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Angular dependence of Resonant Inelastic X-ray Scattering. I. Spherical tensor expansion

Amélie Juhin and Christian Brouder
Institut de Minéralogie et de Physique des Milieux Condensés,
Université Pierre et Marie Curie-Paris 6, CNRS UMR7590,
4 place Jussieu, 75005 Paris, France.

Frank de Groot
Inorganic Chemistry and Catalysis, Department of Chemistry,
Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, Netherlands

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Abstract

A spherical tensor expansion of resonant inelastic x-ray scattering (RIXS) is carried out to express the RIXS cross-section in terms of a sum of products of fundamental RIXS spectra and tensors involving incident and scattered x-ray wavevectors and polarization vectors. Specific terms of this expansion are discussed in detail, in particular magnetic x-ray dichroism and powder samples.

1 Introduction

Resonant inelastic x-ray scattering (RIXS) is a remarkable tool to study electronic and phonon excitations in solids [1]. By selecting the suitable absorption edge one can choose a specific atomic species and orbital in a complex compound. The information content of RIXS is enhanced by the fact that the observed spectra depend on the polarization and direction of the incident and scattered beams. As a matter of fact, there is so much information in RIXS spectra that it is difficult to know whether a specific set of experiments exhausts it or not. The main purpose of our paper is precisely to determine a finite set of fundamental spectra in terms of which all possible experimental spectra can be expressed. More precisely, the RIXS spectrum obtained for a given wavevector and polarization vector of the incident beam (\mathbf{k} and ϵ) and scattered beam (\mathbf{k}_s and ϵ_s) is written as a sum of terms which are a fundamental spectrum [2, 3] (independent of the incident and scattered beam) multiplied by a given polynomial in \mathbf{k} , ϵ , \mathbf{k}_s and ϵ_s .

The number of available fundamental spectra decreases when the sample is a powder or when the polarization of the scattered beam is not measured. For example we show that the RIXS spectrum of a powder sample for electric dipole excitation and electric dipole emission with undetected scattered polarization is the sum of only three fundamental spectra.

This approach was used with great success for the photoemission of localized magnetic systems [4, 5, 6] and in x-ray absorption spectroscopy [2, 3, 7]. Partial results were obtained in the fast collision approximation [8] or for the elastic scattering operator [9, 10, 11] and general results were obtained in specific coordinate systems [12, 13, 14]. But, as far as we know, the fully general formula is new in coordinateless spherical tensor form. We showed for the case of x-ray absorption [7] that such geometric (i.e. coordinateless) expressions are useful (i) to disentangle the properties of the sample from those of the measurement; (ii) to determine specific experimental arrangements aiming at the observation of specific sample properties; (iii) to provide the good starting point for a group subduction leading to the angular dependence of specific crystal symmetries.

Indeed, we show for example that magnetic dichroism might be observed on isotropic (i.e. without remanent magnetization) samples.

The range of validity of our final expression is rather broad. We only assume the validity of the Kramers-Heisenberg formula describing the scattering of light by a quantum system, where we neglect the Thomson scattering and the non-resonant term. We also assume that only the dipole and quadrupole transitions play a role, but this is an excellent approximation in the x-ray range [15]. Our result is a group theoretical consequence of the scattering cross-section. In particular, we do not assume that the states can be described by some LS or LSJ coupling, we do not make the fast collision approximation, we do not assume that some radial dipole and quadrupole matrix elements are independent of energy as in most other works on this subject. We even do not assume that a specific edge is measured. All these additional assumptions can be made in the final expression if necessary.

We chose to give details of the computation to show that our result, even if it looks rather involved, can be obtained by straightforward angular-momentum coupling techniques.

2 General case

2.1 The Kramers-Heisenberg formula

The scattering of light by a quantum system is described by the Kramers-Heisenberg formula, which was obtained before the advent of quantum theory [16]. The first quantum derivation of this formula is due to Dirac [17].

We start from the expression of the scattering cross-section:

$$\begin{aligned} \sigma_{SCAT} = \frac{d\sigma}{d\Omega d\omega_s} &= r_e^2 \frac{\omega_s}{\omega} \sum_F \left| \epsilon_s^* \cdot \epsilon \langle F | e^{i(\mathbf{k}-\mathbf{k}_s) \cdot \mathbf{r}} | I \rangle + \frac{1}{m} \sum_N \frac{\langle F | \epsilon_s^* \cdot \mathbf{P} e^{-i\mathbf{k}_s \cdot \mathbf{r}} | N \rangle \langle N | \epsilon \cdot \mathbf{P} e^{i\mathbf{k} \cdot \mathbf{r}} | I \rangle}{E_I - E_N + \hbar\omega + i\gamma} \right. \\ &\quad \left. + \frac{1}{m} \sum_N \frac{\langle F | \epsilon \cdot \mathbf{P} e^{i\mathbf{k} \cdot \mathbf{r}} | N \rangle \langle N | \epsilon_s^* \cdot \mathbf{P} e^{-i\mathbf{k}_s \cdot \mathbf{r}} | I \rangle}{E_I - E_N - \hbar\omega_s + i\gamma} \right|^2 \delta(E_F + \hbar\omega_s - E_I - \hbar\omega). \end{aligned} \quad (1)$$

r_e is the classical electron radius: $r_e = \alpha_0 \hbar / mc$. $|I\rangle$, $|N\rangle$, $|F\rangle$ are respectively the initial, intermediate and final states. γ is the total width of the intermediate state $|N\rangle$. The incident and scattered photons are characterized by the pulsation, wavevector and polarization vector ω , \mathbf{k} , ϵ and ω_s , \mathbf{k}_s , ϵ_s , respectively. Note that ϵ_s^* denotes the complex conjugate of ϵ_s .

In this expression, the first transition amplitude describes elastic scattering and will not be considered here. E_I being negative and large, $E_I + \hbar\omega$ can be small, and $E_I - \hbar\omega_s$ is large. Hence, we can assume the third matrix element in Eq. 1 can be neglected with respect to the second one (although it could be treated with similar methods). Therefore, only the second amplitude transition remains in the expression of the scattering cross-section, yielding the well-known partial Kramers-Heisenberg formula:

$$\sigma_{RIXS} = \frac{r_e^2 \omega_s}{m^2 \omega} \sum_F \left| \sum_N \frac{\langle F | \epsilon_s^* \cdot \mathbf{P} e^{-i\mathbf{k}_s \cdot \mathbf{r}} | N \rangle \langle N | \epsilon \cdot \mathbf{P} e^{i\mathbf{k} \cdot \mathbf{r}} | I \rangle}{E_I - E_N + \hbar\omega + i\gamma} \right|^2 \delta(E_F + \hbar\omega_s - E_I - \hbar\omega). \quad (2)$$

2.2 Multipole expansion

First we transform the matrix element describing the absorption from the initial state $|I\rangle$ to the intermediate state $|N\rangle$, $\langle N | \epsilon \cdot \mathbf{P} e^{i\mathbf{k} \cdot \mathbf{r}} | I \rangle$.

To calculate $\langle N | \epsilon \cdot \mathbf{P} e^{i\mathbf{k} \cdot \mathbf{r}} | I \rangle$, $e^{i\mathbf{k} \cdot \mathbf{r}}$ is expanded to first order: $e^{i\mathbf{k} \cdot \mathbf{r}} \simeq 1 + i\mathbf{k} \cdot \mathbf{r}$. Hence,

$$\langle N | \epsilon \cdot \mathbf{P} e^{i\mathbf{k} \cdot \mathbf{r}} | I \rangle \simeq \langle N | \epsilon \cdot \mathbf{P} | I \rangle + i \langle N | \mathbf{k} \cdot \mathbf{r} \epsilon \cdot \mathbf{P} | I \rangle.$$

The electric dipole matrix element is transformed by using the equation of motion of \mathbf{P} which is $\mathbf{P} = (m/i\hbar)[\mathbf{r}, H_0]$. [15] Thus,

$$\langle N | \epsilon \cdot \mathbf{P} | I \rangle = (m/i\hbar)(E_I - E_N) \langle N | \epsilon \cdot \mathbf{r} | I \rangle.$$

For the quadrupole matrix element, one uses the identity from Ref. [18],

$$\mathbf{k} \cdot \mathbf{r} \epsilon \cdot \mathbf{P} = -(im/2\hbar)[\epsilon \cdot \mathbf{r} \mathbf{k} \cdot \mathbf{r}, H_0] + 1/2(\mathbf{k} \times \epsilon) \cdot \mathbf{L},$$

where \mathbf{L} is the angular momentum operator. One can neglect the angular momentum term (for an extended justification, see Ref. [15]). Therefore,

$$\begin{aligned}\langle N|\epsilon \cdot \mathbf{P}e^{i\mathbf{k}\cdot\mathbf{r}}|I\rangle &\simeq -\frac{im}{\hbar}(E_I - E_N)\left(\langle N|\epsilon \cdot \mathbf{r}|I\rangle + \frac{i}{2}\langle N|\epsilon \cdot \mathbf{r}\mathbf{k} \cdot \mathbf{r}|I\rangle\right) \\ &= -\frac{im}{\hbar}(E_I - E_N)\sum_{\ell=0}^1 f_\ell \langle N|\epsilon \cdot \mathbf{r}(\mathbf{k} \cdot \mathbf{r})^\ell|I\rangle,\end{aligned}$$

with $f_0 = 1$ and $f_1 = \frac{i}{2}$.

Similarly, we transform the matrix element describing the emission from the intermediate state $|N\rangle$ to the final state $|F\rangle$, $\langle F|\epsilon_s^* \cdot \mathbf{P}e^{-i\mathbf{k}_s \cdot \mathbf{r}}|N\rangle$:

$$\begin{aligned}\langle F|\epsilon_s^* \cdot \mathbf{P}e^{-i\mathbf{k}_s \cdot \mathbf{r}}|N\rangle &\simeq -\frac{im}{\hbar}(E_N - E_F)\left(\langle F|\epsilon_s^* \cdot \mathbf{r}|N\rangle - \frac{i}{2}\langle F|\epsilon_s^* \cdot \mathbf{r}\mathbf{k}_s \cdot \mathbf{r}|N\rangle\right) \\ &= -\frac{im}{\hbar}(E_N - E_F)\sum_{\ell'=0}^1 f_{\ell'}^* \langle F|\epsilon_s^* \cdot \mathbf{r}(\mathbf{k}_s \cdot \mathbf{r})^{\ell'}|N\rangle.\end{aligned}$$

Finally,

$$\begin{aligned}\sigma_{\text{RIXS}} &= \frac{r_e^2 \omega_s}{\hbar^2 \omega} \sum_F \left| \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma} \sum_{\ell, \ell'=0}^1 f_\ell f_{\ell'}^* \langle N|\epsilon \cdot \mathbf{r}(\mathbf{k} \cdot \mathbf{r})^\ell|I\rangle \langle F|\epsilon_s^* \cdot \mathbf{r}(\mathbf{k}_s \cdot \mathbf{r})^{\ell'}|N\rangle \right|^2 \\ &\quad \times \delta(E_F + \hbar\omega_s - E_I - \hbar\omega).\end{aligned}\quad (3)$$

In the following, we shall use:

$$\begin{aligned}C &= \frac{r_e^2 \omega_s}{\hbar^2 \omega}, \\ E_{IFN} &= \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma}, \\ \delta_E &= \delta(E_F + \hbar\omega_s - E_I - \hbar\omega).\end{aligned}$$

Thus, Eq. 3 becomes:

$$\sigma_{\text{RIXS}} = C \delta_E \sum_F \left| \sum_N E_{IFN} \sum_{\ell, \ell'=0}^1 f_\ell f_{\ell'}^* \langle N|\epsilon \cdot \mathbf{r}(\mathbf{k} \cdot \mathbf{r})^\ell|I\rangle \langle F|\epsilon_s^* \cdot \mathbf{r}(\mathbf{k}_s \cdot \mathbf{r})^{\ell'}|N\rangle \right|^2.\quad (4)$$

Eq. 4 is a general expression describing the RIXS intensity for any combination of the absorption and emission transition operators. Each transition operator can be either pure electric dipole (E_1), or pure electric quadrupole (E_2), or a mixture for both ($E_1 + E_2$).

2.3 The Kramers-Heisenberg formula expressed in spherical tensors

In this subsection, the expression of the RIXS cross-section (Eq. 4) is transformed using spherical tensors and their coupling properties. For a short introduction to spherical tensors and their application to x-ray spectroscopies, the reader is referred to Ref. [7] for the case of the X-ray absorption cross-section. Let us first briefly explain the notation. A ℓ^{th} rank spherical tensor T is written as $T^{(\ell)}$. This must not be confused from T^ℓ with is the ℓ -th power of T .

Cartesian vectors, such as ϵ , \mathbf{r} or \mathbf{k} are written in their usual form, i.e., without brackets. However one shall keep in mind that Cartesian vectors correspond to first-rank spherical tensors, and as such they shall indifferently be written as $\epsilon^{(1)}$, $\mathbf{r}^{(1)}$, $\mathbf{k}^{(1)}$.

2.3.1 Expression of $\epsilon \cdot \mathbf{r}(\mathbf{k} \cdot \mathbf{r})^\ell$

Here we show that $\epsilon \cdot \mathbf{r}(\mathbf{k} \cdot \mathbf{r})^\ell$ can be expressed as $g_\ell \left\{ \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)} \otimes \mathbf{r}^{(\ell+1)} \right\}^{(0)}$ where g_ℓ is a constant.

For $\ell = 0$, according to Ref. [7] (Eq. 13):

$$\epsilon \cdot \mathbf{r} = -\sqrt{3} \left(-\frac{1}{\sqrt{3}} \epsilon \cdot \mathbf{r} \right) = -\sqrt{3} \{\epsilon \otimes \mathbf{r}\}^0 = -\sqrt{3} \left\{ \{\epsilon \otimes \mathbf{k}^0\}^{(1)} \otimes \mathbf{r}^{(1)} \right\}^{(0)}.$$

For $\ell = 1$, according to Ref. [7] (pp.5):

$$\epsilon \cdot \mathbf{r} \mathbf{k} \cdot \mathbf{r} = \sqrt{5} \left\{ \{\epsilon \otimes \mathbf{k}\}^{(2)} \otimes \{\mathbf{r} \otimes \mathbf{r}\}^{(2)} \right\}^{(0)} = \sqrt{5} \left\{ \{\epsilon \otimes \mathbf{k}^1\}^{(2)} \otimes \mathbf{r}^{(2)} \right\}^{(0)}$$

Thus, $\epsilon \cdot \mathbf{r}(\mathbf{k} \cdot \mathbf{r})^\ell = g_\ell \left\{ \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)} \otimes \mathbf{r}^{(\ell+1)} \right\}^{(0)}$, with $\mathbf{r}^{(1)} = \mathbf{r}$, $g_0 = -\sqrt{3}$, $\mathbf{r}^{(2)} = \{\mathbf{r} \otimes \mathbf{r}\}^{(2)}$ and $g_1 = \sqrt{5}$.

Then, Eq.4 becomes:

$$\begin{aligned} & \sigma_{\text{RIXS}} \\ &= C\delta_E \sum_F \left| \sum_N E_{IFN} \sum_{\ell, \ell'=0}^1 f_\ell f_{\ell'}^* g_\ell g_{\ell'} \langle N | \left\{ \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)} \otimes \mathbf{r}^{(\ell+1)} \right\}^{(0)} | I \rangle \langle F | \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \mathbf{r}^{(\ell'+1)} \right\}^{(0)} | N \rangle \right|^2 \\ &= C\delta_E \sum_F \left| \sum_N E_{IFN} \sum_{\ell, \ell'=0}^1 f_\ell f_{\ell'}^* g_\ell g_{\ell'} \left\{ \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)} \otimes \langle N | \mathbf{r}^{(\ell+1)} | I \rangle \right\}^{(0)} \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \langle F | \mathbf{r}^{(\ell'+1)} | N \rangle \right\}^{(0)} \right|^2 \\ &= C\delta_E \sum_F \left| \sum_N E_{IFN} \sum_{\ell, \ell'=0}^1 h_\ell h_{\ell'}^* \left\{ \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)} \otimes \langle N | \mathbf{r}^{(\ell+1)} | I \rangle \right\}^{(0)} \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \langle F | \mathbf{r}^{(\ell'+1)} | N \rangle \right\}^{(0)} \right|^2 \quad (5) \end{aligned}$$

with $h_\ell = f_\ell g_\ell$: $h_0 = -\sqrt{3}$, $h_1 = \frac{i}{2}\sqrt{5}$.

If one defines $\mathbf{r}_{NI}^{(\ell+1)} = \langle N | \mathbf{r}^{(\ell+1)} | I \rangle$ and $\mathbf{r}_{FN}^{(\ell'+1)} = \langle F | \mathbf{r}^{(\ell'+1)} | N \rangle$, one gets:

$$\sigma_{\text{RIXS}} = C\delta_E \sum_F \left| \sum_N E_{IFN} \sum_{\ell, \ell'=0}^1 h_\ell h_{\ell'}^* \left\{ \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)} \right\}^{(0)} \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \mathbf{r}_{FN}^{(\ell'+1)} \right\}^{(0)} \right|^2. \quad (6)$$

2.3.2 Recoupling spherical tensors

Here we use the recoupling identity (Ref.[7], Eq.14), which is:

$$\{P^{(a)} \otimes Q^{(a)}\}^{(0)} \{R^{(d)} \otimes S^{(d)}\}^{(0)} = \sum_{g=|a-d|}^{a+d} (-1)^g \frac{\{P^{(a)} \otimes R^{(d)}\}^{(g)} \cdot \{Q^{(a)} \otimes S^{(d)}\}^{(g)}}{\sqrt{(2a+1)(2d+1)}}, \quad (7)$$

where the scalar product \cdot of two spherical tensors $P^{(g)}$ and $Q^{(g)}$ is defined by $P^{(g)} \cdot Q^{(g)} = \sum_{\gamma=-g}^g (-1)^\gamma P_\gamma^{(g)} Q_{-\gamma}^{(g)}$.

Eq. 6 becomes:

$$\sigma_{\text{RIXS}} = C\delta_E \sum_F \left| \sum_N E_{IFN} \sum_{g, \ell, \ell'} \frac{(-1)^g h_\ell h_{\ell'}^*}{\sqrt{(2\ell+3)(2\ell'+3)}} \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)} \right\}^{(g)} \cdot \left\{ \mathbf{r}_{FN}^{(\ell'+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)} \right\}^{(g)} \right|^2,$$

where g runs from $|\ell - \ell'|$ to $(\ell + \ell' + 2)$, ℓ and ℓ' run from 0 to 1.

The first tensor product $\left\{ \left\{ \epsilon_s^* \otimes \mathbf{k}_s^{\ell'} \right\}^{(\ell'+1)} \otimes \left\{ \epsilon \otimes \mathbf{k}^\ell \right\}^{(\ell+1)} \right\}^{(g)}$ gathers the characteristics of the incident beam (ϵ, \mathbf{k}) and of the scattered beam $(\epsilon_s, \mathbf{k}_s)$. The variables dealing with the sample are gathered in the second tensor product $\left\{ \mathbf{r}_{FN}^{(\ell'+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)} \right\}^{(g)}$.

Then, defining

$$A_{FI}^{(g)}(\ell, \ell') = \sum_N E_{IFN} \left\{ \mathbf{r}_{FN}^{(\ell'+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)} \right\}^{(g)} \quad (8)$$

$$= \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma} \left\{ \mathbf{r}_{FN}^{(\ell'+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)} \right\}^{(g)}, \quad (9)$$

one gets

$$\sigma_{\text{RIXS}} = C\delta_E \sum_F \left| \sum_{g, \ell, \ell'} \frac{(-1)^g h_\ell h_{\ell'}^*}{\sqrt{(2\ell+3)(2\ell'+3)}} \left\{ \left\{ \epsilon_s^* \otimes \mathbf{k}_s^{\ell'} \right\}^{(\ell'+1)} \otimes \left\{ \epsilon \otimes \mathbf{k}^\ell \right\}^{(\ell+1)} \right\}^{(g)} \cdot A_{FI}^{(g)}(\ell, \ell') \right|^2. \quad (10)$$

2.3.3 Expansion of the square

Here we square the amplitude inside the sum over the final states in Eq. 10.

When expanding the square, Eq. 10 becomes:

$$\begin{aligned} \sigma_{\text{RIXS}} = C\delta_E \sum_F \sum_{\substack{g_1, \ell_1, \ell'_1 \\ g_2, \ell_2, \ell'_2}} & \frac{(-1)^{g_1+\ell_2+\ell'_2} h_{\ell_1} h_{\ell'_1}^* h_{\ell_2}^* h_{\ell'_2}}{\sqrt{(2\ell_1+3)(2\ell'_1+3)(2\ell_2+3)(2\ell'_2+3)}} \\ & \left\{ \left\{ \epsilon_s^* \otimes \mathbf{k}_s^{\ell'_1} \right\}^{(\ell'_1+1)} \otimes \left\{ \epsilon \otimes \mathbf{k}^{\ell_1} \right\}^{(\ell_1+1)} \right\}^{(g_1)} \cdot A_{FI}^{(g_1)}(\ell_1, \ell'_1) \\ & \left\{ \left\{ \epsilon_s \otimes \mathbf{k}_s^{\ell'_2} \right\}^{(\ell'_2+1)} \otimes \left\{ \epsilon^* \otimes \mathbf{k}^{\ell_2} \right\}^{(\ell_2+1)} \right\}^{(g_2)} \cdot A_{FI}^{(g_2)}(\ell_2, \ell'_2)^*, \quad (11) \end{aligned}$$

where g_i runs from $|\ell_i - \ell'_i|$ to $(\ell_i + \ell'_i + 2)$, with ℓ_i and ℓ'_i equal to 0 or 1.

In the Appendix, we show that $A_{FI}^{(g_2)}(\ell_2, \ell'_2)^* = \overline{A_{IF}^{(g_2)}}(\ell_2, \ell'_2)$. Therefore,

$$\begin{aligned} \sigma_{\text{RIXS}} = C\delta_E \sum_F \sum_{\substack{g_1, \ell_1, \ell'_1 \\ g_2, \ell_2, \ell'_2}} & \frac{(-1)^{g_1+\ell_2+\ell'_2} h_{\ell_1} h_{\ell'_1}^* h_{\ell_2}^* h_{\ell'_2}}{\sqrt{(2\ell_1+3)(2\ell'_1+3)(2\ell_2+3)(2\ell'_2+3)}} \\ & \left\{ \left\{ \epsilon_s^* \otimes \mathbf{k}_s^{\ell'_1} \right\}^{(\ell'_1+1)} \otimes \left\{ \epsilon \otimes \mathbf{k}^{\ell_1} \right\}^{(\ell_1+1)} \right\}^{(g_1)} \cdot A_{FI}^{(g_1)}(\ell_1, \ell'_1) \\ & \left\{ \left\{ \epsilon_s \otimes \mathbf{k}_s^{\ell'_2} \right\}^{(\ell'_2+1)} \otimes \left\{ \epsilon^* \otimes \mathbf{k}^{\ell_2} \right\}^{(\ell_2+1)} \right\}^{(g_2)} \cdot \overline{A_{IF}^{(g_2)}}(\ell_2, \ell'_2) \quad (12) \end{aligned}$$

If one defines

$$X_1^{(g_1)} = \left\{ \left\{ \epsilon_s^* \otimes \mathbf{k}_s^{\ell'_1} \right\}^{(\ell'_1+1)} \otimes \left\{ \epsilon \otimes \mathbf{k}^{\ell_1} \right\}^{(\ell_1+1)} \right\}^{(g_1)}, \quad (13)$$

$$X_2^{(g_2)} = \left\{ \left\{ \epsilon_s \otimes \mathbf{k}_s^{\ell'_2} \right\}^{(\ell'_2+1)} \otimes \left\{ \epsilon^* \otimes \mathbf{k}^{\ell_2} \right\}^{(\ell_2+1)} \right\}^{(g_2)}, \quad (14)$$

$$\Pi_{\ell_1+1, \ell_2+1, \ell'_1+1, \ell'_2+1} = \sqrt{(2\ell_1+3)(2\ell'_1+3)(2\ell_2+3)(2\ell'_2+3)}, \quad (15)$$

one gets

$$\sigma_{\text{RIXS}} = C\delta_E \sum_F \sum_{\substack{g_1, \ell_1, \ell'_1 \\ g_2, \ell_2, \ell'_2}} \frac{(-1)^{g_1 + \ell_2 + \ell'_2} h_{\ell_1} h_{\ell'_1}^* h_{\ell_2}^* h_{\ell'_2}}{\Pi_{\ell_1+1, \ell_2+1, \ell'_1+1, \ell'_2+1}} X_1^{(g_1)} \cdot A_{FI}^{(g_1)}(\ell_1, \ell'_1) X_2^{(g_2)} \cdot \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2). \quad (16)$$

Using the identity $P^{(a)} \cdot Q^{(a)} = (-1)^a \sqrt{2a+1} \{P^{(a)} \otimes Q^{(a)}\}^{(0)}$ (pp.64-65 of Ref. [19]), we have:

$$X_1^{(g_1)} \cdot A_{FI}^{(g_1)}(\ell_1, \ell'_1) = (-1)^{g_1} \sqrt{2g_1+1} \{X_1^{(g_1)} \otimes A_{FI}^{(g_1)}(\ell_1, \ell'_1)\}^{(0)}, \quad (17)$$

$$X_2^{(g_2)} \cdot \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2) = (-1)^{g_2} \sqrt{2g_2+1} \{X_2^{(g_2)} \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(0)}, \quad (18)$$

and then:

$$\sigma_{\text{RIXS}} = C\delta_E \sum_F \sum_{\substack{g_1, \ell_1, \ell'_1 \\ g_2, \ell_2, \ell'_2}} \frac{(-1)^{\ell_2 + \ell'_2 - g_2} h_{\ell_1} h_{\ell'_1}^* h_{\ell_2}^* h_{\ell'_2} \sqrt{(2g_1+1)(2g_2+1)}}{\Pi_{\ell_1+1, \ell_2+1, \ell'_1+1, \ell'_2+1}} \{X_1^{(g_1)} \otimes A_{FI}^{(g_1)}(\ell_1, \ell'_1)\}^{(0)} \{X_2^{(g_2)} \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(0)}. \quad (19)$$

Using Eq. 7, we have:

$$\begin{aligned} & \{X_1^{(g_1)} \otimes A_{FI}^{(g_1)}(\ell_1, \ell'_1)\}^{(0)} \{X_2^{(g_2)} \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(0)} \\ &= \sum_{a=|g_1-g_2|}^{g_1+g_2} \frac{(-1)^a}{\sqrt{(2g_1+1)(2g_2+1)}} \{X_1^{(g_1)} \otimes X_2^{(g_2)}\}^{(a)} \cdot \{A_{FI}^{(g_1)}(\ell_1, \ell'_1) \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(a)} \end{aligned} \quad (20)$$

Then,

$$\sigma_{\text{RIXS}} = C\delta_E \sum_F \sum_{\substack{g_1, \ell_1, \ell'_1 \\ g_2, \ell_2, \ell'_2}} \frac{(-1)^{\ell_2 + \ell'_2 - g_2} h_{\ell_1} h_{\ell'_1}^* h_{\ell_2}^* h_{\ell'_2}}{\Pi_{\ell_1+1, \ell_2+1, \ell'_1+1, \ell'_2+1}} \sum_a (-1)^a \{X_1^{(g_1)} \otimes X_2^{(g_2)}\}^{(a)} \cdot \{A_{FI}^{(g_1)}(\ell_1, \ell'_1) \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(a)},$$

with a running from $|g_1 - g_2|$ to $g_1 + g_2$.

In order to simplify the tensor product:

$$\{X_1^{(g_1)} \otimes X_2^{(g_2)}\}^{(a)} = \left\{ \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'_1}\}^{(\ell'_1+1)} \otimes \{\epsilon \otimes \mathbf{k}^{\ell_1}\}^{(\ell_1+1)} \right\}^{(g_1)} \otimes \left\{ \{\epsilon_s \otimes \mathbf{k}_s^{\ell'_2}\}^{(\ell'_2+1)} \otimes \{\epsilon^* \otimes \mathbf{k}^{\ell_2}\}^{(\ell_2+1)} \right\}^{(g_2)} \right\}^{(a)},$$

one uses the following identity (pp.70 of Ref. [19]):

$$\left\{ \{P^{(a)} \otimes Q^{(b)}\}^{(c)} \otimes \{R^{(d)} \otimes S^{(e)}\}^{(f)} \right\}^{(k)} = \sum_{g,h} \Pi_{c,f,g,h} \begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & k \end{Bmatrix} \left\{ \{P^{(a)} \otimes R^{(d)}\}^{(g)} \otimes \{Q^{(b)} \otimes S^{(e)}\}^{(h)} \right\}^{(k)}, \quad (21)$$

where $|a-d| \leq g \leq a+d$, $|b-e| \leq h \leq b+e$ and $|g-h| \leq k \leq g+h$.

This yields:

$$\{X_1^{(g_1)} \otimes X_2^{(g_2)}\}^{(a)} = \sum_{b,c} \Pi_{g_1, g_2, b, c} \begin{Bmatrix} \ell'_1+1 & \ell_1+1 & g_1 \\ \ell'_2+1 & \ell_2+1 & g_2 \\ b & c & a \end{Bmatrix} \{X\}^{(a)},$$

$$\text{with } \{X\}^{(a)} = \left\{ \left\{ \left\{ \epsilon_s^* \otimes \mathbf{k}_s^{\ell'_1} \right\}^{(\ell'_1+1)} \otimes \left\{ \epsilon_s \otimes \mathbf{k}_s^{\ell'_2} \right\}^{(\ell'_2+1)} \right\}^{(b)} \otimes \left\{ \left\{ \epsilon \otimes \mathbf{k}^{\ell_1} \right\}^{(\ell_1+1)} \otimes \left\{ \epsilon^* \otimes \mathbf{k}^{\ell_2} \right\}^{(\ell_2+1)} \right\}^{(c)} \right\}^{(a)}.$$

According to the triangular conditions, the $9j$ -factor is zero if any of the following conditions is not satisfied

$$\begin{aligned} |\ell'_1 - \ell'_2| &\leq b \leq \ell'_1 + \ell'_2, \\ |\ell_1 - \ell_2| &\leq c \leq \ell_1 + \ell_2, \\ |b - c| &\leq a \leq b + c. \end{aligned}$$

2.3.4 Simplification of $\{X\}^{(a)}$

In $\{X\}^{(a)}$, the variables concerning the scattered beam $(\epsilon_s, \mathbf{k}_s)$ are gathered in the first tensor product, while those concerning the incident beam are gathered in the second product. Therefore in order to simplify $\{X\}^{(a)}$, one shall write it as $\{X\}^{(a)} = \left\{ \{X_{em}\}^{(b)} \otimes \{X_{abs}\}^{(c)} \right\}^{(a)}$ and then simplify $\{X_{em}\}^{(b)}$ and $\{X_{abs}\}^{(c)}$. According to Eq. 21, one gets:

$$\begin{aligned} \{X_{abs}\}^{(c)} &= \left\{ \left\{ \epsilon \otimes \mathbf{k}^{\ell_1} \right\}^{(\ell_1+1)} \otimes \left\{ \epsilon^* \otimes \mathbf{k}^{\ell_2} \right\}^{(\ell_2+1)} \right\}^{(c)} \\ &= \sum_{u,v} \Pi_{\ell_1+1, \ell_2+1, u, v} \begin{Bmatrix} 1 & \ell_1 & \ell_1 + 1 \\ 1 & \ell_2 & \ell_2 + 1 \\ u & v & c \end{Bmatrix} \left\{ \left\{ \epsilon \otimes \epsilon^* \right\}^{(u)} \otimes \left\{ \mathbf{k}^{\ell_1} \otimes \mathbf{k}^{\ell_2} \right\}^{(v)} \right\}^{(c)} \\ &= \sum_{u,v} \Pi_{\ell_1+1, \ell_2+1, u, v} \begin{Bmatrix} 1 & \ell_1 & \ell_1 + 1 \\ 1 & \ell_2 & \ell_2 + 1 \\ u & v & c \end{Bmatrix} \{A\}^{(c)}. \\ \{X_{em}\}^{(b)} &= \left\{ \left\{ \epsilon_s^* \otimes \mathbf{k}_s^{\ell'_1} \right\}^{(\ell'_1+1)} \otimes \left\{ \epsilon_s \otimes \mathbf{k}_s^{\ell'_2} \right\}^{(\ell'_2+1)} \right\}^{(b)} \\ &= \sum_{u',v'} \Pi_{\ell'_1+1, \ell'_2+1, u', v'} \begin{Bmatrix} 1 & \ell'_1 & \ell'_1 + 1 \\ 1 & \ell'_2 & \ell'_2 + 1 \\ u' & v' & b \end{Bmatrix} \left\{ \left\{ \epsilon_s^* \otimes \epsilon_s \right\}^{(u')} \otimes \left\{ \mathbf{k}_s^{\ell'_1} \otimes \mathbf{k}_s^{\ell'_2} \right\}^{(v')} \right\}^{(b)} \\ &= \sum_{u',v'} \Pi_{\ell'_1+1, \ell'_2+1, u', v'} \begin{Bmatrix} 1 & \ell'_1 & \ell'_1 + 1 \\ 1 & \ell'_2 & \ell'_2 + 1 \\ u' & v' & b \end{Bmatrix} \{E\}^{(b)}. \end{aligned}$$

The $9j$ -factors vanish if any of the following triangular conditions is not fulfilled:

$$\begin{aligned} 0 &\leq u \leq 2, \\ |\ell_1 - \ell_2| &\leq v \leq \ell_1 + \ell_2, \\ 0 &\leq u' \leq 2, \\ |\ell'_1 - \ell'_2| &\leq v' \leq \ell'_1 + \ell'_2, \end{aligned}$$

2.4 Final expression of σ_{RIXS}

Finally, one obtains:

$$\begin{aligned} &\sigma_{\text{RIXS}} \\ &= C \sum_F \sum_{\substack{g_1, g_2 \\ \ell_1, \ell_2 \\ \ell'_1, \ell'_2}} \sum_{\substack{a, b, c \\ u, u' \\ v, v'}} (-1)^{a+\ell_2+\ell'_2-g_2} h_{\ell_1} h_{\ell'_1}^* h_{\ell_2}^* h_{\ell'_2} \Pi_{g_1, g_2, b, c, u, v, u', v'} \begin{Bmatrix} 1 & \ell_1 & \ell_1 + 1 \\ 1 & \ell_2 & \ell_2 + 1 \\ u & v & c \end{Bmatrix} \begin{Bmatrix} 1 & \ell'_1 & \ell'_1 + 1 \\ 1 & \ell'_2 & \ell'_2 + 1 \\ u' & v' & b \end{Bmatrix} \begin{Bmatrix} \ell'_1 + 1 & \ell_1 + 1 & g_1 \\ \ell'_2 + 1 & \ell_2 + 1 & g_2 \\ b & c & a \end{Bmatrix} \\ &\quad \cdot \left\{ \{E\}^{(b)} \otimes \{A\}^{(c)} \right\}^{(a)} \cdot \left\{ A_{FI}^{(g_1)}(\ell_1, \ell'_1) \otimes \bar{A}_{IF}^{(g_2)}(\ell_2, \ell'_2) \right\}^{(a)} \delta(E_F + \hbar\omega_s - E_I - \hbar\omega) \end{aligned} \quad (22)$$

with

$$\begin{aligned}
h_0 &= -\sqrt{3} \\
h_1 &= \frac{i}{2}\sqrt{5} \\
C &= \frac{r_e^2 \omega_s}{\hbar^2 \omega} \\
\{A\}^{(c)} &= \left\{ \{\epsilon \otimes \epsilon^*\}^{(u)} \otimes \{\mathbf{k}^{\ell_1} \otimes \mathbf{k}^{\ell_2}\}^{(v)} \right\}^{(c)}, \\
\{E\}^{(b)} &= \left\{ \{\epsilon_s^* \otimes \epsilon_s\}^{(u')} \otimes \{\mathbf{k}_s^{\ell'_1} \otimes \mathbf{k}_s^{\ell'_2}\}^{(v')} \right\}^{(b)}, \\
A_{FI}^{(g)}(\ell, \ell') &= \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma} \{\mathbf{r}_{FN}^{(\ell'+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)}\}^{(g)}, \\
\overline{A}_{IF}^{(g)}(\ell, \ell') &= \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega - i\gamma} \{\mathbf{r}_{IN}^{(\ell+1)} \otimes \mathbf{r}_{NF}^{(\ell'+1)}\}^{(g)}, \\
\mathbf{r}_{NI}^{(\ell+1)} &= \langle N | \mathbf{r}^{(\ell+1)} | I \rangle, \\
\mathbf{r}_{FN}^{(\ell'+1)} &= \langle F | \mathbf{r}^{(\ell'+1)} | N \rangle.
\end{aligned}$$

In Eq. 22 the RIXS cross-section is written as a sum of fundamental spectra, $\left\{ A_{FI}^{(g_1)}(\ell_1, \ell'_1) \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2) \right\}^{(a)}$, which are only sample-dependent for a given couple of transition operators. The fundamental spectra are weighted by coefficients which depend only on the experimental conditions, i.e., transition operator, type of polarization and experimental geometry, in the absorption as well as in the emission. The $\left\{ \{E\}^{(b)} \otimes \{A\}^{(c)} \right\}^{(a)}$ weights are polynomial in ϵ , ϵ_s , \mathbf{k} and \mathbf{k}_s . The three $9j$ -factors (and the related triangular conditions) ensure that these variables are coupled in the RIXS process in a correct (physical) way.

Applications of the general expression to particular cases will be given as examples in the next section.

2.5 Summary: Possible values of the different indices

Here we summarize the possible values taken by the different indices in Eq. 22.

- $0 \leq \ell_i \leq 1$ (for $i = 1, 2$): these indices deal with the transition operator in the absorption. $\ell_i = 0$ for dipole excitation, $\ell_i = 1$ for quadrupole excitation
- $0 \leq \ell'_i \leq 1$ (for $i = 1, 2$): these indices deal with the transition operator in the emission. $\ell'_i = 0$ for dipole emission, $\ell'_i = 1$ for quadrupole emission
- $|\ell_i - \ell'_i| \leq g_i \leq \ell_i + \ell'_i + 2$ (for $i = 1, 2$): these indices couple absorption and emission transition operators.
- $0 \leq u \leq 2$: u deals with the polarization of the incident beam.
- $0 \leq u' \leq 2$: u' deals with the polarization of the scattered beam.
- $|\ell_1 - \ell_2| \leq v \leq \ell_1 + \ell_2$: v deals with the direction of the incident beam.
- $|u - v| \leq c \leq u + v$ and $|\ell_1 - \ell_2| \leq c \leq \ell_1 + \ell_2 + 2$: c gathers all characteristics of the incident beam.
- $|\ell'_1 - \ell'_2| \leq v' \leq \ell'_1 + \ell'_2$: v' deals with the direction of the scattered beam.
- $|u' - v'| \leq b \leq u' + v'$ and $|\ell'_1 - \ell'_2| \leq b \leq \ell'_1 + \ell'_2 + 2$: b gathers all characteristics of the outgoing beam.
- $|b - c| \leq a \leq b + c$ and $|g_1 - g_2| \leq a \leq g_1 + g_2$: a couples everything.

3 Particular cases

In this section we consider several particular cases.

3.1 Conditions due to the type of polarization

When the incident beam is circularly polarized, $u = 0, 1, 2$. When the incident beam is linearly polarized light, $u = 0$ or 2 . Note that there is a basic difference between the polarization of the incident beam and that of the scattered beam. On the one hand, the incident beam is prepared by a synchrotron radiation source and monochromators. Therefore, ϵ can be tuned as one wishes. On the other hand, the polarization state of the scattered beam is entirely determined by the incident beam and the sample. It cannot be tuned. However, we can measure some polarization properties of the scattered beam. If we want to measure the intensity along the polarization direction ϵ_s , then we introduce ϵ_s in the formula. If we do not measure the polarization state, then we take the trace of the density matrix representing the polarization state of the scattered beam. In other words, the measured cross-section is equal to the sum over two perpendicular directions of the scattered polarization (see Appendix 1). In this case $u' = 1$ is zero, since $\langle \{\epsilon \otimes \epsilon^*\}^{(1)} \rangle = 0$.

3.2 Electric dipole excitation, electric dipole emission

We consider the case of an electric dipole transition in the absorption followed by an electric dipole transition in the emission : $\ell_1 = 0, \ell_2 = 0, \ell'_1 = 0$ and $\ell'_2 = 0$. Thus, we have:

$$\begin{aligned} 0 &\leq g_1 \leq 2, \\ 0 &\leq g_2 \leq 2, \\ 0 &\leq a \leq 4, \\ 0 &\leq b \leq 2, \\ 0 &\leq c \leq 2. \end{aligned}$$

Since $\ell_1 = 0, \ell_2 = 0$, we have $v = 0$. This implies $c = u$. Since $\ell'_1 = 0$ and $\ell'_2 = 0$, we have $v' = 0$ and $b = u'$. These conditions allow to calculate the values of some $9j$ symbols.

- The first $9j$ -factor is: $\begin{Bmatrix} 1 & \ell_1 & \ell_1 + 1 \\ 1 & \ell_2 & \ell_2 + 1 \\ u & v & c \end{Bmatrix} = \begin{Bmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ c & 0 & c \end{Bmatrix} = \frac{1}{3\sqrt{2c+1}}$.
- The second $9j$ -factor is: $\begin{Bmatrix} 1 & \ell'_1 & \ell'_1 + 1 \\ 1 & \ell'_2 & \ell'_2 + 1 \\ u' & v' & c' \end{Bmatrix} = \begin{Bmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ b & 0 & b \end{Bmatrix} = \frac{1}{3\sqrt{2b+1}}$.

Thus, we have:

$$\begin{aligned} \sigma_{\text{RIXS}} &= C \sum_F \sum_{g_1, g_2} \sum_{a, b, c} (-1)^{a-g_2} \Pi_{g_1, g_2, b, c} \begin{Bmatrix} 1 & 1 & g_1 \\ 1 & 1 & g_2 \\ b & c & a \end{Bmatrix} \\ &\quad \left\{ \{E\}^{(b)} \otimes \{A\}^{(c)} \right\}^{(a)} \cdot \left\{ A_{FI}^{(g_1)}(0, 0) \otimes \overline{A}_{IF}^{(g_2)}(0, 0) \right\}^{(a)} \delta(E_F + \hbar\omega_s - E_I - \hbar\omega) \quad (23) \end{aligned}$$

Additionally,

$$\begin{aligned} \{E\}^{(b)} &= \left\{ \{\epsilon_s^* \otimes \epsilon_s\}^{(b)} \otimes \{\mathbf{k}_s^0 \otimes \mathbf{k}_s^0\}^{(0)} \right\}^{(b)} = \{\epsilon_s^* \otimes \epsilon_s\}^{(b)}, \\ \{A\}^{(c)} &= \left\{ \{\epsilon \otimes \epsilon^*\}^{(c)} \otimes \{\mathbf{k}^0 \otimes \mathbf{k}^0\}^{(0)} \right\}^{(c)} = \{\epsilon \otimes \epsilon^*\}^{(c)}. \end{aligned}$$

3.3 Electric dipole excitation and emission, powder sample

A further simplification arises when the sample is a powder. The ensuing isotropy implies that $a = 0$. Thus, we can use

$$\begin{Bmatrix} 1 & 1 & g_1 \\ 1 & 1 & g_2 \\ b & c & 0 \end{Bmatrix} = \frac{\delta_{g_1 g_2} \delta_{bc} (-1)^{g_1+b}}{\sqrt{(2g_1+1)(2b+1)}} \begin{Bmatrix} 1 & 1 & g_1 \\ 1 & 1 & b \end{Bmatrix}$$

This implies that $b = c$ and $g_1 = g_2$. Therefore,

$$\begin{aligned} \sigma_{\text{RIXS}} &= C \sum_{g,b} (-1)^b \Pi_{g,b} \begin{Bmatrix} 1 & 1 & g \\ 1 & 1 & b \end{Bmatrix} \left\{ \{E\}^{(b)} \otimes \{A\}^{(b)} \right\}^{(0)} \\ &\quad \sum_F \left\{ A_{FI}^{(g)}(0,0) \otimes \bar{A}_{IF}^{(g)}(0,0) \right\}^{(0)} \delta(E_F + \hbar\omega_s - E_I - \hbar\omega) \end{aligned} \quad (24)$$

- For the term $b = 0$:

$$\begin{Bmatrix} 1 & 1 & g \\ 1 & 1 & 0 \end{Bmatrix} = \frac{(-1)^g}{3},$$

with $g = 0, 1, 2$.

$$\{E\}^{(0)} \otimes \{A\}^{(0)} = \frac{1}{3}.$$

Thus,

$$\sigma_{\text{RIXS}}(b=0) = C \sum_{g=0}^2 (-1)^g \frac{\sqrt{2g+1}}{9} \sum_F \left\{ A_{FI}^{(g)}(0,0) \otimes \bar{A}_{IF}^{(g)}(0,0) \right\}^{(0)} \delta(E_F + \hbar\omega_s - E_I - \hbar\omega).$$

- For the term $b = 1$:

$$\begin{Bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{Bmatrix} = \begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 1 \end{Bmatrix} = \frac{1}{6},$$

$$\begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \end{Bmatrix} = -\frac{1}{3}.$$

$$\{\epsilon \otimes \epsilon^*\}^{(1)} = \frac{i}{\sqrt{2}} \epsilon \times \epsilon^* = -\frac{P_c}{\sqrt{2}} \mathbf{k},$$

where P_c is the rate of circular polarization. Note that P_c is positive for a right circular polarization in the traditional sense (i.e. for a negative helicity). $P_c = 0$ if the polarization is linear.

$$\left\{ \{E\}^{(1)} \otimes \{A\}^{(1)} \right\}^{(0)} = \frac{1}{2\sqrt{3}} P_c P_{c,s} \mathbf{k}_s \cdot \mathbf{k} = \frac{1}{2\sqrt{3}} (|\epsilon \cdot \epsilon_s^*|^2 - |\epsilon \cdot \epsilon_s|^2).$$

This result is interesting. We see that, for an unoriented sample, in particular for a sample without permanent magnetization direction, some circular dichroism can be observed if we measure the

circular polarization of the scattered beam. However, we need to avoid the configuration where the incident and scattered x-ray wavevectors are perpendicular. This remark shows the power of the geometric (coordinateless) approach. Note that, in this expression $P_{c,s}$ does not denote the degree of circular polarization of the scattered beam, but the efficiency of detection of the circularly polarized beam. Note also that $\epsilon \cdot \epsilon_s^*$ and $\epsilon \cdot \epsilon_s$ are the only non-trivial scalars that can be built from ϵ , ϵ_s and their conjugates. Therefore, we could expect them to be involved in this formula.

- For the term $b = 2$:

$$\begin{Bmatrix} 1 & 1 & g \\ 1 & 1 & 2 \end{Bmatrix} = \frac{4}{(2-g)!(3+g)!},$$

with $g = 0, 1, 2$. We have also

$$\left\{ \{E\}^{(2)} \otimes \{A\}^{(2)} \right\}^{(0)} = \frac{1}{\sqrt{5}} \left(\frac{1}{2} |\epsilon^* \cdot \epsilon_s|^2 + \frac{1}{2} |\epsilon \cdot \epsilon_s|^2 - \frac{1}{3} \right).$$

If the polarization of the scattered beam is not detected, then the corresponding term $b = 2$ is calculated using the relation: $\langle \{\epsilon_s \otimes \epsilon_s^*\}^{(2)} \rangle = -\mathbf{k}_s^{(2)}/2$ (see Appendix). Thus,

$$\left\{ \{E\}^{(2)} \otimes \{A\}^{(2)} \right\}^{(0)} = -\frac{1}{2\sqrt{5}} (|\mathbf{k}_s \cdot \epsilon|^2 - \frac{1}{3}).$$

3.4 Electric quadrupole excitation, electric dipole emission

Here we consider the case of an electric quadrupole transition in the absorption followed by an electric dipole transition in the emission: $\ell_1 = 1$, $\ell_2 = 1$, $\ell'_1 = 0$ and $\ell'_2 = 0$. Thus, we have:

$$\begin{aligned} 0 &\leq g_1 \leq 3, \\ 0 &\leq g_2 \leq 3, \\ 0 &\leq a \leq 6, \\ 0 &\leq b \leq 2, \\ 0 &\leq c \leq 4. \end{aligned}$$

Since $\ell_1 = 1$ and $\ell_2 = 1$, we have $0 \leq v \leq 2$. Additionally, $v \neq 1$ since $\{\mathbf{k}^1 \otimes \mathbf{k}^1\}^{(1)} = \frac{i}{\sqrt{2}} \mathbf{k} \times \mathbf{k} = 0$. Thus, $v = 0$ or 2 .

Since $\ell'_1 = 0$ and $\ell'_2 = 0$, we have $v' = 0$ and $b = u'$.

- The first $9j$ -factor is: $\begin{Bmatrix} 1 & \ell_1 & \ell_1 + 1 \\ 1 & \ell_2 & \ell_2 + 1 \\ u & v & c \end{Bmatrix} = \begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 2 \\ u & v & c \end{Bmatrix}$. It is non-zero if $u + v + c$ is even.
- The second $9j$ -factor is: $\begin{Bmatrix} 1 & \ell'_1 & \ell'_1 + 1 \\ 1 & \ell'_2 & \ell'_2 + 1 \\ u' & v' & b \end{Bmatrix} = \begin{Bmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ b & 0 & b \end{Bmatrix}$.
- The third $9j$ -factor is: $\begin{Bmatrix} \ell'_1 + 1 & \ell_1 + 1 & g_1 \\ \ell'_2 + 1 & \ell_2 + 1 & g_2 \\ b & c & a \end{Bmatrix} = \begin{Bmatrix} 1 & 2 & g_1 \\ 1 & 2 & g_2 \\ b & c & a \end{Bmatrix}$.

3.4.1 Powder sample

Isotropy implies that $a = 0$. This implies that $g_1 = g_2$ and $b = c = u'$.

3.4.2 Circularly polarized light

For circularly polarized light we have

$$\{\epsilon \otimes \epsilon^*\}^{(1)} = \frac{i}{\sqrt{2}} \epsilon \times \epsilon^* = -\frac{P_c}{\sqrt{2}} \hat{\mathbf{k}},$$

The first $9j$ -factor is: $\left\{ \begin{matrix} 1 & 1 & 2 \\ 1 & 1 & 2 \\ 1 & v & a \end{matrix} \right\}$.

4 Conclusion

We have presented a detailed derivation of the RIXS cross section in geometric spherical tensor form. Some special cases were studied to illustrate the ability of this expression to describe global properties of the sample (such as being powder).

We have also clarified the meaning of the scattered beam polarization vector as a way to interpret a measurement of that beam.

This general formula is ideally suited for a group subduction corresponding to particular symmetry groups. This will be illustrated in a forthcoming publication.

5 Appendix

One of the most powerful features of geometric expressions is that they can be calculated in a specific coordinate system adapted to a particular problem, and then be valid in any system. We illustrate this by describing the average of the coupling of ϵ and ϵ^* : we show that

$$\begin{aligned} \langle \{\epsilon \otimes \epsilon^*\}^{(0)} \rangle &= -\frac{1}{\sqrt{3}}, \\ \langle \{\epsilon \otimes \epsilon^*\}^{(1)} \rangle &= 0, \\ \langle \{\epsilon \otimes \epsilon^*\}^{(2)} \rangle &= -\frac{\mathbf{k}^{(2)}}{\sqrt{6}} = -\sqrt{\frac{2\pi}{15}} Y_2(\mathbf{k}). \end{aligned}$$

We take a reference frame where \mathbf{k} is along Oz . The linear polarization vector is $\epsilon = (\cos \psi, \sin \psi, 0)$ and the corresponding spherical tensor components are $\epsilon_{\pm 1}^{(1)} = \mp e^{\pm i\psi} / \sqrt{2}$, $\epsilon_0^{(1)} = 0$. Therefore, it is easy to calculate

$$\begin{aligned} \{\epsilon \otimes \epsilon^*\}_{\pm 2}^{(2)} &= \frac{e^{\pm 2i\psi}}{2}, \\ \{\epsilon \otimes \epsilon^*\}_{\pm 1}^{(2)} &= 0, \\ \{\epsilon \otimes \epsilon^*\}_0^{(2)} &= -\frac{1}{\sqrt{6}}. \end{aligned}$$

The average over two perpendicular polarizations (ψ and $\psi + \pi/2$) or the average over all ψ gives us

$$\begin{aligned} \langle \{\epsilon \otimes \epsilon^*\}_{\pm 2}^{(2)} \rangle &= 0, \\ \langle \{\epsilon \otimes \epsilon^*\}_{\pm 1}^{(2)} \rangle &= 0, \\ \langle \{\epsilon \otimes \epsilon^*\}_0^{(2)} \rangle &= -\frac{1}{\sqrt{6}}. \end{aligned}$$

In that reference frame we also have $\mathbf{k}_m^{(2)} = \delta_{m,0} \sqrt{2/3}$. Thus, $\langle \{\epsilon \otimes \epsilon^*\}^{(2)} \rangle = -\mathbf{k}^{(2)}/2$. Moreover, this relation is true in all reference frames because it is a relation between two tensors.

We can also consider elliptically-polarized x-rays. The most general polarization vector in a frame where \mathbf{k} is along Oz is

$$\epsilon = \begin{pmatrix} \cos \chi \cos \psi + i \sin \chi \sin \psi \\ \cos \chi \sin \psi - i \sin \chi \cos \psi \\ 0 \end{pmatrix},$$

for which the degree of circular polarization is $\sin 2\chi$. In particular, $\chi = \pi/4$ for a fully circularly polarized x-ray. Then,

$$\begin{aligned} \{\epsilon \otimes \epsilon^*\}_{\pm 1}^{(1)} &= 0, \\ \{\epsilon \otimes \epsilon^*\}_0^{(1)} &= -\frac{1}{\sqrt{2}} \sin 2\chi, \end{aligned}$$

and

$$\begin{aligned} \{\epsilon \otimes \epsilon^*\}_{\pm 2}^{(2)} &= \frac{1}{2} \cos 2\chi e^{\pm 2i\psi}, \\ \{\epsilon \otimes \epsilon^*\}_{\pm 1}^{(2)} &= 0, \\ \{\epsilon \otimes \epsilon^*\}_0^{(2)} &= -\frac{1}{\sqrt{6}}. \end{aligned}$$

Therefore, by using left and right fully circularly polarized beams, we obtain the same average as with linear polarization.

6 Complex conjugate

We want to calculate the complex conjugate of $A_{FI}^{(g)}(\ell, \ell')$. The operators x , y and z are Hermitian. Therefore

$$\langle N|x|I \rangle = \langle N|x^\dagger|I \rangle = \langle I|x|N \rangle^*,$$

and $\langle N|x|I \rangle^* = \langle I|x|N \rangle$. The same is true for y and z . For the corresponding spherical tensors, we have

$$\langle N|r_1^{(1)}|I \rangle^* = -(1/\sqrt{2})(\langle N|x|I \rangle + i\langle N|y|I \rangle)^* = -(1/\sqrt{2})(\langle I|x|N \rangle - i\langle I|y|N \rangle) = -\langle I|r_{-1}^{(1)}|N \rangle^*.$$

An analogous calculation for the other components of $r^{(1)}$ gives us $\langle N|r_\lambda^{(1)}|I \rangle^* = (-1)^\lambda \langle I|r_{-\lambda}^{(1)}|N \rangle$. For $\ell = 2$, we have

$$\begin{aligned} \langle N|r_\mu^{(2)}|I \rangle^* &= \sum_{\lambda\lambda'} (1\lambda 1\lambda' | 2\mu) \langle N|r_\lambda^{(1)} r_{\lambda'}^{(1)}|I \rangle^* = \sum_{\lambda\lambda'} (1\lambda 1\lambda' | 2\mu) \sum_K \langle N|r_\lambda^{(1)}|K \rangle^* \langle K|r_{\lambda'}^{(1)}|I \rangle^* \\ &= \sum_{\lambda\lambda'} (1\lambda 1\lambda' | 2\mu) (-1)^{\lambda+\lambda'} \sum_K \langle K|r_{-\lambda}^{(1)}|N \rangle \langle I|r_{-\lambda'}^{(1)}|K \rangle. \end{aligned}$$

The Clebsch-Gordan coefficient implies that $\lambda + \lambda' = \mu$. We replace λ and λ' by $-\lambda'$ and $-\lambda$, respectively, and we obtain

$$\begin{aligned} \langle N|r_\mu^{(2)}|I \rangle^* &= (-1)^\mu \sum_{\lambda\lambda'} (1-\lambda' 1-\lambda | 2\mu) \sum_K \langle I|r_{\lambda'}^{(1)}|K \rangle \langle K|r_{-\lambda}^{(1)}|N \rangle \\ &= (-1)^\mu \sum_{\lambda\lambda'} (1-\lambda' 1-\lambda | 2\mu) \langle I|r_\lambda^{(1)} r_{\lambda'}^{(1)}|N \rangle. \end{aligned}$$

Now, we use the symmetry $(\ell_1 m_1 \ell_2 m_2 | \ell_3 m_3) = (\ell_2 - m_2 \ell_1 - m_1 | \ell_3 - m_3)$ to obtain

$$\langle N|r_\mu^{(2)}|I \rangle^* = (-1)^\mu \sum_{\lambda\lambda'} (1\lambda 1\lambda' | 2-\mu) \langle I|r_\lambda^{(1)} r_{\lambda'}^{(1)}|N \rangle = (-1)^\mu \langle I|r_{-\mu}^{(2)}|N \rangle.$$

A recursive use of this argument leads to $\langle N|r_m^{(\ell)}|I\rangle^* = (-1)^\mu \langle I|r_{-m}^{(\ell)}|N\rangle$ for any ℓ .

We proceed with

$$X_\gamma = \{\mathbf{r}_{FN}^{(\ell')} \otimes \mathbf{r}_{NI}^{(\ell)}\}_\gamma^{(g)} = \sum_{m'm} (\ell' m' \ell m | g \gamma) \langle F | \mathbf{r}_{m'}^{(\ell')} | N \rangle \langle N | \mathbf{r}_m^{(\ell)} | I \rangle.$$

The complex conjugate of X_γ is

$$X_\gamma^* = \sum_{m'm} (\ell' m' \ell m | g \gamma) \langle F | \mathbf{r}_{m'}^{(\ell')} | N \rangle^* \langle N | \mathbf{r}_m^{(\ell)} | I \rangle^* = \sum_{m'm} (\ell' m' \ell m | g \gamma) (-1)^{m+m'} \langle N | \mathbf{r}_{-m'}^{(\ell')} | F \rangle \langle I | \mathbf{r}_{-m}^{(\ell)} | N \rangle.$$

The same reasoning as for the complex conjugate of $\langle N|r_\mu^{(2)}|I\rangle$ gives us

$$\left(\{\mathbf{r}_{FN}^{(\ell')} \otimes \mathbf{r}_{NI}^{(\ell)}\}_\gamma^{(g)} \right)^* = (-1)^\gamma \{\mathbf{r}_{IN}^{(\ell)} \otimes \mathbf{r}_{NF}^{(\ell')}\}_{-\gamma}^{(g)}.$$

Finally,

$$A_{FI,\gamma}^{(g)}(\ell, \ell')^* = (-1)^\gamma \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega - i\gamma} \{\mathbf{r}_{IN}^{(\ell+1)} \otimes \mathbf{r}_{NF}^{(\ell'+1)}\}_{-\gamma}^{(g)}. \quad (25)$$

Therefore, if we define

$$\overline{A}_{IF}^{(g)}(\ell, \ell') = \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega - i\gamma} \{\mathbf{r}_{IN}^{(\ell+1)} \otimes \mathbf{r}_{NF}^{(\ell'+1)}\}_\gamma^{(g)}, \quad (26)$$

we have $A_{FI,\gamma}^{(g)}(\ell, \ell')^* = (-1)^\gamma \overline{A}_{IF,-\gamma}^{(g)}(\ell, \ell')$.

In applications, we compute only $\langle N|r_\lambda^{(\ell)}|I\rangle$ and not $\langle I|r_\lambda^{(\ell)}|N\rangle$ that we need to calculate $A_{FI,\gamma}^{(g)}(\ell, \ell')^*$. However, we can easily obtain it by $\langle N|r_\lambda^{(\ell)}|I\rangle = (-1)^\lambda \langle I|r_{-\lambda}^{(\ell)}|N\rangle^*$.

We also have to calculate the complex conjugate of $\left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{\ell'+1} \otimes \{\epsilon \otimes \mathbf{k}^\ell\}^{\ell+1} \right\}_\gamma^{(g)}$. The calculation is very similar. Consider a vector $\mathbf{z} = \mathbf{a} + i\mathbf{b}$, where $\mathbf{a} = (a_x, a_y, a_z)$ and $\mathbf{b} = (b_x, b_y, b_z)$ are real. We have

$$\begin{aligned} (\mathbf{z}_1^{(1)})^* &= -\frac{1}{\sqrt{2}}(a_x + ib_x + i(a_y + ib_y))^* = -\frac{1}{\sqrt{2}}(a_x - ib_x - ia_y - b_y) \\ &= -\frac{1}{\sqrt{2}}(a_x - ib_x - i(a_y - ib_y)) = -(\mathbf{z}^*)_{-1}^{(1)}. \end{aligned}$$

The calculation of the other components gives us $(\mathbf{z}_\lambda^{(1)})^* = (-1)^\lambda (\mathbf{z}^*)_{-\lambda}^{(1)}$. Therefore, $(\epsilon_\lambda)^* = (-1)^\lambda (\epsilon^*)_{-\lambda}$ and $((\epsilon_s^*)_\lambda)^* = (-1)^\lambda (\epsilon_s)_{-\lambda}$. The vector \mathbf{k} is real and $(\mathbf{k}_m^{(\ell)})^* = (-1)^m \mathbf{k}_{-m}^{(\ell)}$. By repeating the proof for $A_{FI}^{(g)}(\ell, \ell')$ we have

$$\left(\{\epsilon \otimes \mathbf{k}^\ell\}_m^{(\ell+1)} \right)^* = (-1)^m \sum_{\lambda\mu} (1 - \lambda\ell - \mu|\ell + 1m) \epsilon_\lambda^* k_\mu^{(\ell)}.$$

Since we do not interchange 1λ and $\ell\mu$, we must use the symmetry relation

$$(\ell_1 m_1 \ell_2 m_2 | \ell_3 m_3) = (-1)^{\ell_1 + \ell_2 - \ell_3} (\ell_1 - m_1 \ell_2 - m_2 | \ell_3 - m_3), \quad (27)$$

to get

$$\left(\{\epsilon \otimes \mathbf{k}^\ell\}_m^{(\ell+1)} \right)^* = (-1)^m \sum_{\lambda\mu} (1\lambda\ell\mu | \ell + 1 - m) \epsilon_\lambda^* k_\mu^{(\ell)} = (-1)^m \{\epsilon^* \otimes \mathbf{k}^\ell\}_{-m}^{(\ell+1)}.$$

Here, the symmetry relation does not bring any additional sign because $\ell_3 = \ell_1 + \ell_2$. Similarly, $\left(\{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}_{m'}^{(\ell'+1)}\right)^* = (-1)^{m'} \{\epsilon_s \otimes \mathbf{k}_s^{\ell'}\}_{-m'}^{(\ell'+1)}$. We now do the same calculation for $\left\{\{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)}\right\}_\gamma^{(g)}$, but here, the sign $(-1)^{\ell+\ell'-g}$ must be retained and we get

$$\left(\left\{\{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)}\right\}_\gamma^{(g)}\right)^* = (-1)^\gamma (-1)^{\ell+\ell'-g} \left\{\{\epsilon_s \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon^* \otimes \mathbf{k}^\ell\}^{(\ell+1)}\right\}_{-\gamma}^{(g)}.$$

Finally, the complex conjugate of $X = \left\{\{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon \otimes \mathbf{k}^\ell\}^{(\ell+1)}\right\}^{(g)} \cdot A_{FI}^{(g)}(\ell, \ell')$ is

$$X^* = (-1)^{\ell+\ell'-g} \left\{\{\epsilon_s \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon^* \otimes \mathbf{k}^\ell\}^{(\ell+1)}\right\}^{(g)} \cdot \overline{A}_{IF}^{(g)}(\ell, \ell').$$

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