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A Theoretical Framework for Dichroism and the Resonance-Enhanced Scattering of X-Rays by Magnetic Materials; Quadrupolar Absorption Events

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A theoretical framework for dichroism and the resonance-enhanced scattering of X-rays by magnetic materials;quadrupolar absorption events.

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Abstract

Work by Lovesey and Balcar with the resonant scattering-length that is based on an atomic model and dipolar absorption events is extended to encompass quadrupolar absorption events. The scattering length is the common element in calculations of the attenuation coefficient, dichroism and the cross-sections for elastic and inelastic resonance-enhanced scattering of X-rays by magnetic materials. Both *jj*-coupling and Russell-Saunders coupling schemes for the atomic electrons are utilized; included are tables of relevant Racah unit tensor operators for the valence shell f^n.

§1. Introduction

A wealth of experience in the interpretation of X-ray spectra for atoms has shown that a useful approach is to classify events according to the power of the wave vector, q, of the X-rays in the operator for their interaction with the atomic electrons. Usually referred to as a multipole expansion of the interaction, the small parameter in the expansion is of the order of (qa_0) where a_0 is the Bohr radius. The leading-order term is an interaction independent of q; in this case, allowed events arise through non-zero matrix elements of the positions of electrons within atoms and the events satisfy the electric dipole selection-rules. At the next level of approximation, events can take place by both electric and magnetic interaction operators. The electric interaction operator in this case is proportional to the square of the electron's position, and the events satisfy the electric quadrupole selection-rules.

The topic of interest here is the use of beams of X-rays to study magnetic properties of materials, which has flourished in the past decade. (By and large, the recent experimental work, which includes the exploitation of the dichroic effect and scattering methods, has been underpinned by sources of X-rays provided by particle accelerators.) Lovesey and Collins

(1996) review a body of experimental and theoretical findings from this emerging field of research.

In a previous paper (Lovesey and Balcar 1996, and hereafter referred to as L & B) we proposed a theoretical framework for absorption and the resonance-enhanced scattering of X-rays by magnetic materials based on an atomic model of electric dipole (E1) events. Here, we extend the framework to include electric quadrupole (E2) events. There is no interference between the two types of event, so the scattering length for resonant processes is just the sum of the contributions from dipole-allowed events, treated by L & B, and quadrupole-allowed events. The expression for our *idealized* resonant scattering-length appropriate for quadrupole-allowed events is found in §3.

Our formulation of attenuation and the resonance-enhanced scattering of X-rays via quadrupole-allowed events is the same in all respects to the formulation of dipole-allowed events reported by L & B. The reader is referred to L & B for a discussion of the basis of the formulation, which entails the neglect of how energies of a subset of the intermediate states in the scattering length depend on their magnetic quantum numbers. While the spectrum of intermediate states available in dipole-allowed and quadrupole-events is the same, for a given configuration of the electrons, the selection rules that operate in the matrix elements, between these states and the initial and final states of the equilibrium configuration of the atom, mean that different parts of the whole spectrum are selected to appear in the dipole-allowed and quadrupole-allowed resonant scattering-lengths. It is to be noted that summation over the quantum numbers of the subset of intermediate states which feature in our formulation is achieved without approximation, and the selection rules for the absorption event (dipole or quadrupole) are fully preserved.

L & B provide some tables of the relevant Racah unit tensor operators for the valence shell f^n. Both *jj*-coupling and Russell-Saunders coupling schemes are utilized. More entries are required for the quadrupole-allowed events, and the additional information is included here. In one respect, at least, empirical data for quadrupole-allowed events is more valuable than for dipole-allowed events, simply because in the former there are more contributions to the representation of the scattering length as a sum of Racah unit tensor operators. On the other hand, the high-order contributions to quadrupole-allowed events, not present in dipole-

allowed events, do not readily admit to simple, physical interpretations in terms of basic equilibrium properties of the magnetic atoms.

The resonant scattering-length including both dipole (E1) and quadrupole (E2) interactions is developed in the next section. The contribution to the idealized scattering-length made by the quadrupole interaction is worked out in §3 following the steps in the formulation by L & B for the dipole interaction. Thereafter, the result for the quadrupole interaction is examined for the special case of a saturated magnetic atom, which can sensibly be used as a model of a magnetic material held at a very low temperature. In §5, the dichroic signal is calculated and compared with the corresponding value generated by the dipole interaction. Scattering cross-sections, for Bragg diffraction and inelastic processes, can be calculated with the aid of the results given in §3 and formulae provided by L & B. A knowledge of the scattering length, and relevant results given by Lovesey and Collins (1996), also permit one to calculate the polarization of the beam of X-rays after scattering, however this topic is not taken up.

§2. **Resonant scattering-length**

The resonant contribution to the scattering length contains matrix elements of $\boldsymbol{\varepsilon}\cdot\mathbf{J}(\mathbf{q})$ where $\mathbf{J}(\mathbf{q})$ is the spatial Fourier transform of the current operator and $\boldsymbol{\varepsilon}$ and $\mathbf{q}$ are the polarization vector and wave vector, respectively, of the primary beam of X-rays. Let $|\mu\rangle$ and $|\eta\rangle$ be eigenstates of the atom, with energies E_μ and E_η, respectively, and define $\Delta = (E_\eta - E_\mu)$. To first order in $\mathbf{q}$ one finds for the matrix element of $\boldsymbol{\varepsilon}\cdot\mathbf{J}(\mathbf{q})$ the result,

$$\langle\eta|\boldsymbol{\varepsilon}\cdot\mathbf{J}(\mathbf{q})|\mu\rangle = (im\Delta/\hbar)\sum_j \langle\eta|\{\boldsymbol{\varepsilon}\cdot\mathbf{R}_j\}(1+\tfrac{i}{2}\mathbf{q}\cdot\mathbf{R}_j)|\mu\rangle + (i\hbar/2)\sum_j \langle\eta|(\mathbf{q}\times\boldsymbol{\varepsilon})\cdot(\mathbf{l}_j+2\mathbf{s}_j)|\mu\rangle . \tag{2.1}$$

In this expression, $\mathbf{R}$, $\mathbf{l}$ and $\mathbf{s}$ are the position, orbital angular momentum and spin operators of an electron, and the sum is taken over all electrons in the atom in question. The last term in (2.1), which involves the magnetic moment of the electrons, is neglected in the present

calculation on the grounds that it is small relative to the first term. The latter is the sum of a dipole (E1) and a quadrupole (E2) contribution.

The scattering length which is the common factor in calculations of the attenuation coefficient and the cross-sections for the resonance-enhanced scattering of X-rays by atoms at sites defined by $\{\mathbf{R}_o\}$ is,

$$f = -(r_e/m)\sum_{\mathbf{R}_o} \exp(i\mathbf{k}\cdot\mathbf{R}_o)\exp\{-W(\mathbf{k})\}\sum_{\eta}\left\{\frac{\langle\mu'|\varepsilon'\cdot\mathbf{J}(-\mathbf{q}')|\eta\rangle\langle\eta|\varepsilon\cdot\mathbf{J}(\mathbf{q})|\mu\rangle}{(E_\mu + E - E_\eta + i\gamma_\eta/2)}\right\}_{\mathbf{R}_o}. \quad (2.2)$$

In this expression, μ and μ' label the initial and final states of the atom, respectively, and η labels the intermediate states. The primary X-rays have an energy $E = \hbar cq = (2\pi\hbar c/\lambda)$, ε' and $\mathbf{q}'$ are the polarization vector and wave vector of the secondary X-rays, and $\mathbf{k} = \mathbf{q} - \mathbf{q}'$. The Debye-Waller factor $\exp\{-W(\mathbf{k})\}$ might depend on the position of an atom, and for this reason in (2.2) it is included in the sum over the position vectors $\{\mathbf{R}_o\}$.

By setting aside the dependence of E_η on the quantum numbers for the subset of intermediate states over which we can perform the sum of the product of matrix elements in (2.2), we arrive at our *idealized* resonant scattering-length,

$$f(\mu,\mu') = -\left(\frac{2\pi e}{\lambda}\right)^2\left(\frac{\Delta'}{\Delta}\right)\{E - \Delta + i\Gamma/2\}^{-1}\sum_{\mathbf{R}_o}\exp(i\mathbf{k}\cdot\mathbf{R}_o)\exp\{-W(\mathbf{k})\}Z(\mu;\mu':\mathbf{R}_o). \quad (2.3)$$

Here, it is assumed that E is tuned close to Δ, which now is a mean energy for the separation in energy between the initial state and the subset of intermediate states. The corresponding energy for the intermediate states and the final state is Δ'. The energy Γ is the total decay width for the subset of intermediate states. Lastly, $Z(\mu;\mu':\mathbf{R}_o)$ is formed from the product of polarization vectors and matrix elements in (2.2). Its dependence on the position of the atom, admittedly not always explicitly displayed in subsequent workings, arises from the dependence of the atomic states on chemical and magnetic order in the sample. An expression for $Z(\mu;\mu')$ appropriate for quadrupole-allowed absorption events is given in the following section.

§3. **Matrix element**

The absorption event in the resonant scattering process involves the transfer of a hole from the valence shell, with angular momentum l, to a core state with angular momentum $\bar{l} \neq l$. The initial and final states of the atom both belong to the valence shell l^n, where n is the number of electrons.

In the idealized scattering length, the matrix element $Z(\mu;\mu')$ is built from the following product of one-particle matrix elements,

$$\sum_{\bar{J}\,\overline{M}} \left\langle lJM\middle|\boldsymbol{\varepsilon}'\cdot\mathbf{J}(-\mathbf{q}')\middle|\bar{l}\bar{J}\,\overline{M}\right\rangle\left\langle\bar{l}\bar{J}\,\overline{M}\middle|\boldsymbol{\varepsilon}\cdot\mathbf{J}(\mathbf{q})\middle|lJ'M'\right\rangle, \tag{3.1}$$

and for the current operator we take the first term in (2.1), which is a sum of electric dipole and quadrupole operators. Because the dipole and quadrupole operators connect the valence shell to different core states, there are no cross terms between matrix elements of these two operators in (3.1) and the latter, therefore, is the sum of a pure dipole contribution and a pure quadrupole contribution.

The sum in (3.1) on $\bar{J}$ and $\overline{M}$ renders the product of matrix elements proportional to a sum of spherical tensors. To these we can apply the methods for equivalent particles developed by Racah and thereby extend the result of our calculation from one hole in a valence shell to a number of holes $n_h \geq 1$. The proper account of Fermi statistics applied to a configuration of n_h equivalent holes is embedded in Racah's unit tensor operators. All the properties of unit tensor operators, for *jj*-coupling and Russell-Saunders coupling, needed in the present work are gathered in L & B.

In the general case, the wave functions of the atomic states are linear combinations of states labelled by the quantum numbers θJM, where θ contains all quantum numbers, over and above J and M, needed for a unique classification of atomic states. Here, we give the matrix element $Z(\mu;\mu')$, which appears in the idealized scattering length, for the states $\mu = \theta JM$ and $\mu' = \theta J'M'$. We have achieved a relatively compact expression for the quadrupole matrix

element through use of a spherical tensor $\mathbf{H}^{(K)}$ that contains the polarization vectors ε and ε′ and the information on the directions of propagation of the primary and secondary beams. It is to be noted that, in the dipole matrix element, treated by L & B, there is no information on the directions of propagation of the X-ray beams. In consequence, the analogue in the dipole matrix element of $\mathbf{H}^{(K)}$ is a much simpler quantity (L & B denote it by $\mathbf{X}^{(K)}$). The definition and properties of $\mathbf{H}^{(K)}$ are the subject of an appendix. The properties of the atom under investigation appear in $Z(\mu;\mu')$ through a tensor operator $T^K_{m_0}$, whose properties are thoroughly discussed by L & B. For the dipole matrix element $0 \le K \le 2$, whereas in the quadrupole matrix element we find the rank extends up to $K = 4$.

It is convenient to lump together several factors that are common to each tensor. Let,

$$\Phi = \tfrac{1}{6}(q'/q)\left\{q\left\langle l|R^2|\bar{l}\right\rangle (l\|C(2)\|\bar{l})\right\}^2, \tag{3.2}$$

where $\left\langle l|R^2|\bar{l}\right\rangle$ is the matrix element of R^2 taken between the valence and core states, and $\left(l\|C(2)\|\bar{l}\right)$ is the reduced matrix element of the normalized spherical harmonic of rank two. We find, for $\bar{l} = l - 2$,

$$\left(l\|C(2)\|\bar{l}\right)^2 = \left\{\frac{3l(l-1)}{2(2l-1)}\right\}. \tag{3.3}$$

Our result for the quadrupole matrix element is,

$$Z(\mu;\mu') = \Phi\sum_K (-1)^K \sqrt{(2K+1)} \begin{Bmatrix} 2 & K & 2 \\ l & \bar{l} & l \end{Bmatrix} \sum_{m_0} \left\langle \theta JM\left|T^K_{m_0}\right|\theta' J'M'\right\rangle H^{(K)}_{-m_0}(-1)^{m_0}. \tag{3.4}$$

A triangle condition in the 6j-symbol limits the integer K to the range $0 \le K \le 4$. The integer m_0 ranges between K and $-K$. We draw attention to the form of the terms in the sum on m_0; this sum has the structure of the standard definition of the scalar product of two tensors, and for $K = 1$ it is identical to the conventional scalar product of two vectors.

The matrix element of $T^K_{m_0}$ satisfies the Wigner-Eckart theorem, namely,

$$\left\langle \theta JM \left| T^K_{m_0} \right| \theta' J' M' \right\rangle = (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & m_0 & M' \end{pmatrix} (\theta J \| T(K) \| \theta' J') \,. \tag{3.5}$$

L & B provide the reduced matrix element in (3.5) for $K = 0$, 1 (see, also, §4) and 2 in both the *jj*-coupling and Russell-Saunders coupling schemes. Here, table 1 lists for $K = 3$ and 4 values of the reduced matrix element of the unit tensor operator $V(K)$ in the two coupling schemes for states of f^n, appropriate to the study of rare earth atoms. The reduced matrix elements $(\theta J \| T(3) \| \theta J)$ are listed in table 2 for values of θJ chosen according to Hund's rules for the ground state of f^n in the coupling scheme of Russell and Saunders. It is interesting to note that $(\theta J \| T(3) \| \theta J)$ is zero for $n = 2$, 5, 9 and 12.

If the wave functions for the initial and final states of the atom are drawn from a single *J*-manifold it might be useful to employ operator equivalents. To this end one re-writes the matrix element (3.5) as,

$$\left\langle \theta JM \left| T^K_{m_0} \right| \theta JM' \right\rangle = \left\langle JM \left| I^{(K)}_{m_0} \right| JM' \right\rangle (\theta J \| T(K) \| \theta J) \,, \tag{3.6}$$

when the tensor $\mathbf{I}^{(K)}$ is defined to have a reduced matrix element equal to one. A consequence of this notation is that the mean value of *Z*, required for both the attenuation coefficient and the scattering length for Bragg diffraction, is a weighted sum of mean values of $\mathbf{I}^{(K)}$, in a scalar product with $\mathbf{H}^{(K)}$. However, this appealing result does not hold in the general case, where the initial and final states of the atom contain contributions from more than one *J*-manifold. Moreover, the use of operator equivalents does not add too much in the way of physical insight for contributions to $\langle Z \rangle$ coming from the terms with $K \geq 3$, simply because the operator equivalents for high-order tensors are complicated objects. By way of an example consider $K = 3$ and $m_0 = 0$, for which we have the result,

$$\left\langle JM \left| I^{(3)}_0 \right| JM \right\rangle = (-1)^{J-M} \begin{pmatrix} J & 3 & J \\ -M & 0 & M \end{pmatrix} = \frac{M\{5M^2 + 1 - 3J(J+1)\}}{\{(J-1)(2J-1)(J+2)(2J+3)\}^{1/2} (J \| J \| J)} \,. \tag{3.7}$$

This result suggests the use of an operator equivalent proportional to an octupole moment operator,

$$J_c\{5J_c^2 + 1 - 3J(J+1)\} = \tfrac{5}{3}\, J_c\{3J_c^2 - J(J+1)\} + \tfrac{1}{3}\, J_c\{3 - 4J(J+1)\}, \qquad (3.8)$$

in which the second form is a sum of J_c and the product of this operator with the diagonal element of the quadrupole operator.

Expressions in terms of the idealized scattering length for the attenuation coefficient and cross-sections, for elastic and inelastic scattering, are given by L & B. These expressions remain valid when the idealized scattering length is taken to be the sum of the dipole and quadrupole scattering lengths, i.e. when Z ($\mu;\mu'$) in (2.3) is the sum of equation (3.10) in L & B and (3.4) in the present paper. In the next section we consider the structure of the quadrupole matrix element (3.4) for the special case of a saturated magnetic atom, which can be a guide to properties observed of a sample held at a low temperature.

§4. Saturated magnetic atom

In some respects, the model of a saturated magnetic atom serves as a useful orientation to the structure and relative magnitudes of the five contributions, labelled by K, to the quadrupole matrix element (3.4). Taking $M = M' = J$ in the latter we find,

$$Z(\mu;\mu) = \Phi \sum_K (-1)^K \sqrt{(2K+1)} \begin{Bmatrix} 2 & K & 2 \\ l & \bar{l} & l \end{Bmatrix} \begin{pmatrix} J & K & J \\ -J & 0 & J \end{pmatrix} (\theta J \| T(K) \| \theta J) H_0^{(K)} . \qquad (4.1)$$

Values of $H_0^{(K)}$ are provided in an appendix.

In the remainder of this section we individually consider the five contributions to (4.1).

<u>$K = 0$:</u> From the result,

$$(\theta J \| T(0) \| \theta' J') = \delta_{\theta,\theta'} \delta_{J,J'}\, n_h \left(\frac{2J+1}{2l+1}\right)^{1/2},$$

we readily find the first contribution to the quadrupole matrix element of a saturated atom,

$$\Phi\left(\tfrac{1}{5}\right)^{1/2}\{n_{\mathrm{h}}/(2l+1)\}H_0^{(0)}\ . \tag{4.2}$$

$\underline{K=1}$: We make use of the results,

$$\begin{Bmatrix} 2 & 1 & 2 \\ l & l-2 & l \end{Bmatrix} = -\left(\tfrac{2}{15}\right)^{1/2}\frac{(l+1)}{(l\|l\|l)},$$

$$\begin{pmatrix} J & 1 & J \\ -J & 0 & J \end{pmatrix} = J/(J\|J\|J),$$

and, for the particular case $J=J'$,

$$(\theta J\|T(1)\|\theta J) = \frac{(J\|J\|J)}{(l\|l\|l)}(2-g),$$

where g is the Landé factor. Assembling the results, the $K=1$ contribution to $Z(\mu;\mu)$ is,

$$\Phi\left(\tfrac{2}{5}\right)^{1/2}\frac{1}{l(2l+1)}(2-g)J\,H_0^{(1)}\ . \tag{4.3}$$

$\underline{K=2}$:

$$\begin{Bmatrix} 2 & 2 & 2 \\ l & l-2 & l \end{Bmatrix} = \frac{(l+1)}{(l\|l\|l)}\left\{\frac{2(2l+3)}{35(2l-1)}\right\}^{1/2},$$

and

$$\begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix} = \frac{J}{(J\|J\|J)}\left\{\frac{(2J-1)}{(2J+3)}\right\}^{1/2}.$$

$K = 3$:

$$\begin{Bmatrix} 2 & 3 & 2 \\ l & l-2 & l \end{Bmatrix} = -\frac{(l+1)}{(l\|l\|l)} \left\{ \frac{(l+2)(2l+3)}{70(l-1)(2l-1)} \right\}^{1/2},$$

and, from (3.7) say,

$$\begin{pmatrix} J & 3 & J \\ -J & 0 & J \end{pmatrix} = \frac{J}{(J\|J\|J)} \left\{ \frac{(J-1)(2J-1)}{(J+2)(2J+3)} \right\}^{1/2}.$$

$K = 4$:

$$\begin{Bmatrix} 2 & 4 & 2 \\ l & l-2 & l \end{Bmatrix} = \frac{(l+1)}{(l\|l\|l)} \left\{ \frac{(l+2)(2l+3)(2l+5)}{630(l-1)(2l-1)(2l-3)} \right\}^{1/2},$$

and,

$$\begin{pmatrix} J & 4 & J \\ -J & 0 & J \end{pmatrix} = \frac{J}{(J\|J\|J)} \left\{ \frac{(J-1)(2J-1)(2J-3)}{(J+2)(2J+3)(2J+5)} \right\}^{1/2}.$$

The reduced matrix elements $(\theta J \| T(K) \| \theta J)$ to go with the foregoing expressions for $K = 2$, 3 and 4 are obtained, for either *jj*-coupling or Russell-Saunders coupling schemes, from tables in L & B and this paper.

§5. **Dichroism**

In our theoretical framework for the attenuation coefficient, γ, one finds that γ is proportional to the mean value of Z evaluated for a forward scattering geometry ($\mathbf{q} = \mathbf{q}'$) and averaged with respect to state of polarization in the primary beam of X-rays. Following L & B, we denote this special value of Z by $\langle Z \rangle_0$. The attenuation coefficient is proportional to the density of particles in the foil, n_0, and in the limit $\Gamma \to 0$,

$$\gamma = 2\pi\lambda n_o \left(\frac{e\Delta}{\hbar c}\right)^2 \delta(E-\Delta)\langle Z\rangle_o . \qquad (5.1)$$

If γ is integrated with respect to E over an interval which includes the subset of intermediate states, whose average energy is defined by Δ, our theoretical framework provides an exact interpretation, within the scope of the atomic model.

For quadrupole-allowed absorption events the mean value of Z, required in (5.1), is calculated using the matrix element (3.4). In the general case, $\langle Z\rangle$ is the linear combination of matrix elements with weights determined by the chemical and physical properties of the target foil. Regarding the dependence of $\langle Z\rangle_o$ on the states of polarization in the primary beam, and it is this dependence which creates a dichroic effect, it is necessary to examine the values of $\mathbf{H}^{(K)}$ calculated for $\mathbf{k} = 0$ and averaged with respect to the states of polarization. If the symmetry of the magnetic state of the atom is cylindrical, or higher, one only needs the diagonal component of $\mathbf{H}^{(K)}$. The appropriate values are listed in table 3, together with all the components, of $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(3)}$, needed to discuss the circular dichroic signal for an arbitrary magnetic symmetry.

The circular dichroic signal is the difference in two values of γ in which the Stokes parameter P_2 is assigned values of equal magnitude and opposite sign. Note that P_2 is the mean helicity of the X-ray beam. Let us define a signal by,

$$\Delta Z = \langle Z(P_2)\rangle_o - \langle Z(-P_2)\rangle_o . \qquad (5.2)$$

Empirical data for the signal has been obtained at the dysprosium L_3 edge by Lang et al. (1995), and at the L_3 edge of Yb in $YbFe_2$ by Giorgetti et al. (1995).

Contributions to $\langle Z\rangle_o$ with $K = 0$, 2 and 4 are independent of P_2 and cancel out in the dichroic signal (5.2). Thus, ΔZ is proportional to the sum of the contributions to $\langle Z\rangle_o$ with ranks $K = 1$ and $K = 3$. Referring to the entries in table 3, the components of $\|\mathbf{H}^{(1)}\|$ and $\|\mathbf{H}^{(3)}\|$ are proportional to P_2. For a given atomic wavefunction, we provide the reader with all necessary information to calculate the dichroic signal.

The relatively simple structure of the reduced matrix element of $T(1)$ enables us to make progress with the physical interpretation of the rank-one contribution to $\langle Z\rangle_o$. Regrettably, and predictably, very little light can be shed on the physical significance of the rank-three contribution, although the reader might find interesting the octupole operator-equivalent for the diagonal element for $K = 3$ given in (3.8).

Let us examine the result for the dichroic signal appropriate to the special case where (i) operator equivalents can be used because the atomic wavefunction is created from one J-manifold and (ii) the rank-three contribution to $\langle Z\rangle_o$ can be safely neglected (with regard to this aspect it is noted that, the rank-three contribution is zero for pure Russell-Saunders coupling and a number of electrons in the valence shell = 2, 5, 9 or 12). For this special case, the circular dichroic signal is (K=1),

$$\Delta Z = -\,\Phi\{P_2 / 5l(2l+1)\}\langle \mathbf{L}\rangle\cdot\hat{\mathbf{q}}, \tag{5.3}$$

and Φ is obtained from (3.2) with $q = q'$. The structure of the result (5.3) is very similar to the dichroic signal with dipole-allowed events; the appropriate result for the latter case is (4.5) in L & B. If we normalize (5.3) by the isotopic contribution to $\langle Z\rangle_o$, generated by the rank-zero contribution,

$$3\Phi\{n_h / 10(2l+1)\},$$

the result is,

$$-\tfrac{2}{3}\,P_2\{\langle \mathbf{L}\rangle\cdot\hat{\mathbf{q}} / ln_h\}.$$

This value is the same as the corresponding quantity obtained for dipole-allowed events apart from the factor (2/3), and most importantly, here we have set aside for the moment the rank-three contribution to the quadrupole matrix element.

To assess the relative sizes of the rank-one and rank-three contributions to the dichroic signal one can appeal to the results in §4 for a saturated magnetic atom. These results lead to

the conclusion that, at a low temperature, the key quantities determining the relative sizes of the two contributions are the reduced matrix elements $(\theta J\|T(1)\|\theta J)$ and $(\theta J\|T(3)\|\theta J)$ and not the 3j and 6j-symbols for which we have given analytic results. The rank-one reduced matrix element is found in §4 , and table 2 contains a listing of the rank-three reduced matrix element evaluated for the ground states of f^n determined by Hund's rules.

We conclude by giving the contribution to the dichroic signal made by the rank-three tensor, i.e. the contribution which when added to (5.3) leads to the total value of the circular dichroic signal. The following contribution is the complete expression for the rank-three contribution to ΔZ in the special case of an atom with cylindrical symmetry, for which terms in (3.4) with $m_o \neq 0$ are zero (no such limitation applies in 5.3). Assuming it is valid to use the operator equivalent (3.8) we find (K=3),

$$\Delta Z = \tfrac{1}{10}\,\Phi\, P_2\, \frac{(l+1)}{(l\|l\|l)} \left\{\frac{(l+2)(2l+3)}{(l-1)(2l-1)}\right\}^{1/2} \qquad (5.4)$$

$$\frac{\left\langle J_c\{5J_c^2+1-3J(J+1)\}\right\rangle}{(J\|J\|J)\{(J-1)(2J-1)(J+2)(2J+3)\}^{1/2}}\ (\theta J\|T(3)\|\theta J)\,(5\hat{q}_c^2-3)\hat{q}_c\,.$$

Here, $(l\|l\|l) = \sqrt{\{l(l+1)(2l+1)\}}$, and a similar expression holds for the reduced matrix element of the total angular momentum.

§6. **Comments**

We have obtained an idealized X-ray resonant scattering-length for quadrupole-allowed absorption events. The formulation follows work by Lovesey and Balcar (1996) for dipole-allowed events. The idealized scattering length provides a description of processes which involve valence electrons in a shell l^n. Where necessary, tables of relevant Racah unit tensor operators for l = 3 are given. Thus, the reader can readily apply the formalism to an atomic model of any rare earth material of interest.

Armed with the resonant scattering-length, it is straightforward to calculate the attenuation coefficient and the cross-sections for scattering. States of polarization in the

primary, and secondary, beams of X-rays are conveniently handled in terms of a Stokes vector (Lovesey and Collins 1996).

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Appendix

The spherical tensor $\mathbf{H}^{(K)}$ in the quadrupole matrix element (3.4) is constructed from spherical tensors of rank two, denoted by $h(Q)$, that are formed out of spherical components of the polarization vector and wave vector. Following the standard convention for creating a spherical tensor by coupling, via a Clebsch-Gordan coefficient, two spherical components of equal rank (Edmonds 1960),

$$h(Q) = \sum_{\nu\nu'} \varepsilon_\nu \hat{q}_{\nu'} (1\nu 1\nu' | 2Q), \tag{A.1}$$

where ε_ν and $\hat{q}_{\nu'}$ are spherical components of the unit vectors ε and $\hat{\mathbf{q}} = (\mathbf{q}/q)$. We choose to have ε purely real. Table 2 in L & B contains the definitions of the spherical components in terms of Cartesian components, and all the components of $h(Q)$. Recall that ε and $\mathbf{q}$ are orthogonal vectors. The spherical tensor constructed from ε' and $\hat{\mathbf{q}}'$, that relate to the secondary beam of X-rays, is denoted by $h'(Q')$.

With the foregoing notation, the definition of the components of $\mathbf{H}^{(K)}$ is,

$$H^{(K)}_{m_0} = \sum_{QQ'} h'(Q')h(Q)(2Q2Q' | Km_0). \tag{A.2}$$

The order of h' and h is significant for K = odd integer. The reason for this is the behaviour of the Clebsch-Gordan coefficient with respect to an interchange of Q and Q', namely,

$$(2Q2Q' | Km_0) = (-1)^K (2Q'2Q | Km_0).$$

Hence, two tensors based on (A.2) and formed out of the primary and secondary variables placed in opposite orders are related by a factor $(-1)^K$. This result permits us to anticipate the finding that odd-order tensors are linear in components of $(\varepsilon' \times \varepsilon)$ and $(\hat{\mathbf{q}}' \times \hat{\mathbf{q}})$, and even-order tensors are unchanged by an interchange of primed and unprimed variables.

Here, and in table 2 of L & B, the Cartesian components of a vector are labelled (a, b, c). (The labels (x, y, z) are reserved for a set of Cartesian axes that are used to describe

the geometry of the experimental arrangement.) For $K = 0$ there is only one component in $\mathbf{H}^{(K)}$, and we find,

$$H_o^{(o)} = \tfrac{1}{2}\left(\tfrac{1}{5}\right)^{1/2}\left\{(\varepsilon'\cdot\varepsilon)(\hat{\mathbf{q}}'\cdot\hat{\mathbf{q}}) + \varepsilon_c'\hat{q}_c(\varepsilon\cdot\hat{\mathbf{q}}') + \varepsilon_c\hat{q}_c'(\varepsilon'\cdot\hat{\mathbf{q}}) - (\varepsilon'\times\varepsilon)_c(\hat{\mathbf{q}}'\times\hat{\mathbf{q}})_c\right\}. \quad \text{(A.3)}$$

For some purposes it is useful to write the sum of the second and third terms in the alternative form,

$$\left\{(\varepsilon'\times\varepsilon)\times(\hat{q}_c'\,\hat{\mathbf{q}} - \hat{q}_c\,\hat{\mathbf{q}}')\right\}_c.$$

Furthermore,

$$H_o^{(2)} = \tfrac{1}{2}\left(\tfrac{1}{14}\right)^{1/2}\{2(\varepsilon'\cdot\varepsilon)(\hat{\mathbf{q}}'\cdot\hat{\mathbf{q}}) - 3\varepsilon_c'\varepsilon_c(\hat{\mathbf{q}}'\cdot\hat{\mathbf{q}}) - 3(\varepsilon'\cdot\varepsilon)\hat{q}_c'\hat{q}_c - \varepsilon_c'\hat{q}_c(\varepsilon\cdot\hat{\mathbf{q}}') - \varepsilon_c\hat{q}_c'(\varepsilon'\cdot\hat{\mathbf{q}}) - 2(\varepsilon'\times\varepsilon)_c(\hat{\mathbf{q}}'\times\hat{\mathbf{q}})_c\}, \quad \text{(A.4)}$$

and,

$$H_o^{(4)} = \tfrac{1}{2}\left(\tfrac{1}{70}\right)^{1/2}\{(\varepsilon'\cdot\varepsilon)(\hat{\mathbf{q}}'\cdot\hat{\mathbf{q}}) + 35\,\varepsilon_c'\varepsilon_c\hat{q}_c'\hat{q}_c - 5\,\varepsilon_c'\varepsilon_c(\hat{\mathbf{q}}'\cdot\hat{\mathbf{q}}) - 5\,(\varepsilon'\cdot\varepsilon)\hat{q}_c'\hat{q}_c - 4\varepsilon_c'\hat{q}_c(\varepsilon\cdot\hat{\mathbf{q}}') - 4\,\varepsilon_c\hat{q}_c'(\varepsilon'\cdot\hat{\mathbf{q}}) - (\varepsilon'\times\varepsilon)_c(\hat{\mathbf{q}}'\times\hat{\mathbf{q}})_c\}. \quad \text{(A.5)}$$

In the calculation of the attenuation coefficient we need $\mathbf{H}^{(K)}$ evaluated for a forward scattering geometry and averaged with respect to states of polarization in the primary beam of X-rays. The average of a quantity with respect to states of polarization is denoted by placing the quantity between double vertical lines. Turning to the result (A.3) for $H_o^{(1)}$ and setting $\mathbf{q} = \mathbf{q}'$ only the first term on the right-hand side does not vanish. With regard to the average over states of polarization we have,

$$\left\|(\varepsilon'\cdot\varepsilon)\right\| = 1,$$

so for $\mathbf{q} = \mathbf{q}'$,

$$\left\|H_o^{(o)}\right\| = \tfrac{1}{2}\left(\tfrac{1}{5}\right)^{1/2}.$$

This result and other results for $\left\|\mathbf{H}^{(K)}\right\|$ required in the calculation of the attenuation coefficient are gathered in table 3. The orientational dependences of $\left\|H_o^{(1)}\right\|$ and $\left\|H_o^{(3)}\right\|$ agree with the findings of Carra et al. (1993) and Giorgetti et al. (1995).

The cross-sections for scattering are proportional to the square of the scattering length averaged with respect to states of polarization in the primary beam. In the event that the scattering length is represented by the term in Z ($\mu;\mu'$) with $K = 0$, the cross-sections are proportional to,

$$\left\|H_o^{(o)} H_o^{(o)}\right\|,$$

and all the terms in this expression that occur on substituting (A.3) for $H_o^{(o)}$ are given by Lovesey and Collins (1996). (The structure of the cross-section for Bragg diffraction is explored by Hill and McMorrow (1996).)

In the remaining discussion of $\mathbf{H}^{(K)}$ we limit ourselves to $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(3)}$. The mean value of Z contains these terms weighted by thermodynamic quantities that vanish if the magnetic state is not ordered. The magnetic quantities that weight $\mathbf{H}^{(2)}$ and $\mathbf{H}^{(4)}$ can be non-zero for a paramagnetic sample.

Looking at (A.3) - (A.5) it might be correctly guessed that the components of $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(3)}$ are somewhat unwiedly. To make the expressions as attractive to the eye as seems possible we use a series of functions $R(p)$, with $p = 1, 2, \ldots, 10$, of the Cartesian components of $\boldsymbol{\varepsilon}, \hat{\mathbf{q}}, \boldsymbol{\varepsilon}'$ and $\hat{\mathbf{q}}'$. It also convenient to use the vectors,

$$\xi = (\hat{\mathbf{q}}' \times \hat{\mathbf{q}}), \text{ and } \varphi = (\boldsymbol{\varepsilon}' \times \boldsymbol{\varepsilon}).$$

We find that $H_o^{(1)}$ and $H_o^{(3)}$ can be expressed as linear combinations of,

$$R(1) = \{h'(1)h(-1) - h'(-1)h(1)\} = \tfrac{i}{2}\{\varepsilon'_c\varepsilon_c\xi_c + \varphi_c\hat{q}'_c\hat{q}_c - \tfrac{1}{2}[\varphi_a(\hat{q}'_a\hat{q}_c + \hat{q}'_c\hat{q}_a)$$

$$+ \varphi_b(\hat{q}'_b\,\hat{q}_c + \hat{q}'_c\,\hat{q}_b) + (\varepsilon'_b\varepsilon_c + \varepsilon'_c\varepsilon_b)\xi_b + (\varepsilon'_a\varepsilon_c + \varepsilon'_c\varepsilon_a)\xi_a]\},$$

and,

$$R(2) = \{h'(-2)h(2) - h'(2)h(-2)\} = \tfrac{i}{2}\{(\varepsilon'\cdot\varepsilon - \varepsilon'_c\varepsilon_c)\xi_c + \varphi_c(\hat{\mathbf{q}}'\cdot\hat{\mathbf{q}} - \hat{q}'_c\hat{q}_c)\}.$$

The results are;

$$H_o^{(1)} = \left(\tfrac{1}{10}\right)^{1/2}\{R(1) + 2R(2)\},$$

and,

$$H_o^{(3)} = \left(\tfrac{1}{10}\right)^{1/2}\{-2R(1) + R(2)\}.$$

These are the only values of $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(3)}$ needed to describe the properties of a magnetic atom with at least cylindrical symmetry with respect to the c-axis.

Defining,

$$R(3) = \{h'(1)h(0) - h'(0)h(1) + h'(0)h(-1) - h'(-1)h(0)\} = \left(\tfrac{3}{2}\right)^{1/2}\{\varphi_b\hat{q}'_c\hat{q}_c + \varepsilon'_c\varepsilon_c\xi_b\},$$

and,

$$R(4) = \{h'(-1)h(2) - h'(2)h(-1) + h'(-2)h(1) - h'(1)h(-2)\} = \tfrac{1}{2}\{\varphi_b(\hat{\mathbf{q}}'\cdot\hat{\mathbf{q}} - \hat{q}'_c\hat{q}_c) + (\varepsilon'\cdot\varepsilon - \varepsilon'_c\varepsilon_c)\xi_b$$

$$-(\varepsilon'_b\varepsilon_c + \varepsilon'_c\varepsilon_b)\xi_c - \varphi_c(\hat{q}'_b\hat{q}_c + \hat{q}'_c\hat{q}_b)\},$$

one has,

$$H_{+1}^{(1)} + H_{-1}^{(1)} = \left(\tfrac{3}{10}\right)^{1/2}R(3) + \left(\tfrac{1}{5}\right)^{1/2}R(4),$$

and,

$$H^{(3)}_{+1} + H^{(3)}_{-1} = -\left(\tfrac{1}{5}\right)^{1/2} R(3) + \left(\tfrac{3}{10}\right)^{1/2} R(4).$$

And, with,

$$R(5) = \left\{h'(1)h(0) - h'(0)h(1) + h'(-1)h(0) - h'(0)h(-1)\right\} = -\,\mathrm{i}\left(\tfrac{3}{2}\right)^{1/2} \{\varepsilon'_c \varepsilon_c \xi_a + \varphi_a \hat{q}'_c \hat{q}_c\},$$

and,

$$R(6) = \left\{h'(-1)h(2) - h'(2)h(-1) - h'(-2)h(1) + h'(1)h(-2)\right\} = \tfrac{\mathrm{i}}{2} \{(\varepsilon'_a \varepsilon_c + \varepsilon'_c \varepsilon_a)\xi_c$$

$$- \varphi_a(\hat{\mathbf{q}}' \cdot \hat{\mathbf{q}} - \hat{q}'_c \hat{q}_c) - (\varepsilon' \cdot \varepsilon - \varepsilon'_c \varepsilon_c)\xi_a + \varphi_c(\hat{q}'_a \hat{q}_c + \hat{q}'_c \hat{q}_a)\},$$

we find,

$$H^{(1)}_{+1} - H^{(1)}_{-1} = \left(\tfrac{3}{10}\right)^{1/2} R(5) + \left(\tfrac{1}{5}\right)^{1/2} R(6),$$

and,

$$H^{(3)}_{+1} - H^{(3)}_{-1} = -\left(\tfrac{1}{5}\right)^{1/2} R(5) + \left(\tfrac{3}{10}\right)^{1/2} R(6).$$

For the remaining components of $\mathbf{H}^{(3)}$ we choose to write,

$$H^{(3)}_{+2} + H^{(3)}_{-2} = \tfrac{\mathrm{i}}{4} (3)^{1/2} R(7),$$

$$H^{(3)}_{+2} - H^{(3)}_{-2} = \tfrac{1}{4} (3)^{1/2} R(8),$$

$$H^{(3)}_{+3} + H^{(3)}_{-3} = \left(\tfrac{1}{2}\right)^{3/2} R(9),$$

and,

$$H^{(3)}_{+3} - H^{(3)}_{-3} = \mathrm{i}\left(\tfrac{1}{2}\right)^{3/2} R(10).$$

We find,

$$R(7) = -\,(\varepsilon'_a\varepsilon_c + \varepsilon'_c\varepsilon_a)\xi_a + (\varepsilon'_b\varepsilon_c + \varepsilon'_c\varepsilon_b)\xi_b + \varphi_b(\hat{q}'_b\hat{q}_c + \hat{q}'_c\hat{q}_b) - \varphi_a(\hat{q}'_a\hat{q}_c + \hat{q}'_c\hat{q}_a),$$

$$R(8) = \varphi_b(\hat{q}'_a\hat{q}_c + \hat{q}'_c\hat{q}_a) + \varphi_a(\hat{q}'_b\hat{q}_c + \hat{q}'_c\hat{q}_b) + (\varepsilon'_a\varepsilon_c + \varepsilon'_c\varepsilon_a)\xi_b + (\varepsilon'_b\varepsilon_c + \varepsilon'_c\varepsilon_b)\xi_a,$$

$$R(9) = \varphi_b(\hat{q}'_b\hat{q}_b - \hat{q}'_a\hat{q}_a) - \varphi_a(\hat{q}'_a\hat{q}_b + \hat{q}'_b\hat{q}_a) + (\varepsilon'_b\varepsilon_b - \varepsilon'_a\varepsilon_a)\xi_b - (\varepsilon'_a\varepsilon_b + \varepsilon'_b\varepsilon_a)\xi_a,$$

and, finally,

$$R(10) = \varphi_a(\hat{q}'_a\hat{q}_a - \hat{q}'_b\hat{q}_b) - \varphi_b(\hat{q}'_a\hat{q}_b + \hat{q}'_b\hat{q}_a) + (\varepsilon'_a\varepsilon_a - \varepsilon'_b\varepsilon_b)\xi_a - (\varepsilon'_a\varepsilon_b + \varepsilon'_b\varepsilon_a)\xi_b.$$

Table 1a

***jj*-coupling scheme:**

The reduced matrix elements $(\nu J\|V(K)\|\nu J)$ for $K = 3$ and 4, and f-electrons in configurations determined by Hund's rules. For the states $f^1 - f^6$ the total angular momentum $j = (5/2)$ and for $f^7 - f^{13}$ it has the value $j = (7/2)$. Values of the reduced matrix element for $K = 0$, 1 and 2 are reported by L & B. As an example of how to read entries in the table consider f^{11}; for this electron shell $j = (7/2)$, the number of electrons in the shell $n = 5$, and the values of reduced matrix elements are appropriate for the number of holes $n_h = (2j + 1 - n) = 3$. NB the signs of the matrix elements for K = even integer depend on whether one is counting electrons or holes, and values for the latter are given in the tables 1a and 1b.

	$(\nu J\|V(3)\|\nu J)$	$(\nu J\|V(4)\|\nu J)$
f^1	$\sqrt{7}$	-3
f^2	$-\sqrt{\left(\frac{11}{14}\right)}$	$\frac{3}{7}\sqrt{\left(\frac{143}{2}\right)}$
f^3	$-\sqrt{\left(\frac{143}{21}\right)}$	0
f^4	$-\sqrt{\left(\frac{11}{14}\right)}$	$-\frac{3}{7}\sqrt{\left(\frac{143}{2}\right)}$
f^5	$\sqrt{7}$	3
f^6	0	0
f^7	$\sqrt{7}$	-3
f^8	$\frac{1}{11}\sqrt{\left(\frac{182}{3}\right)}$	$\frac{1}{11}\sqrt{(442)}$
f^9	$-\sqrt{\left(\frac{3230}{1001}\right)}$	$\frac{9}{7}\sqrt{\left(\frac{646}{143}\right)}$
f^{10}	$-\sqrt{\left(\frac{646}{77}\right)}$	0
f^{11}	$-\sqrt{\left(\frac{3230}{1001}\right)}$	$-\frac{9}{7}\sqrt{\left(\frac{646}{143}\right)}$
f^{12}	$\frac{1}{11}\sqrt{\left(\frac{182}{3}\right)}$	$-\frac{1}{11}\sqrt{(442)}$
f^{13}	$\sqrt{7}$	3

Table 1b

Russell-Saunders coupling scheme:

The value of the reduced matrix elements of $V(3)$ and $V(4)$ for the ground state configuration of tripositive lanthanides derived from Hund's rules, as a function of the number of holes. Results are based on the tables prepared by Nielson and Koster (1963), which cover the p^n, d^n and f^n shells.

Ground state	n_h	$(\theta\|\|V(3)\|\|\theta)$	$(\theta\|\|V(4)\|\|\theta)$
^2F	1	$\sqrt{7}$	3
^3H	2	0	$-2\sqrt{(\frac{13}{7})}$
^4I	3	$-\sqrt{(\frac{182}{33})}$	$-\frac{1}{11}\sqrt{(442)}$
^5I	4	$-\sqrt{(\frac{182}{33})}$	$\frac{1}{11}\sqrt{(442)}$
^6H	5	0	$2\sqrt{(\frac{13}{7})}$
^7F	6	$\sqrt{7}$	-3

Table 2

Values of the reduced matrix elements $(\theta J \| T(3) \| \theta J)$ for the electron configurations f^1 through to f^{13}. The quantum numbers $\theta J = \nu SLJ$ are chosen according to Hund's rules for the ground state configurations in the coupling scheme of Russell and Saunders.

		$(\theta J \| T(3) \| \theta J)$
f^1	$^2F_{5/2}$	$\frac{1}{7}\sqrt{30}$
f^2	$^3H_4$	0
f^3	$^4I_{9/2}$	$-\frac{28}{11}\sqrt{\left(\frac{10}{143}\right)}$
f^4	$^5I_4$	$-\frac{28}{11}\sqrt{\left(\frac{3}{55}\right)}$
f^5	$^6H_{5/2}$	0
f^8	$^7F_6$	$\sqrt{\left(\frac{26}{33}\right)}$
f^9	$^6H_{15/2}$	0
f^{10}	$^5I_8$	$-\frac{1}{14}\sqrt{\left(\frac{323}{2}\right)}$
f^{11}	$^4I_{15/2}$	$-\frac{2}{7}\sqrt{\left(\frac{646}{65}\right)}$
f^{12}	$^3H_6$	0
f^{13}	$^2F_{7/2}$	$\frac{2}{7}\sqrt{11}$

Table 3

Components of the spherical tensor $\mathbf{H}^{(K)}$ evaluated for the forward scattering geometry ($\mathbf{k} = 0$) and averaged with respect to states of polarization in the primary beam of X-rays, described by a Stokes vector $\mathbf{P} = (0, P_2, P_3)$ and defined in agreement with Lovesey and Collins (1996). Cartesian components of the unit vector $\hat{\mathbf{q}}$ are labelled (a, b, c), and this set of axes and the set (x, y, z) are related by Euler angles α, β and γ defined in the same way as L & B and Judd (1975); see tables 3 and 4 in L & B. In the following entries,

$$\left\|\varepsilon_c'\varepsilon_c\right\| = \tfrac{1}{2}\left\{(1+P_3)\cos^2\beta + (1-P_3)\cos^2\alpha\sin^2\beta\right\}.$$

For $\beta = 0$ the axes z and c coincide, and for $\alpha = \beta = (\pi/2)$ the axis of quantization (the c-axis) is aligned with the direction of propagation of the beam of X-rays. The quantity P_2 is the mean helicity in the primary beam.

$$\left\|H_o^{(o)}\right\| = \tfrac{1}{2}\left(\tfrac{1}{5}\right)^{1/2}$$

$$\left\|\mathbf{H}^{(1)}\right\| = -\tfrac{1}{2}\left(\tfrac{1}{10}\right)^{1/2} P_2\hat{\mathbf{q}}$$

$$\left\|H_o^{(2)}\right\| = \tfrac{1}{2}\left(\tfrac{1}{14}\right)^{1/2}\left\{2 - 3\hat{q}_c^2 - 3\left\|\varepsilon_c'\varepsilon_c\right\|\right\}$$

$$\left\|H_o^{(3)}\right\| = \tfrac{1}{2}\left(\tfrac{1}{10}\right)^{1/2} P_2(5\hat{q}_c^2 - 3)\hat{q}_c$$

$$\left\|H_{\pm1}^{(3)}\right\| = \tfrac{1}{4}\left(\tfrac{3}{5}\right)^{1/2} P_2(5\hat{q}_c^2 - 1)\hat{q}_{\pm1}$$

$$\left\|H_{\pm2}^{(3)}\right\| = \tfrac{1}{2}(3)^{1/2} P_2\,\hat{q}_c\,\hat{q}_{\pm1}^2$$

$$\left\|H_{\pm3}^{(3)}\right\| = \tfrac{1}{2} P_2\,\hat{q}_{\pm1}^3$$

$$\left\|H_o^{(4)}\right\| = \tfrac{1}{2}\left(\tfrac{1}{70}\right)^{1/2}\left\{5(7\hat{q}_c^2 - 1)\left\|\varepsilon_c'\varepsilon_c\right\| + 1 - 5\hat{q}_c^2\right\}$$