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A theoretical framework for absorption and resonance-enhanced scattering of x-rays by magnetic materials: IV

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Abstract. The electrostatic resonant scattering of x-rays by an ion is discussed in terms of the relevant part of the scattering length. A formula, which applies for both E1 and E2 absorption events, is given for the product of matrix elements in the scattering length. The formula refers to an intermediate state that is labelled by the full set of quantum numbers of the core state into which a photon is absorbed. Idealized scattering lengths, discussed in our previous papers, are obtained by eliminating one or both quantum numbers of the core state.

In three previous papers we have explored a theoretical framework for the resonant contribution to the scattering length of x-rays, f. This quantity is the common factor in calculations of the attenuation coefficient and scattering cross-sections. Using an atomic model to describe electrons in a partly filled valence shell, we have demonstrated that f can be made to look the same as the scattering length of a direct probe of the valence electrons, e.g. a beam of neutrons, at the expense of discarding some information in f on the intermediate states engaged in the x-ray absorption event. The main advantage in using such an idealized scattering length for the interpretation of x-ray empirical data is that it is *directly* related to atomic quantities of interest, e.g. the spin–orbit interaction and magnetic moment of the valence electrons. As we have just implied, in the idealized scattering length the spectrum of intermediate states no longer obscures the information it contains on properties of the valence electrons of the resonant ion.

In constructing an idealized resonant scattering length for x-rays, the mechanism for discarding information on the spectrum of intermediate states is to perform a sum on the product of matrix elements in f over the quantum numbers of the hole in the core state into which a photon is absorbed. When this act is accompanied by the assumption that the energies of the intermediate states are independent of the said quantum numbers, standard tools in the theory of atomic spectroscopy enable one to carry out a significant simplification of f. The main purpose of the present paper is to report a formula for f in which the quantum numbers of the hole state are explicit, and not summed. As one might anticipate, the formula in question is quite complicated. It is likely that the main use of the formula will be in the interpretation of empirical data for which an idealized scattering length is found to do an inadequate job. The idealized x ray scattering lengths, introduced in our previous papers, are readily recovered from the more general formula given here.

In the following presentation we strive to make the key steps more or less self-contained. However, for the application of the results to calculations of observable quantities and some

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necessary auxiliary quantities, like the combinations of polarization vectors, the reader is referred to our previous papers.

The initial and final equilibrium (discrete) states of the valence electrons of the resonant ion are labelled by quantum numbers $\{\mu\}$ and $\{\mu'\}$. The quasi-discrete intermediate states are labelled by $\{\eta\}$; they have energies $E_\eta - \frac{1}{2}\mathrm{i}\gamma_\eta$ where $(\gamma/\hbar)$ is the total probability of all possible processes by which an intermediate state can decay. It is convenient to define the energy differences $\Delta = E_\eta - E_\mu$ and $\Delta' = E_\eta - E_{\mu'}$. If the primary x-rays have an energy $E = (\hbar cq) = (2\pi\hbar c/\lambda)$, the scattering length for a resonant process in which $E \sim \Delta$ is

$$f_\eta = -\left(\frac{2\pi e}{\lambda}\right)^2 \left(\frac{\Delta'}{\Delta}\right) \left\{ \frac{Z(\mu;\mu')}{E - \Delta + \frac{1}{2}\mathrm{i}\gamma} \right\}_\eta . \tag{1}$$

In general, the matrix element $Z(\mu;\mu')$ will depend on the position of the resonant ion in the sample. Omitted in (1), for simplicity, are the Debye–Waller factor and the spatial coherence factor; see Lovesey (1996). Formulae for the attenuation coefficient and cross-sections for resonance-enhanced elastic and inelastic scattering expressed in terms of f are given by Lovesey and Balcar (1996).

The hole in the intermediate state is labelled by the quantum numbers $\bar{J}$ and $\bar{M}$, and $\bar{J} = \bar{l} \pm \frac{1}{2}$, where $\bar{l}$ is the angular momentum of the core state into which a primary photon is absorbed. We provide results for $Z(\mu;\mu')$ appropriate for electric dipole (E1) and electric quadrupole (E2) absorption events. Let the polarization vectors of the primary and secondary photons be ε and ε', and denote the dipole operator by $\boldsymbol{R}$. If spherical components are labelled by $q = 0, \pm 1$, then, for an E1 event,

$$\begin{aligned} Z_\eta(\mu;\mu') &\equiv \sum_{qq'} (\varepsilon'_q \varepsilon_{q'})^* \langle \mu | R_q | \eta \rangle \langle \eta | R_{q'} | \mu' \rangle \\ &= (l||C(1)||\bar{l})(\bar{l}||C(1)||l) \langle l|R|\bar{l}\rangle^2 \\ &\quad \times \sum_{Km_0} \sum_r (2K+1)^{1/2} (2r+1) X^{(K)}_{-m_0} I^{K(r)}_{m_0} (-1)^{\bar{J}-\bar{M}} \begin{pmatrix} \bar{J} & r & \bar{J} \\ -\bar{M} & 0 & \bar{M} \end{pmatrix} . \end{aligned} \tag{2}$$

The quantity $I^{K(r)}_{m_0}$ is defined after we give the corresponding result for $Z(\mu;\mu')$ calculated for an E2 absorption event. In (2), for $\bar{l} = (l-1)$ the product of reduced matrix elements of the spherical harmonic $C(1)$ has the value $-l$, where l is the angular momentum of the valence shell. The tensor $\mathbf{X}^{(K)}$ contains the polarization vectors and it is defined by Lovesey and Balcar (1996).

For an E2 event,

$$\begin{aligned} Z_\eta(\mu;\mu') &= \tfrac{1}{6}(q'/q)\{q\langle l|R^2|\bar{l}\rangle (l||C(2)||\bar{l})\}^2 \\ &\quad \times \sum_{Km_0} \sum_r (2K+1)^{1/2} (2r+1) (-1)^K H^{(K)}_{-m_0} I^{K(r)}_{m_0} (-1)^{\bar{J}-\bar{M}} \begin{pmatrix} \bar{J} & r & \bar{J} \\ -\bar{M} & 0 & \bar{M} \end{pmatrix} \end{aligned} \tag{3}$$

and $\mathbf{H}^{(K)}$ is defined by Lovesey (1996). The ranges over which the integers K, m_0 and r in (2) and (3) are summed are determined by properties of $I^{K(r)}_{m_0}$.

In our formula for $I^{K(r)}_{m_0}$ we denote the atomic quantum numbers ν, S, and L in μ by θ, and thus μ represents θ, J and M. In the following expression, $t = 1$ (2) for an E1 (E2) event. The definition of $I^{K(r)}_{m_0}$ is based on the function

$$\sum_{qq'} \begin{pmatrix} t & K & t \\ q & -m_0 & q' \end{pmatrix} \sum_{\bar{M}} (-1)^{\bar{J}-\bar{M}} \begin{pmatrix} \bar{J} & r & \bar{J} \\ -\bar{M} & 0 & \bar{M} \end{pmatrix} \langle \mu | C^t_q(\hat{\boldsymbol{R}}) | \eta \rangle \langle \eta | C^t_{q'}(\hat{\boldsymbol{R}}) | \mu' \rangle$$

and the only difference in I is that, purely for convenience, we factor out the reduced matrix elements of the spherical harmonics. We obtain

$$I_{m_0}^{K(r)} = (2\bar{J}+1)(-1)^K \sum_x (-1)^x (2x+1)^{1/2} \begin{pmatrix} K & r & x \\ -m_0 & 0 & m_0 \end{pmatrix} \sum_{ab} \langle \mu | W_{m_0}^{(ab)x} | \mu' \rangle$$
$$\times\ (2a+1)(2b+1) \sum_y (2y+1) \begin{Bmatrix} K & r & x \\ a & b & y \end{Bmatrix} \begin{Bmatrix} t & l & \bar{l} \\ t & l & \bar{l} \\ K & b & y \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \bar{J} & \bar{l} \\ \frac{1}{2} & \bar{J} & \bar{l} \\ a & r & y \end{Bmatrix} \tag{4}$$

where the unit tensor operator has a matrix element

$$\langle \mu | W_{m_0}^{(ab)x} | \mu' \rangle = (-1)^{J-M} \begin{pmatrix} J & x & J' \\ -M & m_0 & M' \end{pmatrix} (\theta J || W^{(ab)x} || \theta' J'). \tag{5}$$

Values of the reduced matrix element in (5) for atomic states determined by Hund's rules are listed by Lovesey and Balcar (1997). From a property of the $3j$-symbol, $m_0 = M - M'$. The $9j$-symbols in (4) are zero unless $(K+b+y)$ and $(a+r+y)$ are even integers. With our notation, which follows Judd (1963), the integers a and b denote the ranks of the spin and orbital tensors in $W^{(ab)x}$.

The quantity that features in our idealized scattering lengths is obtained from $I_{m_0}^{K(r)}$ by setting $r = 0$. For example, Lovesey and Balcar (1997) use

$$\sum_{\bar{M}} \langle \mu | C_q^t | \eta \rangle \langle \eta | C_{q'}^t | \mu' \rangle$$
$$= (l||C(t)||\bar{l})(\bar{l}||C(t)||l)(2\bar{J}+1)^{1/2} \sum_{Km_0} I_{m_0}^{K(0)} (2K+1) \begin{pmatrix} t & K & t \\ q & -m_0 & q' \end{pmatrix}. \tag{6}$$

The idealized scattering length calculated using (6), and the assumption that the energies of intermediate states are degenerate with respect to $\bar{M}$, refers to an absorption edge labelled by $\bar{J}$. An inferior estimate of f is obtained if, in addition to $\bar{M}$, one sums over the two values of $\bar{J}$, and also extends the assumption about the energies of intermediate states to a degeneracy with respect to $\bar{J}$ and $\bar{M}$.

Turning to (4), one finds for $r = 0$ that $x = K$; then (6) tells us that the quantity on the left-hand side, which determines the properties of the resonant scattering length, is a simple sum of unit tensor operators. Hence, by discarding in the scattering length the information labelled by $\bar{M}$ one obtains a dramatic simplification. The idealized scattering length so obtained has the same structure as the scattering length for the magnetic scattering of neutrons.

Perhaps the simplest derivation of (4) comes by using an identity due to Innes and Ufford (1958). More recently, a quantity similar to $I_{m_0}^{K(r)}$ has been exploited by van der Laan (1997a, b) to analyse the role of the spin polarization in the x-ray magnetic circular dichroism spectra of itinerant magnets.

The sequence of steps that we have used to obtain (4) are as follows: the sums on q, q' and $\bar{M}$ which entail four $3j$-symbols, two of which have been made explicit and two more which arise from applications of the Wigner–Eckart theorem to the matrix elements of C_q^t and $C_{q'}^t$, are reduced to a single sum, over x, of two $3j$-symbols and one $9j$-symbol by using a result given by Rotenberg *et al* (1959) equation (3.21)—one of the two $3j$-symbols created in this step is demanded by the Wigner–Eckart theorem as displayed in (5); the $9j$-symbols created in step one multiplied by two $6j$-symbols that arise from the reduced matrix elements of C_q^t and $C_{q'}^t$ are expressed as a sum, over a, b and y, of the product

of one $6j$-symbol and three $9j$-symbols using the identity due to Innes and Ufford (1958), cf. Judd (1963) equation (3-28); the result obtained by steps one and two for a single hole is extended to $(2(2l+1)-n)$ holes in the valence shell l^n by using the standard method due to Racah (see Judd 1963), which leads to the appearance of unit tensor operators in the final expression for $I^{K(r)}_{m_0}$.

It can be useful to separately consider the two contributions to $I^{K(r)}_{m_0}$ labelled by $a=0$ and $a=1$. To this end, we define

$$A_+ = \{\tfrac{1}{2}(2\bar{l}+1-r)(2\bar{l}+2+r)\}^{1/2}/(2\bar{l}+1)$$

and

$$A_- = -\{\tfrac{1}{2}(2\bar{l}-r)(2\bar{l}+1+r)\}^{1/2}/(2\bar{l}+1).$$

For $a=0$ and $\bar{J}=\bar{l}\pm\frac{1}{2}$ we find

$$I^{K(r)}_{m_0} = \pm(-1)^r A_\pm \sum_b (2b+1)\begin{pmatrix} K & r & b \\ -m_0 & 0 & m_0\end{pmatrix}\langle\mu|W^{(0b)b}_{m_0}|\mu'\rangle\begin{Bmatrix} t & l & \bar{l} \\ t & l & \bar{l} \\ K & b & r\end{Bmatrix}. \tag{7}$$

In considering $a=1$ it is convenient to use

$$\alpha = \{(2\bar{l}+1+r)/(2\bar{l}+1-r)\}^{1/2}$$

and

$$\beta = \{(2\bar{l}-r)/(2\bar{l}+2+r)\}^{1/2}.$$

Then,

$$\begin{aligned} I^{K(r)}_{m_0} = (-1)^K\left(\frac{3}{2r+1}\right)^{1/2} A_\pm \sum_x (-1)^x (2x+1)^{1/2}\begin{pmatrix} K & r & x \\ -m_0 & 0 & m_0\end{pmatrix}\sum_b \langle\mu|W^{(1b)x}_{m_0}|\mu'\rangle \\ \times\,(2b+1)\left[\begin{Bmatrix} K & r & x \\ 1 & b & r-1\end{Bmatrix}\begin{Bmatrix} t & l & \bar{l} \\ t & l & \bar{l} \\ K & b & r-1\end{Bmatrix}(r(2r-1))^{1/2}\alpha^{\pm 1}\right. \\ \left. -\,\begin{Bmatrix} K & r & x \\ 1 & b & r+1\end{Bmatrix}\begin{Bmatrix} t & l & \bar{l} \\ t & l & \bar{l} \\ K & b & r+1\end{Bmatrix}((r+1)(2r+3))^{1/2}\beta^{\pm 1}\right]. \end{aligned} \tag{8}$$

Applied to calculations of the dichroic signals in the attenuation coefficient, equations (7) and (8) provide generalizations of the standard sum rules.

Let us now summarize our key findings. In this exercise we will use as the example the scattering length for an E1 absorption event. Our crudest estimate of the x-ray resonant scattering length is obtained by summing the product of matrix elements in Z_η, given in (2), on both of the quantum numbers of the core state, $\bar{J}$ and $\bar{M}$, that are contained in the label η. The effect on (2) of summing it on $\bar{M}$ is to set all terms in the sum over r equal to zero except the term with $r=0$. The effect on (2) of summing it on $\bar{J}$ is to set $a=0$ in the formula (4) for $I^{K(r)}_{m_0}$. In consequence, the idealized scattering length created by summing on $\bar{J}$ and $\bar{M}$ is a sum of matrix elements of $W^{(0K)K}_{m_0}$ with $K=0$, 1 and 2. Note that the circular dichroic absorption signal is proportional to the term in the scattering length with $K=1$ and is proportional to the total orbital angular momentum operator. This and other properties of the idealized scattering length are explored by Lovesey and Balcar (1996).

A more sophisticated estimate of the scattering length is explored by Lovesey and Balcar (1997). This form of the idealized scattering length is created by summing the product of matrix elements in (2) only on $\bar{M}$, leaving it as a function of $\bar{J}$. From what has been said in

the previous paragraph, the idealized scattering length in question is obtained from (2) by setting $r = 0$, which means that it is a sum of the matrix elements of $W_{m_0}^{(ab)K}$ with $K = 0$, 1 and 2. The new terms in the scattering length with $a = 1$ depend on the spin state of the holes in the valence shell.

Lastly, Z_η calculated with the full formula for $I_{m_0}^{K(r)}$ gives our best estimate for the resonant x-ray scattering length. An inspection of (4) shows that it is a nested sum of matrix elements of $W_{m_0}^{(ab)x}$. Of course, of the three different estimates of the scattering length that we have discussed, the one that uses the full formula for $I_{m_0}^{K(r)}$ contains the most information on the holes in the valence shell of the resonant ion.

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