k}) \right) \langle g \mid \sum_i [O(l, l')^{\epsilon^\pm}_{\rho}] g \rangle,
\]

where the geometrical factors \(T^{(x\pm)}(\epsilon^\pm, \hat{\epsilon}, \hat{k})\) are expressed as a function of \(\epsilon^\parallel\) or \(\epsilon^\perp\) and \(\hat{k}\). From Table (1.1) we note that \(T^{(1-)}(\epsilon^\parallel, \hat{\epsilon}, \hat{k})\) is independent of polarization, so that

\[46\]
Figure 2.4: On the left is reported the local DOS for $p$, $d$ and $f$ symmetries in the iodine Wigner-Seitz sphere calculated with the Andersen-Jepsen TB-LMTO-ASA method. (a): Overlap of the $p$ and $d$ DOS; (b): Overlap of the $\{f,d\}$ DOS. On the right is reported the crystal structure of $\alpha$-LiIO$_3$. The blue sphere are associated with the Iodine atoms, the red with the oxygen atoms and the brown with the lithium.

$T^{(1-)}(\vec{e}, \hat{k}) - T^{(1-)}(\vec{e}^\perp, \hat{k})$ vanish, and that $T^{(2+)}(\vec{e}^*, \vec{e}, \hat{k})$ vanishes when $\vec{e}$ is real \footnote{In this case it depends on $\vec{e}^* \times \vec{e}$ that is zero for real polarizations.}. These considerations afford a simplifications of Eq. (2.6), which becomes

\[
\Sigma_{E_1-E_2}^{XNLD} = \sum_{\ell=\ell'=\pm 1} R_{i\ell} R_{i'\ell'}^2 \left\{ C^{(2-)}(l_c, l) \sum_{\rho} (-)^{\rho} \left( T^{(2-)}_\rho(\vec{e}^\parallel, \hat{k}) - T^{(2-)}_\rho(\vec{e}^\perp, \hat{k}) \right) \right. \\
\times \left. \sum_i \langle g | [(\mathbf{n}, \mathbf{L})^{(2-)}]_{l_i}^{l_i'} | f \rangle + C^{(3-)}(l_c, l) \sum_{\rho} (-)^{\rho} \left( T^{(3-)}_\rho(\vec{e}^\parallel, \hat{k}) - T^{(3-)}_\rho(\vec{e}^\perp, \hat{k}) \right) \right. \\
\times \left. \sum_i \langle g | [(\Omega, (\mathbf{n}, \mathbf{L})^{(3-)}]_{l_i}^{l_i'} | f \rangle \right\},
\tag{2.7}
\]

where

\[
T^{(2-)}(\vec{e}, \hat{k}) = \frac{i}{2}((\vec{e}, \vec{e})^2, \hat{k})^2, \quad T^{(3-)}(\vec{e}, \hat{k}) = ((\vec{e}, \vec{e})^2, \hat{k})^3,
\]

\[
C^{(2-)} = \frac{8\pi^2\alpha\sqrt{6}}{3hc}, \quad C^{(3-)} = \frac{16\pi^2\alpha}{hc}.
\]
Equation (2.7) reveals an important difference between ordinary x-ray linear dichroism, which stems from pure electric transitions $E_1, E_2, \ldots$ [5], and non-reciprocal x-ray linear dichroism, which is controlled by the interference $E_1 - E_2$. The former is a time-reversal even effect, the latter is time-reversal odd. This implies that $X\text{MCD}$ spectra do not change upon reversal of an external applied magnetic field, while $X\text{NLD}$ spectra do.

2.4 $(V_{1-x}Cr_x)_{2}O_3$: Goulon experiment

In this section we analyze the $X\text{NLD}$ experiment performed by Goulon at al. [11] on a $Cr$-doped $V_2O_3$ crystal. This experiment appears particularly interesting for the anomalous behavior of the observed signal when an external magnetic field is applied and reversed.

2.4.1 Pure $V_2O_3$ crystallographic properties

Despite the finality of this thesis is not the comprehension of the $V_2O_3$ electronic structure, we decided to discuss its characteristic to clarify the contest in which the Goulon experiment was done. The electronic structure of this compound has been broadly analyzed [68, 69, 70, 71, 72, 73, 74] in past. This system shows metal-insulator transition from a paramagnetic metallic (PM) phase to an anti-ferromagnetic insulator (AFI) phase ($T \simeq 150K$) and from PM phase to a paramagnetic insulator (PI) phase ($T \simeq 500K$) due probably to the interplay between the formation of a band structure (extended states) and the role of Coulomb correlation [75]. It is the only known example among transition-metal oxides that shows a PM to PI transition [75]. This compound (often doped with
Figure 2.5: From Ref. [84]. Corundum structure together with the unit cell for the trigonal and monoclinic phase. Only vanadium ions are shown: filled and empty circles correspond to oxygen octahedra differently oriented in the space. Arrows indicate the directions of the spins.

Cr to eliminate the problems due to the crack that appear when the crystal is cooled) shows a corundum structure (space group $R\bar{3}C$, point group $C_3$)\(^5\) in which the V ions are arranged in $V-V$ couples along the $c$-axis and form an honeycomb in the $ab$ plane (Fig. 2.5).

In a $V_2O_3$ crystal, the vanadium ions are in the $3d^2$ configuration and are surrounded by oxygen octahedra with a small tetragonal distortion that splits the 3-fold degeneracy of $t_{2g}$ orbitals in a non-degenerate $a_{1g}$ and a doubly degenerate $e_g$ orbitals. The energy of

\(^5\)The elements of $R\bar{3}c$ are [76]:

$[\hat{E},0] = \text{Identity}$

$[\hat{I},0] = \text{Inversion around the point O in fig. (2.5)}$

$[\hat{C}_3,0] = \text{Rotation of } \pi/3 \text{ around } c_H$

$[\hat{C}_2,\frac{1}{2}\vec{a}_m] = \text{Rotation of } \pi \text{ around } \vec{b}_m \text{ axis followed by a translation of } \frac{1}{2}\vec{a}_m$
the $e_g$ doublet is lower than the $a_{1g}$ singlet\(^6\), as shown in Fig (2.6). Cooling below $T_N$,

![Figure 2.6: Schematic energy splitting of the 3$d$ level in the corundum structure.](image)

Figure 2.6: Schematic energy splitting of the 3$d$ level in the corundum structure.

![Figure 2.7: The circles denote $V$ ions and the ovals show the $V$ ion pairs. The arrows represent the directions of the tilting of the $V$ ion pairs respect to the $\hat{z}$ axis in the AFI phase.](image)

Figure 2.7: The circles denote $V$ ions and the ovals show the $V$ ion pairs. The arrows represent the directions of the tilting of the $V$ ion pairs respect to the $\hat{z}$ axis in the AFI phase.

a destructive nearly second-order transition occurs and the system enters in a monolitic phase. A particular magnetic structure appears, which consists of ferromagnetic planes orthogonal to the $b_n$ axis and stacked antiferromagnetically. Moreover the monolitic distortion causes a tilting of the $V-V$ bond direction of every $V$ ion pair from the $z$ axis

\(^6\)The $a_1$ orbitals point in the $c$-axis direction forming the bond in the $V$ ions pairs, the $e_g$ orbitals extend their lobes along the directions perpendicular to the $c$-axis.
towards the negative side of the y axis (see Fig. 2.7), thus breaking the three-fold rotation symmetry.

The lattice space group lowers to $I2/a$ with magnetic point group $C_{2h} \otimes \hat{T}$.

In the late seventies, theoretical studies by Castellani et al. [77, 78, 79] pointed out the possibility of an orbitally ordered phase in $V_2O_3$. In their model, $V^{3+}$ was described assuming one electron in the doubly degenerate level $e_g$ and one electron in the strong covalent diamagnetic bound formed by $a_{1g}$ orbital along the vertical pair.

To explain the anti-ferromagnetic structure of $V_2O_3$ in the lower temperature phase, a long range ordering in the occupation of the $e_g$ orbitals was postulated, in agreement with the Goodenough-Kamori-Anderson rules [80, 81, 82].

With the advent of synchrotron radiation, new informations about the ground state properties of the $V_2O_3$ has become available. In particular, accurate measurement of the spin of the vanadium ion, gave the value $\langle S \rangle \approx 0.85 \mu_B$. This fact, together with the result of Park et al. [83] (these authors obtain a 25% occupation of the $a_g$ orbital in the $PM$ phase, 20% in the $PI$ and 17% in the $AFI$ phase; this should be contrasted with the assumption of a 50% occupation in all phases by Castellani et al.), prompted Di Matteo et al. to study of a spin-one orbital order model. Their results are reported in Ref. [84].

The K edge non reciprocal x-ray linear dichroism experiment of Goulon et al. [11] is important in this contest. This experiment, which appears to have probed magnetoelectric properties of the $(V_{0.072}Cr_{0.028})_2O_3$, cannot be interpreted with the model of Ref. [84].

2.4.2 Non-reciprocal x-ray gyrotropy experiment on $(V_{1-x}Cr_x)_2O_3$.

In 1963, $V_2O_3$ was classified as a non-magnetoelectric crystal by Astrov [88]. Notice, however, that $V_2O_3$ is positioned between two magnetoelectric crystals: $Cr_2O_3$ and $Ti_2O_3$.

It could therefore possess a small magnetoelectricity, hardly detectable by standard ex-

\footnote{Also the models of Mila [85], Tanaka [86] and Lovesey [87] on the electronic structure of $V_2O_3$ fail in the interpretation of the results obtained by Goulon.}
experimental methods. (For an extensive review of these experimental techniques see Refs. [43, 89].) X-ray spectroscopies provide a very sensitive tool for a microscopic investigation of electric and magnetic properties of solids. For this reason, Goulon et al. devised an experiment of x-ray linear dichroism to detect the presence of magnetoelectricity, whatever small, in a Cr-doped $V_2O_3$ crystal.

Detecting magnetoelectricity requires magnetoelectric annealing, a standard procedure to select a single magnetoelectric domain. (This experimental techniques is throughly described in Ref. [90].) $ME$ annealing of a $(V_{0.972}Cr_{0.028})_2O_3$ crystal was performed by Goulon et al. by applying modest electric ($5 \cdot 10^3 V/cm$) and magnetic ($H^\pm = \pm0.5T$) fields, in the paramagnetic-insulator phase. The two fields were either parallel or antiparallel to the c-axis. The crystal was then cooled below $T_N$ and the electric field switched off.

![Graph of XNLD spectra](image.png)

Figure 2.8: Non reciprocal $XNLD$ spectra recorder in the monoclinic phase. Magnetoelectric annealing was performed with parallel (+) and anti-parallel (-) electric and magnetic field. The $XNCD$ spectrum displayed at the same scale is hardly visible.
X-ray linear dichroism was measured using linearly polarized photons with $\hat{k}$ parallel to the $c$-axis. The signal was recorded in two configurations ($H^+$ and $H^-$) corresponding to a magnetic field parallel and antiparallel to the electric field $E$, respectively. The recorded spectra are depicted in Fig. (2.8). Two prominent features of these spectra are readily identify.

- They are characterized by a strong increase of the dichroic signal with respect to that recorded in the paramagnetic phase and shown in Fig. (2.9).
- The signal changes sign when the magnetic field is reversed.

The latter feature is really surprising and denotes the peculiarity of this experiment. It has been interpreted as evidence of the presence of magnetoelectricity in the crystal. Theoretically, this conclusion is supported by Eq. (2.7), which contains magnetoelectric effective operators. A possible mechanism for the formation of $ME$ domains could be explained as follows. As previously stated at each vanadium site the point group is $C_3$ [71], in the $PM$ phase. Formation of an electric-dipole moment is thus permitted by

![Figure 2.9: Recorder XANES spectra and XLD spectra in the paramagnetic phase of $(V_{1-x}Cr_x)_2O_3$.](image)

Figure 2.9: Recorder XANES spectra and XLD spectra in the paramagnetic phase of $(V_{1-x}Cr_x)_2O_3$. 

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symmetry. Crystallography also suggests that nearest-neighbor pairs of vanadium atoms are antiferroelectrically ordered along the hexagonal c-axis (the symmetry of a pair is $D_{3h}$), as shown in Fig. 2.10 (left panel). We can thus argue that, at about 300°K in the insulating phase, $(V_{0.972}Cr_{0.028})_2O_3$ is an antiferroelectric (AFE) crystal.

At $T = T_N$, the crystal makes a nearly second-order transition to an $AFM$ monoclinic phase [73]. The driving mechanism of this transition is not fully understood [91]. The lattice space group lowers to $I2/a$, with magnetic point group $C_{2h} \otimes T$ [84]. Notice that this symmetry is incompatible with the observation of XNLD.

However, a reduction of the magnetic symmetry leading to $2/\overline{m}$ and $2/m$ might take place. A lowering of magnetic symmetry could occur as follows. The structural charge to the monolithic phase eliminates the three-fold axis, which characterized the corundum structure. It probably involve a co-operative Jahn-Teller distortion, which tilts the electric moments. A tilting with the pattern depicted in Fig. (2.10) (right panel), would make $(V_{1-x}Cr_x)_2O_3$ an $AFM$, $AFE$ and $ME$ crystal, thus explaining the observations of Goulon and his collaborators.

![Figure 2.10: Left) Antiferroelectric structure of $(V_{0.972}Cr_{0.028})_2O_3$ at high temperature, as inferred from crystallo-
graphic data reported in Ref. [72]. Right) Tilting of the monolithic phase of $(V_{0.972}Cr_{0.028})_2O_3$ (the arrows at about 71°
with respect to the c – axis denote the magnetic moments.](image-url)
2.5 $Cr_2O_3$

In this section we discuss another experiment by Goulon et al. [12]. This experiment aimed at measuring $\Omega$ in a magnetoelectric crystal.

2.5.1 $Cr_2O_3$: crystal properties and $X\chi D$ experiment

$Cr_2O_3$ exhibits a corundum-type crystal structure with two formula per unit cell. Above the Néel temperature the crystal has a three fold axis, three two fold axes and three glide planes (Fig. 2.11). The classical point group is hence $\bar{3}m$.

![Figure 2.11: Basic symmetry operations of the R3C space group of $Cr_2O_3$. The four positions of the chromium ions in the primitive ionic cell are show in the $x - z$ projection. The two-fold axis (solid line) and the glide mirror planes (dashed line) are shown in the $x - y$ projection.](image)

When the system is cooled below $T_N$ ($T_N \approx 310K$) the spins become antiferromagnetically ordered generating two magnetic domains, which can be selected by magnetoelectric annealing. The spins are aligned parallel to the threefold $c$-axis (Fig. 2.12). (The pattern of the magnetic moment $+-+-$ or $-+-+$ breaks both time-reversal and inversion...
symmetry, but leaves their product invariant.

In this phase the magnetic group is $3'm'$. Such a group is compatible with a linear

![Figure 2.12](image)

**Figure 2.12**: Schematic representation of the two $180^\circ$ AFM domains grown by ME annealing with the two possible configuration $H$ parallel $E$ and $H$ anti-parallel $E$.

$ME$ effect with two independent nonzero component of the $ME$ tensor:

$$
\begin{pmatrix}
\alpha_{xx} & 0 & 0 \\
0 & \alpha_{yy} & 0 \\
0 & 0 & \alpha_{zz}
\end{pmatrix},
$$

where $\alpha_{xx} = \alpha_{yy} = \alpha_\perp$, $\alpha_{zz} = \alpha_\parallel$ and

$$
\alpha_{ij} = \frac{\partial^2 F}{\partial E_i \partial H_j} = \frac{\partial P_i}{\partial H_j} = \frac{\partial M_j}{\partial E_i} \quad i, j = x, y, z.
$$

---

The elements of the magnetic group $3'm'$ are a $C_3$ rotation along the trigonal axis, the product of inversion and time reversal $I'$, centered in the origin as chosen in reference [65] and the time-reversed glide plane symmetry $m'$, associated with the trigonal translation $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.  

---

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$F$, $\mathbf{P}$ and $\mathbf{M}$ are respectively the free energy, the polarization and the magnetization of the crystal.

The presence of a external magnetic field $\mathbf{H}_e$ parallel to the $c$-axis lowers the symmetry to $3m'$, without affecting the form of the magneto-electric tensor [92, 93]. Both components $\alpha_{\parallel}$ and $\alpha_{\perp}$ have been carefully studied as a function of temperature and applied magnetic field [94, 95, 96, 97, 98]$^9$.

When $\mathbf{H}_e$ is increased over $\approx 10$ Tesla, a first order transition occurs and the system falls in a spin-flop phase $^{10}$, with the spins oriented perpendicular to the $c$–axis in the basal plane. Plots of electric polarizations as a function of an applied magnetic field are shown in Fig. (2.13).

To investigate the microscopic origin of the magnetoelectricity in $\text{Cr}_2\text{O}_3$ Goulon devised a $X\chi M\chi D$ experiment, which, in some cases, provides a direct measurement of the expectation value of $\mathbf{\Omega}$.

In a $\text{Cr}_2\text{O}_3$ crystal, two magnetic domains are possible, in which the $Cr$ moments have opposite direction with respect to the oxygen ligands. Such domains can be transformed

---

$^9$These studies pointed out that the component $\alpha_{\parallel}$ is much bigger that $\alpha_{\perp}$.

$^{10}$The value of the magnetic field that produce this effect depend to the temperature and is indicated with $H_{s-f}$. 

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into one another by time reversal (see Fig. 2.12.) There is no ME effect and \( X_M \chi D \) vanishes in an equidomain crystal. Magnetoelectric annealing of \( Cr_2O_3 \) was performed by heating the crystal above \( T_N \) and simultaneously applying an electric \( (5 \cdot 10^3 V/cm) \) and a magnetic \( (H^\pm = \pm 0.5T) \) field along the \( c \)-axis, in the parallel or antiparallel configuration.

The crystal was then cooled below \( T_N \) and the electric field switched off\(^{11}\).

X-ray absorption signals \( F(H) \) were recorded with the sample in an equidomain state \([F(0)]\) and in the two single-domain states grown by parallel \([F(H^+)]\) and antiparallel \([F(H^-)]\) ME annealing. Unpolarized light, \( \epsilon^+ + \epsilon^- \) was used. The spectra \( F(H^+) - F(0) \) and \( F(H^-) - F(0) \) are depicted in Fig. 2.14 (left panel). \( F(H^+) - F(H^-) \) is depicted in Fig. 2.14 (right panel).

Only time-reversal odd terms can contribute to the observed spectra. Furthermore, pure

\[ \text{Figure 2.14: } X_M \chi D \text{ from the } K \text{ – edge for the two possible magnetic configuration selected by ME annealing. The equidomain configuration is taken as reference.} \]

\(^{11}\)It is the same procedure used by Goulon for the ME annealing in \((V_{1-x}Cr_x)_2O_3\) crystal.
\( E1 \) transitions are ruled out. By recoupling the integral
\[
\Sigma_{E1 \rightarrow E2}^{XMD} = \int_{j_+ + j_-} \frac{\sigma_x^+(\omega) + \sigma_x^-(\omega)}{(\hbar \omega)^2} d\hbar \omega
\]
it is readily shown that \( XMD \) is controlled by two magnetoelectric tensors: \( \Omega \) and \((\Omega, (L, L)^2)^3\). These tensors are not totally symmetric in \( 3'm' \). \textit{Goulon} and coworker have thus suggested a lower magnetic point group \( 3m \), for \( Cr_2O_3 \), in which \( \Omega \) and \((L, L)^2)^3\) can acquire a non-zero ground state expectation value. Neglecting \((\Omega, (L, L)^2)^3\), \textit{Goulon et al.} obtained \( \langle g \mid \Omega \mid g \rangle = 0.03 \) a.u. for the \( XMD \) spectra

\subsection*{2.5.2 \( XMD \): a Sum Rule.}

The complete integral relation for \( XMD \) reads
\[
\Sigma_{E1 \rightarrow E2}^{XMD} = \int \frac{\sigma_x^+(\omega) + \sigma_x^-(\omega)}{(\hbar \omega)^2} d\hbar \omega = \sum_{x=1}^{3} C^{(x)} \sum_{l=-l_1}^{l_1} \sum_{l'=l_1}^{l_1} R_{l_1 l_2}^1 R_{l_2 l_3}^2 a^{(x)}_{l l'}(l_c, l) \times \sum_p (-)^p \left[ T^{(x)}_{\rho}(\epsilon^-, \epsilon^+, \hat{k}) + T^{(x)}_{\rho}(\epsilon^+, \epsilon^-, \hat{k}) \right] \langle g \mid \sum_i [O(l, l')_{-\rho}]_i \mid g \rangle.
\]
(2.8)

Keep in mind that these experiments are usually performed with \( \hat{k} \parallel \hat{z} \).

Consider
\[
T^{(x)}_{\rho}(\epsilon^-, \epsilon^+, \hat{k}) + T^{(x)}_{\rho}(\epsilon^+, \epsilon^-, \hat{k}),
\]
\footnote{These considerations are based on the hypothesis that the magnetic field of 0.5T, applied during the measurements, is not so strong to influence the magnetic properties of \( Cr_2O_3 \) crystal and to change its magnetic group. In the literature it is reported that an external magnetic field parallel to the \( c \)-axis could lower the symmetry of the \( Cr_2O_3 \) from \( 3'm' \) to \( 3m' \) \cite{92}, but this group is still incompatible with the \( XMD \) observed spectra as \( 3m' \) does not appear among the 36 groups that are compatible with toroidal tensors. The presence of a misalignment among the magnetic field and the \( c \)-axis could explain, on the contrary, this symmetry reduction as pointed out by \textit{Vitebskii} \cite{99}. However such a misalignment would induce, in \( Cr_2O_3 \), also a \( XLD \) signal. This effect was measured by the authors but it was so weak to enable to justify a symmetry reduction to \( 3' \), that thus appears to be the real symmetry of the sample.

There would have been a way to check the effect of the magnetic field on the \( XMD \) measurements; to evaluate the integral \( \Sigma_{E1 \rightarrow E2}^{XMD} \) for different values of the applied magnetic field (say 0.3, 0.5 and 0.7T) looking for a possible dependence of the \( XMD \) (and consequently of the expectation value of \( \Omega \)) on it.}

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we thus have

1. Case \((x\pm)=(1-)\).

From Table (1.1) we have

\[ T^{(1-)}(\epsilon^-, \epsilon^+, \hat{k}) = T^{(1-)}_0(\epsilon^-, \epsilon^+, k_0) = -\frac{1}{2}\sqrt{\frac{3}{5}}k_0 \]

\[ T^{(1-)}(\epsilon^+, \epsilon^-, \hat{k}) = T^{(1-)}_0(\epsilon^+, \epsilon^-, k_0) = -\frac{1}{2}\sqrt{\frac{3}{5}}k_0 \]

and therefore

\[ T^{(1-)}(\epsilon^-, \epsilon^+, k_0) + T^{(1-)}_0(\epsilon^+, \epsilon^-, k_0) = 2T^{(1-)}_0(\epsilon^-, \epsilon^+, k_0) = 2 \left(-\frac{1}{2}\sqrt{\frac{3}{5}}k_0\right) \]

2. Case \((x\pm)=(2+)\).

\[ T^{(2+)}(\epsilon^-, \epsilon^+, \hat{k}) = T^{(2+)}_0(\epsilon^-, \epsilon^+, k_0) = -\frac{\sqrt{3}}{2}C^{2\rho}_{10,1\rho}\epsilon_1\epsilon_{-1}k_\rho \]

that mean, for \(k_\rho = k_0\), that

\[ T^{(2+)}_0(\epsilon^-, \epsilon^+, k_0) = -T^{(2+)}_0(\epsilon^+, \epsilon^-, k_0) = -\frac{\sqrt{2}}{2}\epsilon_1\epsilon_{-1}k_0 \]

or better that

\[ T^{(2+)}_0(\epsilon^-, \epsilon^+, k_0) + T^{(2+)}_0(\epsilon^+, \epsilon^-, k_0) = 0 \]

3. Case \((x\pm)=(2-)\).

\[ T^{(2-)}_0(\epsilon^-, \epsilon^+, \hat{k}) = -\frac{i}{2\sqrt{6}}\epsilon_1\epsilon_{-1}C^{2\rho}_{20,1\rho}k_\rho \]

and

\[ T^{(2-)}(\epsilon^+, \epsilon^-, \hat{k}) = -\frac{i}{2\sqrt{6}}\epsilon_1\epsilon_{-1}C^{2\rho}_{20,1\rho}k_\rho \]

that become, when \(k \parallel z\)

\[ T^{(2-)}_0(\epsilon^-, \epsilon^+, k_0) = T^{(2-)}_0(\epsilon^+, \epsilon^-, k_0) = -\frac{i}{2\sqrt{6}}\epsilon_1\epsilon_{-1}C^{20}_{20,10}k_0 = 0 \]

because of \(C^{20}_{20,10} = 0\). Thus

\[ T^{(2-)}(\epsilon^-, \epsilon^+, k_0) + T^{(2-)}(\epsilon^+, \epsilon^-, k_0) = 0 \]

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4. Case \((x\pm)=(3-)\).

\[
T_{\rho}^{(3-)}(\epsilon^+, \epsilon^-, \hat{k}) = -\frac{1}{\sqrt{6}}\epsilon_1\epsilon_{-1}C_{20,1,\rho}^{\alpha\beta}k_{\rho}
\]

\[
T_{\rho}^{(3-)}(\epsilon^-, \epsilon^+, \hat{k}) = -\frac{1}{\sqrt{6}}\epsilon_1\epsilon_{-1}C_{20,1,\rho}^{\alpha\beta}k_{\rho}.
\]

where \(\epsilon_1\epsilon_{-1} = -1\). Putting \(k_{\rho} = k_0\) and evaluating the Clebsch Gordan coefficient \(C_{20,10} = \sqrt{\frac{3}{5}}\), we have

\[
T_0^{(3-)}(\epsilon^+, \epsilon^-, k_0) = T_0^{(3-)}(\epsilon^-, \epsilon^+, k_0) = \frac{1}{\sqrt{10}}k_0
\]

that is

\[
T_0^{(3-)}(\epsilon^+, \epsilon^-, k_0) + T_0^{(3-)}(\epsilon^-, \epsilon^+, k_0) = 2T_0^{(3-)}(\epsilon^+, \epsilon^-, k_0) = 2\left(\frac{1}{\sqrt{10}}\right)k_0.
\]

Eq. (2.8) takes the form

\[
\Sigma_{E1-E2}^{XMD} = 2C^{(1-)} \sum_{l=\pm 1, l'} \sum_{l=\pm 1, l'} \sum_{l=\pm 1, l'} R_{l,l'}^{l'} T_0^{(1-)}(l, l') T_0^{(1-)}(l, l') \langle g \mid \sum_i [O(l, l')^{(1-)}]_i \mid g \rangle + \]

\[
+ C^{(3-)} \sum_{l=\pm 1, l'} \sum_{l=\pm 1, l'} \sum_{l=\pm 1, l'} R_{l,l'}^{l'} T_0^{(3-)}(l, l') T_0^{(3-)}(l, l') \langle g \mid \sum_i [O(l, l')^{(3-)}]_i \mid g \rangle \]

\]

\[
\tag{2.9}
\]

where:

\[
T_0^{(1-)}(\epsilon^+, \epsilon^-, k_0) = -\frac{1}{2} \sqrt{\frac{3}{5}}k_0 \quad \text{and} \quad T_0^{(3-)}(\epsilon^+, \epsilon^-, k_0) = \frac{1}{\sqrt{10}}k_0.
\]

Using Tables (1.1) and (1.2) we have

\[
\Sigma_{E1-E2}^{XMD} = -\frac{2\pi^2\alpha}{\hbar c} \sum_{l=\pm 1, l'} \sum_{l=\pm 1, l'} R_{l,l'}^{l'} \left[ \frac{2}{5} a^{(1-)}(l, l') k_z \langle g \mid \sum_i [O^{(1-)}]_i \mid g \rangle + \right.
\]

\[
- \frac{16}{\sqrt{10}} a^{(3-)}(l, l') k_z \langle g \mid \sum_i [O, (L, L)^2]^{(3-)}_0 \langle g \rangle \right],
\]

\]

\[
\tag{2.10}
\]

which describes \(XMD\) in the general case.
2.6 Conclusions

In the current chapter we have discussed a set of experiments performed by Goulon and coworkers at the ESRF of Grenoble. They provide the first experimental evidence of \( XNCD \), \( XNLD \) and \( XM\chi D \). Specializing Eq. (1.96) to circular, linear and magnetochiral dichroism, we have shown that integrated \( XNCD \), \( XNLD \) and \( XM\chi D \) are dependent on \((\Omega, L)^2\), on \((n, L)^2\) and \((\Omega, (L, L)^2)^3\), and on \(\Omega\), and \((\Omega, (L, L)^2)^3\) respectively, proving the sensitivity of these effects to polar \( XNCD \) and magnetoelectric \( XNLD \) and \( XM\chi D \) properties of crystals.

2.7 Appendix: x-ray dichroism in noncentrosymmetric crystals

In this section we present a paper accepted for publication in Physical Review B. It consist of three part: a discussion of sum rules for various dichroic phenomena related to \( E1 – E2 \) interference, a proposal for the origin of non-reciprocal dichroism in \((V_{0.972}Cr_{0.028})_2O_3\) and an appendix on Lie Groups.

This paper summarizes the results and the considerations exposed in the first two chapters of the thesis.
X-ray Dichroism in Noncentrosymmetric crystals

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(Dated: December 4, 2002)

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 stems from partly 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.

PACS numbers: PACS numbers: 78.70.Dm, 33.55.Ad

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, E2, ...) transitions, which raise an inner-shell electron to empty valence orbitals.

Linear or circular polarizations are employed in experiments, leading to linear or circular x-ray dichroism, respectively. The former implies a difference between radiations with linear polarizations 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 orbitals.

Following the pioneering work of Templeton and Templeton [1] and Schlitz 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 [3–5] (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, L-transformation) and time reversal (t → −t, R-transformation). They correspond to charge (L-even, R-even) and magnetic (L-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 [3, 4].

It is important to observe that pure electric multipole transitions cannot probe electronic properties that 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 Goulot et al. who reported the observation of three effects

X-ray natural circular dichroism (XNCD), probed in Na2Nd(digly)2NaBF4·6H2O [8] and in α-LiIO3 [9]. [The effect was observed near the Nd L2 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[10].

X-ray magnetochiral dichroism (XMChD), observed at the chromium K edge [11] 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 Goulot 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

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indicate that XNC-D, XNL-D and XM-D are sensitive to polar and magnetoelastic (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. Broad 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: $j = l_{\pm} = l_{\pm} \pm \frac{1}{2}$, where $l_{\pm}$ 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 $I$-odd microscopic operators, revealing the presence of parity nonconserving interactions. We remind the reader that the expectation value of an $I$-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:

- $I$-even and $I$-odd operators corresponding to one-electron polar properties, which arise from a non-centrosymmetric distribution of charge.
- $I$-odd and $R$-odd operators, obviously invariant under the combined symmetry $RI$ and thus describing one-electron ME properties of crystals.

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 1. 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 $k = 0, 1, 2, 3$ contribute to the integrated spectrum, for arbitrary polarisation [5]. In this case, magnetic circular dichroism selects two order parameters: a vector $(k = 1)$ and an octapole $(k = 3)$.

11. 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 [12], a convenient framework for dealing with the angular part of matrix elements. The ensuing results will then be applied to x-ray natural and non-reciprocal dichroism. Our discussion focuses on the physical interpretation of dichroic spectra; technical details of the derivation will be given in an Appendix.

A. Space-odd order parameters

Central to our considerations is the absorption cross section

\[ \sigma^A(\omega) = 4\pi^2a_\hbar\omega \left[ \frac{i}{2} \sum_{f} \sum_{\epsilon} \langle g | e^\epsilon \cdot r_f | f \rangle \left( \frac{1}{2} \right) | \epsilon \cdot r_f \rangle \langle \epsilon \cdot r_f | k \cdot r_f | g \rangle + c.c. \right] \delta(E_f - E_g - \hbar\omega) , \quad (1) \]

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 $\tau$ and $\tau'$; $\alpha = e^\epsilon/\hbar$.

The integrated intensity [14]

\[ \int_{\omega} \frac{\sigma^A(\omega)}{\hbar(\omega)^2} d(\hbar\omega) , \quad (2) \]

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

\[ \sum_{q} T_{q}(\mu, \pm \epsilon)|\epsilon, k \rangle \langle g| \mathcal{O}_{q}(\mu, \pm \epsilon)(l, l')|g\rangle . \]

In the second quantisation formalism, the latter is defined by

\[ \sum_{\epsilon} \mathcal{O}_{q}(\mu, \pm \epsilon)(l, l') = \sum_{m} \langle l'm'| \mathcal{O}_{q}(\mu, \pm \epsilon)| lm \rangle a_{lm}^d a_{lm}^c + c.c. , \quad (3) \]

where $a_{lm}^d$ and $a_{lm}^c$ create and annihilate valence electrons, $| l'm \rangle$ stands for a spherical harmonic, and $l' = l \pm 1$ [15]. All $\mathcal{O}_{q}(\mu, \pm \epsilon)(l, l')$ are odd under space inversion; their behaviour (even or odd) under time reversal is denoted by the superscript $\pm$. 

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

<table>
<thead>
<tr>
<th>Order Parameter</th>
<th>Space Inversion</th>
<th>Time Reversal</th>
<th>X-ray Dichroism</th>
<th>X-ray Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic</td>
<td>even</td>
<td>even</td>
<td>Magnetic Circular</td>
<td>Pure E1 or E2</td>
</tr>
<tr>
<td>Electric</td>
<td>odd</td>
<td>even</td>
<td>Natural Circular</td>
<td>Interference E1-E2</td>
</tr>
<tr>
<td>Magnetoelastic</td>
<td>odd</td>
<td>odd</td>
<td>Nonreciprocal</td>
<td>Interference E1-E2</td>
</tr>
</tbody>
</table>

Four operators $\mathcal{O}^{(p,\pm)}$ 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 $\mathbf{n} = \mathbf{r}/r$, and $\mathbf{\Omega} = (\mathbf{n} \times L - L \times \mathbf{n})/2$, a ME vector.

We find

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

where the couplings are defined via Clebsch-Gordan coefficients

$$[T^{(p)}]_{\mu \nu} \equiv \sum_{\mu', \nu'} C^{(p)}_{\mu \mu'} C^{(p)}_{\nu \nu'} T^{(p)}_{\mu', \nu'}.$$

Equations (4) identify one-electron properties revealed by E1-E2 absorption in the x-ray domain. The corresponding geometrical factors are given in Table II. As $T^{(1,+)}(\mathbf{\epsilon}, \mathbf{k}) = T^{(2,+)}(\mathbf{\epsilon}, \mathbf{k}) \equiv 0$, the polar moments $\mathcal{O}^{(1,+)} = \mathbf{n}$ and $\mathcal{O}^{(2,+)} = \mathcal{O}^{(2,-)}$ do not contribute to expression (2).

The microscopic expressions for the irreducible tensors $\mathcal{O}^{(p,\pm)}$ previously given were obtained as follows. Write Eq. (1) in the second-quantisation formalism and apply the Wigner-Eckart theorem. Then, recoupling the resulting $\mathbf{S}$ symbols by implementing suitable theorems of the Racah-Wigner calculus. This procedure yields a set of irreducible tensors written as pairs of creation and annihilation operators coupled with Clebsch-Gordan coefficients,

$$i \sum_{m, m'} \left( C^{(q)}_{m,l} C^{(q')}_{m', l'} \delta_{m, m'} + C^{(q')}_{m', l'} C^{(q)}_{m, l} \right),$$

with $\delta_{m, m'} = (-1)^{m'-m} \delta_{m, m'}$. Next, identify the physical observables defined by these hermitian one-electron operators. This is accomplished by combining $L$ together with a pair of operators that change the principal orbital quantum number $l$. As made explicit in the Appendix, symmetric and antisymmetric linear combinations of the pair define $\mathbf{n}$ and $\mathbf{\Omega}$, respectively. Symmetries of the triad $L$, $\mathbf{n}$ and $\mathbf{\Omega}$ are then inferred from the pertinent commutation relations.

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 momenta: $l$ and $l' = l \pm 1$, corresponding to $sp$ or $pf$ hybridisation in the actual case. (In our formalism, valence electrons are labelled using uncoupled orbital and spin quantum numbers.)

As shown in previous work [3-5], integrated dichroic spectra which stem from pure E1 or E2 transitions provide a measure of the ground-state expectation value of $L$-even irreducible tensors. Only the diagonal part (in the sense of $\delta_{l,l}$) contributes to the ground-state matrix elements in this case. Angular momentum and parity are good quantum numbers; the known sum rules for linear and circular dichroism are recovered [16].

Integrated E1-E2 dichroic spectra are related to the ground-state expectation value of odd irreducible tensors. Only the off-diagonal part contributes to the

| Table II: Polarisation responses of the E1-E2 interference. |
|-----------------|-----------------|-----------------|
| $T^{(1,+)}(\mathbf{\epsilon}, \mathbf{k}) = \frac{-1}{\sqrt{2}} \sqrt{\mathbf{\epsilon}} \mathbf{k}$ |
| $T^{(2,+)}(\mathbf{\epsilon}, \mathbf{k}) = \frac{1}{\mathbf{\epsilon}} \left[ \mathbf{\epsilon}, \mathbf{\epsilon} \right]^{(2)}$ |
| $T^{(2,-)}(\mathbf{\epsilon}, \mathbf{k}) = \frac{1}{\mathbf{\epsilon}} \left[ \mathbf{\epsilon}, \mathbf{\epsilon} \right]^{(2)}$ |
| $T^{(3,-)}(\mathbf{\epsilon}, \mathbf{k}) = \left[ \mathbf{\epsilon}, \mathbf{\epsilon} \right]^{(2)}$ |
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 $\mathcal{O}^{(\mu, \lambda)}$.

Relations between XNCD, XNLD, XMCD and the order parameters given by Eqs. (4) will be provided below.

$$
\int \frac{\sigma^+_{\mu}(\omega) - \sigma^-_{\mu}(\omega)}{\rho(\omega)} d(\omega) = - \frac{16\pi^4 \alpha}{3 \hbar c} (2l_e + 1) \sum_{l' = -l_e}^{l_e} \sum_{l, \lambda} R_{l, l'}^{(\mu)} R_{l', l}^{(\mu)} a_{l, l'}^{(2, +)}(l_e, l) \sqrt{\frac{\lambda}{2}} T^{(2, +)}(l_e, l') \langle \epsilon^+, \epsilon^-; \mathbf{k} | [\mathbf{L}, \mathbf{S}]^{(2)}_{l, l'}(l_e, l) | \epsilon^+, \epsilon^-; \mathbf{k} \rangle
$$

which reveals the microscopic origin of XNCD spectra. Here, $\epsilon^\pm = \pm (i / \sqrt{2}) (\epsilon_1 \pm i \epsilon_2)$ define circular polarisation states; the index $\epsilon$ runs over valence electrons [17]. Furthermore,

$$
a_{l, l'}^{(2, +)}(l_e, l) = \frac{2(2l + 1)(2l' + 1)[6 + 3l(l_e + 1) - 2l(l + 1) - l'(l' + 1)]}{(l + l' + 1)(l_e - 3l' + 2l)[(l_e + 3l' - 2l + 1)(l_e + l + 2l')]}.
$$

In this case, a recoupling of Eq. (1) leads to the following integral relation

Fig. 1, is readily interpreted with the help of Eq. (5).

We focus on charge properties stemming from $sp$ hybridisation. (The 4d shell of iodine is filled and the crystal displays no magnetism.) At the iodine sites the symmetry is $C_3$. Notice that $\mathcal{O}^{(2, +)} = [\mathbf{L}, \mathbf{S}]^{(2)}_{l, l'}$, known as pseudoelectric 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 threefold 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 pseudoelectricities 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 $l$-odd analog of ferroquadrupolar ordering, which is probed by pure E1 x-ray linear dichroism [5].

2. XNLD

In the case of XNLD, the integral relation reads

The XNCD experiment of Goulon et al. on $\alpha$-LiIO$_3$ [9], whose crystal structure (space group $P6_3$) is depicted in

FIG. 1: Crystal structure of $\alpha$-LiIO$_3$, with $\bullet = Li$, $\bullet = O$, and $\star = I$.
\[
\int_{-\infty}^{\infty} \frac{\sigma_{N}^{1}(\omega) - \sigma_{N}^{2}(\omega)}{h\omega} d(h\omega) = \frac{8\pi^{2}a_{0}}{\hbar c} (2l_{c} + 1) \sum_{l-l\pm 1} \sum_{l-l=1} R_{l}^{(1)} R_{l}^{(2)} \left\{ \sqrt{\frac{2}{3}} a_{l}^{(2)}(l, l) \left( T_{q}^{(2)}(e^{+}, \mathbf{e}) - T_{q}^{(2)}(e^{-}, \mathbf{e}) \right) \right\},
\]

\[
\langle g \sum_{i} [L_{i}, \Pi_{i}^{2}(l, l')] \rangle |g\rangle + 2a_{l}^{(2)}(l, l) \left( T_{q}^{(2)}(e^{+}, \mathbf{e}) - T_{q}^{(2)}(e^{-}, \mathbf{e}) \right) \langle g \sum_{i} [L_{i}, L_{i}^{2}, \Omega_{i}^{(3)}(l, l')] \rangle |g\rangle,
\]

(7)

FIG. 2: Corundum and monoclinic structures of V₂O₅. ( and denote different orientations of the oxygen octahedra.) The AFM structure is also displayed.

where \( \| \) and \( \perp \) denote two orthogonal linear polarization states. The expansion coefficients are given by

\[
a_{l}^{(2,\pm)}(l, l) = \frac{a_{l}^{(2,\pm)}(l, l)}{6 + 3l(l + 1) - 2l(l + 1) - l(l + 1)} - 1,
\]

and

\[
a_{l}^{(2,\pm)}(l, l) = \frac{(l + l' + 1)(l' - l)}{4} a_{l}^{(2,\pm)}(l, l),
\]

with \( a_{l}^{(2,\pm)}(l, l) \) defined by Eq. (6).

Equation (7) 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 [18].) The result implies that Goulon and his co-workers have probed ME properties of \( \{V_{1-\omega}, Cr_{\omega}\}_{3}O_{S} \).

\( \text{V}_{2}\text{O}_{5} \) 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 \( \text{V}_{2}\text{O}_{5} \) are depicted in Fig. 2.

Substitution of \( \text{Cr}^{2+} \) in the \( \text{V}_{2}\text{O}_{5} \) 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 Demier and Marzio [19, 20]. 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 \( \text{C}_{3v} \) [20]. Formation of an electric-dipole moment is thus permitted by symmetry. Crystallography also suggests that nearest-neighbour pairs of vanadium atoms are antiferromagnetically ordered along the hexagonal \( c \) axis (the symmetry of a pair is \( \text{D}_{3h} \) [20]), as shown in Fig. 3. We can thus argue that, at about \( 300^{\circ}\text{K} \) in the insulating phase, \( \{V_{1-\omega}, Cr_{\omega}\}_{3}O_{S} \) is an antiferromagnetic (AFE) crystal [21].

At \( T = T_{N} \), the crystal makes a nearly second-order transition to an AFM monoclinic phase [22]. The driving mechanism of this transition is not fully understood [23]. The lattice space group lowers to \( \text{I}2/\text{a} \), with magnetic point group \( \text{C}_{2h} \otimes \text{R} \) [24]. Notice that this symmetry is incompatible with the observation of XNLD. However, a reduction of magnetic symmetry leading to \( \text{C}_{2h} \otimes \text{C}_{1} \) might take place [25].

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. 4 would render (V1−xCrx)2O3 an AFM, AFE, and ME crystal, thus explaining the observations of Goujon and his collaborators.

A physical interpretation of Eq. (7) is obtained by expanding the "energy" function $W(n, L)$ [26].

The $m$th term in the MacLaurin formula reads:

$$\frac{1}{(n, \partial_\alpha + L, \partial_\alpha)} W(0, 0);$$

here, greek letters denote cartesian components and repeated indexes are summed over. It is readily seen that $[L, n]^{(2)}$, a magnetic quadrupole, stems from the $m = 2$ term and describes a linear ME effect. The contribution $[[L, L], \Omega]^{(3)}$ is found in the $m = 4$ term and accounts for a trilinear ME effect.

3. XM$\chi$D

The third form of E1-E2 x-ray dichroism, namely XM$\chi$D, was probed by Goujon and co-workers [11] at the chromium K-edge in Cr$_2$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 [5], the following integral relationship holds for pure E1 transitions

$$\int_{j \rightarrow j'} \frac{(\sigma^+ + \sigma^-)}{(h\omega)^2} d(h\omega) = 4\pi^2 \alpha \sum I \left\{ \frac{2n_b(l)}{3l+1} + g^{2,+}(l, l) (g \sum_i (3l_i^2 - L^2), |g|) I^{(1)}_{j,l} \right\}, \quad (10)$$

where $n_b(l) = 4l^2 - (g|n|g)$ denotes the number of holes in the valence $l$ shell, and $I^{(1)}_{j,l} = (|l|)|\sqrt{4\pi/3} Y^{(1)}(|l|)| I^{(1)}_{j,l}$.

Furthermore,

$$g^{2,+}(l, l) = \frac{(l+1)[2l(l+1) + 1 - 6l(l+1)] + 3l(l+1)l-3]}{6((2l-1)(2l+1)(l+1)(2l+3)} \quad (11)$$

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

$$\int_{j \rightarrow j'} \frac{(\sigma^+ + \sigma^-)}{(h\omega)^2} d(h\omega) = -\frac{2\pi^2 \alpha}{h\epsilon} (2l^2 + 1) \sum I \left\{ \frac{2n_b(l)}{3l+1} R_{L}^{(2)} \frac{1}{2} a_i^{(1,-)}(l, l, l) \epsilon_i (g \sum \Omega_i (l, l'), |g|) \right\} \quad (12)$$

with

$$a_i^{(1,-)}(l, l) = \frac{(l_+ + l + 1)(l_+ + l - l') h_1(l, l, l')}{(l_+ + l)(l_+ + l + 2)(l + l' + 1)^2}, \quad (13)$$

where $h_1(l, l, l') = l_+ + l' - l + 1$ and $l' = l \pm 1$. We have
set $k = k, \tilde{k}$ in Eqs. (10-12).

Eqs. (10-12) indicate that $XM_3 \xi D$ is observed as follows. Record the $\sigma^0 + \sigma^-$ spectrum in a magnetoelectric crystal annealed in the parallel configuration. Ditto for antiparallel annealing. Subtract the two spectra.

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 $XM_3 \xi D$ respectively in $\alpha$-LiIO$_3$, (V$_{572}$Cr$_{028}$)$_2$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 $E1-E2$ inter-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-odd 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 $\mathcal{O}^{(1,+)} = n$ and $\mathcal{O}^{(3, +)} = \{[L, L]^2, n\}^{(3)}$ (see Section II A), have not entered our discussion of integrated XNCD, XNLD and $XM_3 \xi D$ spectra. As previously observed, $\mathcal{O}^{(1,+)}$ and $\mathcal{O}^{(3, +)}$ 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. [27] 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, AFE and ME structures with x rays at resonance.

In conclusion, the pioneering experiments of Gouin 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

The current Appendix aims at discussing technical aspects of our analysis of $E1-E2$ x-ray dichroism. Emphasis will be on the relation between the vectors $n$ and $\Omega$ and the generators of Lie groups, which have been previously employed in nuclear [28] and particle physics [29, 30].

We follow Carra and Benoist [31, 32] and consider the general framework of a de Sitter algebra: set $\mathfrak{so}(3,2)$ [28, 33]. A realisation of such an algebra is provided by the operators:

$$A^- = i(A - A^\dagger)/2, \quad A^+ = (A + A^\dagger)/2,$$

$$L \quad \text{and} \quad N_0,$$

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

$$A = n f_1(N_0) + \nabla_\Omega f_1(N_0),$$

with $n = r/r, \nabla_\Omega = -i n \times L$ and

$$f_1(N_0) = (N_0 - 1/2) f_2(N_0),$$

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

$A$ and $A^\dagger$ are known as shift operators as their action on $|lm \rangle$ changes $l$ into $l - 1$ and $l + 1$, respectively.

A physical interpretation of $A^-$ is provided by the relation

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

where $[.,.]_\#$ denotes an anticommutator. Eq. (A.6) defines the (purely angular) orbital anapole [34-36].
A physical representation of the generator \( A^+ \) is provided by
\[
A^+ = \sqrt{N_0} n \sqrt{N_0}.
\]
(A.7)

\( L, n \) 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 a homogeneous Lorentz group: SO(3,1). Also \( L \) and
\[
\sqrt{N_0} n \sqrt{N_0}, \text{ where } N_0 [im] = (l + \frac{1}{2})(|m|),
\]
generate SO(3,1). The homogeneous Lorentz group enters our derivation of \( L \)-ciff 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.

[7] X-ray dichroism implies excitations from inner shells, which are filled in the ground state and can therefore be 'integrated out'. As a result, one-electron properties of valence states are probed in the x-ray region.
[14] Integration is over a finite energy interval, which corresponds to the two partners of a spin-orbit split inner shell.
[15] The relation \( l' = l \pm 1 \) holds for \( l_0 = 0, 1 \). In general, \( l \) and \( l' \) must be of opposite parity. As pointed out by C. Brudier (private communication), the values \( l' = l \pm 1 \) and \( l' = l \pm 3 \) are permitted in the matrix element \( \langle l'm'|C^{(3,1)}|lm \rangle \), for \( l_0 = 2 \). A re-definition of \( C^{(3,1)} \) to include \( l' = l \pm 3 \) hybridisation is required in this case.
[16] Sum rules for pure \( E1 \) or \( E2 \) transitions were derived by representing valence-electron states within an \( |lm \rangle \) basis. In this case, the pertinent order parameters are derived from the generators of rotation groups: the components of spin and orbital angular momentum. Such a formulation can be extended to include parity-conserving hybridisation; for example, it can be shown that pure \( E1 \) linear dichroism mixes \( |lm \rangle \) and \( |l \pm 2m \rangle \). Discussion of these effects is beyond the scope of the current paper.
[17] In Eq. (5), the radial integrals are defined by
\[
R_{j,j'}^{(k)} = \int_0^\infty dr \varphi_j (r) r^{L+j+k} \varphi_{j'}(r)
\]
where \( \varphi_j (r) \) and \( \varphi_{j'}(r) \) denote inner-shell and valence radial wave functions, respectively. Our derivation neglects relativistic corrections to the radial part of the atomic wave functions.
[18] It is the magnetic field of the so-called magnetoelectric annealing a standard technique for creating a single magnetoelectric domain in the crystal.
[21] Notice that \( x = 0.038 \) in Ref. 19 and \( x = 0.028 \) in Ref. 10. As shown by the phase diagram of McWhan and Remiika [Phys. Rev. B 2, 3734 (1970)], the two substitutions are equivalent.
[25] These two ME point groups are subgroups of \( C_{2h} \otimes \Re \); in international notation they are denoted by \( 2/m \) and \( 2/m \), respectively.
Chapter 3

$E1-E2$ X-Ray Resonant Scattering
3.1 \( E1-E2 \) x-ray resonant scattering

In the previous chapter we have considered \( E1-E2 \) x-ray dichroism in noncentrosymmetric crystals. In particular we have investigated the microscopic origin of \( XNCD \), \( XNLD \) and \( XMCD \).

It is however important to notice that, recently, a number of publications have stressed the importance of \( E1-E2 \) interference for interpreting unexpected peaks in certain x-ray resonant diffraction spectra; Templeton and Templeton [100] have pointed out the importance of \( E1-E2 \) terms in the tetrahedral anisotropy of x-ray anomalous diffraction in noncentrosymmetric crystals for weak or forbidden Bragg reflections; El’imov et al. [101] have used \( E1-E2 \) transitions to analyze the (660) and (222) resonant x-ray Bragg reflection near the germanium K edge.

A generalization of our derivation to cover the important case of elastic x-ray resonant scattering is thus demanded, and will be discussed in the current chapter. In the case of resonant scattering, however, the amplitude takes a simple, intuitive form only in a particular limit: the fast collision approximation, as thoroughly discussed below.

3.2 X-ray resonant scattering

Consider the \( E1-E2 \) contribution to the x-ray resonant scattering amplitude

\[
f_{E1-E2}(\omega) = 4\pi\bar{\lambda}_0 \left[ \sum_{MM'} \left[ \vec{\varepsilon}_f^* \cdot \mathbf{Y}_{LM}(\hat{k}_f) \right]\left[ \mathbf{Y}_{LM}^e(\hat{k}_0) \cdot \vec{\varepsilon}_0 \right] \langle \psi_f | \mathbf{F}_{LM,LM}(\omega) | \psi_0 \rangle \right] + \left[ \vec{\varepsilon}_f^* \cdot \mathbf{Y}_{LM}(\hat{k}_f) \right]\left[ \mathbf{Y}_{LM}^e(\hat{k}_0) \cdot \vec{\varepsilon}_0 \right] \langle \psi_f | \mathbf{F}_{LM,LM}(\omega) | \psi_0 \rangle \right] \] (3.1)

where \( \vec{\varepsilon}_0, \hat{k}_0 \) and \( \vec{\varepsilon}_f, \hat{k}_f \) denote polarizations and wave vectors of incoming and outgoing photons, respectively; \( \mathbf{Y}_{LM}^e(\theta, \psi) \) is a vector spherical harmonic of electric type\(^1\). The

\(^1\)The vector spherical harmonics are defined by [40]:

\[
\mathbf{Y}_{LM}^e = \frac{1}{\sqrt{L(L+1)}} \nabla_{\Omega} Y_{LM}(\theta, \psi) \] (3.2)
matrix element $\langle \psi_f | F_{L^\prime M^\prime,LM}^e(\omega) | \psi_0 \rangle$ takes the form

$$\langle \psi_f | F_{L^\prime M^\prime,LM}^e(\omega) | \psi_0 \rangle = \sum_I \frac{1}{2\lambda_I} \langle \psi_f | J_{L^\prime M^\prime}^{\dagger} | I \rangle \langle I | J_{LM}^e | \psi_0 \rangle,$$

with the current operator given by

$$J_{LM}^e = \sum_s \langle nlm_s m_s | -\frac{4\pi i k_L}{(2L + 1)!!} \sqrt{\frac{L + 1}{L}} Q_{LM} | n_{e_j} e m_c m_{sc} \rangle \hat{a}_{mlm_s}^\dagger \hat{a}_{jm_{sc}} \hat{b}_{jm_{sc}}.$$

$Q_{LM} = e^{\rho L} Y_{LM}$ is the usual multipole operator, $\hat{a}$ and $\hat{b}$, with appropriate indexes, annihilate valence and core electrons, respectively; $| I \rangle = | (nl)^{+1}(n_{e_j} e)_{-1} \psi_0 \rangle$ represents the intermediate state, where core electron $(n_{e_j} e)$ is excited into the partially filled valence shell $(nl)$. $\Gamma_I$ is the full width at half maximum (FWHM) of the state $| I \rangle$. ( $| \psi_0 \rangle$ and $| \psi_f \rangle$ denote ground and final state of the target, respectively.) Elastic scattering is obtained by setting $| \psi_f \rangle = | \psi_0 \rangle$ [16].

In the context of our derivation, is convenient to rewrite the scattering amplitude as follows

$$f_{E1-E2} = \frac{4\pi \lambda_0}{2L + 1} \sum_c \sum_{M^\prime M^\prime} (-)^{M^\prime+M^\prime} \left[ \hat{e}_f^* \cdot Y_{L^\prime M^\prime}^e(\hat{k}_f) \right] \left[ Y_{LM}^e(\hat{k}_0) \cdot \hat{e}_0 \right] \delta_{M^\prime M^\prime} \delta_{M^\prime M^\prime} \times
\times \langle \psi_f | F_{L^\prime M^\prime,LM}^e(\omega) | \psi_0 \rangle + \sum_c \sum_{M^\prime M^\prime} (-)^{M+M^\prime} \left[ \hat{e}_f^* \cdot Y_{LM}^e(\hat{k}_0) \right] \left[ Y_{L^\prime M^\prime}^e(\hat{k}_f) \cdot \hat{e}_0 \right] \times
\times \langle \psi_f | F_{L^\prime M^\prime,LM}^e(\omega) | \psi_0 \rangle \delta_{M^\prime M^\prime} \delta_{M^\prime M^\prime}.$$

Using the identity

$$\sum_c C_{a_0 b_0}^c C_{a_0 b_0}^c = \delta_{a_0 a_0} \delta_{b_0 b_0},$$

we obtain

$$f_{E1-E2} = \frac{4\pi \lambda_0}{2L + 1} \sum_{x \rho} \sum_{M^\prime M^\prime} C_{LM^\prime,LM}^{E1E2} \left[ \hat{e}_f^* \cdot Y_{L^\prime M^\prime}^e(\hat{k}_f) \right] \left[ Y_{LM}^e(\hat{k}_0) \cdot \hat{e}_0 \right] \times
\times \frac{\nabla(\rho \times \psi)}{\sqrt{L(L + 1)}} Y_{LM}(\theta, \psi).$$

where the suffixes $e,m$ and $l$ indicate electric, magnetic and longitudinal type, respectively.

\begin{align*}
Y_{LM}^m &= \frac{-i}{\sqrt{L(L + 1)}} (n \times \nabla_\theta) Y_{LM}(\theta, \psi) \\
Y_{LM}^l &= n Y_{LM}(\theta, \psi)
\end{align*}
expressing \( f_{E_1 - E_2} \) as a sum of two terms with same structure and \( L \) and \( L' \) interchanged. Generalizing the work of Luo et al. [16], we define recoupled geometrical and electronic factors. They read

\[
T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{LL'} = \sum_{MM'} \sqrt{\frac{2x + 1}{2L + 1} C^{LM}_{LM', MM'} \begin{bmatrix} \epsilon_j^* \cdot Y^{r}_{LM}(\mathbf{k}_0) \end{bmatrix} \begin{bmatrix} Y^{r*}_{LM'}(\mathbf{k}_0) \cdot \epsilon_0 \end{bmatrix} \sqrt{\frac{2x + 1}{2L' + 1} C^{LM'}_{LM', MM'} \begin{bmatrix} \psi_f \end{bmatrix} \begin{bmatrix} F^e_{LM', MM'}(\omega) \end{bmatrix} \begin{bmatrix} \psi_0 \end{bmatrix} \right]},
\]

(3.6)

\[
F^x_\rho(\omega)_{LL'} = \sum_{MM'} \sqrt{\frac{2x + 1}{2L + 1} C^{LM}_{LM', MM'} \begin{bmatrix} \psi_f \end{bmatrix} \begin{bmatrix} F^e_{LL'}(\omega) \end{bmatrix} \begin{bmatrix} \psi_0 \end{bmatrix} \right]},\]

(3.7)

\[
T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{ LL'} = \sum_{MM'} \sqrt{\frac{2x + 1}{2L' + 1} C^{LM'}_{LM, MM'} \begin{bmatrix} \epsilon_j^* \cdot Y^{r}_{LM}(\mathbf{k}_0) \end{bmatrix} \begin{bmatrix} Y^{r*}_{LM'}(\mathbf{k}_0) \cdot \epsilon_0 \end{bmatrix} \sqrt{\frac{2x + 1}{2L + 1} C^{LM'}_{LM', MM'} \begin{bmatrix} \psi_f \end{bmatrix} \begin{bmatrix} F^e_{LM, MM'}(\omega) \end{bmatrix} \begin{bmatrix} \psi_0 \end{bmatrix} \right)},
\]

(3.8)

\[
F^x_\rho(\omega)_{ LL'} = \sum_{MM'} \sqrt{\frac{2x + 1}{2L' + 1} C^{LM'}_{LM, MM'} \begin{bmatrix} \psi_f \end{bmatrix} \begin{bmatrix} F^e_{LL'}(\omega) \end{bmatrix} \begin{bmatrix} \psi_0 \end{bmatrix} \right]},\]

(3.9)

Eq. (3.5) thus becomes:

\[
f_{E_1 - E_2} = 4\pi \tilde{\lambda}_0 \sum_{l+p} \left[ T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{LL'} F^x_\rho(\omega)_{LL'} + T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{ LL'} F^x_\rho(\omega)_{ LL'} \right] = 2\pi \tilde{\lambda}_0 \sum_{l+p} \left[ T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{LL'} + T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{ LL'} \right] \left[ F^x_\rho(\omega)_{LL'} + F^x_\rho(\omega)_{ LL'} \right] + 2\pi \tilde{\lambda}_0 \sum_{l+p} \left[ T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{LL'} - T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{ LL'} \right] \left[ F^x_\rho(\omega)_{LL'} - F^x_\rho(\omega)_{ LL'} \right].
\]

(3.10)

The presence of terms of the form \( F^x_\rho(\omega)_{LL'} \pm F^x_\rho(\omega)_{ LL'} \) and \( T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{LL'} \pm T^x_\rho(\epsilon_f^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{\epsilon}_0)_{ LL'} \) is particularly useful to identify electric and magnetic properties, which are detectable with \( E1-E2 \) x-ray resonant scattering experiments.
3.2.1 Angular factors

To express the scattering amplitude as linear combination of scalar products of pairs of irreducible tensors, we recombine the terms \[ T_{\rho}^{xx}(\mathbf{e}^*_f, \mathbf{k}_f, \mathbf{\hat{e}}_0, \mathbf{\hat{e}}_0)_{LL'} \pm T_{\rho}^{xx}(\mathbf{e}^*_f, \mathbf{k}_f, \mathbf{\hat{e}}_0, \mathbf{\hat{e}}_0)_{L'L} \]
and \[ F_{\rho}^{xx}(\omega)_{LL'} \pm F_{\rho}^{xx}(\omega)_{L'L} \] .

Under complex conjugation, a vector spherical harmonic of electric type transforms as\(^2\)
\[
Y_{\ell M}^e(\theta, \psi) = (-)^M Y_{\ell-M}^e(\theta, \psi).
\]

Eq. (3.6) can thus be given the form:

\[
T_{\rho}^{xx}(\mathbf{e}^*_f, \mathbf{k}_f, \mathbf{\hat{e}}_0, \mathbf{\hat{e}}_0)_{L'L} = \sqrt{\frac{2\ell + 1}{2\ell + 1}} \sum_{\ell', M'} C_{\ell' M', \ell M}^{L M} \left[ \mathbf{\hat{e}}^*_f \cdot Y_{\ell' M'}^e(\mathbf{k}_f) \right] \left[ Y_{\ell M}^e(\mathbf{\hat{e}}_0) \cdot \mathbf{\hat{e}}_0 \right] = \\
\sqrt{\frac{2\ell + 1}{2\ell + 1}} \sum_{\ell', M'} C_{\ell' M', L-M}^{L M} \left[ \mathbf{\hat{e}}^*_f \cdot Y_{\ell' M'}^e(\mathbf{k}_f) \right] \left[ Y_{\ell M}^e(\mathbf{\hat{e}}_0) \cdot \mathbf{\hat{e}}_0 \right] = \\
\sum_{\ell', M'} C_{\ell' M', L-M}^{L M} (-)^{(L'-M'+M)} \left[ \mathbf{\hat{e}}^*_f \cdot Y_{\ell' M'}^e(\mathbf{k}_f) \right] \left[ Y_{\ell-M}^e(\mathbf{\hat{e}}_0) \cdot \mathbf{\hat{e}}_0 \right].
\]

The scalar product between the generic polarization \( \mathbf{\hat{e}} \) and the vector spherical harmonic \( Y_{\ell M}^e(\theta, \psi) \) can be written in terms of ordinary spherical harmonics. The relation reads
\[
\mathbf{\hat{e}} \cdot Y_{\ell M}^e(\mathbf{k}) = \sqrt{\frac{4\pi (2\ell + 1)}{3(\ell + 1)}} \sum_{\alpha \beta} C_{\ell \alpha, L-1, \beta}^{LM} Y_{1 \alpha}(\mathbf{\hat{e}}) Y_{L-1 \beta}(\mathbf{k}),
\]
so that
\[
\mathbf{\hat{e}}^*_f \cdot Y_{\ell' M'}^e(\mathbf{k}_f) = \sqrt{\frac{4\pi (2\ell' + 1)}{3(\ell' + 1)}} \sum_{\mu' \mu} C_{\ell' M', \ell' -1m}^{L'M'} Y_{1 \mu}(\mathbf{\hat{e}}^*_f) Y_{\ell' -1 \mu}(\mathbf{k}_f)
\]
and
\[
Y_{\ell-M}^e(\mathbf{\hat{e}}_0) \cdot \mathbf{\hat{e}}_0 = \sqrt{\frac{4\pi (2\ell + 1)}{3(\ell + 1)}} \sum_{\mu m} C_{\ell \mu, L-1 \mu}^{L M} Y_{1 \mu}(\mathbf{\hat{e}}_0) Y_{L-1 \mu}(\mathbf{\hat{e}}_0)
\]

\(^2\)From relation 39 p. 215 Ref. [40]

\[
Y_{\ell M}^{(\lambda)}(\theta, \psi) = (-)^{(M+\lambda+1)} Y_{\ell-M}^{(\lambda)}(\theta, \psi)
\]

where \( \lambda = 1, 0, -1 \) identify electric, magnetic and longitudinal vector spherical harmonics, respectively.
Setting $L' = 2$ and $L = 1$, remembering that $Y_{00} = \frac{1}{2\sqrt{\pi}}$, we obtain:

$$\hat{c}_f \cdot Y_{2M'}^e(\hat{k}_f) = \sqrt{\frac{15}{12\pi}} \sum_{\mu' m'} C_{1\mu,1m}(\hat{c}_f)_{\mu'}(\hat{k}_f)_{m'},$$

(3.16)

$$Y_{1-M}(\hat{k}_0) \cdot \hat{c}_0 = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sum_{\mu} C_{1\mu,00}(\hat{c}_0)_{\mu}$$

(3.17)

Expressions for $\hat{c}_f \cdot Y_{2M'}^e(\hat{k}_f)$ ($M' = -2, \ldots, 2$) and $Y_{1-M}(\hat{k}_0) \cdot \hat{c}_0$ ($M = -1, \ldots, 1$) are given in Tables 3.1 and 3.2, respectively. The geometrical factors $T_{\rho}^e(\hat{c}_f, \hat{k}_f, \hat{k}_0, \hat{c}_0)_{21}$ and $T_{\rho}^e(\hat{c}_f, \hat{k}_f, \hat{k}_0, \hat{c}_0)_{12}$ are summarized in Table 3.3.

<table>
<thead>
<tr>
<th>$M'$</th>
<th>$\hat{c}<em>f \cdot Y</em>{22}^e(\hat{k}<em>f) = \sqrt{\frac{15}{12\pi}} C</em>{11,11}^{22}(\hat{c}<em>f)</em>{1}(\hat{k}<em>f)</em>{1} = \frac{1}{2} \sqrt{\frac{5}{\pi}} (\hat{c}_f, \hat{k}<em>f)</em>{2}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$\hat{c}<em>f \cdot Y</em>{21}^e(\hat{k}<em>f) = \sqrt{\frac{15}{12\pi}} \sum</em>{\mu' m'} C_{1\mu,1m'}^{21}(\hat{c}<em>f)</em>{\mu'}(\hat{k}<em>f)</em>{m'} = \frac{1}{2} \sqrt{\frac{5}{\pi}} (\hat{c}_f, \hat{k}<em>f)</em>{1}^2$</td>
</tr>
<tr>
<td>0</td>
<td>$\hat{c}<em>f \cdot Y</em>{20}^e(\hat{k}<em>f) = \sqrt{\frac{15}{12\pi}} \sum</em>{\mu' m'} C_{1\mu,1m'}^{20}(\hat{c}<em>f)</em>{\mu'}(\hat{k}<em>f)</em>{m'} = \frac{1}{2} \sqrt{\frac{5}{\pi}} (\hat{c}_f, \hat{k}<em>f)</em>{0}^2$</td>
</tr>
<tr>
<td>-1</td>
<td>$\hat{c}<em>f \cdot Y</em>{2-1}^e(\hat{k}<em>f) = \sqrt{\frac{15}{12\pi}} \sum</em>{\mu' m'} C_{1\mu,1m'}^{2-1}(\hat{c}<em>f)</em>{\mu'}(\hat{k}<em>f)</em>{m'} = \frac{1}{2} \sqrt{\frac{5}{\pi}} (\hat{c}_f, \hat{k}<em>f)</em>{-1}^2$</td>
</tr>
<tr>
<td>-2</td>
<td>$\hat{c}<em>f \cdot Y</em>{2-2}^e(\hat{k}<em>f) = \sqrt{\frac{15}{12\pi}} \sum</em>{\mu' m'} C_{1\mu,1m'}^{2-2}(\hat{c}<em>f)</em>{\mu'}(\hat{k}<em>f)</em>{m'} = \frac{1}{2} \sqrt{\frac{5}{\pi}} (\hat{c}_f, \hat{k}<em>f)</em>{-2}^2$</td>
</tr>
</tbody>
</table>

Table 3.1: In this Table the $(2L'+1)$ scalar products $\hat{c}_f \cdot Y_{2M'}^e(\hat{k}_f)$ are listed.

Algebraic details connecting relation (3.12) and Table 3.3 will be provided in next section.
\( M = 1 \) \[ Y_{1-M}^e(\hat{k}_0) \cdot \hat{e}_0 = \frac{1}{2} \sqrt{\frac{3}{2\pi}} (\epsilon_0)_{-1} \]

\( M = 0 \) \[ Y_{10}^e(\hat{k}_0) \cdot \hat{e}_0 = \frac{1}{2} \sqrt{\frac{3}{2\pi}} (\epsilon_0)_{0} \]

\( M = -1 \) \[ Y_{11}^e(\hat{k}_0) \cdot \hat{e}_0 = \frac{1}{2} \sqrt{\frac{3}{2\pi}} (\epsilon_0)_{1} \]

Table 3.2: In this Table the \((2L + 1)\) scalar products \( Y_{1-M}^e(\hat{k}_0) \cdot \hat{e}_0 \) are given.

\[
\begin{align*}
T_{\rho}^{1s}(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{21} &= \frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\hat{e}_f^*, \hat{k}_f)^2, \hat{e}_0 \right)_{\rho}^4 \\
T_{\rho}^{2s}(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{21} &= \frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\hat{e}_f^*, \hat{k}_f)^2, \hat{e}_0 \right)_{\rho}^2 \\
T_{\rho}^{3s}(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{21} &= \frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\hat{e}_f^*, \hat{k}_f)^2, \hat{e}_0 \right)_{\rho}^3 \\
T_{\rho}^{1s}(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{12} &= -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\hat{e}_f^*, (\hat{e}_0, \hat{k}_0)^2 \right)_{\rho}^4 \\
T_{\rho}^{2s}(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{12} &= -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\hat{e}_f^*, (\hat{e}_0, \hat{k}_0)^2 \right)_{\rho}^2 \\
T_{\rho}^{3s}(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{12} &= -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\hat{e}_f^*, (\hat{e}_0, \hat{k}_0)^2 \right)_{\rho}^3 
\end{align*}
\]

Table 3.3: This Table shows the geometrical factors \( T_{\rho}^x(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{21} \) and \( T_{\rho}^x(\hat{e}_f^*, \hat{k}_f, \hat{k}_0, \hat{e}_0)_{12} \) for \( x = 1, 2, 3 \).

### 3.2.2 Appendix: algebraic details.

This appendix provides algebraic details of the derivation of the results given in Table 3.3. We consider the case \( x = 1 \) only. (The cases \( x = 2, 3 \) represent a straightforward
generalization of the method.

We want to show that

\[ T^{(1^*)}_ρ(\epsilon_f^*, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21} = \frac{\sqrt{15}}{4\pi\sqrt{2}} \left( \langle \epsilon_f^*, \hat{k}_f \rangle^2, \epsilon_0 \right)_ρ \]

and that

\[ T^{(1^*)}_ρ(\epsilon_f^*, \hat{k}_f, \hat{k}_0, \epsilon_0)_{12} = -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( \langle \epsilon_f^*, \epsilon_0, \hat{k}_0 \rangle^2 \right)_ρ \]

To this end we consider Eq. (3.12) for \( x = 1 \). Using the results of Tables 3.1 and 3.2 we obtain:

\[
T^{(1^*)}_ρ(\epsilon_f^*, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21} = C^{10}_{20,10} \left[ \epsilon_f^* \cdot Y_{20}(\hat{k}_f) \right] \left[ Y_{10}(\hat{k}_0) \cdot \epsilon_0 \right] + C^{10}_{21,1-1} \left[ \epsilon_f^* \cdot Y_{21}(\hat{k}_f) \right] \times \\
\times \left[ Y_{1-1}(\hat{k}_0) \cdot \epsilon_0 \right] + C^{10}_{2-1,11} \left[ \epsilon_f^* \cdot Y_{2-1}(\hat{k}_f) \right] \left[ Y_{11}(\hat{k}_0) \cdot \epsilon_0 \right] = C^{10}_{20,10} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_0^2(\epsilon_0) \right] + \\
+ C^{10}_{21,1-1} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_1^2(\epsilon_0) - 1 \right] + C^{10}_{2-1,11} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_{-1}^2(\epsilon_0) \right]_1 = \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle^2, \epsilon_0 \right]_1, \\
\]

\[
T^{(1^*)}_ρ(\epsilon_f^*, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21} = -C^{1-1}_{2-1,11} \left[ \epsilon_f^* \cdot Y_{2-2}(\hat{k}_f) \right] \left[ Y_{11}(\hat{k}_0) \cdot \epsilon_0 \right] - C^{1-1}_{2-1,10} \left[ \epsilon_f^* \cdot Y_{2-1}(\hat{k}_f) \right] \times \\
\times \left[ Y_{10}(\hat{k}_0) \cdot \epsilon_0 \right] - C^{1-1}_{20,1-1} \left[ \epsilon_f^* \cdot Y_{2}(\hat{k}_f) \right] \left[ Y_{1-1}(\hat{k}_0) \cdot \epsilon_0 \right] = -C^{1-1}_{2-1,11} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_{-2}^2(\epsilon_0) \right] + \\
- C^{1-1}_{2-1,10} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_{-1}^2(\epsilon_0) \right] - C^{1-1}_{20,1-1} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_0^2(\epsilon_0) \right]_1 = \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle^2, \epsilon_0 \right]_1, \\
\]

\[
T^{(1^*)}_ρ(\epsilon_f^*, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21} = -C^{11}_{22,1-1} \left[ \epsilon_f^* \cdot Y_{22}(\hat{k}_f) \right] \left[ Y_{1-1}(\hat{k}_0) \cdot \epsilon_0 \right] - C^{11}_{21,10} \left[ \epsilon_f^* \cdot Y_{21}(\hat{k}_f) \right] \times \\
\times \left[ Y_{10}(\hat{k}_0) \cdot \epsilon_0 \right] - C^{11}_{20,11} \left[ \epsilon_f^* \cdot Y_{20}(\hat{k}_f) \right] \left[ Y_{11}(\hat{k}_0) \cdot \epsilon_0 \right] = -C^{11}_{22,1-1} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_{-2}^2(\epsilon_0) \right] + \\
- C^{11}_{21,10} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_{0}^2(\epsilon_0) \right] - C^{11}_{20,11} \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle_{1}^2(\epsilon_0) \right]_1 = \left[ \frac{\sqrt{15}}{4\pi\sqrt{2}} \langle \epsilon_f^*, \hat{k}_f \rangle^2, \epsilon_0 \right]_1.
\]

In a more compact form,
\[ T^{1s}_0(\epsilon_f^*, \hat{k}_f, \hat{\epsilon}_0, \hat{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi \sqrt{2}} \left( (\epsilon_f^*, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_{0} \]

\[ T^{1s}_1(\epsilon_f^*, \hat{k}_f, \hat{\epsilon}_0, \hat{\epsilon}_0)_{21} = -\frac{\sqrt{15}}{4\pi \sqrt{2}} \left( (\epsilon_f^*, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_{-1} \]

\[ T^{-1s}_1(\epsilon_f^*, \hat{k}_f, \hat{\epsilon}_0, \hat{\epsilon}_0)_{21} = -\frac{\sqrt{15}}{4\pi \sqrt{2}} \left( (\epsilon_f^*, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_{1} \]

or \(^3\)

\[ T^{1}_0(\epsilon_f^*, \hat{k}_f, \hat{\epsilon}_0, \hat{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi \sqrt{2}} \left( (\epsilon_f^*, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_{0} \]

\[ T^{-1}_1(\epsilon_f^*, \hat{k}_f, \hat{\epsilon}_0, \hat{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi \sqrt{2}} \left( (\epsilon_f^*, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_{1} \]

that is

\[ T^{1}_{\rho}(\epsilon_f^*, \hat{k}_f, \hat{\epsilon}_0, \hat{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi \sqrt{2}} \left( (\epsilon_f^*, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_{\rho}. \quad (3.18) \]

Similarly

\[ T^{1s}_{0}(\epsilon_f^*, \hat{k}_f, \hat{\epsilon}_0, \hat{\epsilon}_0)_{12} = -C^{10}_{10,20} \left[ \epsilon_f^* \cdot Y^*_{10}(\hat{k}_f) \right] \left[ Y^e_{20}(\hat{\epsilon}_0) \cdot \hat{\epsilon}_0 \right] - C^{10}_{11,21} \left[ \epsilon_f^* \cdot Y^e_{11}(\hat{k}_f) \right] \times \left[ Y^e_{21}(\hat{\epsilon}_0) \cdot \hat{\epsilon}_0 \right] - C^{10}_{11,21} \left[ \epsilon_f^* \cdot Y^e_{11}(\hat{k}_f) \right] \left[ Y^e_{21}(\hat{\epsilon}_0) \cdot \hat{\epsilon}_0 \right] = -C^{10}_{10,20} \left[ \frac{\sqrt{15}}{4\pi \sqrt{2}} (\epsilon_f^* \cdot Y^e_{10}(\hat{\epsilon}_0, \hat{\epsilon}_0))^2 \right] + \]

\[ -C^{10}_{11,21} \left[ \frac{\sqrt{15}}{4\pi \sqrt{2}} (\epsilon_f^* \cdot Y^e_{11}(\hat{\epsilon}_0, \hat{\epsilon}_0))^2 \right] - C^{10}_{11,21} \left[ \frac{\sqrt{15}}{4\pi \sqrt{2}} (\epsilon_f^* \cdot Y^e_{11}(\hat{\epsilon}_0, \hat{\epsilon}_0))^2 \right] = -\frac{\sqrt{15}}{4\pi \sqrt{2}} \left( (\epsilon_f^*, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_{0} \]

\(^3\)We use the relation of p. 61, Ref. [40],

\[ (M_{JM})^* = (-)^M M_{-M} \]

where \(M_{JM}\) is an irreducible tensor.
\[
T_{11}^{1s}(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{12} = C_{1-1,20}^{11} \left[ \hat{\epsilon}_f^* \cdot Y_{11}^e(\hat{k}_f) \right] \left[ Y_{20}^e(\hat{k}_0) \cdot \hat{\epsilon}_0 \right] + C_{11,2-1}^{11} \left[ \hat{\epsilon}_f^* \cdot Y_{10}^e(\hat{k}_f) \right] \times
\]
\[
\times \left[ Y_{22}^e(\hat{k}_0) \cdot \hat{\epsilon}_0 \right] + C_{11,2-2}^{11} \left[ \hat{\epsilon}_f^* \cdot Y_{11}^e(\hat{k}_f) \right] \left[ Y_{2-2}^e(\hat{k}_0) \cdot \hat{\epsilon}_0 \right] = C_{1-1,20}^{11} \left[ \frac{\sqrt{15}}{4\pi \sqrt{2}} (\hat{\epsilon}_f^*)_{-1} (\hat{\epsilon}_0, \hat{k}_0)_{-1} \right] +
\]
\[
+ C_{11,2-1}^{11} \left[ \frac{\sqrt{15}}{4\pi \sqrt{2}} (\hat{\epsilon}_f^*)_0 (\hat{\epsilon}_0, \hat{k}_0)_{-1} \right] + C_{11,2-2}^{11} \left[ \frac{\sqrt{15}}{4\pi \sqrt{2}} (\hat{\epsilon}_f^*)_1 (\hat{\epsilon}_0, \hat{k}_0)_{-1} \right] = \frac{\sqrt{15}}{4\pi \sqrt{2}} \left( \hat{\epsilon}_f^*, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_{-1}.
\]

In a more compact form

\[
T_{11}^{1s}(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{12} = -\frac{\sqrt{15}}{4\pi \sqrt{2}} \left( \hat{\epsilon}_f^*, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_0
\]

\[
T_{11}^{1s}(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi \sqrt{2}} \left( \hat{\epsilon}_f^*, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_{-1}
\]

\[
T_{11}^{1s}(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi \sqrt{2}} \left( \hat{\epsilon}_f^*, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_1
\]

or

\[
T_{11}^{1s}(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = -\frac{\sqrt{15}}{4\pi \sqrt{2}} \left( \hat{\epsilon}_f^*, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_0
\]

\[
T_{11}^{1s}(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = -\frac{\sqrt{15}}{4\pi \sqrt{2}} \left( \hat{\epsilon}_f^*, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_1
\]

\[
T_{11}^{1s}(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = -\frac{\sqrt{15}}{4\pi \sqrt{2}} \left( \hat{\epsilon}_f^*, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_{-1}
\]

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that is
\[ T^1_\rho(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{12} = \frac{-\sqrt{15}}{4\pi\sqrt{2}} \left( \hat{\epsilon}_f, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)_\rho. \]  
(3.19)

### 3.2.3 Geometrical factors

Using the results of Table 3.3, this section provides a useful form for the terms

\[ T^{x*}_\rho(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{12} \pm T^{x*}_\rho(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} \]

evaluated for \( x = 1, 2, 3. \)

1. **Case \( x = 1 \)**

We have
\[ T^{1*}_\rho(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{12} \pm T^{1*}_\rho(\hat{\epsilon}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = \frac{-\sqrt{15}}{4\pi\sqrt{2}} \left\{ \left( \hat{\epsilon}_f, (\epsilon_0, \hat{k}_0)^2 \right)_\rho \mp \left( (\epsilon_f, \hat{k}_f)^2, \hat{\epsilon}_0 \right)_\rho \right\}. \]

(3.20)

The foregoing relation can be simplified using the identity [40]
\[ ((A, B)^2, C)^1 = \sqrt{\frac{3}{5}} \left\{ \frac{1}{3} C(A \cdot B) - \frac{1}{2} B(A \cdot C) - \frac{1}{2} C(A \cdot C) \right\}, \]

with \( A, B \) and \( C \) rank one irreducible tensors. We obtain
\[ \left( \hat{\epsilon}_f, \hat{k}_f \right)^1_\rho = \sqrt{\frac{3}{5}} \left\{ \frac{1}{3} \hat{\epsilon}_f (\hat{\epsilon}_0 \cdot \hat{k}_f) - \frac{1}{2} \hat{k}_f (\hat{\epsilon}_f \cdot \hat{\epsilon}_0) - \frac{1}{2} \hat{\epsilon}_f (\hat{k}_0 \cdot \hat{\epsilon}_0) \right\}_\rho = \]
\[ = \frac{1}{2} \sqrt{\frac{3}{5}} \left\{ \hat{k}_f (\hat{\epsilon}_0 \cdot \hat{\epsilon}_0) + \hat{\epsilon}_f (\hat{k}_f \cdot \hat{\epsilon}_0) \right\}_\rho \]

and
\[ \left( \hat{\epsilon}_f, (\hat{\epsilon}_0, \hat{k}_0)^2 \right)^1_\rho = \left( \hat{\epsilon}_0, (\hat{k}_0)^2 \right)^1_\rho = \sqrt{\frac{3}{5}} \left\{ \frac{1}{3} \hat{\epsilon}_f (\hat{\epsilon}_0 \cdot \hat{k}_0) - \frac{1}{2} \hat{k}_0 (\hat{\epsilon}_0 \cdot \hat{\epsilon}_f) - \frac{1}{2} \hat{\epsilon}_0 (\hat{k}_0 \cdot \hat{\epsilon}_f) \right\}_\rho = \]
\[ = \frac{1}{2} \sqrt{\frac{3}{5}} \left\{ \hat{k}_0 (\hat{\epsilon}_0 \cdot \hat{\epsilon}_f) + \hat{\epsilon}_0 (\hat{k}_0 \cdot \hat{\epsilon}_f) \right\}_\rho. \]
Eq. (3.20) thus becomes

\[
T_\rho^{1*}(\vec{e}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{12} + T_\rho^{1*}(\vec{e}_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = \frac{3}{8\pi \sqrt{2}} \left\{ (\hat{\epsilon}_0 \cdot \vec{e}_f) (\hat{k}_0 \cdot \hat{\epsilon}_f + \hat{\epsilon}_0 \cdot \hat{\epsilon}_f) - (\hat{\epsilon}_f \cdot \hat{k}_f) + (\hat{\epsilon}_f \cdot \hat{k}_f) \right\},
\]

(3.21)

The term

\[
(\hat{\epsilon}_f \cdot \hat{k}_f) = (\hat{\epsilon}_0 \cdot \hat{k}_0) = 0
\]

(3.22)

is analyzed by separately treating the contributions with positive and negative sign. Remembering that

\[
[(A \times B) \times C] = -[A(B \cdot C) - B(A \cdot C)]
\]

and

\[
(\hat{\epsilon}_f \cdot \hat{k}_f) = (\hat{\epsilon}_0 \cdot \hat{k}_0) = 0
\]

one has

\[
(\hat{\epsilon}_0 \cdot \hat{k}_0) - (\hat{\epsilon}_f \cdot \hat{k}_f) = \left\{ \hat{\epsilon}_0 (\hat{k}_0 \cdot \hat{\epsilon}_f + \hat{\epsilon}_0 \cdot \hat{\epsilon}_f) - \hat{\epsilon}_f (\hat{\epsilon}_0 \cdot \hat{k}_f) + \right\}
\]

\[
= \left\{ \hat{\epsilon}_0 \left[ (\hat{k}_f + \hat{k}_0) \cdot \hat{\epsilon}_f - \hat{\epsilon}_f \left[ (\hat{k}_f + \hat{k}_0) \cdot \hat{\epsilon}_0 \right] \right] \right\}_\rho =
\]

\[
\left[ (\hat{\epsilon}_f \times \hat{\epsilon}_0) \times (\hat{k}_f + \hat{k}_0) \right]_\rho
\]

(3.23)

and

\[
(\hat{\epsilon}_f \cdot \hat{k}_f) + (\hat{\epsilon}_0 \cdot \hat{k}_f) = \left\{ (\hat{\epsilon}_f) (\hat{k}_f \cdot \hat{\epsilon}_0) + (\hat{\epsilon}_0) (\hat{k}_0 \cdot \hat{\epsilon}_f) - (\hat{\epsilon}_0) (\hat{k}_f \cdot \hat{\epsilon}_f) + \right\}
\]

\[
= \left\{ \hat{\epsilon}_f \left[ (\hat{k}_f - \hat{k}_0) \cdot \hat{\epsilon}_0 \right] - \hat{\epsilon}_0 \left[ (\hat{k}_f - \hat{k}_0) \cdot \hat{\epsilon}_f \right] \right\}_\rho =
\]

\[
\left[ (\hat{\epsilon}_f \times \hat{\epsilon}_0) \times (\hat{k}_0 - \hat{k}_f) \right]_\rho.
\]

(3.24)

Expression (3.22) can thus be rewritten as

\[
(\hat{\epsilon}_0 \cdot \hat{k}_0) + (\hat{\epsilon}_f \cdot \hat{k}_f) = \left[ (\hat{\epsilon}_f \times \hat{\epsilon}_0) \times (\hat{k}_0 \pm \hat{k}_f) \right]_\rho
\]
so that expression (3.21) takes the form
\[
T_\rho^{1s}(\vec{\epsilon}_f, \vec{k}_f, \vec{k}_0, \vec{\epsilon}_0)_{12} \pm T_\rho^{1s}(\vec{\epsilon}_f, \vec{k}_f, \vec{k}_0, \vec{\epsilon}_0)_{21} = \frac{3}{8\pi\sqrt{2}} \left\{ (\vec{\epsilon}_0 \cdot \vec{\epsilon}_f)(\vec{k}_0 \mp \vec{k}_f) + \right.
\]
\[
\left. + (\vec{\epsilon}_f \times \vec{\epsilon}_0) \times (\vec{k}_0 \pm \vec{k}_f) \right\}_\rho \quad (3.25)
\]

2. Case \( x = 2 \)

The cases \( x = 2 \) and \( x = 3 \) will be treated by recoupling techniques. (These techniques have been discussed in chapter one, see for example Sect. 1.3.1.)

For \( x = 2 \) we have
\[
T_\rho^2(\vec{\epsilon}_f, \vec{k}_f, \vec{k}_0, \vec{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi\sqrt{2}} \left( \vec{\epsilon}_f, \vec{k}_f \right)^2 = -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( \vec{\epsilon}_0, \vec{\epsilon}_f, \vec{k}_f \right)^2 =
\]
\[
= -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left\{ \sum_{\nu'\beta} -\sqrt{5(2\nu+1)} \left\{ \begin{array}{ccc} 1 & 1 & \nu \\ 1 & 2 & 2 \end{array} \right\} C_{1\beta,1\alpha} C_{\nu\nu',1\beta} \vec{\epsilon}_0 \vec{\epsilon}_f^* \vec{k}_{f\beta} \right\} =
\]
\[
= -\frac{15}{8\pi\sqrt{10}} \left( \vec{\epsilon}_0, \vec{\epsilon}_f^* \right)^2 - \frac{\sqrt{15}}{8\pi\sqrt{2}} \left( \vec{\epsilon}_0, \vec{\epsilon}_f^* \right)^2 \rho .
\]

and
\[
T_\rho^2(\vec{\epsilon}_f, \vec{k}_f, \vec{k}_0, \vec{\epsilon}_0)_{12} = -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( \vec{\epsilon}_f, \vec{k}_0 \right)^2 \rho =
\]
\[
= -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left\{ \sum_{\nu'\beta} (-)\sqrt{5(2\nu+1)} \left\{ \begin{array}{ccc} 1 & 1 & \nu \\ 1 & 2 & 2 \end{array} \right\} C_{1\beta,1\alpha} C_{\nu\nu',1\beta} \vec{\epsilon}_0 \vec{\epsilon}_f^* \vec{k}_{0\beta} \right\} =
\]
\[
= \frac{15}{8\pi\sqrt{10}} \left( \vec{\epsilon}_0, \vec{\epsilon}_f^* \right)^2 - \frac{\sqrt{15}}{8\pi\sqrt{2}} \left( \vec{\epsilon}_0, \vec{\epsilon}_f^* \right)^2 \rho .
\]

(Numerical values for the 6J Symbols, in the case of \( \nu = 0, 1, 2 \) are given on section 1.5).

We obtain
\[
T_\rho^2(\vec{\epsilon}_f, \vec{k}_f, \vec{k}_0, \vec{\epsilon}_0)_{12} \pm T_\rho^2(\vec{\epsilon}_f, \vec{k}_f, \vec{k}_0, \vec{\epsilon}_0)_{21} = \frac{15}{8\pi\sqrt{10}} \left( \vec{\epsilon}_0, \vec{\epsilon}_f^* \right)^2 +
\]
\[
- \frac{\sqrt{15}}{8\pi\sqrt{2}} \left( \vec{\epsilon}_0, \vec{\epsilon}_f^* \right)^2 \rho . \quad (3.26)
\]
3. Case $x = 3$

Again, from the same recoupling relations, we get

$$T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \hat{\epsilon}_0)_{21} = \frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\epsilon^*_f, \epsilon_0)^2, \hat{k}_f \right)^3_{\rho}$$

and

$$T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{12} = -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\epsilon^*_f, \epsilon_0)^2, (\hat{k}_0 + \hat{k}_f) \right)^3_{\rho}.$$ 

Consequently

$$T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{12} + T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21} = -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\epsilon^*_f, \epsilon_0)^2, (\hat{k}_0 + \hat{k}_f) \right)^3_{\rho}.$$  \hspace{1cm} (3.27)

The geometrical factors of $E1-E2$ x-ray resonant diffraction are summarized in Table 3.4.

| $T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{12} + T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21}$ | $= \frac{3}{8\pi\sqrt{2}} \left\{ (\epsilon_0 \cdot \epsilon^*_{\rho}) (\hat{k}_0 + \hat{k}_f) + (\epsilon^*_{\rho} \times \epsilon_0) \times (\hat{k}_0 + \hat{k}_f) \right\}$ |
| $T^2_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{12} + T^2_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21}$ | $= \frac{15}{8\pi\sqrt{10}} \left( (\epsilon_0, \epsilon^*_{\rho})^1, (\hat{k}_0 + \hat{k}_f) \right)^2 - \frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\epsilon_0, \epsilon^*_{\rho})^2, (\hat{k}_0 + \hat{k}_f) \right)^2$ |
| $T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{12} + T^3_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21}$ | $= -\frac{\sqrt{15}}{4\pi\sqrt{2}} \left( (\epsilon^*_f, \epsilon_0)^2, (\hat{k}_0 + \hat{k}_f) \right)^3_{\rho}$ |

Table 3.4: All possible combinations $T^x_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{12} + T^x_{\rho}(\epsilon^*_f, \hat{k}_f, \hat{k}_0, \epsilon_0)_{21}$.

### 3.3 Electronic properties

This section examines the electronic components $F^x_{\rho}(\omega)_{L/L'}$ of the scattering amplitude. We consider $E1-E2$ resonant processes, i.e. $L' = 2, L = 1$ and $L' = 1, L = 2$. These contributions will be expressed in terms of effective one electron operators.

Following the work of Luo et al. [16], we have introduced the tensor

$$F^x_{\rho}(\omega)_{L/L'} = \sqrt{\frac{2x + 1}{2L + 1}} \sum_{MM'} C^{LM}_{L'M'x\rho} \langle \psi_f | F^e_{L'M',LM}(\omega) | \psi_0 \rangle,$$
where
\[
\langle \psi_f | \mathbf{F}_{L'M',LM}^e | \psi_0 \rangle = \sum_I \frac{\langle \psi_f | \mathbf{J}_{L'M'}^e | I \rangle \langle I | \mathbf{J}_{LM}^e | \psi_0 \rangle}{2\lambda_{IO} (E_I - E_0 - \hbar \omega - i\frac{\Gamma_I}{2})}. \tag{3.28}
\]

Putting
\[
\mathbf{J}_{L'M'}^\dagger = \sum_{m'_c m'_s} \sum_{l'_m' m'_s} \sum_{l_m m_s} \sum_{l'_m m'_s} \langle \psi_f | \mathbf{c}_{j c m'_j c m'_j} \mathbf{a}_{l'_m m'_s} \mathbf{c}_{j c m_j c} | I \rangle \langle I | \mathbf{c}_{l_m m_s} \mathbf{a}_{l'_m m'_s} \mathbf{c}_{j c m_j c} | \psi_0 \rangle
\]
and
\[
\mathbf{J}_{LM} = \sum_{m_c m_s} \sum_{l_m m_s} \sum_{l'_m m'_s} \sum_{l'_m m'_s} \langle \psi_f | \mathbf{c}_{j c m'_j c m'_j} \mathbf{a}_{l'_m m'_s} \mathbf{c}_{j c m_j c} | I \rangle \langle I | \mathbf{c}_{l_m m_s} \mathbf{a}_{l'_m m'_s} \mathbf{c}_{j c m_j c} | \psi_0 \rangle
\]
Eq. (3.28) becomes
\[
\langle \psi_f | \mathbf{F}_{L'M',LM}^e | \psi_0 \rangle = \sum_I \frac{\langle \psi_f | \mathbf{c}_{j c m'_j c m'_j} \mathbf{a}_{l'_m m'_s} \mathbf{c}_{j c m_j c} | I \rangle \langle I | \mathbf{c}_{l_m m_s} \mathbf{a}_{l'_m m'_s} \mathbf{c}_{j c m_j c} | \psi_0 \rangle}{2\lambda_{IO} (E_I - E_0 - \hbar \omega - i\frac{\Gamma_I}{2})}.
\tag{3.29}
\]

We will only consider the case of elastic scattering (| \psi_f \rangle = | \psi_0 \rangle) and work in the "fast collision approximation", which is equivalent to neglecting the dispersion of the intermediate states; \(E_I\) and \(\Gamma_I\) can be taken as constants, and the expansion for the resonant denominator:
\[
\frac{1}{E_I - E_0 - \hbar \omega - i\frac{\Gamma_I}{2}} = \frac{1}{E_I} - \frac{1}{E_I} \times \frac{E_I - E_0 - \hbar \omega - i\frac{\Gamma_I}{2}}{E_I - E_0 - \hbar \omega - i\frac{\Gamma_I}{2}} \times \sum_{l=0}^{\infty} \left( \frac{E_I - E_0 - \hbar \omega - i\frac{\Gamma_I}{2}}{E_I - E_0 - \hbar \omega - i\frac{\Gamma_I}{2}} \right)^l
\]
truncated at \(n = 0\). The physical interpretation of this approximation is described in Ref. [16], which we verbatim quote:

4We have
\[
\mathbf{Y}_{LM} = \langle l_m | \langle \frac{1}{2} m_s | - \frac{4\pi}{2L+1} \mathbf{Q}_{LM} | n_{c,jc m_{j_c}} \rangle | \frac{1}{2} m_{s_c} \rangle C_{l_m m_s} C_{j_c m_{j_c}}
\]
and
\[
\mathbf{Y}_{L'M'} = \langle n_{c,jc m'_{j_c}} | \langle \frac{1}{2} m'_{s_c} | - \frac{4\pi}{2L'+1} \mathbf{Q}_{L'M'} | l'' m'' \rangle | \frac{1}{2} m'' \rangle C_{l'' m''} C_{j_c m_{j_c}}
\]
Core and valence states have been written using respectively relations 1.6 and 1.7.

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“... this is the fast collision approximation: when the core electron is initially injected into an empty orbital of the valence shell, then generally it and the core hole exert torques on each other and the state of these electrons. The rate at which these charges take places however, is determined by $\Delta E_I$ and to a good approximation they can be neglected if $\Delta E_I T$ is small, where $T = |\Delta \omega - i\frac{\Gamma}{2}|^{-1}$ measures the collision duration $^5$ ...”

In Ref. [16] the limits of this approximation are clearly stated$^6$. They read:

“... the fast collision results should be rather good for resonant scattering at the $l$ and $L_3$ edges in the rare earths and actinides as well as for the $M_4$ and $M_5$ edges in the actinides, for which ($\Delta \ll \Gamma$) and the splitting is not resolved$^7$ ...

When these conditions are not verified

“... the simplicity of the fast collision approximation can be regained by tuning off resonance so that $\Delta \ll \Delta \omega$ ...”

By making the fast collision approximation, putting $< E_I > = \bar{E}_I$ and $< \Gamma_I > = \Gamma$, Eq. (3.29) can be written as:

$$
\langle \psi_0 \mid F_{L'M',LM}^0 \mid \psi_0 \rangle = \frac{1}{2\lambda(E_I - E_0 - \hbar \omega - i\frac{\Gamma}{2})} \sum_{m_j, m_{j'} c} \sum_{l_{m_l m_s}} \sum_{m_{c c'} l_{m_l m_s}} \langle \psi_0 \mid \hat{c}^\dagger_{j' m_{j'} c} \gamma_{L'M'} \hat{a}_{l m_{l} m_{s} c} \times

\hat{c}_{j m_{j} c} \gamma_{L M} \hat{a}^\dagger_{l m_{l} m_{s}} \mid \psi_0 \rangle.
$$

(3.30)

$^5\Delta \omega = E_I - E_0 - \hbar \omega.$

$^6$See also references [102, 103, 104, 105, 106].

$^7$Delta represent the energy splitting of the valence multiplet.
After a considerable amount of algebra, the foregoing result can be expressed as:

\[
\langle \psi_0 | \mathbf{F}_{L',M',LM} (\omega) | \psi_0 \rangle = (-)^{l' + y - l + L - x} \frac{4\pi e^2 i L (i L')^{\dagger} k^{L + L'}}{(2L' + 1)!!(2L + 1)!!} \times \\
\times (2l_c + 1)(2y + 1) \sqrt{\frac{(L + 1)(L' + 1)(2L + 1)(2L' + 1)}{2(2L' + 1)}(2j_c + 1)(2\alpha + 1)R_{l'l'}^L R_{l'l'}^{L'} \delta_{m_s,m_s'} \times \\
\times \delta_{m_{sc},m_{sc}'} C^{d_0}_{l',0,L'0} C^{d_0}_{l,0,L0} \left\{ \begin{array}{ccc}
l_c & l_c & \alpha \\
\frac{1}{2} & \frac{1}{2} & j_c \end{array} \right\} \left\{ \begin{array}{ccc}L' & l' & l_c \\
L & l & l_c \\
x & y & \alpha \end{array} \right\} C^{\alpha_\gamma}_{L' - M',LM} C^{i m_{l',y - \mu}}_{l'm_{l',y - \mu}} C^{\beta_\delta}_{m_{sc} \alpha \beta} C^{\alpha_\gamma}_{y - \mu, \alpha \beta} \times \\
\times \frac{\langle \psi_0 | \mathbf{a}_{l'm_{l',y - \mu}}^{\dagger} \mathbf{a}_{l'm_{l',y - \mu}} | \psi_0 \rangle}{(E_I - E_0 - \hbar \omega - i \frac{1}{2})}.\]

(3.31)

Eq. (3.7) takes then the form:

\[
F^x_\rho (\omega)_{L'L} = (-)^{l' + y - l + L - x} \frac{4\pi e^2 i L (i L')^{\dagger} k^{L + L'}}{(2L' + 1)!!(2L + 1)!!} \times \\
\times \sqrt{\frac{(L + 1)(L' + 1)(2L + 1)(2L' + 1)}{2(2L' + 1)}(2j_c + 1)(2\alpha + 1)R_{l'l'}^L R_{l'l'}^{L'} \delta_{m_s,m_s'} \delta_{m_{sc},m_{sc}'} C^{d_0}_{l',0,L'0} \times \\
\times C^{d_0}_{l,0,L0} \left\{ \begin{array}{ccc}l_c & l_c & \alpha \\
\frac{1}{2} & \frac{1}{2} & j_c \end{array} \right\} \left\{ \begin{array}{ccc}L' & l' & l_c \\
L & l & l_c \\
x & y & \alpha \end{array} \right\} C^{i m_{l',y - \mu}}_{l'm_{l',y - \mu}} C^{\beta_\delta}_{m_{sc} \alpha \beta} \frac{\langle \psi_0 | \mathbf{a}_{l'm_{l',y - \mu}}^{\dagger} \mathbf{a}_{l'm_{l',y - \mu}} | \psi_0 \rangle}{(E_I - E_0 - \hbar \omega - i \frac{1}{2})}.\]

(3.32)

where $l'$ and $l$ represent the final states reached through the transition operator $\mathbf{J}^\dagger_{L'M'}$ and $\mathbf{J}_{LM}$. [A similar expression for Eq. (3.9) is obtained from the (3.32) by exchanging $L$ with $L'$, $l$ with $l'$ and $m_l$ with $m_l'$.] Using the symmetry properties

\[
\left\{ \begin{array}{ccc}L' & l' & l_c \\
L & l & l_c \\
x & y & \alpha \end{array} \right\} = (-)^R \left\{ \begin{array}{ccc}L & l & l_c \\
L' & l' & l_c \\
x & y & \alpha \end{array} \right\}
\]

The mathematical details, which are very similar to those described in chapter 1 for x-ray dichroism, will be omitted.
(R = \sum_{i,j} a_{ij} with a_{i,j} generic element of the 9J Symbol), it is possible express the combinations $F^\pi_\rho(\omega)_{LL'} \pm F^\pi_\rho(\omega)_{L'L}$ and $F^\pi_\rho(\omega)_{LL'} - F^\pi_\rho(\omega)_{L'L}$ as follows

$$F^\pi_\rho(\omega)_{LL'} \pm F^\pi_\rho(\omega)_{L'L} = (-)\langle \psi_0 | \sum_{lm_l m_s} \sum_{lm'_l m'_s} \frac{1}{2\lambda(E_I - E_0 - \hbar \omega - i\frac{\hbar}{2})} (-)^{j_c + \frac{1}{2} y - x - l + L} \times$$

$$\times \frac{4\pi e^2 i\ell' (iL')^l k^{L+L'}}{(2L'+1)! (2L+1)!} \sqrt{(L+1)(L'+1)(2L+1)(2L'+1)/(2(L'L))} (2y+1)(2l_c+1)(2j_c+1) \times$$

$$\times (2\alpha + 1) R_{l_c}^{L_c} R_{l'_c}^{L'_c} C_{l_0,0,L_0}^{C_{l_0,0}} \left\{ \frac{l_c}{2}, \frac{l_c}{2}, \frac{l_c}{2}, \frac{l_c}{2}, j_c \right\} \times \left\{ L \ l \ l_c \right\} \times$$

$$\times \left\{ L' \ l' \ l_c \right\} \times \left\{ x \ y \ \alpha \right\} \times$$

$$\left[ \frac{C_{l'_m, y - \mu C_{l'_m, y - \mu}^* \hat{\alpha}_{l'_m m_s} \hat{\alpha}_{l' m_s^*}}}{\sqrt{2l'+1}} \mp (-)^R \frac{C_{l''_m, y - \mu C_{l''_m, y - \mu}^* \hat{\alpha}_{l'' m_s} \hat{\alpha}_{l'' m_s^*}}}{\sqrt{2l+1}} \right] C_{y - \mu, \alpha \beta} \langle \psi_0 \rangle.$$  \hspace{1cm} (3.33)

We will consider the case $L' = 2$ and $L = 1$ ($E_1E_2$ transition).

### 3.4 K edge excitations

This section analyzes a particular case of x-ray resonant scattering: the K edge, where no spin contributions are present in the observed signal. Such a case corresponds to setting $\alpha = 0$ in Eq. (3.33). As a consequence,

$$\left\{ \begin{array}{ccc} L & l & l_c \\ L' & l' & l_c \\ x & x & 0 \end{array} \right\} = \frac{(-)^{(l+L'+l_c+x)}}{\sqrt{(2l_c+1)(2x+1)}} \left\{ \begin{array}{ccc} L & l & l_c \\ l' & L' & x \end{array} \right\}$$

so that Eq. (3.33) becomes

$$F^\pi_\rho(\omega)_{LL'} \pm F^\pi_\rho(\omega)_{L'L} = \frac{4\pi e^2 i\ell' (iL')^l k^{L+L'}}{2\lambda(E_I - E_0 - \hbar \omega - i\frac{\hbar}{2})(2L'+1)! (2L+1)!} (2j_c + 1) \times$$

---

9The absence of the spin orbit interaction in the s orbitals forbid the observation of the spin proprieties through x-ray scattering (and x-ray absorption) experiments.
\[ \times \sum_{L'} (-)^x R_{l_{t'}} R_{l_{t}L'} \sqrt{(L+1)(L'+1)(2L+1)(2L'+1)(2x+1)} C_{t_{l_{t}L'}t_{L'0}}^{t_{l_{t}L}t_{0}L} \{ L \ l \ l_c \} \times \]

\[ \times \left[ \sum_{m_{l_{t}m_{l}}'} \langle \psi_0 | \frac{C_{l_{m_{l}m_{l}}'} a_{l_{m_{l}m_{l}}'} a_{t_{m_{l}}}}{\sqrt{2l' + 1}} \right] = 1 \langle \psi_0 | \psi_0 \rangle \right]. \tag{3.34} \]

This relation is further simplified by evaluating the product

\[ C_{t_{l_{t}L'}t_{L'0}}^{t_{l_{t}L}t_{0}L} \{ L \ l \ l_c \} \]

for \( x = 1, 2, 3 \) and \( L' = 2, L = 1 \), and by expressing

\[ \frac{C_{l_{m_{l}m_{l}}'} a_{l_{m_{l}m_{l}}'} a_{t_{m_{l}}}}{\sqrt{2l' + 1}} \]

as combination of one-electron operators. As described in chapter 1, the combination

\[ \frac{C_{l_{m_{l}m_{l}}'} a_{l_{m_{l}m_{l}}'} a_{t_{m_{l}}}}{\sqrt{2l' + 1}} + \frac{C_{l_{m_{l}m_{l}}'} a_{l_{m_{l}m_{l}}'} a_{t_{m_{l}}}}{\sqrt{2l' + 1}} \]

can be expressed in terms of a rank \( x \) effective operator which is obtained coupling \( \Omega \) and \( L \). The case of

\[ \frac{C_{l_{m_{l}m_{l}}'} a_{l_{m_{l}m_{l}}'} a_{t_{m_{l}}}}{\sqrt{2l' + 1}} - \frac{C_{l_{m_{l}m_{l}}'} a_{l_{m_{l}m_{l}}'} a_{t_{m_{l}}}}{\sqrt{2l' + 1}} \]

correspond to a rank \( x \) effective operator, which is obtained coupling \( n \) and \( L \). Separating the contributions \( x = 1, 2, 3 \) in Eq. (3.34), we write the scattering amplitude \( f_{E1-E2} \) as

\[ f_{E1-E2} = f_{x=1} + f_{x=2} + f_{x=3}. \tag{3.36} \]

From Eq. (3.10), using the tensors given in Table (3.4) and expressing Eq. (3.34) in terms of one electron effective operators, we obtain

\[ f_{x=1} = -2\pi \frac{\lambda^2 \pi^3}{20 \lambda^2} \sum_{l_{t}l_{t'}} R_{l_{t}l_{t'}}^2 (-)^x \left\{ a_{l_{t'}}(l_{t}, l_{c})(\hat{\epsilon}_0 \cdot \hat{\epsilon}_f)(\hat{k}_f + \hat{k}_0) + (\hat{\epsilon}_f^* \times \hat{\epsilon}_0) \times (\hat{k}_0 - \hat{k}_f) \right\} \times \]

\[ \times \langle \psi_0 | \sum_i |O(l, l')^{(1-)}|_i \psi_0 \rangle - i a_{l_{t'}}(l_{t}, l_{c})(\hat{\epsilon}_0 \cdot \hat{\epsilon}_f)(\hat{k}_f - \hat{k}_0) + (\hat{\epsilon}_f^* \times \hat{\epsilon}_0) \times (\hat{k}_f + \hat{k}_0) \right\} \times \]

\[ \times \langle \psi_0 | \sum_i |O(l, l')^{(1+)}|_i \psi_0 \rangle \right\}. \tag{3.37} \]
The effective operators for $E_1-E_2$ x-ray resonant scattering are listed in Table 3.5. The

<table>
<thead>
<tr>
<th>$x$</th>
<th>$O^{(x+)}$</th>
<th>$O^{(x-)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\hat{n}$</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>2</td>
<td>$(\Omega, L)^2$</td>
<td>$(n, L)^2$</td>
</tr>
<tr>
<td>3</td>
<td>$(n, (L, L)^2)^3$</td>
<td>$(\Omega, (L, L)^2)^3$</td>
</tr>
</tbody>
</table>

Table 3.5: Six effective operators detectable by x-ray scattering from the K edge.

coefficients $a^{(x \pm)}$ ($x = 1, 2, 3$) are depicted in Table 3.6. Relations (3.36-3.39) identify properties of the valence electrons which can be probed by x-ray resonant diffraction in noncentrosymmetric crystals when the “fast-collision approximation” hold.

Given their different angular dependences, the various terms $O^{(x \pm)}$ can be selected experimentally. In particular relations (3.36-3.39) indicate the possibility of detecting fer-
Explicitly, for...

Going over the geometrical setting of Blume and Gibbs [107], we introduce a set of basis vectors $U_i$ which are defined by

$$U_1 = \frac{\hat{k}_0 + \hat{k}_f}{2\cos\theta}, \quad U_2 = \frac{\hat{k}_0 \times \hat{k}_f}{2\sin\theta}, \quad U_3 = \frac{\hat{k}_0 - \hat{k}_f}{2\sin\theta}.$$

To reproduce typical experimental conditions, it is convenient to write the scattering amplitude in the basis of two set of orthogonal vectors:

$$\tilde{\epsilon}_{0\parallel} = \sin\theta U_1 - \cos\theta U_3 \quad \tilde{\epsilon}_{0\perp} = -U_2$$

$$\tilde{\epsilon}_{f\parallel} = -(\sin\theta U_1 + \cos\theta U_3) \quad \tilde{\epsilon}_{f\perp} = -U_2.$$

In this formalism, the resonant scattering amplitude can be written as a $2 \times 2$ matrix.

Explicitly, for $x = 1$, the $2 \times 2$ matrix takes the form:

$$X = \begin{pmatrix}
    f_{x=1}(\epsilon_{f\parallel}, \hat{k}_f, \hat{k}_0, \epsilon_{0\parallel}) & f_{x=1}(\epsilon_{f\perp}, \hat{k}_f, \hat{k}_0, \epsilon_{0\perp}) \\
    f_{x=1}(\epsilon_{f\parallel}, \hat{k}_f, \hat{k}_0, \epsilon_{0\perp}) & f_{x=1}(\epsilon_{f\perp}, \hat{k}_f, \hat{k}_0, \epsilon_{0\perp})
\end{pmatrix} = -2\pi \lambda \frac{e^2 \pi^3}{20\lambda^4} \sum_{ll'} R_{l,l'}^1 R_{l,l'}^2 \begin{pmatrix}
    X_{11} & X_{12} \\
    X_{21} & X_{22}
\end{pmatrix},$$

Table 3.6: The numerical coefficients to be used in Rel. (3.39)

roelectric and antiferroelectric Bragg peaks, using x-ray resonant diffraction. These not-yet-observed resonant reflections would be determined by $O^{(1+)} = n$. 

Blume and Gibbs [107], we introduce a set of basis vectors $U_i$ which are defined by

$$U_1 = \frac{\hat{k}_0 + \hat{k}_f}{2\cos\theta}, \quad U_2 = \frac{\hat{k}_0 \times \hat{k}_f}{2\sin\theta}, \quad U_3 = \frac{\hat{k}_0 - \hat{k}_f}{2\sin\theta}.$$

To reproduce typical experimental conditions, it is convenient to write the scattering amplitude in the basis of two set of orthogonal vectors:

$$\tilde{\epsilon}_{0\parallel} = \sin\theta U_1 - \cos\theta U_3 \quad \tilde{\epsilon}_{0\perp} = -U_2$$

$$\tilde{\epsilon}_{f\parallel} = -(\sin\theta U_1 + \cos\theta U_3) \quad \tilde{\epsilon}_{f\perp} = -U_2.$$

In this formalism, the resonant scattering amplitude can be written as a $2 \times 2$ matrix.

Explicitly, for $x = 1$, the $2 \times 2$ matrix takes the form:

$$X = \begin{pmatrix}
    \frac{4(2x+1)(l_0+l+1)(l_0+2l'-l+1)}{(l+l_0)(l+l_0+2)(l'+l+1)} \\
    \frac{2(2x+1)(2l'+1)(2l'+2)(l_0+l_0+2)(l+2l'-2l'+l+1)}{(l+l_0)(l+l_0+2)(l'+l+1)(l'+l+2)}
\end{pmatrix} = -2\pi \lambda \frac{e^2 \pi^3}{20\lambda^4} \sum_{ll'} R_{l,l'}^1 R_{l,l'}^2 \begin{pmatrix}
    X_{11} & X_{12} \\
    X_{21} & X_{22}
\end{pmatrix},$$

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Figure 3.1: \( U_1, U_2, U_3 \) define a basis set. \( \vec{e}_\perp \) and \( \vec{e}_\parallel \) are the components of the polarization perpendicular and parallel to the diffraction plane.

where

\[
X_{11} = a^{(1-)} \left[ -2\cos\theta \left( 1 - 4\sin^2\theta \right) \right] \langle \psi_0 | U_1 \cdot \Omega | \psi_0 \rangle - i a^{(1+)} \left[ 2\sin\theta \left( 1 - 4\cos^2\theta \right) \right] \langle \psi_0 | U_3 \cdot n | \psi_0 \rangle
\]

\[
X_{12} = -\sin 2\theta \left( -a^{(1-)} \langle \psi_0 | U_2 \cdot \Omega | \psi_0 \rangle - i a^{(1+)} \langle \psi_0 | U_2 \cdot n | \psi_0 \rangle \right)
\]

\[
X_{21} = \sin 2\theta \left( -a^{(1-)} \langle \psi_0 | U_2 \cdot \Omega | \psi_0 \rangle + i a^{(1+)} \langle \psi_0 | U_2 \cdot n | \psi_0 \rangle \right)
\]

\[
X_{22} = -2a^{(1-)} \cos\theta \langle \psi_0 | U_1 \cdot \Omega | \psi_0 \rangle + 2i a^{(1+)} \sin \theta \langle \psi_0 | U_3 \cdot n | \psi_0 \rangle
\]

The matrix elements \( X_{ij} \) \((i,j = 1,2)\) provide the angular dependence of \( f_{x=1} \) when a well defined “polarization channel” \( \langle \vec{e}_{i\parallel} | \vec{e}_{f\parallel} | \vec{e}_{i\perp} | \vec{e}_{f\perp} \rangle \) or \( \langle \vec{e}_{i\perp} | \vec{e}_{f\perp} \rangle \) is chosen. As an example, consider \( X_{11} \), which refers to the case of ingoing and outgoing photons parallel to the diffraction plane. It is then clear that \( f_{x=1} \) picks out \( \Omega \) (projected along the \( U_1 \) axis) and \( n \) (projected along \( U_3 \) axis). Choosing the scattering angle so that \( 1 - \sin^2 \theta = 0 \) would select \( n \) only. In this case, Bragg peaks from ferro- or antiferroelectric structures could be observed.
3.4.1 Appendix: case $\alpha = 1$

This section completes the analysis of the scattering amplitude to include the terms which arise when $\alpha = 1$ in Eq. (3.33). As shown in Sect. 3.2, the angular factor

$$T^{x*}_\rho(\mathbf{c}_f, \mathbf{k}_f, \mathbf{k}_0, \mathbf{c}_0)_{12} \pm T^{x*}_\rho(\mathbf{c}_f, \mathbf{k}_f, \mathbf{k}_0, \mathbf{c}_0)_{21}$$

is independent of $\alpha$. On the contrary, the function $F^x_\rho(\omega)_{12} \pm F^x_\rho(\omega)_{21}$ is given by the sum of two terms, one corresponding to $\alpha = 0$ (see Sect. 3.4) and the other corresponding to $\alpha = 1$.

Consider the term

$$\left[ C^m_{lm_1,y;\mu} C^m_{lm_2,\alpha\beta} \hat{a}^\dagger_{lm_1 m_2} \hat{a}_{lm_2 m_1} \right] \pm (-)^R \left[ C^m_{lm_1,y;\mu} C^m_{lm_2,\alpha\beta} \hat{a}^\dagger_{lm_1 m_2} \hat{a}_{lm_2 m_1} \right] C^{x\rho}_{y;\mu,\alpha\beta} (3.40)$$

which identifies a spin and orbital rank-x effective operator. As shown below, the physical operators which stem from expression (3.40) are readily identified by applying the Wigner-Eckart theorem.

Again, we distinguish two cases, which correspond to the plus and minus sign in Eq. (3.40). In the former case (plus sign), effective tensors are obtained by coupling the spin operator $\mathbf{S}$ to $\mathbf{O}^{(1-)}$, $\mathbf{O}^{(2+)}$ and $\mathbf{O}^{(3-)}$ respectively. In the latter case (minus sign), $\mathbf{S}$ is coupled to $\mathbf{O}^{(1+)}$, $\mathbf{O}^{(2-)}$ and $\mathbf{O}^{(3+)}$. These spin and orbital operators will be denoted by

$$\mathbf{S}^{(y\alpha)x,\pm} = (\mathbf{O}^{(y,\pm)}, \mathbf{S})^{x,\pm},$$

for $\alpha = 1$. Needless to say that, for $\alpha = 0$,

$$\mathbf{S}^{(y\alpha)x,\pm} = 2\mathbf{O}^{(y,\pm)}.$$  

We thus have

$$f_{E1-E2} = \sum_{y\alpha \pm} \sum_{R^{l\pm}_l} R^{l\pm}_l R^{l\pm}_l (-)^{l_1} \hat{T}^{x,\pm}_\rho(\mathbf{c}_f, \mathbf{k}_f, \mathbf{k}_0, \mathbf{c}_0) \langle g | \mathbf{S}^{(y\alpha)x,\pm}_\rho | g \rangle .$$

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with
\[
\hat{T}^{(1\pm)}(\mathbf{c}^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{e}_0) = \frac{3}{8\pi \sqrt{2}} \left\{ (\mathbf{c}_0 \cdot \mathbf{c}_f) (\mathbf{k}_0 \mp \mathbf{k}_f) + (\mathbf{c}_f^* \times \mathbf{e}_0) \times (\mathbf{k}_0 \pm \mathbf{k}_f) \right\}
\]
\[
\hat{T}^{(2\pm)}(\mathbf{c}^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{e}_0) = \frac{15}{8\pi \sqrt{10}} (\mathbf{e}_0, \mathbf{e}_f^*) (\mathbf{k}_0 \mp \mathbf{k}_f)^2 - \frac{\sqrt{15}}{8\pi \sqrt{2}} ((\mathbf{e}_0, \mathbf{e}_f^*)^2, (\mathbf{k}_0 \pm \mathbf{k}_f))^2
\]
and
\[
\hat{T}^{(3\pm)}(\mathbf{c}^*, \mathbf{k}_f, \mathbf{k}_0, \mathbf{e}_0) = -\frac{\sqrt{15}}{4\pi \sqrt{2}} ((\mathbf{e}_f, \mathbf{e}_0)^2, (\mathbf{k}_0 \mp \mathbf{k}_f))^3.
\]

Explicit expressions for \(S^{(y\alpha)\pm}\) are given in Table 3.7. Notice that sum rules for \(E1-\)

| \(y = 1, \alpha = 0, x = 1\) | \(2\Omega\) | \(2\mathbf{n}\) |
| \(y = 2, \alpha = 0, x = 2\) | \(2(\mathbf{n}, \mathbf{L})^2\) | \(2(\Omega, \mathbf{L})^2\) |
| \(y = 3, \alpha = 0, x = 3\) | \(2(\Omega, (\mathbf{L}, \mathbf{L})^2)^3\) | \(2(\mathbf{n}, (\mathbf{L}, \mathbf{L})^2)^3\) |
| \(y = 1, \alpha = 1, x = 1\) | \(\mathbf{n} \times \mathbf{S}\) | \(\Omega \times \mathbf{S}\) |
| \(y = 1, \alpha = 1, x = 2\) | \((\mathbf{n}, \mathbf{S})^2\) | \((\Omega, \mathbf{S})^2\) |
| \(y = 2, \alpha = 1, x = 1\) | \((\Omega, \mathbf{L})^2, \mathbf{S})^1\) | \((\mathbf{n}, \mathbf{L})^2, \mathbf{S})^1\) |
| \(y = 2, \alpha = 1, x = 2\) | \((\Omega, \mathbf{L})^2, \mathbf{S})^2\) | \((\mathbf{n}, \mathbf{L})^2, \mathbf{S})^2\) |
| \(y = 2, \alpha = 1, x = 3\) | \((\Omega, \mathbf{L})^2, \mathbf{S})^3\) | \((\mathbf{n}, \mathbf{L})^2, \mathbf{S})^3\) |
| \(y = 3, \alpha = 1, x = 2\) | \((\mathbf{n}, (\mathbf{L}, \mathbf{L})^2)^3, \mathbf{S})^2\) | \((\Omega, (\mathbf{L}, \mathbf{L})^2)^3, \mathbf{S})^2\) |
| \(y = 3, \alpha = 1, x = 3\) | \((\mathbf{n}, (\mathbf{L}, \mathbf{L})^2)^3, \mathbf{S})^3\) | \((\Omega, (\mathbf{L}, \mathbf{L})^2)^3, \mathbf{S})^3\) |
| \(y = 4, \alpha = 1, x = 3\) | \((\Omega, \mathbf{L})^2, (\mathbf{L}, \mathbf{L})^2)^4, \mathbf{S})^3\) | \((\mathbf{n}, \mathbf{L})^2, (\mathbf{L}, \mathbf{L})^2)^4, \mathbf{S})^3\) |

Table 3.7: Effective operators detectable by x-ray scattering.

\(E2\) x-ray dichroism, integrated over a single partner of a spin orbit split core level, are readily obtained from Table 3.7 by considering the forward scattering limit\(^\text{10}\). Only the

\(^{10}\text{Absorption cross section and scattering amplitude are connected by the relation:}
\[
\sigma_{E1-E2} = \frac{4\pi Im[f_{E1-E2}(\omega)\mathbf{k}_f=\mathbf{k}_0]}{|\mathbf{k}|}
\]

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operators depicted in red (see Table 3.7) contribute in this case. In particular, it can be shown that integrated $XNCD$, $XNLD$ and $XMCD$ are proportional to a linear combination of $(\Omega, L)^2$, $(\Omega, S)^2$, $(n, L)^2, S^2$ and $((\Omega, (L, L)^2)^3, S)^2$, of $(n, L)^2$, $(\Omega, (L, L)^2)^3$, $(n, S)^2$, $((\Omega, L)^2, S)^2$, $(n, (L, L)^2)^3, S^2$, $((\Omega, L)^2, S)^3$ and of $n, (L, L)^2)^3, S^3$ and $((n, (L, L)^2)^3, S)^3$ respectively.

3.5 Conclusions

In the current chapter we have extended our derivation to cover the important case of $E1-E2$ x-ray anomalous diffraction. By making the “fast collision approximation”, we have obtained a simple form for the resonant scattering amplitude which points out the possibility of observing resonant Bragg peaks from ferro- and antiferroelectric structures. By considering the forward scattering limit, we have also discussed $E1-E2$ x-ray dichroism sum rules, when dichroic spectra are integrated over a single partner of a spin-orbit split core level.

\[ \text{Im}[f_{E1-E2}(\omega)] \] is the imaginary part of the scattering amplitude.
Final conclusions

In this thesis, we have studied $E1$-$E2$ x-ray absorption spectroscopy as a probe of ground state electronic and magnetic properties of hybridized valence states in non-centrosymmetric crystals.

To this end we have derived new integral relations for parity-breaking x-ray dichroism. This was achieved by employing a single-ion model and implementing the methods of Racah-Wigner calculus. In particular, we have provided a microscopic interpretation of $XNCD$, $XNLD$ and $XM\chi D$ experiments, which are sensitive to polar and magnetoelectric properties of crystals. We have also extended our derivation to cover the important case of $E1$-$E2$ x-ray anomalous diffraction. In this case, by making the “fast collision approximation”, a particular simple form for the resonant amplitude was obtained, indicating the possibility of observing ferro- and antiferroelectric Bragg peaks with x-ray energy at the resonance.

Our discussion is general. To treat specific cases numerical work is necessary. New quantum chemistry codes capable to reproducing $E1$-$E2$ x-ray dichroic spectra are currently being developed by ESRF theory group.
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Publications and Articles Submitted


2) P. Carra, A. Jerez and I. Marri, X-Ray Dichroism and Orbital Anapole cond-mat/0104582.


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- Poster presented at the VII convegno SILS, Aquila (Italy), July 1-3, 1999.
   Title: Resonant X-Ray Magnetic Scattering from $U_{1-x}Np_xRu_2Si_2$ Alloys.

- Poster presented at the INFM Meeting, Bari (Italy), June 24-28, 2002.
   Title: Integral relation for E1-E2 transitions.

- Oral presentation X convegno SILS, Roma (Italy), July 11-13, 2002.
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Bibliography


[41] P. Curie, Symmetrie d’un Champ Électric et d’un Champ magnetique, J. Physique, 3 Serie, III, 393, (Reprinted in Euvres de Pierre Curie, Gauthier-Villars, Paris 1908)


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