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Electric-dipole absorption and the scattering of x-rays: analytic results for a $3d^9$ ion in an octahedral crystal field

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Abstract. A formulation describing electric-dipole absorption and resonance-enhanced diffraction of x-rays is applied to a $3d^9$ ion in an octahedral crystal field and subject to a magnetic field. Analytical results are given for both the idealized and the complete forms of the scattering length. The contributing atomic quantities are discussed in detail, e.g. the spin–orbit interaction and the quadrupole moment of the valence holes.

The model calculation was chosen to illustrate the use of a completely general formulation of the scattering length, from which one obtains the attenuation coefficient and cross-sections for elastic and inelastic scattering. Relevant tensor operators are referred both to unit tensors, and to appropriately coupled operators of spin and orbital angular momentum. The quantities that appear in the linear dichroic signal differ from corresponding results in the literature, and reasons for this finding are discussed.

1. Introduction

While steady progress has been made in the development of a theoretical framework for the interpretation of absorption and the resonance-enhanced scattering of x-rays by magnetic materials, there are relatively few worked examples in the published literature. One of the first illustrative examples is due to van der Laan and Thole (1990). A major value of worked examples in this emerging field of research is that they provide some insight into the atomic quantities that naturally enter the interpretation of experimental data. Furthermore, they make concrete the theoretical developments in atomic physics that might, at first sight, be inscrutable.

In this spirit, Sainctavit *et al* (1995) examined the x-ray absorption spectra of a $3d^9$ ion in an octahedral environment. They calculated the matrix elements of the dipole operator for the transition of the hole in the 3d shell to a 2p core state, and from these matrix elements constructed the absorption spectra. The spin–orbit interaction on the 2p state splits the six levels into two groups, with total angular momenta $\bar{J} = \frac{1}{2}$ and $\bar{J} = \frac{3}{2}$. The levels in each group are degenerate in energy, and they make up the L_2 and L_3 absorption edges. It was shown that sum rules on the circular dichroic spectra at the two absorption edges agree with the results predicted by Carra *et al* (1993b) on the basis of a more general approach. In addition, Sainctavit *et al* (1995) carefully explored the properties of the mean value of the magnetic-dipole operator, which arises in one of the sum rules.

Here, we present the diagonal matrix element, or mean value, of the *idealized* scattering length (Lovesey and Balcar 1997) for the same model $3d^9$ ion. It is used among other things to demonstrate that the circular dichroic signal derived from the idealized scattering length

8679

is exactly the same as the one directly calculated by Sainctavit *et al* (1995). Moreover, all of the atomic quantities in the isotropic signal and the linear dichroic signal are given here, and their properties explored, e.g. the spin–orbit interaction and the quadrupole operator for the orbit. In addition, we explore for the model ion a *complete* scattering length that carries all quantum numbers of the core state. For a $3d^9$ ion the spectrum contains six components, as already mentioned, and we explore how these depend on the parameters that define the ground-state wave function. Another topic taken up is the cross-section for Bragg diffraction.

An appendix to the paper contains general expressions for the matrix elements in the idealized scattering length written in terms of atomic quantities. For the linear dichroic signal our results are not the same as those reported by Carra *et al* (1993a).

The configuration $3d^9$ is appropriate to the ions Ni^+ and Cu^{2+}. In an octahedral crystal environment the orbital for the ground state has the symmetry Γ_3. (NB van der Laan and Thole (1990) consider a $3d^9$ ion in a tetragonal crystal environment.) This state is non-magnetic, and a magnetic field has no matrix elements connecting the two orbital states of Γ_3; see, for example, page 459 of Abragam and Bleaney (1970). In addition, the spin–orbit interaction has no matrix elements within the Γ_3 doublet. The ground-state wave function for $3d^9$ obtained with the crystal-field, spin–orbit and Zeeman energies is given in section 2. In this case, the wave function explicitly depends on the ordering of the spin and orbital angular momenta chosen in the coupling scheme.

The idealized scattering length for an E1 event is briefly reviewed in section 3, together with the seven atomic quantities that enter it. The idealized scattering length is constructed on the assumption that the states for an absorption edge are degenerate with respect to their energy. This assumption is satisfied in the model used by Sainctavit *et al* (1995). Thereafter, in the idealized scattering length the algebra for coupling angular momenta is used to reformulate the product of matrix elements, of the dipole operator, in terms of a linear combination of standard atomic quantities.

The results in section 3 are used in sections 4 and 5, respectively, to calculate the dichroic signals in the attenuation coefficient and the unit-cell structure factor for Bragg diffraction. Section 6 contains the details of the complete spectrum that contributes to the scattering length for the wave function specified in section 2. A brief summary is found in section 7. An appendix is given over to a précis of the idealized scattering length in terms of the atomic quantities discussed in section 3. Of course, a $3d^9$ ion is an example of the simplest type, since it contains one hole in the valence shell. The results in the appendix, and Lovesey and Balcar (1997), apply to any configuration of the valence electrons.

2. The wave function of $3d^9$

The ground-state wave function of Cu^{2+} ($3d^9$) is a linear combination of states with total spin $S = \frac{1}{2}$ and orbital angular momentum $L = 2$, and it contains wave functions with total angular momenta $J = \frac{3}{2}$ and $\frac{5}{2}$. It is derived by diagonalizing a Hamiltonian that contains the spin–orbit interaction, a crystal-field interaction of O_h symmetry and a Zeeman energy created by a magnetic field applied along the (001) axis of the crystal field. In terms of the states $|J, M\rangle$ the wave function for the ground state of the ion is

$$|\psi\rangle = \sin\theta \left|\frac{3}{2}, \frac{3}{2}\right\rangle + \frac{1}{\sqrt{6}} \cos\theta \left\{ \left|\frac{5}{2}, \frac{3}{2}\right\rangle + \sqrt{5} \left|\frac{5}{2}, -\frac{5}{2}\right\rangle \right\}. \tag{2.1}$$

The sign of $\cos\theta$ in (2.1) is different from the sign in the wave function derived by Sainctavit, Arrio and Brouder (1995), hereafter referred to as SAB. The sign difference arises because

we use a widespread convention in which spin and orbital angular momenta are coupled in the order S and L, whereas SAB use the less-favoured reverse ordering of the angular momenta.

Two other features of (2.1) merit comment. First, the photon is absorbed into a 2p state, with total angular momentum $\bar{J} = \frac{1}{2}(L_2)$ or $\bar{J} = \frac{3}{2}(L_3)$. In an E1 absorption event the total angular momentum changes by at most ± 1. Hence, an E1 event at the L_2 edge engages in $|\psi\rangle$ the state with $J = \frac{3}{2}$, and not the state $J = \frac{5}{2}$. So, we anticipate that the matrix element of the dipole operator for an L_2 edge is proportional to $\sin\theta$. The second feature relates to the values of the magnetic quantum number in $|\psi\rangle$. A matrix element created with $|\psi\rangle$ contains contributions in which $\Delta M = 0$ and ± 4. However, the product of dipole matrix elements, which is here denoted by Z, is a sum of tensors of rank $K = 0$, 1 and 2. Thus, the contributions with $\Delta M = \pm 4$ do not appear in Z, and, for the wave function $|\psi\rangle$ studied here, Z is diagonal with respect to M. The latter feature is responsible for the relative simplicity of the expression for the scattering length which is given in the next section.

3. Scattering length

The Cu^{2+} ions are located at positions $\{R_0\}$ on a lattice. In the resonant scattering process the x-rays change their wave vector by k. If the primary x-ray has an energy, $E = (2\pi\hbar c/\lambda)$, that almost matches the energy of the absorption edge labelled by the total angular momentum of the core state $\bar{J}$, the mean value of the resonant scattering length is

$$\langle f \rangle = -\left(\frac{2\pi e}{\lambda}\right)^2 \sum_{R_0} \left\{\frac{\langle Z \rangle}{E - \Delta + (i/2)\Gamma}\right\}_{\bar{J}} \exp\{ik \cdot R_0 - W\}. \tag{3.1}$$

In this expression, $\exp(-W)$ is the Debye–Waller factor, and Δ and Γ, respectively, are the position in energy and the width in energy of the absorption line. Our expression for Z is based on the dipole approximation to the absorption mechanism, and it does not include the diamagnetic contribution created by the field applied to the Cu^{2+} ion. The matrix element, or mean value, of Z as denoted by $\langle Z \rangle \equiv \langle \psi | Z | \psi \rangle$ is discussed in an appendix.

In this section we focus on the physical properties of $\langle Z \rangle$ for an ion described by the wave function (2.1). We give the result for $\langle Z \rangle$ in terms of its three contributions that are labelled by the rank, K, of the tensor which is involved. In principle, the contributions can be measured by observing the attenuation coefficient and the Bragg diffraction pattern. In the following expressions, $\langle R \rangle = \langle 2p|R|3d \rangle$ is the radial matrix element and $\bar{J} = 1 \pm \frac{1}{2}$. Writing

$$\langle Z \rangle = \sum_K \langle Z \rangle^{(K)} \tag{3.2}$$

we find the following expressions for the two allowed values of $\bar{J}$:

$$\langle Z \rangle^{(0)} = -\frac{1}{15\sqrt{3}} \langle R \rangle^2 X_0^{(0)} \left\{ (2\bar{J} + 1) \pm 2\langle S \cdot L \rangle \right\} \tag{3.3a}$$

$$\langle Z \rangle^{(1)} = \frac{1}{30\sqrt{2}} \langle R \rangle^2 X_0^{(1)} \left\{ (2\bar{J} + 1)\langle L_0 \rangle \pm \frac{4}{3} [2\langle S_0 \rangle + 7\langle T_0 \rangle] \right\} \tag{3.3b}$$

and

$$\langle Z \rangle^{(2)} = -\frac{1}{45\sqrt{6}} \langle R \rangle^2 X_0^{(2)} \left\{ (2\bar{J} + 1)\langle Q_0 \rangle \pm \frac{12}{5} [\langle P_0 \rangle + \langle R_0 \rangle] \right\}. \tag{3.3c}$$

In these expressions, $X_0^{(K)}$ represents combinations of the polarization vectors of the primary (ε) and secondary (ε') x-rays and

$$X_0^{(0)} = -\frac{1}{\sqrt{3}}(\varepsilon' \cdot \varepsilon) \qquad X_0^{(1)} = \frac{\mathrm{i}}{\sqrt{2}}(\varepsilon' \times \varepsilon)_0 \qquad X_0^{(2)} = \frac{1}{\sqrt{6}}(3\varepsilon_0'\varepsilon_0 - \varepsilon' \cdot \varepsilon). \tag{3.4}$$

We note that only the diagonal elements of the spherical tensor $\boldsymbol{X}^{(K)}$ are required for $\langle Z \rangle^{(K)}$, on account of the fact that for the wave function considered here all of the matrix elements are diagonal with respect to the magnetic quantum numbers, M.

Evidently, the scattering length for Bragg diffraction can contain all three contributions to $\langle Z \rangle$. However, the nature of the magnetic order in the sample can lead to the absence of a contribution to a particular Bragg peak. For this to occur the chemical and magnetic order must be different. The dichroic signal in the attenuation coefficient which is selected by changes in the helicity in the primary beam is proportional to $\langle Z \rangle^{(1)}$, while the signal picked out by changing from σ- to π-polarization is proportional to $\langle Z \rangle^{(2)}$. For unpolarized x-rays the attenuation coefficient is determined by $\langle Z \rangle^{(0)}$.

Let us turn now to the various atomic quantities in (3.3). The mean value of the spin–orbit interaction

$$\langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle = \frac{1}{2}(2 - 5\sin^2\theta). \tag{3.5}$$

Note that the physical range of θ gives $\langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle$ a positive-definite value. The quantity (3.5) vanishes for $\sin\theta = -(2/5)^{1/2}$, which corresponds to a zero value for the spin–orbit interaction, ζ. An equation for θ in terms of the ratio of ζ to the strength of the crystal-field potential, $10Dq$, is given by SAB, namely,

$$\tan(2\theta) = \frac{-4\sqrt{6}}{\{2 + 25(\zeta/10Dq)\}}. \tag{3.6}$$

One sees that $\zeta = 0$ is consistent with $\sin\theta = -(2/5)^{1/2}$. At the other extreme, $\zeta = \infty$ and $\theta = 0$. The corresponding value $\langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle = 1$ is expected for $S = \frac{1}{2}$ and $L = 2$ and an infinite value of the spin–orbit interaction.

The atomic quantities that enter $\langle Z \rangle^{(1)}$ are given by SAB. In our notation, and using $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$,

$$\langle J_0 \rangle = \frac{1}{6}(20\sin^2\theta - 11) \qquad \langle S_0 \rangle = -\frac{1}{30}(9\sin^2\theta - 2\sqrt{6}\sin 2\theta + 11\cos^2\theta) \tag{3.7a}$$

and

$$\langle T_0 \rangle = -\frac{1}{105}\left(63\sin^2\theta + \frac{7}{2}\sqrt{6}\sin 2\theta + 22\cos^2\theta\right). \tag{3.7b}$$

These results are displayed in figure 1 as a function of the spin–orbit interaction. For the special case $\zeta = 0$, one finds $\langle L_0 \rangle = 0$,

$$\langle J_0 \rangle = \langle S_0 \rangle = -\frac{1}{2} \qquad \text{and} \qquad \langle T_0 \rangle = -\frac{2}{7}.$$

Setting $\theta = 0$ in (3.7), which corresponds to $\zeta = \infty$,

$$\langle J_0 \rangle = -\frac{11}{6}$$

and this value is also readily obtained directly from $|\psi\rangle$ evaluated for $\theta = 0$. The corresponding values for $\langle S_0 \rangle$, $\langle L_0 \rangle$ and $\langle T_0 \rangle$ obtained from (3.7) are

$$\langle L_0 \rangle = 4\langle S_0 \rangle = 7\langle T_0 \rangle = -\frac{22}{15}.$$
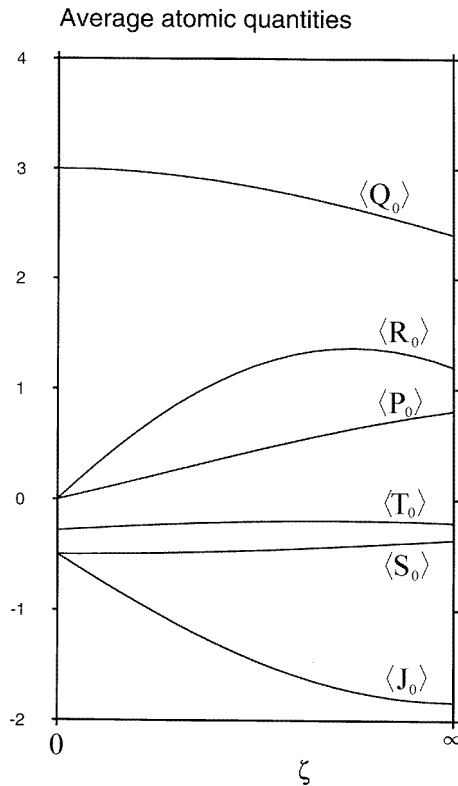
Average atomic quantities

Figure 1. The mean values, or diagonal matrix elements, of the atomic quantities relevant for the idealized scattering length are displayed as functions of the spin–orbit interactions ζ. Due to the simplicity of the wave function for the $3d^9$ ion only the zeroth component of each spherical tensor operator is required in the scattering length. The most general case is covered by the results (A.17)–(A.19).

For these values and $\bar{J} = \frac{1}{2}$ one finds that $\langle Z \rangle^{(1)}$ is zero. This is a consequence of a more general result that $\langle Z \rangle^{(K)}$ at the L_2 edge is proportional to $\sin^2 \theta$. Other studies of $\langle T_0 \rangle$ for different ions have been made by Collins *et al* (1995) and Crocombette *et al* (1996).

The atomic quantities in $\langle Z \rangle^{(2)}$ are

$$\langle P_0 \rangle = \frac{3}{10}\left(-\sin^2 \theta + \frac{1}{2}\sqrt{6}\sin 2\theta + \frac{8}{3}\cos^2 \theta\right) \tag{3.8a}$$

$$\langle Q_0 \rangle = \frac{3}{10}(7\sin^2 \theta - \sqrt{6}\sin 2\theta + 8\cos^2 \theta) \tag{3.8b}$$

and

$$\langle R_0 \rangle = -\frac{3}{5}\left(7\sin^2 \theta + \frac{2}{3}\sqrt{6}\sin 2\theta - 2\cos^2 \theta\right). \tag{3.8c}$$

Expressions for the operators P_0, Q_0 and R_0 are obtainable from (A.12)–(A.14); Q_0 is the quadrupole operator for orbital angular momentum while P_0 and R_0, like T_0, combine spin and orbital angular momenta. The results (3.8) are displayed in figure 1. Considering again the limiting cases, for $\zeta = 0$ one finds

$$\langle P_0 \rangle = \langle R_0 \rangle = 0 \qquad \text{and} \qquad \langle Q_0 \rangle = 3.$$

Hence, when the spin–orbit interaction on the 3d electrons is set to zero, the spin-dependent parts of $\langle Z \rangle^{(0)}$ and $\langle Z \rangle^{(2)}$ are zero. By contrast, for the same value of ζ the spin-dependent parts of $\langle Z \rangle^{(1)}$ are non-zero, and $\langle L_0 \rangle = 0$. The null value of $\langle L_0 \rangle$ for $\zeta = 0$ reflects the fact that the Γ_3 orbital is non-magnetic. When the spin and orbital angular momenta are fully aligned, by an infinite spin–orbit interaction,

$$\langle P_0 \rangle = \frac{1}{3}\langle Q_0 \rangle = \frac{2}{3}\langle R_0 \rangle = \frac{4}{5}.$$

As we have mentioned, the expressions for $\langle Z \rangle^{(K)}$ simplify at the L_2 edge. Setting $\bar{J} = \frac{1}{2}$ in (3.3) and using (3.5), (3.7) and (3.8) one finds

$$\langle Z \rangle^{(0)} = -\frac{1}{3\sqrt{3}}\langle R \rangle^2 X_0^{(0)} \sin^2 \theta \tag{3.9a}$$

$$\langle Z \rangle^{(1)} = \frac{1}{3\sqrt{2}}\langle R \rangle^2 X_0^{(1)} \sin^2 \theta \tag{3.9b}$$

and

$$\langle Z \rangle^{(2)} = -\frac{1}{3\sqrt{6}}\langle R \rangle^2 X_0^{(2)} \sin^2 \theta. \tag{3.9c}$$

The collapse of the expressions evaluated for $\bar{J} = \frac{1}{2}$ to these anticipated simple results gives us confidence that we have correctly calculated the contributions to $\langle Z \rangle$.

It is often the case that it is very convenient to calculate the wave function of the valence shell of the absorbing ion in a set of local, Cartesian axes that do no coincide with the axes used to define the geometry of the experiment. In such a case one needs to obtain the atomic matrix elements in $Z(\mu; \mu')$ for the axes in which $X^{(K)}$ is calculated from the atomic matrix elements calculated in the local axes. The mathematical structure of the relationship between the two sets of matrix elements is quite simple if in the local axes the atomic matrix elements are diagonal with respect to the magnetic quantum numbers. In fact, one usually selects the local axes such that the dominant matrix elements are diagonal, to a good approximation. For the model 3d ion all of the atomic matrix elements in $\langle Z \rangle$ are diagonal, as we have seen.

The local axes are obtained by rotating the axes in which $X^{(K)}$ is calculated by a transformation defined by three Euler angles; cf. (4.3). For the simple case at hand only two angles, α and β, are required. Using, by way of an example, the rank-two operator $\boldsymbol{R}$, the atomic matrix element $\langle \mu | R_{m_0} | \mu' \rangle$ in the set of axes, (x, y, z), in which $X^{(2)}$ is calculated is

$$\langle \mu | R_{m_0} | \mu' \rangle_{(xyz)} = C_{m_0}^{(2)}(\beta, \alpha)\langle \mu | R_0 | \mu' \rangle. \tag{3.10}$$

Here, $C_{m_0}^{(K)}(\beta, \alpha)$ is a spherical harmonic normalized such that $C_0^{(0)}(\beta, \alpha) = 1$. The same expression is used for $\boldsymbol{P}$ and $\boldsymbol{Q}$, while for $\boldsymbol{L}$, $\boldsymbol{S}$ and $\boldsymbol{T}$ the spherical harmonic is of rank one.

4. Dichroic signals in the attenuation coefficient

The attenuation coefficient is obtained from the imaginary part of mean value of the scattering length, evaluated for a geometry of forward scattering and averaged with respect to states of partial polarization in the primary beam. The polarization of the primary beam is defined by a Stokes vector $\boldsymbol{P} = (0, P_2, P_3)$ in which P_2 is the mean helicity, and $P_3 > 0$ is σ linear polarization and $P_3 < 0$ is π linear polarization. The dichroic signals are defined

as the changes in the attenuation coefficient on changing P_2 to $-P_2$, or P_3 to $-P_3$. The corresponding changes in the amplitudes of the signals are, respectively, the changes in $\langle Z \rangle^{(1)}$ or $\langle Z \rangle^{(2)}$, and the changes in the amplitudes are here denoted by $\Delta Z(C)$ and $\Delta Z(L)$.

From the results in (3.3) we find,

$$\Delta Z(C) = -\frac{1}{30}\langle R \rangle^2 P_2 \hat{q}_0 \left\{ (2\bar{J}+1)\langle L_0 \rangle \pm \frac{4}{5}[2\langle S_0 \rangle + 7\langle T_0 \rangle] \right\} \tag{4.1}$$

where $\hat{q}_0$ is the projection of primary beam on the axis of magnetic quantization. The linear dichroic signal is proportional to

$$\Delta Z(L) = \frac{1}{90}\langle R \rangle^2 P_3 (\cos^2 \alpha \sin^2 \beta - \cos^2 \beta) \left\{ (2\bar{J}+1)\langle Q_0 \rangle \pm \frac{12}{5}[\langle P_0 \rangle + \langle R_0 \rangle] \right\}. \tag{4.2}$$

Here, α and β are two of the three Euler angles required to define the axes of quantization relative to the geometry of the experiment. Following the discussion given by Lovesey and Collins (1996), the latter is specified by Cartesian coordinates (x, y, z) with the primary beam along the y-axis. The magnetic axis of quantization is

$$m = \hat{x} \cos \alpha \sin \beta + \hat{y} \sin \alpha \sin \beta + \hat{z} \cos \beta. \tag{4.3}$$

From the last expression we find $\hat{q}_0 = \sin \alpha \sin \beta$. The values of (4.1) and (4.2) averaged with respect to the direction of m are zero, of course.

The results (4.1) and (4.2) embody the sum rules for the dichroic signals for the Cu^{2+} ion. The sum rules are applied to empirical data for the attenuation coefficient to extract values for the various atomic quantities that are involved. The differences between (4.2) and the corresponding result given by Carra *et al* (1993a) are discussed in the appendix to this paper.

5. Bragg diffraction

The cross-section for Bragg diffraction is derived from $|\langle f \rangle|^2$. To obtain the observed quantity, $|\langle f \rangle|^2$ must be averaged with respect to states of partial polarization in the primary beam, and this problem has been addressed by Lovesey and Balcar (1996). In keeping with their work, we examine a case for which $\langle Z \rangle$ is diagonal with respect to the magnetic quantum numbers. As we have shown, this is realized for the Cu^{2+} ion.

For one ion per unit cell, $\langle Z \rangle$ is in fact the unit-cell structure factor introduced by Lovesey and Balcar, and this is expressed in the form

$$F = \langle Z \rangle = A_1(\varepsilon' \cdot \varepsilon) + iA_2 m \cdot (\varepsilon' \times \varepsilon) + A_3(\varepsilon' \cdot m)(\varepsilon \cdot m). \tag{5.1}$$

In this expression, m is a unit vector that defines the axis of magnetic quantization. From the results (3.4) and (A.17)–(A.19) one finds

$$A_1 + \frac{1}{3}A_3 = \frac{l\langle R \rangle^2}{6(4l^2-1)} \left\{ (2\bar{J}+1)n_h \pm 4\left(\frac{l-1}{l}\right)\left\langle \sum s \cdot l \right\rangle \right\} \tag{5.2a}$$

$$A_2 = \frac{\langle R \rangle^2}{4(4l^2-1)} \left\{ (2\bar{J}+1)\langle L_0 \rangle \pm \frac{4}{3}(l-1)[l\langle S_0 \rangle + (2l+3)\langle T_0 \rangle] \right\} \tag{5.2b}$$

and

$$A_3 = \frac{-\langle R \rangle^2}{2(4l^2-1)(2l-1)} \left\{ (2\bar{J}+1)\langle Q_0 \rangle \pm \frac{4}{5}[(l-1)(2l-1)\langle P_0 \rangle + 3\langle R_0 \rangle] \right\}. \tag{5.2c}$$

In these expressions $\langle R \rangle$ is the radial integral connecting the core state, with $\bar{l} = l-1$, and the valence state. Note that the thermodynamic properties of A_2 and A_3 can be expected to

be quite different. For example, A_2 will vanish in the paramagnetic phase in the absence of a magnetic field, whereas for the same conditions A_3 can be different from zero.

A general expression for the average value of $|F|^2$ is known. Here, we will consider two cases of the expression that are of particular interest for experiments. First, let m be directed perpendicularly to the plane defined by the primary and secondary beams of x-rays. In this case $|F|^2$ is independent of the helicity in the primary beam. If the x-rays are deflected through an angle φ (=twice the Bragg angle),

$$|F|^2 = \frac{1}{2}(1 + P_3)(A_1 + A_3)^2 + \frac{1}{2}(1 - P_3)\left\{(A_1 \cos \varphi)^2 + (A_2 \sin \varphi)^2\right\} \qquad m \perp \text{plane.}$$
(5.3)

In the standard setting at a synchrotron source of x-rays the primary radiation is almost pure σ-polarization, described by $P_3 = 1$, in which case the unit-cell structure factor is independent of the magnetization.

Secondly, let m lie in the plane of scattering and be parallel to the scattering vector, k. In this case $|F|^2$ contains an overlap between A_2, and A_1 and A_3 that is induced by the helicity in the primary beam. One finds

$$|F|^2 = \frac{1}{2}(1 + P_3)A_1^2 + \frac{1}{2}(1 - P_3)\left\{\left(A_1 + \frac{1}{3}A_3\right)\cos \varphi + \frac{1}{6}A_3(3 + \cos \varphi)\right\}^2$$
$$+ \left(A_2 \sin \frac{1}{2}\varphi\right)^2 + P_2 A_2 \sin \frac{1}{2}\varphi\left\{\left(A_1 + \frac{1}{3}A_3\right)(\cos \varphi - 1)\right.$$
$$+ \left.\frac{1}{6}A_3(5 + \cos \varphi)\right\} \qquad m \parallel k.$$
(5.4)

The quantity $A_1 + A_3/3$ is not likely to depend strongly on the temperature. As in (5.3), the contribution to $|F|^2$ in (5.4) from A_2 is multiplied by a factor that includes $\sin(\varphi/2)$, so the magnetization does not contribute strongly to low-order diffraction peaks. The overlap induced by P_2 is allowed by a ferromagnetic order, created by a spontaneous ordering or an external magnetic field. The overlap is forbidden at a purely magnetic reflection in a material for which the chemical and magnetic ordering is different, e.g. a collinear antiferromagnet.

Let us consider the L_2 edge of the Cu^{2+} ion, for which the scattering length is very simple. For a ferromagnetic configuration of the moments and (3.9) one finds $A_1 = A_2 = -A_3$, and

$$A_1 = \frac{1}{6}\langle R \rangle^2 \sin^2 \theta.$$

Thus, for m perpendicular to the plane of scattering,

$$|F|^2 = \frac{1}{2}A_1^2(1 - P_3)$$

and, writing $s = \sin(\varphi/2)$, for m parallel to k,

$$|F|^2 = \frac{1}{2}A_1^2\left\{(1 + P_3) + (1 - P_3)s^4 + 2s^2 - 2P_2 s(1 + s^2)\right\}.$$

It is interesting to note that for pure σ-polarization ($P_3 = 1$), in the first case the diffraction cross-section is zero, and in the second case it is simply

$$|F|^2 = A_1^2(1 + s^2).$$

6. The complete scattering length

The idealized scattering length that we have used in previous sections is created from the complete scattering length by summing it over quantum numbers for the hole in the core state. These are collectively denoted by η, and the magnetic quantum number for the core state is $\bar{M}$. With this notation, the matrix elements of Z used in the preceding sections and the matrix elements used here for the complete scattering length, $\langle Z \rangle^{(K)}$ and $\langle Z_\eta \rangle^{(K)}$, respectively, are related by

$$\langle Z \rangle^{(K)} = \sum_{\bar{M}} \langle Z_\eta \rangle^{(K)}.$$

The degeneracy with respect to $\bar{M}$ will be lifted by the exchange field at the core electron created by the unpaired valence electrons.

It has been shown that the complete scattering length can be expressed as a nested sum of the Racah unit tensors used for the idealized scattering length (Lovesey 1997). To round out our discussion of the $3d^9$ ion described by the wave function (2.1) we give the components of the complete scattering length. This demands a knowledge of more unit tensors than those in the idealized scattering length, i.e. the complete scattering length contains more information on the atomic properties of the valence electrons than is to be found in the idealized variant. In the case of one hole in the valence shell the unit tensors are relatively easy to calculate because no coefficients of fractional parentage are used. All of the relevant details for the $3d^9$ ion are contained in the paper by Lovesey and Balcar (1997).

We consider separately the two values of $\bar{J}$. For $\bar{J} = \frac{1}{2}$ we find

$$\langle Z_\eta \rangle^{(0)} = -\frac{1}{6} \left(\frac{1}{3} \right)^{1/2} \langle R \rangle^2 X_0^{(0)} \sin^2 \theta (1 + 2\bar{M}) \tag{6.1a}$$

$$\langle Z_\eta \rangle^{(1)} = \frac{1}{6} \left(\frac{1}{2} \right)^{1/2} \langle R \rangle^2 X_0^{(1)} \sin^2 \theta (1 + 2\bar{M}) \tag{6.1b}$$

and

$$\langle Z_\eta \rangle^{(2)} = -\frac{1}{6} \left(\frac{1}{6} \right)^{1/2} \langle R \rangle^2 X_0^{(2)} \sin^2 \theta (1 + 2\bar{M}). \tag{6.1c}$$

On summing on $\bar{M}$ these results reduce to (3.9), as expected. The results in (6.1) are zero for $\bar{M} = -\frac{1}{2}$, and this condition stems from the values of the magnetic quantum numbers in the wave function (2.1) and the selection inherent in an E1 adsorption event. The results (6.1) also vanish for an infinite value of the spin–orbit interaction in the 3d valence state, which is described by $\theta = 0$.

For $\bar{J} = \frac{3}{2}$, of course, the scattering length also is zero for $\bar{M} = -\frac{1}{2}$. We find that $\langle Z_\eta \rangle^{(1)}$ is zero for $\bar{M} = \frac{3}{2}$. The non-zero values are as follows.

(i) $\bar{M} = \frac{1}{2}$:

$$\langle Z_\eta \rangle^{(0)} = -\frac{1}{75} \left(\frac{1}{3} \right)^{1/2} \langle R \rangle^2 X_0^{(0)} (2 \sin^2 \theta - \sqrt{6} \sin 2\theta + 3 \cos^2 \theta) = \langle R \rangle^2 X_0^{(0)} \Sigma \left(\frac{1}{2} \right)$$

$$\langle Z_\eta \rangle^{(1)} = -\left(\frac{3}{2} \right)^{1/2} \langle R \rangle^2 X_0^{(1)} \Sigma \left(\frac{1}{2} \right) \tag{6.2a}$$

$$\langle Z_\eta \rangle^{(2)} = \left(\frac{1}{2} \right)^{1/2} \langle R \rangle^2 X_0^{(2)} \Sigma \left(\frac{1}{2} \right).$$

(ii) $\bar{M} = \frac{3}{2}$:

$$\langle Z_\eta \rangle^{(0)} = -\frac{1}{75}\left(\frac{1}{3}\right)^{1/2} \langle R \rangle^2 X_0^{(0)} (3\sin^2\theta + \sqrt{6}\sin 2\theta + 2\cos^2\theta) = \langle R \rangle^2 X_0^{(0)} \Sigma\left(\frac{3}{2}\right)$$

(6.2b)

$$\langle Z_\eta \rangle^{(2)} = -\sqrt{2}\langle R \rangle^2 X_0^{(2)} \Sigma\left(\frac{3}{2}\right).$$

(iii) $\bar{M} = -\frac{3}{2}$:

$$\langle Z_\eta \rangle^{(0)} = -\frac{1}{3}\left(\frac{1}{3}\right)^{1/2} \langle R \rangle^2 X_0^{(0)} \cos^2\theta$$

$$\langle Z_\eta \rangle^{(1)} = -\frac{1}{3}\left(\frac{1}{2}\right)^{1/2} \langle R \rangle^2 X_0^{(1)} \cos^2\theta$$

(6.2c)

$$\langle Z_\eta \rangle^{(2)} = -\frac{1}{3}\left(\frac{1}{6}\right)^{1/2} \langle R \rangle^2 X_0^{(2)} \cos^2\theta.$$

For $\bar{M} = -\frac{3}{2}$ there are no contributions proportional to $\sin^2\theta$ and $\sin 2\theta$ because the corresponding wave functions create matrix elements with $|\bar{J}, \bar{M}\rangle$ in which ΔM exceeds the rank (unity) of the dipole operator.

It is interesting to note what happens to the foregoing results for the case of zero spin–orbit interaction. One finds that $\Sigma(\frac{1}{2}) = -1/15\sqrt{3}$ while $\Sigma(\frac{3}{2}) = 0$. Hence, the spectrum of states in the scattering length involves only $\bar{M} = \frac{1}{2}$ and $-\frac{3}{2}$. In the opposite extreme of an infinite spin–orbit interaction all of the foregoing contributions are different from zero.

Lastly, we note that by adding the $\bar{M}$-contributions in (6.2) one recovers the results for the idealized scattering length displayed in section 3. In one sense, the contributions (6.2) can be regarded as components of higher-order sum rules for the attenuation coefficient.

7. Summary

The absorption and resonance-enhanced scattering of x-rays by a magnetic material has been discussed in the framework of an atomic model and the scattering length. Idealized versions of the latter incorporate the assumption that the core state involved in the E1 absorption event is degenerate. The degeneracy will be lifted by an exchange interaction created by unpaired electrons in the valence shell. In the event that this type of interaction is a significant perturbation the assumption no longer is justified and the so-called complete scattering length must be used to calculate the attenuation coefficient and cross-sections for scattering.

General expressions are given for atomic quantities in the idealized scattering length, for an electric-dipole absorption event. Use of the expressions has been illustrated in a thorough discussion of a $3d^9$ ion, for which the wave function contains states from two J-manifolds. We have used the wave function derived by Sainctavit *et al* (1995), and have confirmed and extended their findings for the atomic quantities necessary for the description of the scattering length. Our results are applied to a discussion of the dichroic signals in the attenuation coefficient and the cross-sections.

Acknowledgment

Appendix

We gather here the key results for the idealized scattering length used in the text. The valence electrons are in the shell l^n, and a photon is absorbed in to a shell with angular momentum $\bar{l} = l - 1$. The core hole has a total angular momentum $\bar{J} = \bar{l} \pm \frac{1}{2}$. For an E1 event, the matrix element $Z(\mu; \mu')$ is

$$Z(\mu; \mu') = -l\langle l|R|\bar{l}\rangle^2 \sum_K (2K + 1)^{1/2} \begin{Bmatrix} 1 & K & 1 \\ l & \bar{l} & l \end{Bmatrix} \sum_{m_0} \langle \mu|T_{m_0}^K|\mu'\rangle X_{-m_0}^{(K)}(-1)^{m_0}. \tag{A.1}$$

The components $X_0^{(K)}$ are given in the text, and the remaining components are found in Lovesey and Balcar (1996).

The quantum numbers of the valence state are ν, S, L, J and M, and they are collectively denoted by μ in (A.1). In forming a matrix element of $T_{m_0}^K$ the magnetic quantum numbers factor out in terms of a $3j$-symbol, by virtue of the Wigner–Eckart theorem. In the following material we elect to continue with the use of μ as a shorthand for all of the quantum numbers other than M. A reduced matrix element is defined by

$$\langle \mu M|T_{m_0}^K|\mu' M'\rangle = (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & m_0 & M' \end{pmatrix} (\mu||T(K:\bar{J})||\mu'). \tag{A.2}$$

In what follows we give results for

$$\begin{Bmatrix} 1 & K & 1 \\ l & l-1 & l \end{Bmatrix} (\mu||T(K:\bar{J})||\mu') \tag{A.3}$$

for a given $\bar{J}$ and $K = 0$, 1 and 2. The atomic quantities that enter the results are discussed later. For (A.3) we have, for $\bar{J} = \bar{l} \pm \frac{1}{2}$, the following results.

(i) $K = 0$:

$$\frac{1}{(2l - 1)} \left\{ \frac{1}{6(2l + 1)} \right\}^{1/2} \left\{ (2\bar{J} + 1)(\mu||W^{(00)0}||\mu') \right.$$
$$\left. \mp 6(l - 1)\left(\frac{l+1}{l}\right)^{1/2} (\mu||W^{(11)0}||\mu') \right\}. \tag{A.4}$$

Here, the reduced matrix elements of the unit tensors are

$$(\mu||W^{(00)0}||\mu') = \delta_{\mu,\mu'} n_h \left\{ \frac{2J + 1}{2(2l + 1)} \right\}^{1/2} \tag{A.5}$$

where $n_h = (2(2l + 1) - n)$, and

$$(\mu||W^{(11)0}||\mu') = -\frac{\sqrt{2}}{3} \frac{1}{(l||l||l)} (\mu||\sum_j (s \cdot l)_j||\mu') \tag{A.6}$$

in which j ranges over all holes in the valence shell, and the reduced matrix element $(l||l||l) = \{l(l + 1)(2l + 1)\}^{1/2}$.

(ii) $K = 1$:

$$-\frac{1}{2\sqrt{6}} \frac{1}{l(4l^2 - 1)} \left\{ (2\bar{J} + 1)(\mu||L||\mu') \pm \frac{4}{3}(l - 1)\left[l(\mu||S||\mu') + (2l + 3)(\mu||T||\mu')\right] \right\}. \tag{A.7}$$

In this result,

$$(\mu||L||\mu') = \sqrt{2}(l||l||l)(\mu||W^{(01)1}||\mu') \tag{A.8}$$

$$(\mu||S||\mu') = \left\{\frac{3}{2}(2l+1)\right\}^{1/2}(\mu||W^{(10)1}||\mu') \tag{A.9}$$

and

$$(\mu||T||\mu') = -(\mu||\sum_j (3\hat{R}_0(\hat{\mathbf{R}} \cdot \mathbf{s}) - s_0)_j||\mu')$$

$$= -\left\{\frac{15}{(2l-1)(2l+3)}\right\}^{1/2}(l||l||l)(\mu||W^{(12)1}||\mu') \tag{A.10}$$

where $\hat{\mathbf{R}}$ is a unit position vector.

(iii) $K = 2$:

$$\left(\frac{1}{30}\right)^{1/2}\frac{1}{l(2l-1)^2(2l+1)}\left\{(2\bar{J}+1)(\mu||Q||\mu')\right.$$

$$\left.\pm\frac{4}{5}\left[(l-1)(2l-1)(\mu||P||\mu') + 3(\mu||R||\mu')\right]\right\}. \tag{A.11}$$

Here,

$$2(\mu||P||\mu') = (\mu||\sum_j (3s_0l_0 - \mathbf{s} \cdot \mathbf{l})_j||\mu') = 3(l||l||l)(\mu||W^{(11)2}||\mu') \tag{A.12}$$

$$2(\mu||Q||\mu') = (\mu||\sum_j (3l_0^2 - l(l+1))_j||\mu')$$

$$= (l||l||l)\{2(2l-1)(2l+3)\}^{1/2}(\mu||W^{(02)2}||\mu') \tag{A.13}$$

and

$$-2(\mu||R||\mu') = (\mu||\sum_j \{(2l(l+1)+1)s_0l_0 + (l(l+1)-2)\mathbf{s} \cdot \mathbf{l} - 5l_0(\mathbf{s} \cdot \mathbf{l})l_0\}_j||\mu')$$

$$= (l||l||l)\left\{\frac{7}{2}(l-1)(2l-1)(l+2)(2l+3)\right\}^{1/2}(\mu||W^{(13)2}||\mu'). \tag{A.14}$$

The definitions of the reduced matrix elements of P and Q agree with the ones adopted by Carra *et al* (1993a). Our definition of R differs from the one that they give by a factor of 2, i.e. on the left-hand side of (A.14) they have a factor 4. Regarding the result (A.11), Carra *et al* (1993a) have the opposite relative sign between Q, and P and R, which we believe is a mistake. Furthermore, our numerical results for mean values of these operators differ in sign from the entries in their table 2. One might speculate that the sign difference can be attributed to the difference in the sign of even-rank tensors for configurations of electrons and holes, respectively. In the scattering length it is natural to use valence hole states.

Lovesey and Balcar (1997) provide tables of the reduced matrix elements of the unit tensors that appear in the foregoing results. The reduced matrix elements of the atomic quantities follow from the standard definition of a spherical tensor formed from a product of two spherical tensors:

$$X_Q^{(ab)K} = \sum_{qq'}\sum_j (z_q^{(a)}y_{q'}^{(b)})_j(aqbq'|KQ) \tag{A.15}$$

in which $z^{(a)}$ and $y^{(b)}$ are tensors acting on the spin and on the orbit, respectively, and $(aqbq'|KQ)$ is a Clebsch–Gordan coefficient. The definition of the unit tensor is such that the reduced matrix element

$$(\mu||X^{(ab)K}||\mu') = (s||z(a)||s)(l||y(b)||l)(\mu||W^{(ab)K}||\mu'). \tag{A.16}$$

For $a = 0$, $(s||z(0)||s) = (2s+1)^{1/2} = \sqrt{2}$ and for $a = 1$, $(s||z(1)||s) = (s||s||s) = (3/2)^{1/2}$. From these results one immediately gets (A.8) and (A.9). To obtain (A.14), the most complicated of the results, to a total of three orbital operators apply twice the tensor coupling defined in (A.15) to form a tensor of rank 3, and couple this tensor to one spin operator, again using (A.15), to form a tensor of rank 2. The prefactor in (A.14) is the reduced matrix element of the orbital tensor of rank 3, i.e. in (A.16) the reduced matrix element of $y(3)$.

In the main text we calculate the diagonal matrix element, or the mean value, of the scattering length. In general, this quantity is proportional to a sum of matrix elements $Z(\mu; \mu)$ and $Z(\mu; \mu')$ weighted by factors that are determined by interactions that perturb the valence electrons, e.g. the ligand crystal-field. For the wave function (2.1) in $\langle f \rangle$ there are five matrix elements. We refer to this linear combination of matrix elements $Z(\mu; \mu')$ as the mean value of Z, and denote it by $\langle Z \rangle$. The notation for a mean value is extended to the atomic quantities, e.g. the mean value of $\boldsymbol{R}$, which is a tensor of rank two with the reduced matrix element (A.14), is denoted by $\langle \boldsymbol{R} \rangle$.

The mean value $\langle Z \rangle$ in its most general form is constructed according to (3.2) using the results

(i) $K = 0$:

$$\langle Z \rangle^{(0)} = -\frac{1}{2\sqrt{3}}\langle R \rangle^2 X_0^{(0)}\left(\frac{l}{4l^2-1}\right)\left\{(2\bar{J}+1)n_h \pm 4\left(\frac{l-1}{l}\right)\left\langle\sum \boldsymbol{s} \cdot \boldsymbol{l}\right\rangle\right\}. \tag{A.17}$$

(ii) $K = 1$:

$$\langle Z \rangle^{(1)} = \frac{1}{2\sqrt{2}}\langle R \rangle^2\left(\frac{1}{4l^2-1}\right)X^{(1)} \cdot \left\{(2\bar{J}+1)\langle \boldsymbol{L} \rangle \pm \frac{4}{3}(l-1)\left[l\langle \boldsymbol{S} \rangle + (2l+3)\langle \boldsymbol{T} \rangle\right]\right\}. \tag{A.18}$$

(iii) $K = 2$:

$$\langle Z \rangle^{(2)} = -\frac{1}{\sqrt{6}}\langle R \rangle^2\left(\frac{1}{(2l-1)^2(2l+1)}\right)X^{(2)} \cdot \left\{(2\bar{J}+1)\langle \boldsymbol{Q} \rangle \right.$$
$$\left. \pm \frac{4}{5}\left[(l-1)(2l-1)\langle \boldsymbol{P} \rangle + 3\langle \boldsymbol{R} \rangle\right]\right\}. \tag{A.19}$$

The results (A.17)–(A.19) are the basis for the calculations leading to (3.3). In the foregoing results the scalar product with $X^{(K)}$ is defined in the standard manner, e.g.

$$\boldsymbol{X}^{(2)} \cdot \langle \boldsymbol{R} \rangle = \sum_{m_0} X^{(2)}_{-m_0}\langle R_{m_0} \rangle(-1)^{m_0}. \tag{A.20}$$

Applied to $K = 1$, equation (A.20) is equivalent to the standard scalar product of two vectors. In the event that the atomic matrix element is calculated in local principal axes the atomic matrix element in (A.20) is obtained by a standard application of rotation matrices, e.g. (3.10).

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