The total fluorescence yield from magnetic materials obtained using circularly polarized x-rays

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Abstract. The circular dichroic signal in the total cross-section for resonance-enhanced electric dipole scattering is calculated by an analytic method. Applied to lanthanide ions, our results shows that the signal is proportional to the mean value of the orbital magnetic moment, to a good approximation. This finding is the same as that found, without approximations, for the dichroic signal in the attenuation coefficient. Thus, the finding supports the use of the total fluorescence yield as a method of measuring the information known to be in the coefficient. An ion with a half-filled valence shell is shown to be an exceptional case. For f^7 the signal in the cross-section is proportional to the product of the (spin) magnetic moment and the difference between the total decay widths for the M_4 and M_5 absorption lines. For all cases, we give the angular dependence of the total cross-section, with respect to the direction of the primary radiation and the axis of quantization for the atomic states.

1. Introduction

The experimental technique that is based on the dichroic effect in the absorption of x-rays is emerging as a useful means by which to obtain information, at the atomic level of detail, on the magnetic properties of materials. Exploitation of the technique is underpinned by the sources of x-rays from particle accelerators, and its future development is assured by new, third-generation, sources.

Both linearly and circularly polarized beams of x-rays are useful (for a review of recent work, see, for example, Lovesey and Collins (1996) and Ebert (1996)). However, it appears that the use of circular polarization in absorption experiments has the most to offer when it comes to the study of the magnetic properties of materials. For one thing, the helicity in the polarized beam can detect the preferred axis for the net magnetization in the sample. In the absence of a magnetic field, the circular dichroic signal is zero for a paramagnetic and an antiferromagnetic configuration of magnetic moments. For a ferromagnetic configuration the signal tends to zero as the sample's temperature is raised through the critical temperature for the onset of spontaneous magnetic order. A paramagnetic material subjected to a strong magnetic field will show a dichroic signal for circular polarization. The information which can be extracted from the dichroic signal includes the mean value of the orbital contribution to the magnetic moment. The analysis required for this purpose is an integration of the dichroic signal, with respect to energy, across the absorption edge, and the use of so-called sum rules which have been derived on the basis of an atomic (localized) model of magnetic materials (Thole *et al* 1992, Ankudinov and Rehr 1995).

The absorption experiments are performed by measuring the attenuation of a beam of x-rays and, also, by detecting the yield of photoelectrons or the total fluorescence yield (Agarwal (1991), and section 4.2.6 in Lovesey and Collins (1996)). While a transmission measurement of the attenuation coefficient, using a foil made from the material of interest, presents itself as an ideal method, regrettably, it is often not possible to implement. The main reason is that the strong attenuation, of which a small part is due to the magnetic properties of the foil, demands that the foil is very thin, particularly when using soft x-rays, and only in a few cases are the properties of the sample such that a very thin foil can be realized.

At the moment, there is not a consensus on the efficacy of the indirect method of measuring the attenuation coefficient which is based on the detection of fluorescence photons; see Ma (1994), de Groot *et al* (1994) and van Veenendaal *et al* (1996). de Groot *et al* (1994) have strongly called into question fluorescence yield detection as a method of reliably measuring the attenuation coefficient of a magnetic material. Their argument has been further refined by van Veenendaal *et al* (1996) who conclude from their study, which uses a computer simulation and analytic methods, that fluorescence yield detection is probably a safe route to the attenuation coefficient for both 3d transition-metal ions and light lanthanide ions, and it is not safe for the investigation of heavy lanthanide ions.

The present contribution to the subject analyses, by an analytic method, a model of the fluorescence yield that is based on the total cross-section for resonance-enhanced scattering; the same model was used by van Veenendaal *et al* (1996) in their computer simulation. We apply our results to lanthanide ions, for which the localized, or atomic picture of the magnetic properties should be ideally suited. One finds that the difference in the total cross-section, caused by switching from right- to left-handed circular polarization in the primary beam of x-rays, to a good approximation is proportional to mean value of the orbital contribution to the magnetic moment. The analysis also gives the angular distribution of the difference signal, which might be exploited in experiments to reinforce our understanding of the underlying fluorescence process. (Self-absorption effects are not included in our work.) It is found that the configuration f^7 (Gd^{3+}) is an exceptional case, and the difference signal is proportional to the product of the (spin) magnetic moment and the difference in the total decay widths for the two absorption lines, namely the M_4 and M_5 lines.

The next section of the paper briefly reviews the resonant contribution to the scattering length, which is the instrument that is common to the calculation of the attenuation coefficient and the cross-section for scattering. A calculation of the total cross-section is taken up in section 3, and most of the mathematical work is relegated to an appendix. The application of our findings to lanthanide ions is the subject of section 4. A discussion of our results, and circular dichroism in the attenuation coefficient, is found in section 5.

2. Scattering lengths

The attenuation coefficient for the absorption, and the cross-section for the scattering of x-rays can be derived from the scattering length, f. In fact, the attenuation coefficient is proportional to the mean value of f, and the cross-section is proportional to the square of the absolute value of matrix elements of f. We start this section by discussing the cross-section for inelastic scattering, which is considered to result in one emitted photon and an electron transferred into a bound state.

Let us label the initial and final discrete states of the electrons in an absorbing atom by μ and μ', respectively, and denote the corresponding matrix elements of the scattering length by $f(\mu; \mu')$. If the change in the energy of the x-rays from E to E', caused by scattering,

is $\hbar\omega$ then conservation of energy in a scattering event requires that $\hbar\omega = E_{\mu'} - E_{\mu}$. The Boltzmann factor for the initial state of the atom p_{μ} satisfies $\sum p_{\mu} = 1$. With this notation the cross-section for the scattering of x-rays is

$$\left(\frac{d\sigma}{dE'}\right) = \left(\frac{E'}{E}\right) \sum_{\mu\mu'} p_{\mu} \delta(\hbar\omega + E_{\mu} - E_{\mu'}) |f(\mu; \mu')|^2. \tag{2.1}$$

Our development of this expression for the cross-section for the case of resonance-enhanced scattering will follow the formulation set out by Lovesey and Balcar (1996) and Lovesey and Balcar (1997), and the cited papers are hereafter referred to as papers I and III. Åberg and Tulkki (1985) review the calculation of the cross-section for materials that are not magnetic.

The energies of the quasi-discrete intermediate states engaged in an absorption event usually make two distinct clusters that can be labelled by the two values of the total angular momentum of the associated core state, $\bar{J}$. For an electric dipole (E1) absorption event by a lanthanide ion the two clusters constitute the M_4 and the M_5 absorption lines.

In the formulation set out in paper III, to each cluster one assigns a mean energy and a total decay width, Γ. The energy measured relative to the energy of the initial state of the atom is denoted by Δ, and relative to the final energy of the atom it is denoted by Δ'. When the energy of the primary x-rays $E = 2\pi\hbar c/\lambda$ is close to Δ, a matrix element of the scattering length is

$$f(\mu; \mu') = -\left(\frac{2\pi e}{\lambda}\right)^2 \sum_{\bar{J}} \left\{ \left(\frac{\Delta'}{\Delta}\right) \frac{Z(\mu; \mu')}{(E - \Delta + (i/2)\Gamma)} \right\}_{\bar{J}}. \tag{2.2}$$

Here, inside the curly brackets all quantities, apart from E, depend on $\bar{J}$. The quantity not mentioned before, $Z(\mu; \mu')$, includes the polarization vectors for the primary and secondary beams, the radial integral for the electric dipole absorption event, and various reduced matrix elements for the configuration of the valence electrons of the absorbing atom.

The expression for the cross-section obtained with (2.2) has to be averaged with respect to the states of polarization in the primary beam. A method for doing this, which uses a density matrix, is described by Berestetskii *et al* (1982) and Lovesey and Collins (1996). We are interested in the variation of the total cross-section with respect to the handedness of circular polarization in the primary beam. In terms of a Stokes vector to describe polarization in the primary beam, its component P_2 is the mean value of the helicity in the beam. Hence, for our immediate purpose, after taking the average we only need that part of the cross-section which is proportional to P_2. We find that it is useful to define a difference signal as the change in the total cross-section caused by reversing the handedness of the helicity, from right ($P_2 > 0$) to left ($P_2 < 0$) handed. Our most general result for the difference signal is derived from (A.4), and it is discussed in the next two sections.

As the last topic in this section we turn to the attenuation coefficient. This observable is a bulk quantity. It depends on the mean value of the scattering length, and in this respect it is the same as the scattering length which determines the cross-section for Bragg scattering. In terms of the formulation that we are using, the attenuation coefficient is actually proportional to the mean value of Z averaged over the states of polarization in the primary beam and evaluated for a forward-scattering geometry. This special value of Z is denoted by $\langle Z \rangle_0$. In terms of this quantity, we define a circular dichroic signal:

$$\Delta Z = \langle Z(P_2) \rangle_0 - \langle Z(-P_2) \rangle_0. \tag{2.3}$$

We will return to this expression in section 5, after we have reported the result for its analogue in scattering.

3. The total cross-section

The total cross-section is derived from (2.1) by integrating with respect to the energy of the secondary x-rays, E'. Evidently, the key quantity needed to understand the information which is contained in the total cross-section is the mean value of $|f|^2$, namely

$$\langle |f|^2 \rangle = \sum_{\mu\mu'} p_\mu |f(\mu; \mu')|^2. \tag{3.1}$$

Our difference signal is thus

$$\langle |f|^2 \rangle_{P_2} - \langle |f|^2 \rangle_{-P_2}$$

and this can be calculated by using the expression (A.4). The latter is built from quantities denoted by $\{A_0(K; K')\}$ which are constructed from energies, and reduced matrix elements, for the absorption lines labelled by $\bar{J}$. The integers K and K' are the ranks of the tensor operators that contribute to $A_0(K; K')$.

In the remainder of this section, and the following section, we consider a simplification to the expression (A.4) that is brought about by setting aside the dependence on $\bar{J}$ of the energies and reduced matrix elements. The appropriate value of the simplified scattering length is (A.9), and in paper I it is called the idealized scattering length. From (A.9) one sees that the difference signal is

$$\left\{ \frac{2}{\Gamma} \left(\frac{2\pi e}{\lambda} \right)^2 \right\}^2 \Delta Z^2 \tag{3.2}$$

where

$$\Delta Z^2 = \langle Z^2(P_2) \rangle - \langle Z^2(-P_2) \rangle$$

has the dimension of (length)^4. A value for ΔZ^2 is derived from (A.4) and (A.5) by replacing A_0 by A, which is defined in (A.8), and by replacing M and M^3 by the thermal averages $\langle J_c \rangle$ and $\langle J_c^3 \rangle$, respectively. Of course, $\langle J_c \rangle$ is proportional to the magnetic moment of the atom, while $\langle J_c^3 \rangle$ could be expressed in terms of the magnetic octupole.

4. Lanthanide ions

The quantities $A(K; K')$ which arise in the difference signal ΔZ^2 are defined by (A.8), and they can be computed by using the tables given in papers I and III. By way of an illustration, we will continue with an investigation of ΔZ^2 for lanthanide ions, for which the localized model of the magnetic ion that we are using is ideally suited (Jensen and Mackintosh 1991).

The two quantities $A(0; 1)$ and $A(1; 1)$ are quite simple functions of atomic variables, and the tables are not necessary. We find, following the definition in (A.5) and using (A.8),

$$Q(1) = 2\left\{ \frac{2}{3} J(J+1) \right\}^{1/2} A(0; 1) = -n_h(2-g)\frac{2l}{3(2l+1)^2}(J||J||J)^2\langle R \rangle^4 \tag{4.1a}$$

and

$$A(1; 1) = (2-g)^2 \frac{(J||J||J)^2}{2(2l+1)^2}\langle R \rangle^4. \tag{4.1b}$$

In these expressions, n_h is the number of holes in the valence shell, whose angular momentum is l, and g is the Landé factor. (For convenience, values of g for lanthanide ions are included in table 1.) The reduced matrix element is

$$(J||J||J) = \{J(J+1)(2J+1)\}^{1/2}.$$

Table 1. Entries in the table are in units of $\langle R \rangle^4$, apart from the Landé factor in the right-hand column. The other entries are $A(1; 1)$ defined by (A.8), and $Q(1)$, $Q(2)$ and $Q(3)$ that are defined in accord with (A.5) and evaluated with $A(K; K')$ in place of $A_0(K; K')$. The ground states of the configuration f^n are determined by Hund's rules.

	$Q(1)$	$A(1; 1)$	$Q(2)$	$Q(3)$	g
f^1	-31.85	0.70	0.05	0.02	6/7
f^2	-105.78	2.64	0.07	0.01	4/5
f^3	-141.42	4.09	0.03	0.00	8/11
f^4	-102.85	3.60	-0.03	0.00	3/5
f^5	-33.07	1.57	-0.06	0.01	2/7
f^8	-66.85	1.39	0.04	0.01	3/2
f^9	-138.76	4.63	0.07	0.01	4/3
f^{10}	-149.86	7.02	0.03	0.00	5/4
f^{11}	-99.90	6.66	-0.03	0.00	6/5
f^{12}	-37.14	3.87	-0.07	0.01	7/6
f^{13}	-4.41	0.94	-0.05	0.02	8/7

The remaining two quantities in (A.4), $Q(2)$ and $Q(3)$, which are defined in accord with (A.5), do not have simple values in terms of atomic variables. However, they are readily calculated in terms of reduced matrix elements of Racah unit spherical tensors $(\theta J || W^{(0K)K} || \theta J)$ that are tabulated in paper III. The appropriate expressions are

$$A(1; 2) = -\left\{ \frac{1}{3} \frac{(2l+3)}{(2l-1)} \right\}^{1/2} \frac{l(l+1)}{(2l+1)} \langle R \rangle^4 (\theta J || W^{(01)1} || \theta J)(\theta J || W^{(02)2} || \theta J)$$

and

$$A(2; 2) = \left\{ \frac{l(l+1)(2l+3)}{3(2l-1)(2l+1)} \right\} \langle R \rangle^4 (\theta J || W^{(02)2} || \theta J)^2.$$

Here, θ is an abbreviation for the atomic quantum numbers ν (seniority), S and L.

Values of $Q(1)$, $A(1; 1)$, $Q(2)$ and $Q(3)$, in units of $\langle R \rangle^4$, for lanthanide ions are given in table 1. The electronic state of an ion is determined by Hund's rules. For the configurations f^6 and f^7 all of the quantities are zero.

An inspection of the entries in table 1 shows that for the lanthanide ions it is an excellent approximation to neglect $Q(2)$ and $Q(3)$ in the evaluation of ΔZ^2. In this instance, our result for the difference signal defined through (3.2) is

$$\Delta Z^2 = \frac{P_2 \langle L_c \rangle \langle R \rangle^4}{2\{2(2l+1)\}^2} \left\{ -\frac{4}{3} ln_h [3\cos\varphi + \cos(\varphi - 2\theta)] + (2 - g)[\cos\varphi - \cos(\varphi - 2\theta)] \right\}.$$

(4.2)

Here $\langle L_c \rangle = (2 - g)\langle J_c \rangle$ is the orbital part of the magnetic moment of the absorbing atom. Also, θ is the angle between the directions of the primary and secondary beams, and the primary beam lies at an angle φ to the axis of quantization of the atomic states, which is the c-axis. If the difference signal ΔZ^2 is averaged with respect to the direction of the secondary beam it is proportional to $\cos\varphi$, and thus this signal vanishes if the primary beam is directed at right angles to the axis of quantization.

We are obliged to turn to our most general result for the difference signal to complete a discussion of two lanthanides, namely, $Eu^{3+}(f^6)$ and $Gd^{3+}(f^7)$. First, the ground state of f^6 has $J = 0$. For this case our general result (A.4) is zero, because $M = 0$, and thus the difference signal for f^6 is predicted to be zero.

According to the estimate (4.2) one gets for f^7 the same, null, result. However, this result is an aberration caused by the approximation that takes us from (A.4) to (4.2), and the correct value of the difference signal for f^7 is possibly non-zero.

In order to derive the signal for f^7 one must use (A.4), because for f^7 all of the relevant reduced matrix elements of the Racah unit tensor with $K > 0$ apart from one are zero; the one non-zero reduced matrix element is $(\theta J||W^{(10)1}||\theta J) = 2\sqrt{3}$. This finding tells us that there is no meaning attached to working with

$$(\theta J||T(K)||\theta J) = \sum_{\bar{J}} (\theta J||T(K:\bar{J})||\theta J)$$

because it is zero, for f^7 and $K > 0$. Turning, then, to (A.5) one finds that $Q_0(2) = Q_0(3) = 0$, and therefore the signal (A.4) is solely due to $Q_0(1)$ and $A_0(1;1)$, which are evaluated from (A.6). For f^7 we find a difference signal

$$\langle|f|^2\rangle_{P_2} - \langle|f|^2\rangle_{-P_2} = \frac{1}{2}P_2\langle S_c\rangle\left\{\frac{4}{35}\left(\frac{2\pi e}{\lambda}\right)^2\right\}^2 \langle R\rangle^4\left(\frac{1}{\Gamma_-} - \frac{1}{\Gamma_+}\right)$$
$$\times \left\{7[3\cos\varphi + \cos(\varphi - 2\theta)]\left(\frac{2}{\Gamma_-} + \frac{3}{\Gamma_+}\right)\right.$$
$$\left. + [\cos\varphi - \cos(\varphi - 2\theta)]\left(\frac{1}{\Gamma_-} - \frac{1}{\Gamma_+}\right)\right\} \tag{4.3}$$

where Γ_+ and Γ_- are, respectively, the widths of the $\bar{J} = \frac{5}{2}$ (M_5) and $\bar{J} = \frac{3}{2}$ (M_4) absorption lines. Hence, it is now perfectly clear that, applied to f^7, the approximation which assumes that the two widths are equal predicts that the difference signal is zero. Lifting this approximation leads to the possibility of a non-zero value for the signal, and the prediction for f^7 is the result (4.3). For lanthanides other than $Gd^{3+}(f^7)$ it is meaningful to use (4.2) to estimate the difference signal, of course.

5. Discussion

Let us begin the section by briefly reviewing the circular dichroic signal in the attenuation coefficient. The signal is found to be proportional to the projection of the mean value of the orbital magnetic moment on the direction of propagation of the beam of x-rays. Let φ be the angle between the c-axis, chosen for the quantization of the atomic states of the absorbing ion, and the direction of propagation of the beam. Using exactly the same theoretical framework as we have used in the body of this paper, the circular dichroic signal in the attenuation coefficient (2.3) is found to be

$$\Delta Z = -\langle R\rangle^2 P_2\langle L_c\rangle \cos\varphi/(2l + 1) \tag{5.1}$$

where P_2 is the mean helicity in the primary beam, $\langle L_c\rangle = (2-g)\langle J_c\rangle$ is the orbital moment, and l is the angular momentum of the valence shell.

The quantity calculated here is the difference, or dichroic, signal in the total cross-section for resonance-enhanced electric dipole scattering. *Averaged over the direction of propagation of the secondary beam*, in the plane defined by the primary and secondary beams, the difference signal for lanthanide ions, to a very good approximation, is

$$\Delta Z^2 = \frac{1}{8}\langle R\rangle^4 \frac{P_2\langle L_c\rangle \cos\varphi}{(2l + 1)^2}\{-4ln_h + 2 - g\}. \tag{5.2}$$

In this expression, n_h is the number of holes in the valence shell. The conditions under which (5.2) is valid are violated by an ion with a valence shell that is half full of electrons.

The appropriate expression for f^7 (Gd^{3+}) is found to be

$$\Delta Z^2 = 2\langle R\rangle^4 P_2\langle S_c\rangle \cos\varphi \left(\frac{\Gamma}{35}\right)^2 \left(\frac{1}{\Gamma_-} - \frac{1}{\Gamma_+}\right)\left(\frac{43}{\Gamma_-} + \frac{62}{\Gamma_+}\right) \tag{5.3}$$

in which Γ_+ and Γ_- are the total decay widths for the M_5 and M_4 absorption lines, and $\langle S_c\rangle$ is the spin moment. Like (5.1), these expressions refer to the combined information from the two absorption lines. It is noted that (5.2) and (5.3) are not inconsistent with the simulation data for the model that we have studied (van Veenendaal *et al* 1996).

The similarity between the dichroic signal in the attenuation coefficient (5.1) and the dichroic signal in the directionally averaged total cross-section (5.2) supports the view that a measurement of the total fluorescence yield is a reliable method by which to obtain the mean value of the orbital magnetic moment of the absorbing ion. For a half-filled shell, with $\langle L_c\rangle = 0$, the dichroic signal in the total cross-section is not necessarily zero, and it is proportional to the mean value of the magnetic moment.

As we have mentioned, the results (5.2) and (5.3) apply to the case in which the signal is averaged over all directions of the secondary beam of x-rays. The directional information in the more general expressions, found in section 4, could usefully be tested with the appropriate experiments.

In the event that (5.2) is found wanting, a better estimate of the dichroic signal can be found with the expression (A.4) taken in conjunction with (A.6). To evaluate the latter expression one needs values for the total decay widths. Use of the better estimate is essential for an absorbing atom with a valence shell that is half full, and its application to such a case is illustrated for f^7 in the results (4.3) and (5.3).

Acknowledgments

Appendix

Referring to paper III, a matrix element of the resonant contribution to the scattering length is

$$f(\mu;\mu') = \sum_{Km_0}(-1)^{J-M+m_0}\begin{pmatrix} J & K & J' \\ -M & -m_0 & M' \end{pmatrix}X_{m_0}^{(K)}\sum_{\bar{J}}F(K;\bar{J}). \tag{A.1}$$

Here, μ is an abbreviation for the atomic quantum numbers ν, S, L, J and M, and $\bar{J}$ is the total angular momentum of the core state involved in the E1 absorption event. The quantity $F(K;\bar{J})$ is complex, on account of the non-zero decay width in the energy denominator, and so is $X_{m_0}^{(K)}$, which carries all the information on the states of polarization of the primary and secondary beams of x-rays.

The cross-section for one atom is proportional to

$$|f(\mu;\mu')|^2 = \sum_{K,K'}\sum_{m_0}\{X_{m_0}^{(K)}\}^*X_{m_0}^{(K')}\begin{pmatrix} J & K & J' \\ -M & -m_0 & M' \end{pmatrix}\begin{pmatrix} J & K' & J' \\ -M & -m_0 & M' \end{pmatrix}$$
$$\times \{A_0(K;K') + iB_0(K;K')\} \tag{A.2}$$

where

$$A_0(K; K') + iB_0(K; K') = \sum_{\bar{J}, \bar{J}'} F^*(K; \bar{J})F(K'; \bar{J}'). \tag{A.3}$$

In the calculation of the average of $|f|^2$ over the states of polarization in the primary beam one uses the properties $A_0(K; K') = A_0(K'; K)$ and $B_0(K; K') = -B_0(K'; K)$, which are directly proved from (A.3).

The part of the averaged value of $|f|^2$ which is of interest is the part that changes sign when the mean helicity in the primary beam is reversed. Following Lovesey and Collins (1996), this entails finding the part of the average value of $|f|^2$ that depends on the component of P_2 of the Stokes vector which is used to describe the polarization of the primary beam. It can be shown that in the average value of $|f|^2$ the coefficient of $P_2 B_0(K; K')$ is zero. This result hinges on two facts, namely, that $B_0(K; K')$ is odd with respect to an interchange of K and K', and that $|f|^2$ is diagonal with respect to $m_0 = M' - M$.

In order to give an explicit expression for the average value of $|f|^2$ it is necessary to define the geometry of the scattering experiment. The x-rays are deflected through an angle θ. The axis of magnetic quantization, which is taken to be the c-axis in the Cartesian components (a, b, c), lies in the plane defined by the primary and secondary beams, the a-axis is perpendicular to the plane, and the primary beam is at an angle φ to the c-axis.

If μ is the density matrix for the states of partial polarization in the primary beam, the average value of $|f|^2$ is

$$\text{Tr}(\mu|f|^2)$$

where the trace operation is carried out with respect to the polarization vectors in $\{X_{m_0}^{(K)}\}^* X_{m_0}^{(K')}$. The difference signal is derived from

$$\text{Tr}(\mu|f|^2)_{P_2} - \text{Tr}(\mu|f|^2)_{-P_2}$$

and we obtain for this quantity the following result, which is correct for one J-manifold:

$$\begin{aligned}
\frac{1}{2} P_2 \frac{M}{(J||J||J)^2} \Big\{ & Q_0(1)[\cos\varphi + \cos\psi \cos\theta] + A_0(1; 1)\sin\psi \sin\theta \\
& + 6M^2(Q_0(2) - Q_0(3))[\sin\varphi \sin 2\psi + \cos\varphi(3\cos^2\psi - 1)] \\
& - 2Q_0(2)[J(J+1)\{\sin\varphi \sin 2\psi + \cos\varphi(7\cos^2\psi - 5)\} + 3\cos\varphi \sin^2\psi] \\
& + \frac{3}{2}Q_0(3)\Big[2J(J+1)\{\sin\varphi \sin 2\psi + 4\cos\varphi \cos^2\psi\} \\
& - \frac{1}{2}\sin\varphi \sin 2\psi - \cos\varphi(3\cos^2\psi + 1)\Big] \Big\}. \tag{A.4}
\end{aligned}$$

In this result, $\psi = (\theta - \varphi)$ and

$$Q_0(1) = 2\left\{\frac{2}{3}J(J+1)\right\}^{1/2} A_0(0; 1) \tag{A.5a}$$

$$Q_0(2) = A_0(1; 2)/\{3(2J-1)(2J+3)\}^{1/2} \tag{A.5b}$$

and

$$Q_0(3) = 2A_0(2; 2)/\{(2J-1)(2J+3)\}. \tag{A.5c}$$

The factors of M and J in these expressions arise from use of algebraic formulae for the $3j$-symbols in (A.2), evaluated with $J = J'$.

Concerning (A.4), it is interesting to note that when an average is taken with respect to the direction of the secondary beam the coefficient of M^3 vanishes, since the averages of $\sin 2\psi$ and $\cos^2 \psi$ are 0 and 1/3, respectively. Also after directional averaging,

$$\{\cos \varphi + \cos \psi \cos \theta\} \to \frac{4}{3} \cos \varphi \qquad \sin \psi \sin \theta \to \frac{2}{3} \cos \varphi$$

and one finds that (A.4) is proportional to $\cos \varphi$.

It remains for us to give the expression for $A_0(K; K')$. The following result, (A.6), is derived from work reported in paper III and the definitions (A.1) and (A.3).

First, some necessary definitions. The primary radiation has an energy $E = 2\pi\hbar c/\lambda$, and the E1 radial integral is $\langle R \rangle$. The angular momentum of the valence shell is l, and for the core state $\bar{l} = l - 1$, and $\bar{J} = \bar{l} \pm \frac{1}{2}$.

It is assumed that the spectrum of intermediate states contain two quite distinct clusters that can be labelled by the two values of $\bar{J}$. The total decay width of a cluster of states is $\Gamma_{\bar{J}}$. We find

$$A_0(K; K') = \left\{ 2\left(\frac{2\pi e}{\lambda}\right)^2 l\langle R\rangle^2 \right\}^2 \{(2K + 1)(2K' + 1)\}^{1/2} \begin{Bmatrix} 1 & K & 1 \\ l & \bar{l} & l \end{Bmatrix}$$

$$\times \begin{Bmatrix} 1 & K' & 1 \\ l & \bar{l} & l \end{Bmatrix} \sum_{\bar{J},\bar{J}'} (\theta J \| T(K : \bar{J}) \| \theta' J')(\theta J \| T(K' : \bar{J}') \| \theta' J')/(\Gamma_{\bar{J}} \Gamma_{\bar{J}'}).$$

(A.6)

The reduced matrix element of the spherical tensor operator $T(K : \bar{J})$ is defined in paper III. It can be expressed in terms of various nj-symbols and the reduced matrix elements of Racah unit spherical tensors. In (A.6), the integer K takes the values $K = 0, 1$ and 2 by virtue of a triangle condition in the $6j$-symbol.

The expressions (A.4) and (A.6) together form our result for the difference signal in the total cross-section for the resonance-enhanced scattering of x-rays. In the main body of the text we consider a simplification to $A_0(K; K')$ that occurs when the dependence on $\bar{J}$ of Δ, Δ' and Γ is set aside. For this case one finds, for E close to Δ,

$$A_0(K; K') = \left(\left(\frac{2\pi e}{\lambda}\right)^2 \left(\frac{\Delta'}{\Delta}\right)\right)^2 \frac{A(K; K')}{|E - \Delta + (i/2)\Gamma|^2}$$

where $A(K; K')$ is

$$(l\langle R\rangle^2)^2 \{(2K + 1)(2K' + 1)\}^{1/2} \begin{Bmatrix} 1 & K & 1 \\ l & \bar{l} & l \end{Bmatrix} \begin{Bmatrix} 1 & K' & 1 \\ l & \bar{l} & l \end{Bmatrix} (\theta J \| T(K) \| \theta' J')(\theta J \| T(K') \| \theta' J').$$

(A.7)

In this last expression, the reduced matrix element $(\theta J \| T(K) \| \theta' J')$ is defined and discussed in paper I. Lastly, we give the corresponding expression for a matrix element of the scattering length, which in paper I is referred to as the idealized scattering length:

$$f_0(\mu; \mu') = -\left(\frac{2\pi e}{\lambda}\right)^2 \left(\frac{\Delta'}{\Delta}\right) \frac{Z(\mu; \mu')}{(E - \Delta + (i/2)\Gamma)}$$

$$= \left(\frac{2\pi e}{\lambda}\right)^2 \left(\frac{\Delta'}{\Delta}\right) \frac{l\langle R\rangle^2 (-1)^{J-M}}{(E - \Delta + (i/2)\Gamma)} \sum_K (2K + 1)^{1/2}$$

$$\times \begin{Bmatrix} 1 & K & 1 \\ l & \bar{l} & l \end{Bmatrix} \sum_{m_0} (-1)^{m_0} X_{m_0}^{(K)} \begin{pmatrix} J & K & J' \\ -M & -m_0 & M' \end{pmatrix} (\theta J \| T(K) \| \theta' J'). \qquad \text{(A.8)}$$

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