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Angular dependence of resonant inelastic x-ray scattering: a spherical tensor expansion

Research Article

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Abstract: A spherical tensor expansion is carried out to express the resonant inelastic scattering cross-section as a sum of products of fundamental spectra with tensors involving wavevectors and polarization vectors of incident and scattered photons. The expression presented in this paper differs from that of the influential article by Carra et al. (Phys. Rev. Lett. 74, 3700, 1995) because it does not omit interference terms between electric dipole and quadrupole contributions when coupling each photon to itself. Some specific cases of the spherical tensor expansion are discussed. For example the case of isotropic samples is considered and the cross-section is expressed as a combination of only three fundamental spectra for the situation where electric dipole or electric quadrupole transitions in the absorption process are followed by electric dipole transitions in the emission. This situation includes the case of untextured powder samples, which corresponds to the most frequent situation met experimentally. Finally, it is predicted that some circular dichroism may be observed on isotropic samples provided that the circular polarization of the scattered beam can be detected.

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1. Introduction

Resonant inelastic scattering (RIS) spectroscopies are remarkable tools to study electronic, magnetic and vibrational properties of materials [1]. They span a broad energy range, from infrared frequencies for phonon excitations, through optical photons for electronic excitations to x-ray energies for Resonant Inelastic X-ray Scattering (RIXS). The richness of these spectroscopies is due to the large number of possible spectra obtained by varying the energy, direction and polarization state of the incident and scattered electromagnetic waves. As a matter of fact, there is so much information in the spectra that it is difficult to know whether a specific set of experiments measures all potential information. The main purpose of this paper is

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to determine a finite set of fundamental spectra in terms of which all possible experimental spectra can be expressed. More precisely, the resonant inelastic scattering 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 fundamental spectra [2, 5] (independent of the incident and scattered beam) multiplied by an explicit polynomial in $\mathbf{k}$, ϵ, $\mathbf{k}_s$ and ϵ_s.

The fundamental spectra will be computed by a spherical tensor analysis, which was used with great success for the x-ray photoemission of localized magnetic systems [6, 8–11] and in x-ray absorption spectroscopy [2, 4, 5, 7, 12]. For the case of x-ray absorption [12] such geometric (*i.e.* coordinateless) and fully-decoupled 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 most convenient starting point to investigate the reduction of the number of fundamental spectra due to crystal symmetries.

Following the same idea in the present case, the resonant inelastic scattering cross-section is expressed as the smallest possible combination of fundamental spectra. To do so, the remarkable angular momentum recoupling techniques developed by the Lithuanian school [13, 14] are used. As an application of the general results, the most common experimental case of an isotropic sample (disordered molecules, liquids, polycrystals or powders) is described in detail. It is demonstrated that the spectrum of an isotropic sample for electric dipole excitation and electric dipole emission with undetected scattered polarization is the sum of only three fundamental spectra, compared to 19 in the general spherical-tensor-based expression (and versus the 81 components of a general fourth-rank Cartesian tensor).

The starting point of this work is the Kramers-Heisenberg formula [15, 16], extended to take electric quadrupole transitions into account. The Thomson scattering term is not explicitly considered but it can be easily included (see below). For simplicity, the non-resonant term in the Kramers-Heisenberg formula is neglected (i.e., assuming the vicinity of an absorption edge). If the non-resonant term is sizeable [3], it can be taken into account by similar methods. It would also be possible to take variable decay lifetimes into account [17], but in this paper only the standard Kramers-Heisenberg formulation is considered for simplicity. Electric dipole and quadrupole transitions contribute significantly in the x-ray range [19]. Using x-ray photons, typically from a synchrotron radiation source, one can choose a specific atomic species and orbital in a complex compound by selecting the suitable absorption edge. The sample can be magnetic, it can be submitted to an external electric or magnetic field, as long as the orientation of the external fields remains constant with respect to the sample. Thus, the results presented in this paper are a pure group theoretical consequence of the resonant scattering cross-section formula. Such an expansion does not need to assume that a specific edge is measured (*i.e.*, only the nature of the transitions involved is specified) nor to assume that the states involved in the transitions are localized or delocalized.

The paper consists of three parts. In the first part, the spherical tensor expression is derived for the resonant scattering amplitude. Similar expressions were already published [20, 22–24]. The second part of this paper consists of a full recoupling of the scattering amplitude to obtain the spherical tensor decomposition of the scattering cross-section. At this stage, several works in the literature make specific approximations, for example by considering a localized initial state or by using the fast collision approximation (which is not generally valid [25]). Finally, recoupling techniques are used to separate the incident beam from the scattered beam in the cross section and to separate the polarization part from the wavevector part. This enables to treat the frequent experimental case where the polarization state of the scattered beam is not measured.

Related results were obtained in specific experimental conditions [26, 27] or in specific coordinate systems [28–30] but this general expression is new. Its coordinateless form enables descriptions of the general form of the resonant inelastic spectroscopy of isotropic samples. Other works use an approach similar to that presented in this paper [1, 20, 31], but they do not take into account the interference between electric dipole and electric quadrupole transitions which generates natural circular dichroism [32, 33], or they carry out a different coupling.

A consequence of the formula presented in this paper is that circular dichroism can be observed for isotropic (in particular not magnetically oriented) samples, if the polarization of the scattered beam can be measured experimentally. The third part of the paper contains appendices giving the detail of the derivations.

2. General case

2.1. The Kramers-Heisenberg formula

The scattering of light by a quantum system is described by an equation derived by Kramers and Heisenberg before the advent of quantum theory [15]. Its first quantum derivation (in the electric-dipole approximation) is due to

Dirac [34]. The multipole scattering cross-section is [35]:

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

where m is the electron mass, r_e is the classical electron radius: $r_e = e^2/(4\pi\epsilon_0 mc^2)$, $|I\rangle$, $|N\rangle$, $|F\rangle$ are respectively the initial, intermediate and final states, γ is the total width of the intermediate state $|N\rangle$, $\mathbf{P}$ and $\mathbf{r}$ are the momentum and position operators. The incident and scattered photons are characterized by the pulsation, wavevector and polarization vectors $\omega, \mathbf{k}, \epsilon$ and $\omega_s, \mathbf{k}_s, \epsilon_s$, respectively. Note that ϵ_s^* denotes the complex conjugate of ϵ_s.

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

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

For notational convenience, a single variable $\mathbf{P}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}$ is written instead of a sum over all electrons of the system $\sum_{j=1}^{N} \mathbf{P}_j \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}_j}$.

2.2. Multipole expansion

First the matrix element $\langle N|\epsilon\cdot\mathbf{P}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}|I\rangle$, describing the absorption from the initial state $|I\rangle$ to the intermediate state $|N\rangle$, is transformed by expanding $\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}$ to first order: $\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} \simeq 1 + i\mathbf{k}\cdot\mathbf{r}$. Hence,

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

The electric dipole matrix element is transformed by using the equation of motion of $\mathbf{P}$ which is $\mathbf{P} = (m/i\hbar)[\mathbf{r}, H_0]$ [19]. 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. [36],

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

where $\mathbf{L}$ is the angular momentum operator. In this work the second (magnetic dipole) term is not taken into account because it is small in the x-ray range [19]. Therefore

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

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

Similarly, on transforming the matrix element describing the emission from the intermediate state $|N\rangle$ to the final state $|F\rangle$,

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

Finally,

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

where $\delta_E = \delta(E_F + \hbar\omega_s - E_I - \hbar\omega)$. Denoting $C = r_e^2\omega_s/(\hbar^2\omega)$ and

$$F_{I,N,F} = \sum_{\ell,\ell'=0}^{1} f_\ell f_{\ell'}^* \langle N|\epsilon\cdot\mathbf{r}(\mathbf{k}\cdot\mathbf{r})^\ell|I\rangle\langle F|\epsilon_s^*\cdot\mathbf{r}(\mathbf{k}_s\cdot\mathbf{r})^{\ell'}|N\rangle,$$

Equation (3) becomes:

$$\sigma_{\mathrm{KH}} = C\sum_F \Big|\sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma} F_{I,N,F}\Big|^2 \delta_E. \quad (4)$$

Equation (4) is a general expression describing the resonant inelastic scattering 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 of both ($E_1 + E_2$).

2.3. The Kramers-Heisenberg formula expressed in terms of spherical tensors

The expression of the $F_{I,N,F}$ intensity factor appearing in the Kramers-Heisenberg equation (Equation (4)) is transformed using spherical tensors and their coupling properties. This transformation is detailed in Appendices A.1 and A.2. For a short introduction to spherical tensors and their application to x-ray spectroscopies, the reader is referred to Ref. [12] for the case of the X-ray absorption cross-section. First the notation is briefly explained.

An ℓth-rank spherical tensor T is written as $T^{(\ell)}$, not to be mistaken for T^{ℓ}, the ℓth 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 should keep in mind that Cartesian vectors correspond to first-rank spherical tensors, and as such they shall also be written as $\epsilon^{(1)}$, $\mathbf{r}^{(1)}$, $\mathbf{k}^{(1)}$ or ϵ^{1}, $\mathbf{r}^{1}$, $\mathbf{k}^{1}$.

After the transformation of $F_{I,N,F}$ (see Appendices A.1 and A.2), Equation (4) becomes:

$$\sigma_{\mathrm{KH}} = C\sum_F \left| \sum_N \sum_{g,\ell,\ell'} \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma} \frac{(-1)^g h_\ell h^*_{\ell'}}{\sqrt{(2\ell+3)(2\ell'+3)}} \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon \otimes \mathbf{k}^{\ell}\}^{(\ell+1)} \right\}^{(g)} \cdot \left\{ \mathbf{r}_{FN}^{(\ell'+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)} \right\}^{(g)} \right|^2 \delta_E,$$

where g runs from $|\ell - \ell'|$ to $(\ell + \ell' + 2)$, ℓ and ℓ' run from 0 to 1. The h_ℓ factors are defined by $h_0 = -\sqrt{3}$, $h_1 = \frac{i}{2}\sqrt{5}$.

In Refs. [20, 31], a similar formula was obtained in terms of vector spherical harmonics. The present coupling is chosen (as in [20]) to avoid irrelevant powers of $\sqrt{4\pi}$ in the final result.

The first tensor product $\left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon \otimes \mathbf{k}^{\ell}\}^{(\ell+1)} \right\}^{(g)}$ characterizes the incident beam $(\epsilon, \mathbf{k})$ and the scattered beam $(\epsilon_s, \mathbf{k}_s)$. The variables describing 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

$$A_{FI}^{(g)}(\ell,\ell') = \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma} \{\mathbf{r}_{FN}^{(\ell'+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)}\}^{(g)}, \tag{5}$$

one obtains

$$\sigma_{\mathrm{KH}} = C\sum_F \left| \sum_{g,\ell,\ell'} \frac{(-1)^g h_\ell h^*_{\ell'}}{\sqrt{(2\ell+3)(2\ell'+3)}} \left\{ \{\epsilon_s^* \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \{\epsilon \otimes \mathbf{k}^{\ell}\}^{(\ell+1)} \right\}^{(g)} \cdot A_{FI}^{(g)}(\ell,\ell') \right|^2 \delta_E. \tag{6}$$

Note that Thomson scattering can be taken into account as a contribution to the term $A_{FI}^{(0)}(0,0)$. In the case of x-rays, at this stage of the spherical tensor expansion, the local nature of the initial core orbital is often used in the literature to specify the absorption edge [37]. Such an approach is powerful to derive sum rules, for instance. In this paper a general initial state is used.

As remarked by Carra and coll. [31], it is much more convenient to work with each photon coupled to itself instead of with the incident photon coupled to the scattered one as in Eq. (6). This is achieved by expanding the square modulus in Eq. (6) and recoupling the spherical tensors describing the incident and scattered beams. In the influential Ref. [31] the authors note that "This is a rather technical part in our derivation, and will not be discussed here." The calculation is indeed lengthy and a detailed derivation is given in Appendices A.3 and A.4). This allows the derivation of the final expression for σ_{KH}, which now has fully decoupled sample- and beam-dependent parts:

$$\sigma_{\mathrm{KH}} = \sum_{g_1,g_2,\ell_1,\ell_2,\ell_1',\ell_2'} \sum_{a,b,c,u,u',v,v'} (-1)^{a+\ell_2+\ell_2'-g_2} h_{\ell_1} h^*_{\ell_1'} h^*_{\ell_2} h_{\ell_2'} \Pi_{g_1,g_2,b,c,u,v,u',v'} \begin{Bmatrix} \ell_1'+1 & \ell_1+1 & g_1 \\ \ell_2'+1 & \ell_2+1 & g_2 \\ b & c & a \end{Bmatrix} \begin{Bmatrix} 1 & \ell_1 & \ell_1+1 \\ 1 & \ell_2 & \ell_2+1 \\ u & v & c \end{Bmatrix} \begin{Bmatrix} 1 & \ell_1' & \ell_1'+1 \\ 1 & \ell_2' & \ell_2'+1 \\ u' & v' & b \end{Bmatrix} \gamma^{bca}_{UL} \cdot S_L^{g_1 g_2 a}, \tag{7}$$

where $h_0 = -\sqrt{3}$, $h_1 = \frac{i}{2}\sqrt{5}$, $U = (u, v, u', v')$ and $L = (\ell_1, \ell_2, \ell_1', \ell_2')$. The tensors γ^{bca}_{UL} describe the incident and scattered x-rays, the tensor $S_L^{g_1 g_2 a}$ describes the sample. More precisely,

$$\gamma^{bca}_{UL} = \left\{ \mathrm{Out}^{(b)}_{UL} \otimes \mathrm{In}^{(c)}_{UL} \right\}^{(a)}, \tag{8}$$

is obtained by coupling the tensors $\mathrm{In}^{(c)}_{UL}$ of the incident beam and the tensors $\mathrm{Out}^{(b)}_{UL}$ of the scattered (outgoing) beam, where

$$\mathrm{Out}^{(b)}_{UL} = \left\{ \{\epsilon_s^* \otimes \epsilon_s\}^{(u')} \otimes \{\mathbf{k}_s^{\ell_1'} \otimes \mathbf{k}_s^{\ell_2'}\}^{(v')} \right\}^{(b)}, \tag{9}$$

$$\mathrm{In}^{(c)}_{UL} = \left\{ \{\epsilon \otimes \epsilon^*\}^{(u)} \otimes \{\mathbf{k}^{\ell_1} \otimes \mathbf{k}^{\ell_2}\}^{(v)} \right\}^{(c)}. \tag{10}$$

The tensors describing the sample are

$$S_L^{g_1 g_2 a} = \frac{r_e^2 \omega_s}{\hbar^2 \omega} \sum_F \left\{ A^{(g_1)}_{FI}(\ell_1, \ell_1') \otimes \overline{A}^{(g_2)}_{IF}(\ell_2, \ell_2') \right\}^{(a)} \delta(E_F + \hbar\omega_s - E_I - \hbar\omega), \tag{11}$$

where

$$A^{(g)}_{FI}(\ell, \ell') = \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma} \{\langle F|\mathbf{r}^{(\ell'+1)}|N\rangle \otimes \langle N|\mathbf{r}^{(\ell+1)}|I\rangle\}^{(g)},$$

$$\overline{A}^{(g)}_{IF}(\ell, \ell') = \sum_N \frac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega - i\gamma} \{\langle I|\mathbf{r}^{(\ell+1)}|N\rangle \otimes \langle N|\mathbf{r}^{(\ell'+1)}|F\rangle\}^{(g)}.$$

The spherical tensors $S_L^{g_1 g_2 a}$ are the fundamental spectra from which all experimental spectra can be expressed. These fundamental spectra are weighted by coefficients γ^{bca}_{UL} which are polynomials in ϵ, ϵ_s, $\mathbf{k}$ and $\mathbf{k}_s$ and which describe the experimental conditions. The three 9-j-symbols (and the related triangular conditions) ensure that these variables are coupled in the scattering process in a correct (physical) way.

The result presented in this paper differs from that of Ref. [31] because, as noted by Ferriani [21], these authors neglect some interference effects. More precisely, they replace the square modulus of the sum $|\sum_{\ell\ell'} \ldots|^2$ in eq. (4) of the present paper by the sum of the square moduli $\sum_{\ell\ell'} |\ldots|^2$. Since this approximation is not made here, there is an additional 9j recoupling coefficient describing the interference between electric dipole and quadrupole contributions when each photon is coupled to itself. These interference terms are physically relevant since, even in the simpler case of x-ray absorption, they lead to important effects such as natural circular dichroism [32, 33], non-reciprocal gyrotropy [38] and magnetochiral dichroism [39].

The sum rules derived in Ref. [31, 37] may have a restricted range of validity inasmuch as they neglect these interference terms. In subsequent articles [1, 20], the multipole matrix elements are coupled in a different way, which avoids the additional 9j-coefficients but is no longer compatible with sum rules or Green function representations.

Applications of the above general expression to particular cases will be given as examples in Section 3, but before

that the range of values of the different variables in Eq. (7) is specified.

2.4. Possible values of the different indices appearing in Equation (7)

The "selection rules" of the 9-j symbols give the following possible values taken by the angular variables in Equation (7).

- $0 \leq \ell_i \leq 1$ (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. Applications to special cases

In this section several special cases of Equation (7) are considered.

3.1. Conditions due to the type of polarization

Knowing the type of beam polarization reduces the number of values that the indices u and u' are allowed to take. When the incident beam is linearly polarized, then $u = 0$ or 2. Note that there is a basic difference between the polarization of the incident beam and that of the scattered beam. Indeed, the incident beam is prepared by the experimental setup (ϵ can be tuned as one wishes) while the polarization state of the scattered beam is entirely determined by the incident beam and the sample. It cannot be tuned. However, the polarization properties of the scattered beam can be measured. If the requirement is to measure the intensity along the polarization direction ϵ_s, then that ϵ_s is introduced in the formula. If the polarization state is not measured, then the trace of the density matrix representing the polarization state of the scattered beam can be taken. In other words, the measured cross-section is equal to the sum over two perpendicular directions of the scattered polarization (see Appendix C). In this case the term corresponding to $u' = 1$ in Equation (7) vanishes since $\langle \{\epsilon_s \otimes \epsilon_s^*\}^{(1)} \rangle = 0$.

It is important to discuss the case where the polarization of the scattered beam is not measured. As proved in Appendix C, this corresponds to an average of polarizations but not to an "isotropic photon". The concept of isotropic photon was used in the literature [1, 20, 31, 37, 40, 41]. An isotropic incoming photon would correspond to $b = 0$ in Eq. (10) and an isotropic outgoing photon to $c = 0$ in Eq. (9). At first, it was mistakenly stated that an isotropic photon is an unpolarized photon [37]. As shown in Appendix C, this is not the case and an unpolarized incident photon (for example) is the sum of a contribution $c = 0$ and a contribution $c = 2$. Indeed, the photon polarization vector ϵ is always perpendicular to the photon direction $\mathbf{k}$. Thus, an unpolarized photon is not isotropic in all space, it is only isotropic in the plane perpendicular to $\mathbf{k}$. For example, angle-dependent x-ray absorption can be carried out with unpolarized beams [19]. This anisotropy of unpolarized light is the origin of the $b = 2$ contribution to the scattered beam. The multipole (*i.e.* $b = 0$ and $b = 2$) nature of unpolarized light was clarified by Veenendaal and Benoist [20]. The identification of isotropic and unpolarized photons was corrected in Ref. [37].

In the next sections, RIXS spectra are discussed for electric dipole emission (i.e. $(\ell'_1, \ell'_2) = (0, 0)$), and either electric dipole excitation (i.e. $(\ell_1, \ell_2) = (0, 0)$) or electric quadrupole excitation (i.e. $(\ell_1, \ell_2) = (1, 1)$). Mixed excitations (i.e. $(\ell_1, \ell_2) = (0, 1)$ and $(1, 0)$) are deferred to a forthcoming paper.

3.2. Electric dipole excitation, electric dipole emission

Let an electric dipole transition in the absorption be followed by an electric dipole transition in the emission:

$\ell_1 = 0$, $\ell_2 = 0$, $\ell'_1 = 0$ and $\ell'_2 = 0$. Thus:

$$0 \le g_1 \le 2, \quad 0 \le g_2 \le 2, \quad 0 \le a \le 4,$$
$$0 \le b \le 2, \quad 0 \le c \le 2.$$

Since $\ell_1 = 0$, $\ell_2 = 0$, then $v = 0$. This implies $c = u$. Since $\ell'_1 = 0$ and $\ell'_2 = 0$, then $v' = 0$ and $b = u'$. These conditions allow the calculation of the values of all $9j$ symbols needed (see Appendix D.1).

The scattering cross section simplifies to:

$$\sigma_{\mathrm{KH}}^{E1E1} = \sum_{g_1,g_2}\sum_{a,b,c}(-1)^{a-g_2}\Pi_{g_1,g_2,b,c}\begin{Bmatrix}1 & 1 & g_1\\ 1 & 1 & g_2\\ b & c & a\end{Bmatrix}\left\{\{\epsilon_s^*\otimes\epsilon_s\}^{(b)}\otimes\{\epsilon\otimes\epsilon^*\}^{(c)}\right\}^{(a)}\cdot S_{L_0}^{g_1g_2a}, \tag{12}$$

where $L_0 = (0,0,0,0)$.

3.3. Electric dipole excitation and dipole emission, isotropic sample

A further simplification arises when the sample is isotropic. This corresponds to the case of a liquid or a powder sample, with no prefered orientation and no remanent magnetization. The ensuing isotropy implies that $a = 0$ and

$$\begin{Bmatrix}1 & 1 & g_1\\ 1 & 1 & g_2\\ b & c & 0\end{Bmatrix} = \frac{\delta_{g_1g_2}\delta_{bc}(-1)^{g_1+b}}{\sqrt{(2g_1+1)(2b+1)}}\begin{Bmatrix}1 & 1 & g_1\\ 1 & 1 & b\end{Bmatrix}.$$

Therefore,

$$\sigma_{\mathrm{KH}}^{E1E1} = \sum_{g,b}(-1)^b\Pi_{g,b}\begin{Bmatrix}1 & 1 & g\\ 1 & 1 & b\end{Bmatrix}\gamma_{L_0U}^{bb0}S_{L_0}^{gg0}. \tag{13}$$

Note that the variables g can take the values 0, 1 and 2, so that only three fundamental spectra are needed to generate all the spectra that can be measured on a powder. The variable b describing the incident and scattered beams can take the value 0, 1 and 2.

- For $b = 0$:

$$\sigma_{\mathrm{KH}}^{E1E1}(b=0) = \sum_{g=0}^{2}(-1)^g\frac{\sqrt{2g+1}}{9}S_{L_0}^{gg0}.$$

- For $b = 1$:

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

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. Similarly, $P_{c,s}$ is defined by $P_{c,s} = i\epsilon_s^*\times\epsilon_s$ and

$$\gamma_{L_0U}^{bb0} = \frac{1}{2\sqrt{3}}P_cP_{c,s}\mathbf{k}_s.\mathbf{k} = \frac{1}{2\sqrt{3}}(|\epsilon\cdot\epsilon_s^*|^2 - |\epsilon\cdot\epsilon_s|^2).$$

Thus

$$\sigma_{\mathrm{KH}}^{E1E1}(b=1) = \sum_{g=0}^{2} -\frac{\sqrt{2g+1}}{2}\begin{Bmatrix}1 & 1 & g\\ 1 & 1 & 1\end{Bmatrix}(|\epsilon\cdot\epsilon_s^*|^2 - |\epsilon\cdot\epsilon_s|^2)S_{L_0}^{gg0}. \tag{14}$$

This result is interesting: for an unoriented sample, in particular for a powder sample without permanent magnetization direction and in the absence of magnetic dipole transitions, some circular dichroism can be observed when measuring the circular polarization of the scattered beam, for example using the polarization analysis device described in Ref. [42]. However, the incident and scattered wavevectors must not be perpendicular. This remark shows the power of the geometric (coordinateless) approach. Note that $\epsilon\cdot\epsilon_s^*$ and $\epsilon\cdot\epsilon_s$ are expected to be involved in this formula because they are the only non-trivial scalars that can be built from ϵ, ϵ_s and their conjugates.

- For $b = 2$:

$$\sigma_{\mathrm{KH}}^{E1E1}(b=2) = \sum_{g=0}^{2}\frac{4\sqrt{2g+1}}{(2-g)!(3+g)!}\left(\frac{1}{2}|\epsilon^*\cdot\epsilon_s|^2 + \frac{1}{2}|\epsilon\cdot\epsilon_s|^2 - \frac{1}{3}\right)S_{L_0}^{gg0}.$$

The final expression of the Kramers–Heisenberg cross-section for an isotropic sample, electric dipole absorption and dipole emission is:

$$\sigma_{\rm KH}^{E1E1}=\sum_{g=0}^{2}\left((-1)^g\frac{\sqrt{2g+1}}{9}-\frac{\sqrt{2g+1}}{2}\begin{Bmatrix}1&1&g\\1&1&1\end{Bmatrix}(|\epsilon\cdot\epsilon_s^*|^2-|\epsilon\cdot\epsilon_s|^2)+\frac{4\sqrt{2g+1}}{(2-g)!(3+g)!}\left(\frac{1}{2}|\epsilon^*\cdot\epsilon_s|^2+\frac{1}{2}|\epsilon\cdot\epsilon_s|^2-\frac{1}{3}\right)\right)S_{L_0}^{gg0}. \tag{15}$$

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

$$\left\langle\gamma_{L_0U}^{bb0}\right\rangle = -\frac{1}{2\sqrt{5}}\left(|\mathbf{k}_s\cdot\epsilon|^2-\frac{1}{3}\right). \tag{16}$$

In this case,

$$\left\langle\sigma_{\rm KH}^{E1E1}\right\rangle = \sum_{g=0}^{2}\left((-1)^g\frac{\sqrt{2g+1}}{9}-\frac{2\sqrt{2g+1}}{(2-g)!(3+g)!}\left(|\mathbf{k}_s\cdot\epsilon|^2-\frac{1}{3}\right)\right)S_{L_0}^{gg0}. \tag{17}$$

3.4. Electric quadrupole excitation, electric dipole emission

This section considers the case of electric quadrupole transitions in the absorption followed by electric dipole transitions in the emission: $\ell_1=1$, $\ell_2=1$, $\ell_1'=0$ and $\ell_2'=0$. Thus:

$$1\le g_1\le 3,\quad 1\le g_2\le 3,\quad 0\le a\le 6,\quad 0\le b\le 2,\quad 0\le c\le 4.$$

Since $\ell_1=1$ and $\ell_2=1$, $0\le v\le 2$. Additionally, $v\neq 1$ since $\{\mathbf{k}\otimes\mathbf{k}\}^{(1)}=\frac{i}{\sqrt{2}}\mathbf{k}\times\mathbf{k}=0$. Thus, $v=0$ or 2. Since $\ell_1'=0$ and $\ell_2'=0$, $v'=0$ and $b=u'$. The values of all $9j$ symbols needed are given in Appendix D.2.

Thus,

$$\sigma_{\rm KH}^{E2E1}=\sum_{g_1,g_2}\sum_{a,b,c,u,v}\frac{5}{4}(-1)^{a+1-g_2}\Pi_{g_1,g_2,b,c,u,v}\begin{Bmatrix}1&1&2\\1&1&2\\u&v&c\end{Bmatrix}\begin{Bmatrix}1&2&g_1\\1&2&g_2\\b&c&a\end{Bmatrix}\gamma_{UL_1}^{bca}S_{L_1}^{g_1g_2a}, \tag{18}$$

where $L_1=(1,1,0,0)$.

3.5. Electric quadrupole excitation, electric dipole emission, isotropic sample

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

$$\sigma_{\rm KH}^{E2E1}=\sum_{g}\sum_{b,u,v}\frac{5}{4}(-1)^{1-g}(2g+1)(2b+1)\Pi_{u,v}\begin{Bmatrix}1&1&2\\1&1&2\\u&v&b\end{Bmatrix}\begin{Bmatrix}1&2&g\\1&2&g\\b&b&0\end{Bmatrix}\gamma_{UL_1}^{bb0}S_{L_1}^{gg0},$$

with $U = (u, v, b, 0)$.
As in the case of electric dipole absorption and emission, only three fundamental spectra are needed to describe all the experimental spectra of a powder. The tensors $\gamma^{bb0}_{UL_1}$, are evaluated for all possible values of (u, b, v) (see Appendix D.3). This leads to the final expression of the Kramers-Heisenberg cross-section for an isotropic sample, in the case of quadrupole absorption with dipole emission:

$$\sigma^{E2E1}_{\mathrm{KH}} = \sum_{g=1}^{3}\left((-1)^g\frac{\sqrt{2g+1}}{120} + \frac{1}{16\sqrt{5}}\sqrt{2g+1}\begin{Bmatrix}1&2&g\\2&1&1\end{Bmatrix} \times (|\epsilon\cdot\epsilon_s^*|^2 - |\epsilon\cdot\epsilon_s|^2) + \frac{\sqrt{3}}{4\sqrt{7}}\sqrt{2g+1}\begin{Bmatrix}1&2&g\\2&1&2\end{Bmatrix} \times \left(\frac{1}{3} - \frac{1}{4}|\epsilon^*\cdot\epsilon_s|^2 - \frac{1}{4}|\epsilon\cdot\epsilon_s|^2 - \frac{1}{2}|\mathbf{k}\cdot\epsilon_s^*|^2\right)\right) S^{gg0}_{L_1}, \tag{19}$$

where: $\begin{Bmatrix}1&2&g\\2&1&2\end{Bmatrix} = \frac{1}{5\sqrt{21}}$ for $g=3$, $\frac{\sqrt{7}}{10\sqrt{3}}$ for $g=2$, $\frac{\sqrt{7}}{10\sqrt{3}}$ for $g=1$, $\begin{Bmatrix}1&2&g\\2&1&1\end{Bmatrix} = \frac{1}{3\sqrt{5}}$ for $g=3$, $\frac{1}{6\sqrt{5}}$ for $g=2$, and $-\frac{1}{2\sqrt{5}}$ for $g=1$.
If the polarization of the scattered beam is not detected the polarization average yields:

$$\left\langle\sigma^{E2E1}_{\mathrm{KH}}\right\rangle = \sum_{g=1}^{3}\left((-1)^g\frac{\sqrt{2g+1}}{120} + \frac{\sqrt{3}}{4\sqrt{7}}\sqrt{2g+1}\begin{Bmatrix}1&2&g\\2&1&2\end{Bmatrix} \times \left(-\frac{1}{6} + \frac{1}{4}|\mathbf{k}\cdot\mathbf{k}_s|^2 + \frac{1}{4}|\epsilon\cdot\mathbf{k}_s|^2\right)\right) S^{gg0}_{L_1}. \tag{20}$$

4. Conclusion

This paper presents a detailed derivation of the resonant inelastic scattering cross section in geometric spherical tensor form. Starting from the Kramers-Heisenberg equation and using angular-momentum coupling techniques, this expression is derived without any assumption on the nature of the states involved in the scattering process. The use of spherical tensors allows to drastically reduce the number of fundamental spectra that shall be measured in order to extract the full information from a sample. For example, for electric dipole absorption followed by electric dipole emission transitions, 19 fundamental spectra (versus 81 for a general fourth-rank Cartesian tensor) are required, that reduce to three for a powder.
Angular momentum techniques are used to recouple each photon (incident and scattered) with itself. This step is required to discuss the common case where the polarization of the scattered beam is not measured.
Some special cases were studied to illustrate the ability of this expression to describe global properties of the sample. In the case of isotropic samples, which are most often measured experimentally, the electric dipole absorption-electric dipole emission and electric quadrupole absorption-electric dipole emission cross-sections are each expressed as a combination of only three fundamental spectra. This method predicts that circular dichroism may be observed on isotropic samples provided that the circular polarization of the scattered beam is detected.

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A. Derivation of Kramers-Heisenberg formula using spherical tensors

A.1. Expression of $\epsilon\cdot\mathbf{r}(\mathbf{k}\cdot\mathbf{r})^\ell$

First it is shown 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. [12] (Eq. 13):

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

For $\ell = 1$, according to Ref. [12][p. 5]:

$$\epsilon \cdot \mathbf{r}\mathbf{k} \cdot \mathbf{r} = \sqrt{5}\{\{\epsilon \otimes \mathbf{k}\}^{(2)} \otimes \{\mathbf{r} \otimes \mathbf{r}\}^{(2)}\}^{(0)} = \sqrt{5}\Big\{\{\epsilon \otimes \mathbf{k}\}^{(2)} \otimes \mathbf{r}^{(2)}\Big\}^{(0)}. \tag{A.2}$$

Thus, $\epsilon \cdot \mathbf{r}(\mathbf{k} \cdot \mathbf{r})^{\ell} = g_{\ell}\Big\{\{\epsilon \otimes \mathbf{k}^{\ell}\}^{(\ell+1)} \otimes \mathbf{r}^{(\ell+1)}\Big\}^{(0)}$, with $\mathbf{r}^{(1)} = \mathbf{r}$, $g_0 = -\sqrt{3}$, $\mathbf{r}^{(2)} = \{\mathbf{r} \otimes \mathbf{r}\}^{(2)}$ and $g_1 = \sqrt{5}$.
Defining $E_{IFN} = \dfrac{(E_I - E_N)(E_N - E_F)}{E_I - E_N + \hbar\omega + i\gamma}$, Equation (4) becomes:

$$\sigma_{\mathrm{KH}} = C\sum_F \Big|\sum_N E_{IFN} \sum_{\ell,\ell'=0}^{1} f_{\ell} f^*_{\ell'} g_{\ell} g_{\ell'} \langle N|\Big\{\{\epsilon \otimes \mathbf{k}^{\ell}\}^{(\ell+1)} \otimes \mathbf{r}^{(\ell+1)}\Big\}^{(0)}|I\rangle\langle F|\Big\{\{\epsilon^*_s \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \mathbf{r}^{(\ell'+1)}\Big\}^{(0)}|N\rangle\Big|^2 \delta_E, \tag{A.3}$$

and

$$\sigma_{\mathrm{KH}} = C\sum_F \Big|\sum_N E_{IFN} \sum_{\ell,\ell'=0}^{1} h_{\ell} h^*_{\ell'} \Big\{\{\epsilon \otimes \mathbf{k}^{\ell}\}^{(\ell+1)} \otimes \langle N|\mathbf{r}^{(\ell+1)}|I\rangle\Big\}^{(0)} \Big\{\{\epsilon^*_s \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \langle F|\mathbf{r}^{(\ell'+1)}|N\rangle\Big\}^{(0)}\Big|^2 \delta_E, \tag{A.4}$$

with $h_{\ell} = f_{\ell} g_{\ell}$. If one now 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 obtains:

$$\sigma_{\mathrm{KH}} = C\sum_F \Big|\sum_N E_{IFN} \sum_{\ell,\ell'=0}^{1} h_{\ell} h^*_{\ell'} \Big\{\{\epsilon \otimes \mathbf{k}^{\ell}\}^{(\ell+1)} \otimes \mathbf{r}_{NI}^{(\ell+1)}\Big\}^{(0)} \Big\{\{\epsilon^*_s \otimes \mathbf{k}_s^{\ell'}\}^{(\ell'+1)} \otimes \mathbf{r}_{FN}^{(\ell'+1)}\Big\}^{(0)}\Big|^2 \delta_E. \tag{A.5}$$

A.2. Recoupling spherical tensors

Now using the recoupling identity (Ref. [12], Eq. 14), which is:

$$\{P^{(a)} \otimes Q^{(a)}\}^{(0)}\{R^{(d)} \otimes S^{(d)}\}^{(0)} = \sum_{g=|a-d|}^{a+d} (-1)^g \frac{\{P^{(a)} \otimes R^{(d)}\}^{(g)} \cdot \{Q^{(a)} \otimes S^{(d)}\}^{(g)}}{\sqrt{(2a+1)(2d+1)}}, \tag{A.6}$$

where the scalar product $\cdot$ of two spherical tensors $P^{(g)}$ and $Q^{(g)}$ is defined by: $P^{(g)} \cdot Q^{(g)} = \sum_{\gamma=-g}^{g} (-1)^{\gamma} P_{\gamma}^{(g)} Q_{-\gamma}^{(g)}$, Equation (A.5) becomes:

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

where g runs from $|\ell - \ell'|$ to $(\ell + \ell' + 2)$, ℓ and ℓ' run from 0 to 1. This is Equation (5).

A.3. Expansion of the square in Equation (6)

Now the modulus of the amplitude inside the sum over the final states in Equation (6) is squared. When expanding the square, Equation (6) becomes:

$$\begin{aligned}\sigma_{\mathrm{KH}} = C\sum_F \sum_{g_1,\ell_1,\ell'_1,g_2,\ell_2,\ell'_2} & h_{\ell_1} h^*_{\ell'_1} h^*_{\ell_2} h_{\ell'_2} \frac{(-1)^{g_1+\ell_2+\ell'_2}}{\sqrt{(2\ell_1+3)(2\ell'_1+3)(2\ell_2+3)(2\ell'_2+3)}} \\ & \Big\{\{\epsilon^*_s \otimes \mathbf{k}_s^{\ell'_1}\}^{(\ell'_1+1)} \otimes \{\epsilon \otimes \mathbf{k}^{\ell_1}\}^{(\ell_1+1)}\Big\}^{(g_1)} \cdot A_{FI}^{(g_1)}(\ell_1, \ell'_1) \\ & \Big\{\{\epsilon_s \otimes \mathbf{k}_s^{\ell'_2}\}^{(\ell'_2+1)} \otimes \{\epsilon^* \otimes \mathbf{k}^{\ell_2}\}^{(\ell_2+1)}\Big\}^{(g_2)} \cdot A_{FI}^{(g_2)}(\ell_2, \ell'_2)^* \delta_E,\end{aligned} \tag{A.7}$$

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 Appendix B, it is shown that $A_{FI}^{(g_2)}(\ell_2, \ell'_2)^* = \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)$.
Therefore,

$$\begin{aligned}\sigma_{\mathrm{KH}} = C \sum_F \sum_{g_1,\ell_1,\ell'_1,g_2,\ell_2,\ell'_2} h_{\ell_1} h^*_{\ell'_1} h^*_{\ell_2} h_{\ell'_2} \frac{(-1)^{g_1+\ell_2+\ell'_2}}{\sqrt{(2\ell_1+3)(2\ell'_1+3)(2\ell_2+3)(2\ell'_2+3)}} \\ \left\{\{\epsilon^*_s \otimes \mathbf{k}_s^{\ell'_1}\}^{(\ell'_1+1)} \otimes \{\epsilon \otimes \mathbf{k}^{\ell_1}\}^{(\ell_1+1)}\right\}^{(g_1)} \cdot A_{FI}^{(g_1)}(\ell_1, \ell'_1) \\ \left\{\{\epsilon_s \otimes \mathbf{k}_s^{\ell'_2}\}^{(\ell'_2+1)} \otimes \{\epsilon^* \otimes \mathbf{k}^{\ell_2}\}^{(\ell_2+1)}\right\}^{(g_2)} \cdot \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\delta_E.\end{aligned}$$

If one defines

$$X_1^{(g_1)} = \left\{\{\epsilon^*_s \otimes \mathbf{k}_s^{\ell'_1}\}^{(\ell'_1+1)} \otimes \{\epsilon \otimes \mathbf{k}^{\ell_1}\}^{(\ell_1+1)}\right\}^{(g_1)}, \tag{A.8}$$

$$X_2^{(g_2)} = \left\{\{\epsilon_s \otimes \mathbf{k}_s^{\ell'_2}\}^{(\ell'_2+1)} \otimes \{\epsilon^* \otimes \mathbf{k}^{\ell_2}\}^{(\ell_2+1)}\right\}^{(g_2)}, \tag{A.9}$$

$$\Pi_{\ell_1+1,\ell_2+1,\ell'_1+1,\ell'_2+1} = \sqrt{(2\ell_1+3)(2\ell'_1+3)(2\ell_2+3)(2\ell'_2+3)}, \tag{A.10}$$

one obtains

$$\sigma_{\mathrm{KH}} = C \sum_F \sum_{g_1,\ell_1,\ell'_1,g_2,\ell_2,\ell'_2} \frac{(-1)^{g_1+\ell_2+\ell'_2} h_{\ell_1} h^*_{\ell'_1} h^*_{\ell_2} h_{\ell'_2}}{\Pi_{\ell_1+1,\ell_2+1,\ell'_1+1,\ell'_2+1}} X_1^{(g_1)} \cdot A_{FI}^{(g_1)}(\ell_1, \ell'_1)\ X_2^{(g_2)} \cdot \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\delta_E. \tag{A.11}$$

The identity $P^{(a)} \cdot Q^{(a)} = (-1)^a \sqrt{2a+1}\ \{P^{(a)} \otimes Q^{(a)}\}^{(0)}$ [43, pp. 64-65]) becomes:

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

and then:

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

Using Equation (A.6):

$$\begin{aligned}\{X_1^{(g_1)} \otimes A_{FI}^{(g_1)}(\ell_1, \ell'_1)\}^{(0)} \{X_2^{(g_2)} \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(0)} = \sum_{a=|g_1-g_2|}^{g_1+g_2} \frac{(-1)^a}{\sqrt{(2g_1+1)(2g_2+1)}} \{X_1^{(g_1)} \otimes X_2^{(g_2)}\}^{(a)} \\ \cdot \{A_{FI}^{(g_1)}(\ell_1, \ell'_1) \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(a)}.\end{aligned} \tag{A.12}$$

Then,

$$\sigma_{\mathrm{KH}} = C \sum_F \sum_{g_1,\ell_1,\ell'_1,g_2,\ell_2,\ell'_2} \frac{(-1)^{\ell_2+\ell'_2-g_2} h_{\ell_1} h^*_{\ell'_1} h^*_{\ell_2} h_{\ell'_2}}{\Pi_{\ell_1+1,\ell_2+1,\ell'_1+1,\ell'_2+1}} \sum_a (-1)^a \{X_1^{(g_1)} \otimes X_2^{(g_2)}\}^{(a)} \{A_{FI}^{(g_1)}(\ell_1, \ell'_1) \otimes \overline{A}_{IF}^{(g_2)}(\ell_2, \ell'_2)\}^{(a)} \delta_E, \tag{A.13}$$

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

In order to transform the tensor product:

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

one uses the following identity [43, p. 70]:

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

where $|a-d| \leq g \leq a+d$, $|b-e| \leq h \leq b+e$ and $|g-h| \leq k \leq g+h$. This recoupling transforms the coupling of the incident photon with the scattered photons into a coupling of each photon with itself. The 9-j symbol that appears in this formula was overlooked in ref. [31]. This yields:

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

with

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

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

$$|\ell_1' - \ell_2'| \leq b \leq \ell_1' + \ell_2', \quad |\ell_1 - \ell_2| \leq c \leq \ell_1 + \ell_2, \quad |b-c| \leq a \leq b + c \quad .$$

A.4. Recoupling 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. However, to treat the case of a partially polarized incident or scattered beam, it is required to couple the polarization vectors with themselves: in $\{X\}^{(a)} = \left\{\{X_{\text{out}}\}^{(b)} \otimes \{X_{\text{in}}\}^{(c)}\right\}^{(a)}$ the polarization vectors in $\{X_{\text{out}}\}^{(b)}$ and $\{X_{\text{in}}\}^{(c)}$ are recoupled. According to Eq. (A.14), one obtains:

$$\{X_{\text{in}}\}^{(c)} = \{\{\epsilon \otimes \mathbf{k}^{\ell_1}\}^{(\ell_1+1)} \otimes \{\epsilon^* \otimes \mathbf{k}^{\ell_2}\}^{(\ell_2+1)}\}^{(c)} = \sum_{u,v} \Pi_{\ell_1+1,\ell_2+1,u,v} \begin{Bmatrix} 1 & \ell_1 & \ell_1+1 \\ 1 & \ell_2 & \ell_2+1 \\ u & v & c \end{Bmatrix} \text{In}_{UL}^{(c)},$$

where $\text{In}_{UL}^{(c)} = \left\{\{\epsilon \otimes \epsilon^*\}^{(u)} \otimes \{\mathbf{k}^{\ell_1} \otimes \mathbf{k}^{\ell_2}\}^{(v)}\right\}^{(c)}$ and

$$\{X_{\text{out}}\}^{(b)} = \{\{\epsilon_s^* \otimes \mathbf{k}_s^{\ell_1'}\}^{(\ell_1'+1)} \otimes \{\epsilon_s \otimes \mathbf{k}_s^{\ell_2'}\}^{(\ell_2'+1)}\}^{(b)} = \sum_{u',v'} \Pi_{\ell_1'+1,\ell_2'+1,u',v'} \begin{Bmatrix} 1 & \ell_1' & \ell_1'+1 \\ 1 & \ell_2' & \ell_2'+1 \\ u' & v' & b \end{Bmatrix} \text{Out}_{UL}^{(b)},$$

where $\text{Out}_{UL}^{(b)} = \left\{\{\epsilon_s^* \otimes \epsilon_s\}^{(u')} \otimes \{\mathbf{k}_s^{\ell_1'} \otimes \mathbf{k}_s^{\ell_2'}\}^{(v')}\right\}^{(b)}$. In these expressions the multi-indices U and L stand for $U = (u, v, u', v')$ and $L = (\ell_1, \ell_2, \ell_1', \ell_2')$. A similar recoupling of the polarization vector with itself was also carried out by Veenendaal and Benoist [20].

The 9-j-symbols vanish if any of the following triangular conditions is not fullfilled:

$$0 \leq u \leq 2, \quad |\ell_1 - \ell_2| \leq v \leq \ell_1 + \ell_2, \quad 0 \leq u' \leq 2, \quad |\ell_1' - \ell_2'| \leq v' \leq \ell_1' + \ell_2'.$$

B. Complex conjugate

It is required to calculate the complex conjugate of $A^{(g)}_{FI}(\ell,\ell')$. The position operator x is 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,

$$\langle N|r^{(1)}_1|I\rangle^* = -(1/\sqrt{2})\big(\langle N|x|I\rangle + i\langle N|y|I\rangle\big)^* = -(1/\sqrt{2})\big(\langle I|x|N\rangle - i\langle I|y|N\rangle\big) = -\langle I|r^{(1)}_{-1}|N\rangle^*.$$

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

$$\begin{aligned}\langle N|r^{(2)}_\mu|I\rangle^* &= \sum_{\lambda\lambda'}(1\lambda1\lambda'|2\mu)\langle N|r^{(1)}_\lambda r^{(1)}_{\lambda'}|I\rangle^* = \sum_{\lambda\lambda'}(1\lambda1\lambda'|2\mu)\sum_K\langle N|r^{(1)}_\lambda|K\rangle^*\langle K|r^{(1)}_{\lambda'}|I\rangle^*\\ &= \sum_{\lambda\lambda'}(1\lambda1\lambda'|2\mu)(-1)^{\lambda+\lambda'}\sum_K\langle K|r^{(1)}_{-\lambda}|N\rangle\langle I|r^{(1)}_{-\lambda'}|K\rangle.\end{aligned}$$

The Clebsch-Gordan coefficient $(1\lambda1\lambda'|2\mu)$ implies that $\lambda+\lambda' = \mu$. By replacing λ and λ' by $-\lambda'$ and $-\lambda$, respectively, the following is obtained

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

Now, the symmetry $(\ell_1m_1\ell_2m_2|\ell_3m_3) = (\ell_2 - m_2\ell_1 - m_1|\ell_3 - m_3)$ is used to obtain

$$\langle N|r^{(2)}_\mu|I\rangle^* \;=\; (-1)^\mu\sum_{\lambda\lambda'}(1\lambda1\lambda'|2-\mu)\langle I|r^{(1)}_\lambda r^{(1)}_{\lambda'}|N\rangle = (-1)^\mu\langle I|r^{(2)}_{-\mu}|N\rangle.$$

A recursive use of this argument leads to $\langle N|r^{(\ell)}_m|I\rangle^* = (-1)^m\langle I|r^{(\ell)}_{-m}|N\rangle$ for any ℓ.
A similar calculation can be carried out for

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

The complex conjugate of X_γ is

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

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

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

Finally,

$$A^{(g)}_{FI,\gamma}(\ell,\ell')^* = (-1)^\gamma\sum_N\frac{(E_I-E_N)(E_N-E_F)}{E_I-E_N+\hbar\omega-i\gamma}\{\mathbf{r}^{(\ell+1)}_{IN}\otimes\mathbf{r}^{(\ell'+1)}_{NF}\}^{(g)}_{-\gamma}. \tag{A.14}$$

Therefore, defining

$$\overline{A}^{(g)}_{IF}(\ell,\ell') \;=\; \sum_N \frac{(E_I-E_N)(E_N-E_F)}{E_I-E_N+\hbar\omega-i\gamma}\{\mathbf{r}^{(\ell+1)}_{IN}\otimes\mathbf{r}^{(\ell'+1)}_{NF}\}^{(g)}, \tag{A.15}$$

the final result $A^{(g)}_{FI,\gamma}(\ell,\ell')^* = (-1)^\gamma \overline{A}^{(g)}_{IF,-\gamma}(\ell,\ell')$ follows.
The relation $\langle N|r^{(\ell)}_\lambda|I\rangle = (-1)^\lambda\langle I|r^{(\ell)}_{-\lambda}|N\rangle^*$ is standard and it just remains to calculate the complex conjugate of $\Big\{\{\epsilon^*_s\otimes \mathbf{k}^{\ell'}_s\}^{(\ell'+1)}\otimes\{\epsilon\otimes\mathbf{k}^{\ell}\}^{(\ell+1)}\Big\}^{(g)}_\gamma$. The polarization vectors ϵ and ϵ_s are complex. For a complex 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, the complex conjugate of the spherical component $\mathbf{z}^{(1)}_\lambda$ for $\lambda=1$ is

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

The calculation of the other components gives $\big(\mathbf{z}^{(1)}_\lambda\big)^* = (-)^\lambda(\mathbf{z}^*)^{(1)}_{-\lambda}$. Therefore, $(\epsilon_\lambda)^* = (-1)^\lambda(\epsilon^*)_{-\lambda}$ and $\big((\epsilon^*_s)_\lambda\big)^* = (-1)^\lambda(\epsilon_s)_{-\lambda}$. The vector $\mathbf{k}$ is real and $(\mathbf{k}^{(\ell)}_m)^* = (-1)^m\mathbf{k}^{(\ell)}_{-m}$. The same proof as for $A^{(g)}_{FI}(\ell,\ell')$ leads to

$$\Big(\{\epsilon\otimes\mathbf{k}^\ell\}^{(\ell+1)}_m\Big)^* \;=\; (-1)^m\sum_{\lambda\mu}(1\,-\lambda\,\ell\,-\mu|\ell+1,m)\epsilon^*_\lambda k^{(\ell)}_\mu.$$

Since 1λ and $\ell\mu$ are not interchanged, another symmetry relation must be used

$$(\ell_1 m_1\ell_2 m_2|\ell_3 m_3) \;=\; (-1)^{\ell_1+\ell_2-\ell_3}(\ell_1\,-m_1\,\ell_2\,-m_2|\ell_3\,-m_3), \tag{A.16}$$

to obtain

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

Here, the symmetry relation does not bring any additional sign because $\ell_3=\ell_1+\ell_2$. Similarly, $\Big(\{\epsilon^*_s\otimes\mathbf{k}^{\ell'}_s\}^{(\ell'+1)}_{m'}\Big)^* = (-1)^{m'}\{\epsilon_s\otimes\mathbf{k}^{\ell'}_s\}^{(\ell'+1)}_{-m'}$.

In the calculation of the complex conjugate of $\Big\{\{\epsilon^*_s\otimes\mathbf{k}^{\ell'}_s\}^{(\ell'+1)}\otimes\{\epsilon\otimes\mathbf{k}^\ell\}^{(\ell+1)}\Big\}^{(g)}_\gamma$, the sign $(-1)^{\ell+\ell'-g}$ must be retained to obtain

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

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

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

C. Average over polarizations

One of the most powerful features of the 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. This is illustrated by describing the average of the coupling of ϵ and ϵ^*:

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

Taking 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 $\epsilon^{(1)}_{\pm1} = \mp e^{\pm i\psi}/\sqrt{2}$, $\epsilon^{(1)}_0 = 0$. Therefore, it is easy to calculate

$$\begin{aligned}\{\epsilon\otimes\epsilon^*\}^{(2)}_{\pm2} &= \frac{e^{\pm2i\psi}}{2},\\ \{\epsilon\otimes\epsilon^*\}^{(2)}_{\pm1} &= 0,\\ \{\epsilon\otimes\epsilon^*\}^{(2)}_{0} &= -\frac{1}{\sqrt{6}}.\end{aligned}$$

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

$$\begin{aligned}\langle\{\epsilon\otimes\epsilon^*\}^{(2)}_{\pm2}\rangle &= 0,\\ \langle\{\epsilon\otimes\epsilon^*\}^{(2)}_{\pm1}\rangle &= 0,\\ \langle\{\epsilon\otimes\epsilon^*\}^{(2)}_{0}\rangle &= -\frac{1}{\sqrt{6}}.\end{aligned}$$

In that reference frame $\mathbf{k}^{(2)}_m = \delta_{m,0}\sqrt{2/3}$. Thus, $\langle\{\epsilon\otimes\epsilon^*\}^{(2)}\rangle = -\mathbf{k}^{(2)}/2$ and this relation is true in any reference frame because it is a relation between two tensors. Considering 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 $\sin2\chi$. In particular, $\chi = \pi/4$ for a fully circularly polarized x-ray. Then,

$$\begin{aligned}\{\epsilon\otimes\epsilon^*\}^{(1)}_{\pm1} &= 0,\\ \{\epsilon\otimes\epsilon^*\}^{(1)}_{0} &= -\frac{1}{\sqrt{2}}\sin2\chi,\end{aligned}$$

and

$$\begin{aligned}\{\epsilon\otimes\epsilon^*\}^{(2)}_{\pm2} &= \frac{1}{2}\cos2\chi e^{\pm2i\psi},\\ \{\epsilon\otimes\epsilon^*\}^{(2)}_{\pm1} &= 0,\\ \{\epsilon\otimes\epsilon^*\}^{(2)}_{0} &= -\frac{1}{\sqrt{6}}.\end{aligned}$$

Therefore, by using left and right fully circularly polarized beams, the same average as with linear polarization is obtained.
Similarly, it can be shown that $\langle|\mathbf{a}\cdot\epsilon|^2\rangle = (|\mathbf{a}|^2 - |\mathbf{a}\cdot\mathbf{k}|^2)/2$.

D. Values of 9-j-factors and geometric coefficients for particular cases of Equation (6)

D.1. Electric dipole excitation, electric dipole emission

- The first 9-j-symbol 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 9-j-symbol 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:

$$\sigma^{E1E1}_{\mathrm{KH}} = \sum_{g_1,g_2}\sum_{a,b,c}(-1)^{a-g_2}\Pi_{g_1,g_2,b,c}\begin{Bmatrix}1&1&g_1\\1&1&g_2\\b&c&a\end{Bmatrix}\gamma^{bca}_{UL_0}\cdot S^{g_1g_2a}_{L_0}, \tag{A.17}$$

where $L_0 = (0,0,0,0)$ because $\ell_1 = \ell_2 = \ell'_1 = \ell'_2 = 0$ for electric dipole emission and absorption and $U = (b,0,c,0)$. Additionnally, recall that $\gamma^{bca}_{UL_0} = \{\mathrm{Out}^{(b)}_{UL}\otimes \mathrm{In}^{(c)}_{UL_0}\}^{(a)}$, where $\mathrm{Out}^{(b)}_{UL} = \{\epsilon^*_s\otimes\epsilon_s\}^{(b)}$ and $\mathrm{In}^{(c)}_{UL_0} = \{\epsilon\otimes\epsilon^*\}^{(c)}$. Further simplifications arise when the sample is a powder (*i.e.* $a=0$).
It can be shown that:

$$\begin{Bmatrix}1&1&g_1\\1&1&g_2\\b&c&0\end{Bmatrix} = \frac{\delta_{g_1g_2}\delta_{bc}(-1)^{g_1+b}}{\sqrt{(2g_1+1)(2b+1)}}\begin{Bmatrix}1&1&g_1\\1&1&b\end{Bmatrix}.$$

- For $b = 0$:

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

with $g = 0, 1, 2$, and $\gamma_{UL_0}^{000} = \frac{1}{3}$.

Thus,

$$\sigma_{\mathrm{KH}}^{E1E1}(b=0) = \sum_{g=0}^{2}(-1)^g \frac{\sqrt{2g+1}}{9} S_{L_0}^{gg0}.$$

- For $b = 1$:

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

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

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

where P_c is the rate of circular polarization.

$$\gamma_{UL_0}^{110} = \frac{1}{2\sqrt{3}} P_c P_{c,s} \mathbf{k}_s \cdot \mathbf{k} = \frac{1}{2\sqrt{3}}(|\epsilon \cdot \epsilon_s^*|^2 - |\epsilon \cdot \epsilon_s|^2).$$

Thus,

$$\sigma_{\mathrm{KH}}^{E1E1}(b=1) = \sum_{g=0}^{2} -\frac{\sqrt{2g+1}}{2} \begin{Bmatrix} 1 & 1 & g \\ 1 & 1 & 1 \end{Bmatrix} (|\epsilon \cdot \epsilon_s^*|^2 - |\epsilon \cdot \epsilon_s|^2) S_{L_0}^{gg0}.$$

- For $b = 2$:

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

with $g = 0, 1, 2$.

$$\gamma_{UL_0}^{220} = \frac{1}{\sqrt{5}}\left(\frac{1}{2}|\epsilon^* \cdot \epsilon_s|^2 + \frac{1}{2}|\epsilon \cdot \epsilon_s|^2 - \frac{1}{3}\right).$$

Thus,

$$\sigma_{\mathrm{KH}}^{E1E1}(b=2) = \sum_{g=0}^{2} \frac{4\sqrt{2g+1}}{(2-g)!(3+g)!} \left(\frac{1}{2}|\epsilon^* \cdot \epsilon_s|^2 + \frac{1}{2}|\epsilon \cdot \epsilon_s|^2 - \frac{1}{3}\right) S_{L_0}^{gg0}.$$

This leads to Equation (15).

If the polarization of the scattered beam is not detected, then the term $b = 2$ is calculated using the relation: $\langle\{\epsilon_s \otimes \epsilon_s^*\}^{(2)}\rangle = -\mathbf{k}_s^{(2)}/2$ and Eq. (17) is obtained because

$$\left\langle \gamma_{UL_0}^{220} \right\rangle = -\frac{1}{2\sqrt{5}}\left(|\mathbf{k}_s \cdot \epsilon|^2 - \frac{1}{3}\right). \qquad \text{(A.18)}$$

D.2. Electric quadrupole excitation, electric dipole emission

In the case of electric quadrupole transitions in the absorption followed by electric dipole transitions in the emission, $\ell_1 = 1$, $\ell_2 = 1$, $\ell_1' = 0$ and $\ell_2' = 0$. Thus,

$$1 \le g_1 \le 3, \quad 1 \le g_2 \le 3, \quad 0 \le a \le 6,$$
$$0 \le b \le 2, \quad 0 \le c \le 4.$$

Since $\ell_1 = 1$ and $\ell_2 = 1$, $0 \le v \le 2$. Additionally, $v \ne 1$ 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 $\ell_2' = 0$, $v' = 0$ and $b = u'$.

Therefore:

- The first 9-j-symbol 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 zero if $u + v + c$ is odd.

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

- The third 9-j-symbol is:
$$\begin{Bmatrix} \ell_1'+1 & \ell_1+1 & g_1 \\ \ell_2'+1 & \ell_2+1 & g_2 \\ b & c & a \end{Bmatrix} = \begin{Bmatrix} 1 & 2 & g_1 \\ 1 & 2 & g_2 \\ b & c & a \end{Bmatrix}.$$

D.3. Electric quadrupole excitation, electric dipole emission, powder sample

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

$$\sigma_{\mathrm{KH}}^{E2E1} = C\sum_F\sum_g\sum_{b,u,v}(-1)^{1-g}h_1h_0^*h_1^*h_0\Pi_{g,g,b,b,u,v,b}\begin{Bmatrix}1&1&2\\1&1&2\\u&v&b\end{Bmatrix}\begin{Bmatrix}1&0&1\\1&0&1\\b&0&b\end{Bmatrix}\begin{Bmatrix}1&2&g\\1&2&g\\b&b&0\end{Bmatrix}\gamma_{UL_1}^{bb0}S_{L_1}^{gg0},$$

with $L_1 = (1,1,0,0)$ and $U = (u,v,u',v') = (u,v,b,0)$. The angular term is

$$\gamma_{UL_1}^{bb0} = \left\{\left\{\{\epsilon\otimes\epsilon^*\}^{(u)}\otimes\{\mathbf{k}\otimes\mathbf{k}\}^{(v)}\right\}^{(b)}\otimes\{\epsilon_s^*\otimes\epsilon_s\}^{(b)}\right\}^{(0)}.$$

More precisely,

- $b=0,u=0,v=0$: $\gamma_{UL_1}^{bb0} = -\frac{1}{3\sqrt{3}}$.
- $b=0,u=2,v=2$: $\gamma_{UL_1}^{bb0} = \frac{1}{3\sqrt{15}}$.
- $b=1,u=1,v=0$: $\gamma_{UL_1}^{bb0} = -\frac{1}{6}P_cP_{c,s}\mathbf{k}\cdot\mathbf{k}_s$.
- $b=1,u=1,v=2$: $\gamma_{UL_1}^{bb0} = -\frac{1}{3\sqrt{5}}P_cP_{c,s}\mathbf{k}\cdot\mathbf{k}_s$.
- $b=2,u=2,v=0$: $\gamma_{UL_1}^{bb0} = -\frac{1}{\sqrt{15}}\left(\frac{1}{2}|\epsilon^*\cdot\epsilon_s|^2+\frac{1}{2}|\epsilon\cdot\epsilon_s|^2-\frac{1}{3}\right)$.
- $b=2,u=0,v=2$: $\gamma_{UL_1}^{bb0} = -\frac{1}{\sqrt{15}}\left(|\mathbf{k}\cdot\epsilon_s|^2-\frac{1}{3}\right)$.
- $b=2,u=2,v=2$: $\gamma_{UL_1}^{bb0} = \frac{1}{3\sqrt{105}}(6|\mathbf{k}\cdot\epsilon_s|^2-4+3|\epsilon\cdot\epsilon_s^*|^2+3|\epsilon\cdot\epsilon_s|^2)$.

This leads to Equation (19). Note that the term $b=2,u=2,v=2$ is obtained by using classical invariant theory [44, 45]:
If the polarization of the scattered beam is not detected, then $\left\langle\gamma_{UL_1}^{110}\right\rangle = 0$ and the polarization average yields:

$$\left\langle\left\{\left\{\{\epsilon\otimes\epsilon^*\}^{(2)}\otimes\{\mathbf{k}\otimes\mathbf{k}\}^{(2)}\right\}^{(2)}\otimes\{\epsilon_s^*\otimes\epsilon_s\}^{(2)}\right\}^{(0)}\right\rangle = \frac{2-3|\mathbf{k}\cdot\mathbf{k}_s|^2-3|\epsilon\cdot\mathbf{k}_s|^2}{3\sqrt{105}}.$$

$$\left\langle\left\{\left\{\{\epsilon\otimes\epsilon^*\}^{(0)}\otimes\{\mathbf{k}\otimes\mathbf{k}\}^{(2)}\right\}^{(2)}\otimes\{\epsilon_s^*\otimes\epsilon_s\}^{(2)}\right\}^{(0)}\right\rangle = -\frac{1}{2\sqrt{15}}\left(\frac{1}{3}-|\mathbf{k}\cdot\mathbf{k}_s|^2\right).$$

$$\left\langle\left\{\left\{\{\epsilon\otimes\epsilon^*\}^{(2)}\otimes\{\mathbf{k}\otimes\mathbf{k}\}^{(0)}\right\}^{(2)}\otimes\{\epsilon_s^*\otimes\epsilon_s\}^{(2)}\right\}^{(0)}\right\rangle = -\frac{1}{2\sqrt{15}}\left(\frac{1}{3}-|\epsilon\cdot\mathbf{k}_s|^2\right).$$

This leads to Equation (20).

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