A theoretical framework for absorption (dichroism) and the resonance-enhanced scattering of x-rays by magnetic materials: III. Contributions from atomic spins

# A theoretical framework for absorption (dichroism) and the resonance-enhanced scattering of x-rays by magnetic materials: III. Contributions from atomic spins

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**Abstract.**  A report is given of a study of the resonant contribution to the scattering length for x-rays, evaluated using an atomic picture of the electrons. Armed with the scattering length one can calculate the attenuation coefficient, dichroic signal and cross-sections for the elastic and inelastic scattering of x-rays by magnetic materials. The formulation is more finely honed than the one used in two previous studies. The additional information in the scattering length relates to the spins of the electrons in the unfilled valence shell. For the $d^n$ and $f^n$ configurations, tables of Racah unit spherical tensors are provided for ground states determined by Hund's rules.

## 1. Introduction

In two previous papers, we have investigated a theoretical framework, using an atomic description of electron states, for the interpretation of the attenuation and resonance-enhanced scattering of x-rays by magnetic materials.  The instrument used in the investigation is the resonant scattering length from which one can readily calculate the attenuation coefficient, dichroic signal, and the cross-sections for elastic and inelastic scattering.  On reducing some information on the plethora of intermediate states in the scattering length, by summing over a judiciously chosen subset of intermediate-state quantum numbers, we created a framework in which the measurable quantities are expressed in terms of familiar atomic variables, e.g. magnetic multipoles and unit spherical tensors. Our scattering length, to which we attached the soubriquet *idealized*, has been shown by us to have much to recommend it.

   In the present study we explore, in much the same vein, a more finely honed reduction of the information on intermediate states in the resonant scattering length. On the one hand the new scattering length is an improvement, in as much that it contains more information on the valence electrons than the idealized scattering length, but weighed against this is an increased technical complexity. A way of describing the difference between the two scattering lengths is to note that the idealized one does not distinguish between the two spin–orbit-split partners of a core state whereas the new one can.

   As before, we aim to make full use of Racah unit spherical tensors to describe the equivalent holes in the partly filled valence shell. Values of the tensors are listed for the $d^n$ and $f^n$ configuration, appropriate for transition elements, lanthanides and actinides. Given a wave function for the valence shell d or f electrons couched in terms of atomic orbitals it is straightforward to calculate the scattering length, and from it the measurable quantities

that we have mentioned. In the event that a realistic wave function can be constructed from states in one $J$-manifold, the concept of operator equivalents brings the mean value of the scattering length, required to calculate both the dichroic signal and cross-section for Bragg diffraction, to a relatively simple and attractive form.

In the field of atomic spectroscopy, it seems that the possibility of performing a restricted sum over the intermediate-state quantum numbers in the first-order correction to a matrix element was first explored by Griffith (1960), Judd (1962) and Ofelt (1962). Although the objective for their work was different from ours, Judd and Ofelt reported work in which they faced calculations not unlike the one we report. A different view of the physical picture of summing over intermediate-state quantum numbers, with an ambition different from ours, was given by Trammell (1962). In the latter work, Trammell expressed the energy denominator in the matrix element, that provides for a resonance enhancement, in terms of an integral in time. He then investigated approximations based on the limits of fast and slow collisions; features of a fast-collision approximation for x-ray scattering were briefly reported by Luo *et al* (1993).

The measurable quantities of interest are presented in the next section, together with the resonant contribution to the scattering length. These topics are fully discussed in our two previous papers on the subject: Lovesey and Balcar (1996) and Lovesey (1996), and hereafter referred to as papers I and II, respectively. The following two sections focus on the information in the scattering length that is new relative to the idealized scattering length. To illustrate some aspects of the spin contributions to the scattering length, not found in the idealized scattering length, we give in section 5 two examples of the calculation of the circular dichroic signals for E1 and E2 absorption events. We choose not to give any examples of the cross-sections for Bragg diffraction and inelastic scattering. These two topics are discussed in paper I, and it is a straightforward exercise to repeat the calculations reported there using in place of the idealized scattering length the more complete version given here in section 3.

## 2. The attenuation coefficient and cross-sections

Let the primary and secondary x-rays in a scattering process have energies $E$ and $E'$, respectively, and wave vectors $q$ and $q'$; then

$$E = \hbar c q = 2\pi \hbar c / \lambda$$

with similar expressions for $E'$ in terms of $q'$ or $\lambda'$. The initial and final (equilibrium) states of the target atoms are defined by labels $\mu$ and $\mu'$, about which we have more to say later on. A matrix element of the scattering length for these two states is denoted by $f(\mu; \mu')$, and its mean value is denoted by $\langle f \rangle$. This last quantity determines the cross-section for Bragg scattering, namely,

$$\sigma = || \, |\langle f \rangle|^2 \, || \tag{2.1}$$

where the double vertical bars indicate that an average is taken with respect to the states of polarization in the primary beam of x-rays. A method for performing the average, in which the polarization of the beam of x-rays is defined in terms of a Stokes vector, is described by Lovesey and Collins (1996). The differential cross-section for inelastic scattering is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}E'} = \left( \frac{E'}{E} \right) \sum_{\mu\mu'} p_\mu \delta(\hbar\omega + E_\mu - E_{\mu'}) || \, |f(\mu; \mu')|^2 \, ||. \tag{2.2}$$

Here, we have defined

$$\hbar\omega = E - E'$$

and $E_\mu$ ($E_{\mu'}$) is the energy of the initial (final) atomic state. The factor $p_\mu$ is the probability for the initial state to be available in the scattering process, and the sum of the $p_\mu$ is unity.

For resonance-enhanced scattering, the scattering length in (2.1) and (2.2) is just the resonant contribution to the scattering length. The latter quantity, evaluated for the forward-scattering geometry ($q = q'$) and averaged with respect to the states of polarization in the primary beam, determines the attenuation coefficient $\gamma$. We will give a result for $\gamma$ expressed in terms of our formulation of the resonant scattering length.

Let $\Delta$ be the difference between the mean energy of the absorption edge and $E_\mu$, and let $\Delta'$ be the corresponding energy difference with respect to $E_{\mu'}$. More than likely, $\Delta$ and $\Delta'$ will be different for E1 and E2 absorption events. The resonant scattering length evaluated for $E$ close to $\Delta$ is taken to be

$$f(\mu; \mu') = -\left(\frac{2\pi e}{\lambda}\right)^2 \left(\frac{\Delta'}{\Delta}\right) \left\{E - \Delta + \frac{\mathrm{i}}{2}\Gamma\right\}^{-1} \sum_{R_0} \exp\{-W(k) + \mathrm{i}k \cdot R_0\} Z(\mu; \mu' : R_0).$$

(2.3)

In this expression, the vectors $\{R_0\}$ define the positions of the atoms, and $\Gamma$ is the total decay width. The Debye–Waller factor might depend on $R_0$, and it is unity in the forward direction of scattering, for which

$$k = q - q' = 0.$$

The matrix element $Z(\mu; \mu' : R_0)$, which is the principal subject of the paper, depends on $R_0$ through chemical and magnetic order in the target sample.

We are now in a position to give our result for the attenuation coefficient, for a foil in which the density of particles is $n_0$. The mean value of $Z$ averaged with respect to states of polarization in the primary beam, and evaluated for a forward-scattering geometry is denoted by $\langle Z \rangle_0$. Taking the limit $\Gamma \to 0$,

$$\gamma = 2\pi\lambda n_0 \left(\frac{e\Delta}{\hbar c}\right)^2 \delta(E - \Delta)\langle Z \rangle_0.$$

(2.4)

The action of the delta function in (2.4) is to set $\lambda = (12.40/\Delta)$ Å with $\Delta$ expressed in units of keV. Calculations of the attenuation coefficient using a band-structure description of electronic states are reviewed by Ebert (1996).

## 3. Matrix elements

Here, we provide an expression for the matrix element $Z(\mu; \mu')$; for the most part, we omit the label $R_0$ to save on notation.

In paper I we consider an E1 absorption event. Using an atomic model, so $\mu$ and $\mu'$ are shorthand for atomic quantum numbers $\nu$ (seniority), $S, L, J$ and $M$, we derive the expression

$$Z(\mu; \mu') = (l||C(1)||\bar{l})(\bar{l}||C(1)||l)\langle l|R|\bar{l}\rangle^2 \sum_K (2K+1)^{1/2} \begin{Bmatrix} 1 & K & 1 \\ l & \bar{l} & l \end{Bmatrix}$$

$$\times \sum_{m_0} \langle \theta J M|T^K_{m_0}|\theta' J' M'\rangle X^{(K)}_{-m_0}(-1)^{m_0}.$$

(3.1)

In this expression, $(l||C(1)||\bar{l})$ is the reduced matrix element of a spherical harmonic, normalized in the manner proposed by Racah, of rank one taken between states of angular momentum $l$ and $\bar{l}$. The physical process that (3.1) describes is the transfer of a hole from a valence shell $l^n$ to a filled core state with angular momentum $\bar{l}$, and $\langle l|R|\bar{l}\rangle$ is the radial integral for the E1 event. The sum on $K = 0$, 1 and 2 and $m_0$ ($-K \leqslant m_0 \leqslant K$) involves a matrix element ($\theta = \nu SL$) of a spherical tensor operator, $T^K_{m_0}$, appropriate to $n_h$ holes in the valence shell. We return to this operator in a moment. The tensor $\mathbf{X}^{(K)}$ depends only on the polarization vectors for the primary and secondary x-rays, and its components are listed in paper I, together with averages of $\mathbf{X}^{(K)}$, required to evaluate (2.4) for the attenuation coefficient, and averages of $|\mathbf{X}^{(K)}|^2$ required to evaluate cross-sections.

The expression for $Z(\mu; \mu')$ for an E2 event, that corresponds to (3.1) for an E1 event, has a structure very similar to (3.1). There are two really significant differences between the expressions for E1 and E2 events. For the latter case the sum on $K$ extends up to 4, and in place of $\mathbf{X}^{(K)}$ there is a more complicated tensor, denoted by $\mathbf{H}^{(K)}$ in paper II, that is formed from the polarization vectors of the primary and secondary x-rays, and unit vectors $\hat{q}$ and $\hat{q}'$ which define the directions of propagation of the two beams. The spherical tensor operator $T^K_{m_0}$, which reflects the hole configuration in the valence shell, is common to the matrix elements for E1, E2 and higher-order events.

We now give an expression for the matrix element of $T^K_{m_0}$. The matrix element satisfies the Wigner–Eckart theorem:

$$\langle\theta JM|T^K_{m_0}|\theta'J'M'\rangle = (-1)^{J-M}\begin{pmatrix} J & K & J' \\ -M & m_0 & M' \end{pmatrix}(\theta J||T(K:\bar{J})||\theta'J') \quad (3.2)$$

where the quantity which multiplies the phase factor and $3j$-symbol is the reduced matrix element for the absorption edge with total angular momentum $\bar{J} = \bar{l} \pm \frac{1}{2}$. Of course, two matrix elements with $\bar{J} = \bar{l} + \frac{1}{2}$ and $\bar{J} = \bar{l} - \frac{1}{2}$ can be used to describe a case in which an absorption edge does not closely correspond to one value of $\bar{J}$. Such a situation will arise if the strength of the spin–orbit interaction for the core state and the Coulomb interaction, measured in terms of Slater integrals, are similar in magnitude, and, in consequence, the core state contains sizable amounts of both of the spin–orbit core states (Teramura *et al* 1996). In papers I and II we described physical processes using the foregoing expressions and a reduced matrix element:

$$(\theta J||T(K)||\theta'J') = \sum_{\bar{J}}(\theta J||T(K:\bar{J})||\theta'J') \quad (3.3)$$

and the corresponding scattering length was named an idealized scattering length.

Our expression for $T(K:\bar{J})$ involves unit spherical tensors $W^{(a,b)K}$, which are standard quantities in the theory of atomic spectra. The indices $a$ and $b$ refer to different parts of the atomic system, and $K$ is the rank of the unit tensor. With our notation, which follows the one adopted by Judd (1963), the index $a$ is the rank of the spin operator and $b$ is the rank of the orbital operator. The ordering of spin versus orbital operators is tied to the coupling of spin and orbital quantum numbers in a Clebsch–Gordan coefficient, which we choose to be $(SM_sLM_L|JM)$ (NB a mixture in a calculation of $SL$- and $LS$-coupling schemes can produce non-trivial errors). The reduced matrix elements of $T(K)$ and $W^{(0,K)K}$ are related, of course, and differ only by a numerical factor which is given in (A.2). For the convenience of the reader, an appendix to this paper contains the salient features of the unit spherical tensors. Also, we give in tables listings of values of the reduced matrix elements of $W^{(a,b)K}$ appropriate to the ground states of $d^n$ and $f^n$ as determined by Hund's rules—see later.

We have arranged our result for the reduced matrix element of $T(K \colon \bar{J})$ so as to highlight the information from $a = 1$ that is additional to the information from $a = 0$, which is all contained in the reduced matrix element of $T(K)$. One finds, for $\bar{J} = \bar{l} \pm \frac{1}{2}$,

$$\left[(\theta J || T(K \colon \bar{J}) || \theta' J') - \left\{\frac{(2\bar{J}+1)}{2(2\bar{l}+1)}\right\}(\theta J || T(K) || \theta' J')\right]\left\{\begin{matrix} t & K & t \\ l & \bar{l} & l \end{matrix}\right\}$$

$$= \pm (-1)^{K+1}\left(\frac{6\bar{l}(\bar{l}+1)}{(2K+1)(2\bar{l}+1)}\right)^{1/2}$$

$$\times \sum_b (\theta J || W^{(1,b)K} || \theta' J')(2b+1)\left\{\begin{matrix} \bar{l} & l & t \\ \bar{l} & l & t \\ 1 & b & K \end{matrix}\right\}. \tag{3.4}$$

It is at once clear that (3.4) satisfies (3.3), since the right-hand side of (3.4) has an equal magnitude and opposite sign for the two allowed values of $\bar{J}$, which describes the total angular momentum of the hole in the core state. The variable $t$ depends on the nature of the absorption event; for an E1 event $t = 1$ and for an E2 event $t = 2$. The range of the sum on the integer $b$ is restricted by two triangle conditions in the $9j$-symbol, namely, $0 \leqslant b \leqslant 2l$ and $|K - 1| \leqslant b \leqslant (K + 1)$. A further restriction on $b$ placed by the $9j$-symbol is that $b + K$ must be an odd integer, otherwise the symbol is zero (this follows on noting that the $9j$-symbol is unaltered by interchanging its top two rows, and this move also multiplies it by a phase factor $(-1)^{1+b+K}$). Many values of the $9j$-symbol which are required in the study of rare-earth atoms are tabulated by Balcar and Lovesey (1989), together with short tables of $3j$- and $6j$-symbols. An extensive compilation of $3j$- and $6j$-symbols is given by Rotenberg *et al* (1959). Lastly, $\bar{l} + l + t$ is an even integer, by virtue of a property of $(\bar{l} || C(t) || l)$.

We conclude this section with a few words about the derivation of (3.4), and an alternative form of the result that is useful in the description of valence electrons subjected to a strong electrostatic field from the ligand ions. For one hole, the resonant scattering length contains a product of one-particle matrix elements:

$$\langle l J M | C_q^t(\hat{\boldsymbol{R}}) | \bar{l} \bar{J} \bar{M} \rangle \langle \bar{l} \bar{J} \bar{M} | C_{q'}^t(\hat{\boldsymbol{R}}) | l J' M' \rangle \tag{3.5}$$

where $q$ and $q'$ label spherical components. In the energy denominator associated with (3.5) is the energy of the intermediate state, $\bar{l} \bar{J} \bar{M}$. If we set aside the dependence of this energy on $\bar{J}$ and $\bar{M}$, say, we can perform a sum over these labels in the product of matrix elements. This is the basis of the formulation given in papers I and II. The result is extended to describe a valence shell with $n_h$ holes by using Racah's methods for equivalent particles in an atomic shell, and the energy of the intermediate state is replaced by some mean value that remains to be chosen. The current work follows the same line of reasoning, except that at the start we sum over $\bar{M}$, and leave $\bar{J}$ as a variable.

The exercise that brings us to the result (3.4) is relatively straightforward, uses standard identities for $nj$-symbols, and can be described in a few sentences. First, use

$$\langle l J M | C_q^t(\hat{\boldsymbol{R}}) | \bar{l} \bar{J} \bar{M} \rangle = (-1)^{J-M}\begin{pmatrix} J & t & \bar{J} \\ -M & q & \bar{M} \end{pmatrix}$$

$$\times (l || C(t) || \bar{l})(-1)^{3/2-J+l}[(2J+1)(2\bar{J}+1)]^{1/2}\left\{\begin{matrix} J & t & \bar{J} \\ \bar{l} & \frac{1}{2} & l \end{matrix}\right\} \tag{3.6}$$

and a similar expression for the second matrix element in (3.5). The result (3.6) is given by Judd (1963) as equation (3-38) (a small printing error in (3-38), which has round brackets (indicating a $3j$-symbol) instead of curly brackets, is a glitch at first sight). The sum on $\bar{M}$

can be converted to a sum over products of $3j$- and $6j$-symbols. Here, the key step is to arrange one of the $3j$-symbols to be of the form demanded by the Wigner–Eckart theorem (3.2). The next step is to isolate $\bar{J}$ in one $6j$-symbol, achieved by twice using the sum rule of Biedenharn and Elliott. Having reached this point the remaining product of four $6j$-symbols, that do not contain $\bar{J}$ in their arguments, can be expressed as a product of two $9j$-symbols. The identities used in the foregoing are found in Rotenberg *et al* (1959), equations (2.8), (2.19), (3.1) and (3.22). The result for the one-particle matrix element is extended to $n_h$ equivalent holes by the method proposed by Racah, and results in the appearance of unit spherical tensors. Finally, to get the result for the reduced matrix element of $T(K:\bar{J})$ as it appears in (3.4) we have used an analytic expression for the one $6j$-symbol which contains $\bar{J} = \bar{l} \pm \frac{1}{2}$.

The properties of the reduced matrix element (3.4) evaluated for a shell with one hole merit comment. First, one should note that the two triangle conditions on $\bar{J}$ in (3.6) lead to the result that for one hole in an otherwise full shell of electrons and $J = l + \frac{1}{2}$ the absorption event for $\bar{J} = \bar{l} - \frac{1}{2}$ is forbidden. Turning to (3.4) only one of the two triangle conditions on $\bar{J}$ is explicit in the result, namely, $\bar{J} = \bar{l} \pm \frac{1}{2}$. It can be shown, however, that for $\bar{J} = \bar{l} - \frac{1}{2}$ the reduced matrix element of $T(K:\bar{J})$ given in (3.4) is zero. So, the restriction placed on the absorption event, by the two triangle conditions on $\bar{J}$, is indeed preserved even after performing the sum on $\bar{M}$ to create the reduced matrix element of $T(K:\bar{J})$.

In applying the results to the calculation of the cross-sections and attenuation coefficient one may be faced with atomic wave functions that contain several atomic states. The additions to the state determined purely by Hund's rules will result from the actions of inter-atomic forces, and perturbations to the valence shell created by the environment of the atom, including like atoms. A specific case that can lead to a wave function for the ground state, and excited states, with two or more values of $J$ is when the magnitude of the electrostatic field from the ligand ions is so large that it and the spin–orbit interaction must be treated on an equal footing. In this regard, note that the dependence on the magnetic quantum numbers $M$ and $M'$ of a matrix element of $T_{m_0}^K$ appears solely in the $3j$-symbol which features in the Wigner–Eckart theorem. Hence, if the degeneracy with respect to these quantum numbers if lifted, e.g. by an external field or a molecular field capable of inducing long-range magnetic order in the sample, the averaging to be done involves effecting the averaging of $3j$-symbols.

Some observable quantities take on a very simple structure when the atomic wave function is drawn from one $J$-manifold. In this case one can adopt the practice, widespread in other branches of spectroscopy, of using operator equivalents, e.g.,

$$\langle JM|I_0^{(K)}|JM\rangle = (-1)^{J-M}\begin{pmatrix} J & K & J \\ -M & 0 & M \end{pmatrix}.$$

The average with respect to the magnetic quantum numbers is then represented by displaying the operator in angular brackets, $\langle I_0^{(K)}\rangle$, which is in accord with our chosen notation of angular brackets to denote the mean value of the enclosed quantity. For $K = 1$, which appears in (A.9),

$$\langle JM|I_0^{(1)}|JM\rangle = M/(J||J||J)$$

where $(J||J||J)$ is the reduced matrix element of the angular momentum, and

$$\langle I_0^{(1)}\rangle = \langle J_c\rangle/(J||J||J) \tag{3.7}$$

in which $c$ labels the magnetic quantization axis.

For some problems, the most natural basis in which to write the wave function of the ground state is the $SM_SLM_L$-basis, whereas the foregoing results are given in the $SLJM$-basis. The transformation from the latter to $SM_SLM_L$ leads to a matrix element of $T_{m_0}^K$ expressed in terms of unit spherical tensors $W^{(a,b)}$; the relation between the reduced matrix elements $(\theta J || W^{(a,b)K} || \theta' J')$ and $(\theta || W^{(a,b)} || \theta')$ is (A.1), and table 1 contains listings of the diagonal reduced matrix elements appropriate to 3d transition elements and rare-earth elements. To work in the $SM_SLM_L$-basis one replaces

$$(-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & m_0 & M' \end{pmatrix} (\theta J || W^{(a,b)K} || \theta J')$$

which appears in $\langle \theta J M | T_{m_0}^K | \theta J' M' \rangle$, by

$$(-1)^{a+b+m_0} \left\{ \frac{(2K+1)}{(2a+1)(2b+1)} \right\}^{1/2} (\theta || W^{(a,b)} || \theta) \sum_{m,n} \begin{pmatrix} a & K & b \\ -m & m_0 & -n \end{pmatrix}$$

$$\times (-1)^{S-M_S} \begin{pmatrix} S & a & S \\ -M_S & m & M'_S \end{pmatrix} (-1)^{L-M_L} \begin{pmatrix} L & b & L \\ -M_L & n & M'_L \end{pmatrix}. \tag{3.8}$$

Notice that the result that we give applies to the construction of $\langle SM_SLM_L | T_{m_0}^K | SM'_SLM'_L \rangle$ which is diagonal in the total spin and total orbital angular momentum. The result (3.8) is the product of the Wigner–Eckart theorem applied to the spin and orbital operators, of rank $a$ and $b$, respectively, working in a tensor of rank $K$. For either $a = 0$ or $b = 0$, equation (3.8) takes a very simple form, e.g. $a = 0$ means $m = M_S - M'_S = 0$ and $n = M_L - M'_L = m_0$.

## 4. Spin-dependent contributions

In what follows we focus on the physical interpretation of the contributions to the resonant scattering length on the right-hand side of (3.4), using the $SLJM$-basis. These new contributions arise from $a = 1$ and are additions to the idealized scattering length obtained for $a = 0$. The dependence of the new contributions on the atomic spin is quite simply seen in the rank-one term $W^{(1,0)1}$. For $J = J'$, $W^{(1,0)1}$ is proportional to $g - 1$ where $g$ is the Landé factor. This finding married with (3.7), which is valid within a $J$-manifold, leads to a contribution to $\langle f \rangle$ and to $\langle Z \rangle_0$ that is proportional to $(g - 1)\langle J_c \rangle = \langle S_c \rangle$.

It seems natural to consider the contributions according to their rank $K$, because the value of $K$ determines the nature of the thermodynamic quantity. In simple cases, the thermodynamic quantity is a magnetic multipole, e.g. the magnetic moment ($K = 1$) or quadrupole moment ($K = 2$). The reduced matrix elements of $W^{(a,b)K}$ are nothing more than weighting factors, although, having said this, they can have a profound effect on the observed quantity. As an example of what can occur consider an $f^n$ configuration and $K = 3$. For $n = 2$, 5, 9 and 12 and Hund-rules ground states $W^{(0,3)} = 0$, so in this instance there is no pure orbital contribution to the idealized scattering length. However, both $W^{(1,2)}$ and $W^{(1,4)}$ are non-zero for these configurations and therefore, there are non-zero spin-dependent contributions to the scattering length.

As a step toward giving a physical interpretation of the rank-zero contribution we note that the reduced matrix element of the spin–orbit coupling in the valence shell is proportional to the reduced matrix element of $W^{(1,1)0}$; if $j$ labels the electrons in the valence shell, we find

$$(\theta J || \sum_j (s \cdot l)_j || \theta' J') = -\sqrt{3}(s||s||s)(l||l||l)(\theta J || W^{(1,1)0} || \theta' J'). \tag{4.1}$$

**Table 1.** Racah unit spherical tensors which appear in (3.4), (3.8), (A.1) and (A.2) are listed for $d^n$ and $f^n$ valence shells. The quantum numbers are determined by the application of Hund's rules. Note that our unit spherical tensors are for holes, not electrons. This means that for $a + b =$ even integer $> 0$ our unit spherical tensors have an opposite sign to those for electrons; for $a + b =$ odd integer, values for holes and electrons are the same. For the special case $a = b = 0$ one has $(\theta||W^{(0,0)}||\theta') = \delta_{\theta,\theta'} n_h \{(2S + 1)(2L + 1)/[2(2l + 1)]\}^{1/2}$ and $(\theta J||W^{(0,0)0}||\theta' J') = \delta_{\theta,\theta'} \delta_{J,J'} n_h \{(2J + 1)/[2(2l + 1)]\}^{1/2}$ where $n_h$ is the number of holes in the valence shell. Also, for $n_h = 1$, $(\theta||W^{(a,b)}||\theta) = \{(2a + 1)(2b + 1)\}^{1/2}$ and, for $n_h = 4l + 1$, $(\theta||W^{(a,b)}||\theta) = (-1)^{a+b+1}\{(2a + 1)(2b + 1)\}^{1/2}$.

| $Ti^{3+}$ $\quad d^1$ $\quad n_h = 9$ | | | |
|---|---|---|---|
| $(^2D||W^{(0,1)}||^2D)$ | $\sqrt{3}$ | $(^2D_{3/2}||W^{(0,1)1}||^2D_{3/2})$ | $\dfrac{3}{5}$ |
| $(^2D||W^{(0,2)}||^2D)$ | $-\sqrt{5}$ | $(^2D_{3/2}||W^{(0,2)2}||^2D_{3/2})$ | $-\dfrac{1}{5}\sqrt{7}$ |
| $(^2D||W^{(1,1)}||^2D)$ | $-3$ | $(^2D_{3/2}||W^{(1,1)0}||^2D_{3/2})$ | $-\sqrt{\dfrac{1}{15}}$ |
| $(^2D||W^{(1,0)}||^2D)$ | $\sqrt{3}$ | $(^2D_{3/2}||W^{(1,0)1}||^2D_{3/2})$ | $-\dfrac{1}{5}\sqrt{2}$ |
| $(^2D||W^{(1,2)}||^2D)$ | $\sqrt{15}$ | $(^2D_{3/2}||W^{(1,2)1}||^2D_{3/2})$ | $\dfrac{1}{5}\sqrt{\dfrac{14}{5}}$ |
| $(^2D||W^{(1,1)}||^2D)$ | $-3$ | $(^2D_{3/2}||W^{(1,1)2}||^2D_{3/2})$ | $\dfrac{1}{5}\sqrt{\dfrac{2}{3}}$ |
| $(^2D||W^{(1,3)}||^2D)$ | $-\sqrt{21}$ | $(^2D_{3/2}||W^{(1,3)2}||^2D_{3/2})$ | $-\dfrac{2}{5}$ |
| $V^{3+}$ $\quad d^2$ $\quad n_h = 8$ | | | |
| $(^3F||W^{(0,1)}||^3F)$ | $3\sqrt{\dfrac{7}{5}}$ | $(^3F_2||W^{(0,1)1}||^3F_2)$ | $\dfrac{2}{3}\sqrt{2}$ |
| $(^3F||W^{(0,2)}||^3F)$ | $-3\sqrt{\dfrac{1}{5}}$ | $(^3F_2||W^{(0,2)2}||^3F_2)$ | $-\dfrac{6}{35}\sqrt{2}$ |
| $(^3F||W^{(1,1)}||^3F)$ | $-3\sqrt{\dfrac{14}{5}}$ | $(^3F_2||W^{(1,1)0}||^3F_2)$ | $-\dfrac{2}{3}\sqrt{\dfrac{1}{3}}$ |
| $(^3F||W^{(1,0)}||^3F)$ | $2\sqrt{\dfrac{21}{5}}$ | $(^3F_2||W^{(1,0)1}||^3F_2)$ | $-\dfrac{2}{3}$ |
| $(^3F||W^{(1,2)}||^3F)$ | $3\sqrt{\dfrac{2}{5}}$ | $(^3F_2||W^{(1,2)1}||^3F_2)$ | $\dfrac{4}{5}\sqrt{\dfrac{1}{35}}$ |
| $(^3F||W^{(1,1)}||^3F)$ | $-3\sqrt{\dfrac{14}{5}}$ | $(^3F_2||W^{(1,1)2}||^3F_2)$ | $\dfrac{4}{3}\sqrt{\dfrac{1}{21}}$ |
| $(^3F||W^{(1,3)}||^3F)$ | $3\sqrt{\dfrac{7}{5}}$ | $(^3F_2||W^{(1,3)2}||^3F_2)$ | $\dfrac{3}{7}\sqrt{\dfrac{2}{7}}$ |

The selection rules for $W^{(1,1)0}$ are thus the same as those familiar to us for the spin–orbit coupling. This contrasts with the selection rules in $T(0)$, which is diagonal with respect to the total angular momentum, and diagonal with respect to $\theta = \nu SL$.

For an E1 event in an atomic state that satisfies Hund's rules we find $(K = 0)$

$$Z(\mu; \mu) = \frac{1}{3}(\varepsilon' \cdot \varepsilon)\langle l|R|\bar{l}\rangle^2 \left\{ \frac{l}{2(2\bar{l} + 1)(2l + 1)} \right\}$$
$$\times \left[ n_h(2\bar{J} + 1) \mp \left(\frac{1}{S}\right)\left(\frac{l - 1}{l}\right)[L(L + 1) + S(S + 1) - J(J + 1)] \right]. \quad (4.2)$$

In this expression, derived from (3.1) and (A.12), $\varepsilon$ and $\varepsilon'$ are the polarization vectors for

**Table 1.** (Continued)

| | | | |
|---|---|---|---|
| $Cr^{3+}$ $d^3$ $n_h = 7$ | | | |
| $(^4F\|\|W^{(0,1)}\|\|^4F)$ | $2\sqrt{\dfrac{21}{5}}$ | $(^4F_{3/2}\|\|W^{(0,1)1}\|\|^4F_{3/2})$ | $\dfrac{4}{5}$ |
| $(^4F\|\|W^{(0,2)}\|\|^4F)$ | $2\sqrt{\dfrac{3}{5}}$ | $(^4F_{3/2}\|\|W^{(0,2)2}\|\|^4F_{3/2})$ | $\dfrac{12}{25}\sqrt{\dfrac{1}{7}}$ |
| $(^4F\|\|W^{(1,1)}\|\|^4F)$ | $-2\sqrt{7}$ | $(^4F_{3/2}\|\|W^{(1,1)0}\|\|^4F_{3/2})$ | $-\dfrac{4}{3}\sqrt{\dfrac{1}{15}}$ |
| $(^4F\|\|W^{(1,0)}\|\|^4F)$ | $\sqrt{42}$ | $(^4F_{3/2}\|\|W^{(1,0)1}\|\|^4F_{3/2})$ | $-\dfrac{3}{5}\sqrt{2}$ |
| $(^4F\|\|W^{(1,2)}\|\|^4F)$ | $-2$ | $(^4F_{3/2}\|\|W^{(1,2)1}\|\|^4F_{3/2})$ | $-\dfrac{12}{25}\sqrt{\dfrac{2}{35}}$ |
| $(^4F\|\|W^{(1,1)}\|\|^4F)$ | $-2\sqrt{7}$ | $(^4F_{3/2}\|\|W^{(1,1)2}\|\|^4F_{3/2})$ | $\dfrac{4}{15}\sqrt{\dfrac{2}{3}}$ |
| $(^4F\|\|W^{(1,3)}\|\|^4F)$ | $\sqrt{14}$ | $(^4F_{3/2}\|\|W^{(1,3)2}\|\|^4F_{3/2})$ | $\dfrac{6}{35}$ |
| $Mn^{3+}$ $d^4$ $n_h = 6$ | | | |
| $(^5D\|\|W^{(1,1)}\|\|^5D)$ | $-\dfrac{3}{2}\sqrt{5}$ | $(^5D_0\|\|W^{(1,1)0}\|\|^5D_0)$ | $-\dfrac{1}{2}\sqrt{\dfrac{1}{15}}$ |
| $Fe^{3+}$ $d^5$ $n_h = 5$ | | | |
| $(^6S\|\|W^{(1,0)}\|\|^6S)$ | $\sqrt{21}$ | $(^6S_{5/2}\|\|W^{(1,0)1}\|\|^6S_{5/2})$ | $\sqrt{7}$ |
| $Co^{3+}$ $d^6$ $n_h = 4$ | | | |
| $(^5D\|\|W^{(0,1)}\|\|^5D)$ | $\sqrt{\dfrac{15}{2}}$ | $(^5D_4\|\|W^{(0,1)1}\|\|^5D_4)$ | $\dfrac{1}{2}\sqrt{3}$ |
| $(^5D\|\|W^{(0,2)}\|\|^5D)$ | $-5\sqrt{\dfrac{1}{2}}$ | $(^5D_4\|\|W^{(0,2)2}\|\|^5D_4)$ | $-\dfrac{3}{14}\sqrt{11}$ |
| $(^5D\|\|W^{(1,1)}\|\|^5D)$ | $\dfrac{3}{2}\sqrt{5}$ | $(^5D_4\|\|W^{(1,1)0}\|\|^5D_4)$ | $-\sqrt{\dfrac{1}{15}}$ |
| $(^5D\|\|W^{(1,0)}\|\|^5D)$ | $2\sqrt{15}$ | $(^5D_4\|\|W^{(1,0)1}\|\|^5D_4)$ | $\sqrt{6}$ |
| $(^5D\|\|W^{(1,2)}\|\|^5D)$ | $-\dfrac{5}{2}\sqrt{3}$ | $(^5D_4\|\|W^{(1,2)1}\|\|^5D_4)$ | $\sqrt{\dfrac{3}{70}}$ |
| $(^5D\|\|W^{(1,1)}\|\|^5D)$ | $\dfrac{3}{2}\sqrt{5}$ | $(^5D_4\|\|W^{(1,1)2}\|\|^5D_4)$ | $\sqrt{\dfrac{11}{42}}$ |
| $(^5D\|\|W^{(1,3)}\|\|^5D)$ | $\dfrac{1}{2}\sqrt{105}$ | $(^5D_4\|\|W^{(1,3)2}\|\|^5D_4)$ | $-\dfrac{3}{28}\sqrt{\dfrac{11}{7}}$ |

the primary and secondary x-rays, and the sign $\mp$ is dictated by the sign in $\bar{J} = \bar{l} \pm \frac{1}{2}$. The sign of the term $1/S$ is appropriate for $n_h \leqslant (2l + 1)$, and it is reversed for $n_h > (2l + 1)$. This dependence of the sign on $n_h$ stems from the value of an even-order unit tensor, in this case $W^{(1,1)}$, for a state and its conjugate, namely, for the two states $(\theta\|\|W^{(1,1)}\|\|\theta)$ has equal magnitudes and opposite signs.

The thermodynamic properties of the odd-rank contributions to the matrix element of $Z$ are sensitive to the existence of long-range magnetic order in the target sample, and feature in the circular dichroic signal. Taking $K = 1$ there are two values for $b$, namely $b = 0$ and $b = 2$. The reduced matrix element of $W^{(1,0)1}$ is found in (A.7); it is diagonal with respect to $\theta$, and $|J - 1| \leqslant J' \leqslant (J + 1)$. Hence, this term allows inelastic scattering to occur

**Table 1.** (Continued)

|  | $Ni^{3+}$ | $d^7$ | $n_h = 3$ |  |
| --- | --- | --- | --- | --- |
| $(^4F\|\|W^{(0,1)}\|\|^4F)$ | $2\sqrt{\dfrac{21}{5}}$ | $(^4F_{9/2}\|\|W^{(0,1)1}\|\|^4F_{9/2})$ | $\sqrt{\dfrac{11}{6}}$ |
| $(^4F\|\|W^{(0,2)}\|\|^4F)$ | $-2\sqrt{\dfrac{3}{5}}$ | $(^4F_{9/2}\|\|W^{(0,2)2}\|\|^4F_{9/2})$ | $-\dfrac{1}{2}\sqrt{\dfrac{11}{21}}$ |
| $(^4F\|\|W^{(1,1)}\|\|^4F)$ | $2\sqrt{7}$ | $(^4F_{9/2}\|\|W^{(1,1)0}\|\|^4F_{9/2})$ | $-\sqrt{\dfrac{1}{6}}$ |
| $(^4F\|\|W^{(1,0)}\|\|^4F)$ | $\sqrt{42}$ | $(^4F_{9/2}\|\|W^{(1,0)1}\|\|^4F_{9/2})$ | $\sqrt{\dfrac{11}{3}}$ |
| $(^4F\|\|W^{(1,2)}\|\|^4F)$ | $-2$ | $(^4F_{9/2}\|\|W^{(1,2)1}\|\|^4F_{9/2})$ | $\dfrac{1}{3}\sqrt{\dfrac{11}{105}}$ |
| $(^4F\|\|W^{(1,1)}\|\|^4F)$ | $2\sqrt{7}$ | $(^4F_{9/2}\|\|W^{(1,1)2}\|\|^4F_{9/2})$ | $\dfrac{1}{3}\sqrt{\dfrac{11}{2}}$ |
| $(^4F\|\|W^{(1,3)}\|\|^4F)$ | $-\sqrt{14}$ | $(^4F_{9/2}\|\|W^{(1,3)2}\|\|^4F_{9/2})$ | $\dfrac{1}{14}\sqrt{\dfrac{11}{3}}$ |

|  | $Cu^{3+}$ | $d^8$ | $n_h = 2$ |  |
| --- | --- | --- | --- | --- |
| $(^3F\|\|W^{(0,1)}\|\|^3F)$ | $3\sqrt{\dfrac{7}{5}}$ | $(^3F_4\|\|W^{(0,1)1}\|\|^3F_4)$ | $\dfrac{3}{4}\sqrt{3}$ |
| $(^3F\|\|W^{(0,2)}\|\|^3F)$ | $3\sqrt{\dfrac{1}{5}}$ | $(^3F_4\|\|W^{(0,2)2}\|\|^3F_4)$ | $\dfrac{3}{28}\sqrt{11}$ |
| $(^3F\|\|W^{(1,1)}\|\|^3F)$ | $3\sqrt{\dfrac{14}{5}}$ | $(^3F_4\|\|W^{(1,1)0}\|\|^3F_4)$ | $-\dfrac{1}{2}\sqrt{\dfrac{3}{5}}$ |
| $(^3F\|\|W^{(1,0)}\|\|^3F)$ | $2\sqrt{\dfrac{21}{5}}$ | $(^3F_4\|\|W^{(1,0)1}\|\|^3F_4)$ | $\sqrt{\dfrac{3}{2}}$ |
| $(^3F\|\|W^{(1,2)}\|\|^3F)$ | $3\sqrt{\dfrac{2}{5}}$ | $(^3F_4\|\|W^{(1,2)1}\|\|^3F_4)$ | $-\dfrac{1}{2}\sqrt{\dfrac{3}{70}}$ |
| $(^3F\|\|W^{(1,1)}\|\|^3F)$ | $3\sqrt{\dfrac{14}{5}}$ | $(^3F_4\|\|W^{(1,1)2}\|\|^3F_4)$ | $\dfrac{1}{2}\sqrt{\dfrac{33}{14}}$ |
| $(^3F\|\|W^{(1,3)}\|\|^3F)$ | $-3\sqrt{\dfrac{7}{5}}$ | $(^3F_4\|\|W^{(1,3)2}\|\|^3F_4)$ | $\dfrac{3}{28}\sqrt{\dfrac{11}{7}}$ |

|  | $Zn^{3+}$ | $d^9$ | $n_h = 1$ |  |
| --- | --- | --- | --- | --- |
| $(^2D\|\|W^{(0,1)}\|\|^2D)$ | $\sqrt{3}$ | $(^2D_{5/2}\|\|W^{(0,1)1}\|\|^2D_{5/2})$ | $\dfrac{1}{5}\sqrt{14}$ |
| $(^2D\|\|W^{(0,2)}\|\|^2D)$ | $\sqrt{5}$ | $(^2D_{5/2}\|\|W^{(0,2)2}\|\|^2D_{5/2})$ | $\dfrac{2}{5}\sqrt{3}$ |
| $(^2D\|\|W^{(1,1)}\|\|^2D)$ | $3$ | $(^2D_{5/2}\|\|W^{(1,1)0}\|\|^2D_{5/2})$ | $-\dfrac{1}{3}\sqrt{\dfrac{2}{5}}$ |
| $(^2D\|\|W^{(1,0)}\|\|^2D)$ | $\sqrt{3}$ | $(^2D_{5/2}\|\|W^{(1,0)1}\|\|^2D_{5/2})$ | $\dfrac{1}{5}\sqrt{7}$ |
| $(^2D\|\|W^{(1,2)}\|\|^2D)$ | $\sqrt{15}$ | $(^2D_{5/2}\|\|W^{(1,2)1}\|\|^2D_{5/2})$ | $-\dfrac{2}{5}\sqrt{\dfrac{1}{5}}$ |
| $(^2D\|\|W^{(1,1)}\|\|^2D)$ | $3$ | $(^2D_{5/2}\|\|W^{(1,1)2}\|\|^2D_{5/2})$ | $\dfrac{2}{15}\sqrt{14}$ |
| $(^2D\|\|W^{(1,3)}\|\|^2D)$ | $\sqrt{21}$ | $(^2D_{5/2}\|\|W^{(1,3)2}\|\|^2D_{5/2})$ | $-\dfrac{1}{5}\sqrt{\dfrac{3}{7}}$ |

**Table 1.** (Continued)

| $Ce^{3+}$ $f^1$ $n_h = 13$ | | | |
|---|---|---|---|
| $(^2F\|\|W^{(0,1)}\|\|^2F)$ | $\sqrt{3}$ | $(^2F_{5/2}\|\|W^{(0,1)1}\|\|^2F_{5/2})$ | $\frac{2}{7}\sqrt{5}$ |
| $(^2F\|\|W^{(0,2)}\|\|^2F)$ | $-\sqrt{5}$ | $(^2F_{5/2}\|\|W^{(0,2)2}\|\|^2F_{5/2})$ | $-\frac{3}{7}\sqrt{2}$ |
| $(^2F\|\|W^{(0,3)}\|\|^2F)$ | $\sqrt{7}$ | $(^2F_{5/2}\|\|W^{(0,3)3}\|\|^2F_{5/2})$ | $\frac{1}{7}\sqrt{15}$ |
| $(^2F\|\|W^{(0,4)}\|\|^2F)$ | $-3$ | $(^2F_{5/2}\|\|W^{(0,4)4}\|\|^2F_{5/2})$ | $-\frac{1}{7}\sqrt{11}$ |
| $(^2F\|\|W^{(1,1)}\|\|^2F)$ | $-3$ | $(^2F_{5/2}\|\|W^{(1,1)0}\|\|^2F_{5/2})$ | $-\frac{2}{3}\sqrt{\frac{1}{7}}$ |
| $(^2F\|\|W^{(1,0)}\|\|^2F)$ | $\sqrt{3}$ | $(^2F_{5/2}\|\|W^{(1,0)1}\|\|^2F_{5/2})$ | $-\frac{1}{7}\sqrt{5}$ |
| $(^2F\|\|W^{(1,2)}\|\|^2F)$ | $\sqrt{15}$ | $(^2F_{5/2}\|\|W^{(1,2)1}\|\|^2F_{5/2})$ | $\frac{2}{7}\sqrt{\frac{6}{5}}$ |
| $(^2F\|\|W^{(1,1)}\|\|^2F)$ | $-3$ | $(^2F_{5/2}\|\|W^{(1,1)2}\|\|^2F_{5/2})$ | $\frac{2}{21}\sqrt{5}$ |
| $(^2F\|\|W^{(1,3)}\|\|^2F)$ | $-\sqrt{21}$ | $(^2F_{5/2}\|\|W^{(1,3)2}\|\|^2F_{5/2})$ | $-\frac{3}{7}\sqrt{\frac{5}{7}}$ |
| $(^2F\|\|W^{(1,2)}\|\|^2F)$ | $\sqrt{15}$ | $(^2F_{5/2}\|\|W^{(1,2)3}\|\|^2F_{5/2})$ | $-\frac{1}{7}\sqrt{\frac{6}{5}}$ |
| $(^2F\|\|W^{(1,4)}\|\|^2F)$ | $3\sqrt{3}$ | $(^2F_{5/2}\|\|W^{(1,4)3}\|\|^2F_{5/2})$ | $\frac{2}{21}\sqrt{\frac{55}{3}}$ |
| $(^2F\|\|W^{(1,3)}\|\|^2F)$ | $-\sqrt{21}$ | $(^2F_{5/2}\|\|W^{(1,3)4}\|\|^2F_{5/2})$ | $\frac{2}{7}\sqrt{\frac{1}{7}}$ |
| $(^2F\|\|W^{(1,5)}\|\|^2F)$ | $-\sqrt{33}$ | $(^2F_{5/2}\|\|W^{(1,5)4}\|\|^2F_{5/2})$ | $-\frac{1}{7}\sqrt{10}$ |

| $Pr^{3+}$ $f^2$ $n_h = 12$ | | | |
|---|---|---|---|
| $(^3H\|\|W^{(0,1)}\|\|^3H)$ | $\frac{3}{2}\sqrt{\frac{55}{7}}$ | $(^3H_4\|\|W^{(0,1)1}\|\|^3H_4)$ | $3\sqrt{\frac{6}{35}}$ |
| $(^3H\|\|W^{(0,2)}\|\|^3H)$ | $-\frac{1}{2}\sqrt{\frac{715}{21}}$ | $(^3H_4\|\|W^{(0,2)2}\|\|^3H_4)$ | $-\frac{13}{5}\sqrt{\frac{2}{33}}$ |
| $(^3H\|\|W^{(0,3)}\|\|^3H)$ | $0$ | $(^3H_4\|\|W^{(0,3)3}\|\|^3H_4)$ | $0$ |
| $(^3H\|\|W^{(0,4)}\|\|^3H)$ | $\sqrt{\frac{78}{7}}$ | $(^3H_4\|\|W^{(0,4)4}\|\|^3H_4)$ | $\frac{1}{11}\sqrt{26}$ |
| $(^3H\|\|W^{(1,1)}\|\|^3H)$ | $-3\sqrt{\frac{55}{14}}$ | $(^3H_4\|\|W^{(1,1)0}\|\|^3H_4)$ | $-\sqrt{\frac{3}{14}}$ |
| $(^3H\|\|W^{(1,0)}\|\|^3H)$ | $2\sqrt{\frac{33}{7}}$ | $(^3H_4\|\|W^{(1,0)1}\|\|^3H_4)$ | $-2\sqrt{\frac{6}{35}}$ |
| $(^3H\|\|W^{(1,2)}\|\|^3H)$ | $\sqrt{\frac{715}{42}}$ | $(^3H_4\|\|W^{(1,2)1}\|\|^3H_4)$ | $\frac{26}{15}\sqrt{\frac{1}{35}}$ |
| $(^3H\|\|W^{(1,1)}\|\|^3H)$ | $-3\sqrt{\frac{55}{14}}$ | $(^3H_4\|\|W^{(1,1)2}\|\|^3H_4)$ | $2\sqrt{\frac{3}{55}}$ |
| $(^3H\|\|W^{(1,3)}\|\|^3H)$ | $0$ | $(^3H_4\|\|W^{(1,3)2}\|\|^3H_4)$ | $0$ |
| $(^3H\|\|W^{(1,2)}\|\|^3H)$ | $\sqrt{\frac{715}{42}}$ | $(^3H_4\|\|W^{(1,2)3}\|\|^3H_4)$ | $-\frac{13}{5}\sqrt{\frac{1}{165}}$ |
| $(^3H\|\|W^{(1,4)}\|\|^3H)$ | $-2\sqrt{\frac{39}{7}}$ | $(^3H_4\|\|W^{(1,4)3}\|\|^3H_4)$ | $-\frac{26}{33}\sqrt{\frac{2}{15}}$ |
| $(^3H\|\|W^{(1,3)}\|\|^3H)$ | $0$ | $(^3H_4\|\|W^{(1,3)4}\|\|^3H_4)$ | $0$ |
| $(^3H\|\|W^{(1,5)}\|\|^3H)$ | $\sqrt{\frac{429}{7}}$ | $(^3H_4\|\|W^{(1,5)4}\|\|^3H_4)$ | $\frac{2}{11}\sqrt{\frac{65}{11}}$ |

**Table 1.** (Continued)

| | Nd$^{3+}$  f$^3$  $n_h = 11$ | |
|---|---|---|
| $(^4I\|\|W^{(0,1)}\|\|^4I)$ | $\sqrt{39}$ | $(^4I_{9/2}\|\|W^{(0,1)1}\|\|^4I_{9/2})$ $\dfrac{1}{2}\sqrt{\dfrac{105}{11}}$ |
| $(^4I\|\|W^{(0,2)}\|\|^4I)$ | $-\sqrt{\dfrac{65}{33}}$ | $(^4I_{9/2}\|\|W^{(0,2)2}\|\|^4I_{9/2})$ $-\dfrac{5}{11}\sqrt{\dfrac{7}{22}}$ |
| $(^4I\|\|W^{(0,3)}\|\|^4I)$ | $-2\sqrt{\dfrac{91}{33}}$ | $(^4I_{9/2}\|\|W^{(0,3)3}\|\|^4I_{9/2})$ $-\dfrac{28}{11}\sqrt{\dfrac{5}{143}}$ |
| $(^4I\|\|W^{(0,4)}\|\|^4I)$ | $\dfrac{2}{11}\sqrt{221}$ | $(^4I_{9/2}\|\|W^{(0,4)4}\|\|^4I_{9/2})$ $\dfrac{68}{363}\sqrt{\dfrac{35}{13}}$ |
| $(^4I\|\|W^{(1,1)}\|\|^4I)$ | $-\sqrt{65}$ | $(^4I_{9/2}\|\|W^{(1,1)0}\|\|^4I_{9/2})$ $-\dfrac{1}{6}\sqrt{\dfrac{35}{3}}$ |
| $(^4I\|\|W^{(1,0)}\|\|^4I)$ | $\sqrt{\dfrac{390}{7}}$ | $(^4I_{9/2}\|\|W^{(1,0)1}\|\|^4I_{9/2})$ $-3\sqrt{\dfrac{15}{77}}$ |
| $(^4I\|\|W^{(1,2)}\|\|^4I)$ | $\dfrac{5}{3}\sqrt{\dfrac{13}{11}}$ | $(^4I_{9/2}\|\|W^{(1,2)1}\|\|^4I_{9/2})$ $\dfrac{1}{11}\sqrt{\dfrac{35}{22}}$ |
| $(^4I\|\|W^{(1,1)}\|\|^4I)$ | $-\sqrt{65}$ | $(^4I_{9/2}\|\|W^{(1,1)2}\|\|^4I_{9/2})$ $\dfrac{1}{3}\sqrt{\dfrac{35}{11}}$ |
| $(^4I\|\|W^{(1,3)}\|\|^4I)$ | $\dfrac{2}{3}\sqrt{\dfrac{455}{11}}$ | $(^4I_{9/2}\|\|W^{(1,3)2}\|\|^4I_{9/2})$ $\dfrac{4}{11}\sqrt{\dfrac{5}{11}}$ |
| $(^4I\|\|W^{(1,2)}\|\|^4I)$ | $\dfrac{5}{3}\sqrt{\dfrac{13}{11}}$ | $(^4I_{9/2}\|\|W^{(1,2)3}\|\|^4I_{9/2})$ $-\dfrac{7}{11}\sqrt{\dfrac{5}{286}}$ |
| $(^4I\|\|W^{(1,4)}\|\|^4I)$ | $-\dfrac{2}{11}\sqrt{\dfrac{1105}{3}}$ | $(^4I_{9/2}\|\|W^{(1,4)3}\|\|^4I_{9/2})$ $-\dfrac{952}{3267}\sqrt{\dfrac{5}{13}}$ |
| $(^4I\|\|W^{(1,3)}\|\|^4I)$ | $\dfrac{2}{3}\sqrt{\dfrac{455}{11}}$ | $(^4I_{9/2}\|\|W^{(1,3)4}\|\|^4I_{9/2})$ $-\dfrac{8}{11}\sqrt{\dfrac{5}{143}}$ |
| $(^4I\|\|W^{(1,5)}\|\|^4I)$ | $-\dfrac{1}{3}\sqrt{\dfrac{2210}{11}}$ | $(^4I_{9/2}\|\|W^{(1,5)4}\|\|^4I_{9/2})$ $-\dfrac{85}{121}\sqrt{\dfrac{14}{143}}$ |

between states $J$ and $J \pm 1$, and in the mean value of $f$ or $Z$ it will give contributions if the wave function contains admixtures of these manifolds. For the special case where $J = J'$ the reduced matrix element of $W^{(1,0)1}$ is very simple and the result is (A.8).

Turning to $W^{(1,2)1}$, we note that

$$(\theta J\|\sum_j \{3\hat{R}(\hat{R} \cdot s) - s\}_j\|\theta'J')$$

$$= \left\{ \frac{15}{(2l-1)(2l+3)} \right\}^{1/2} (l\|l\|l)(\theta J\|W^{(1,2)1}\|\theta'J')$$

$$= -(\theta J\|\mathbf{T}\|\theta'J') \tag{4.3}$$

where $\hat{R}$ is a unit position vector for an electron. This result is the basis of a discussion in the appendix which leads us to conclude that the thermal average value of the magnetic dipole operator is proportional to $\langle J_c \rangle$ multiplied by a factor that contains the right-hand side of (4.3). Following Carra *et al* (1993), it is usual to denote this value of the magnetic dipole operator by $-\langle T_c \rangle$.

The $9j$-symbol that accompanies $W^{(1,0)1}$ in $T(1; \bar{J})$ is proportional to a $6j$-symbol that can be evaluated analytically with a formula in Edmonds (1960). With $W^{(1,2)1}$ it is useful

**Table 1.** (Continued)

<table>
<tr><td colspan="4" align="center">Pm$^{3+}$  f$^4$  $n_h = 10$</td></tr>
<tr><td>$(^5I\|W^{(0,1)}\|^5I)$</td><td>$\frac{1}{2}\sqrt{195}$</td><td>$(^5I_4\|W^{(0,1)1}\|^5I_4)$</td><td>$\sqrt{\frac{21}{10}}$</td></tr>
<tr><td>$(^5I\|W^{(0,2)}\|^5I)$</td><td>$\frac{5}{2}\sqrt{\frac{13}{33}}$</td><td>$(^5I_4\|W^{(0,2)2}\|^5I_4)$</td><td>$\frac{7}{11}\sqrt{\frac{3}{22}}$</td></tr>
<tr><td>$(^5I\|W^{(0,3)}\|^5I)$</td><td>$-\sqrt{\frac{455}{33}}$</td><td>$(^5I_4\|W^{(0,3)3}\|^5I_4)$</td><td>$-\frac{14}{11}\sqrt{\frac{6}{55}}$</td></tr>
<tr><td>$(^5I\|W^{(0,4)}\|^5I)$</td><td>$-\frac{1}{11}\sqrt{1105}$</td><td>$(^5I_4\|W^{(0,4)4}\|^5I_4)$</td><td>$-\frac{238}{363}\sqrt{\frac{2}{13}}$</td></tr>
<tr><td>$(^5I\|W^{(1,1)}\|^5I)$</td><td>$-\frac{3}{2}\sqrt{\frac{65}{2}}$</td><td>$(^5I_4\|W^{(1,1)0}\|^5I_4)$</td><td>$-\frac{1}{2}\sqrt{\frac{7}{6}}$</td></tr>
<tr><td>$(^5I\|W^{(1,0)}\|^5I)$</td><td>$2\sqrt{\frac{195}{7}}$</td><td>$(^5I_4\|W^{(1,0)1}\|^5I_4)$</td><td>$-4\sqrt{\frac{6}{35}}$</td></tr>
<tr><td>$(^5I\|W^{(1,2)}\|^5I)$</td><td>$-\frac{5}{2}\sqrt{\frac{13}{22}}$</td><td>$(^5I_4\|W^{(1,2)1}\|^5I_4)$</td><td>$-\frac{1}{11}\sqrt{\frac{7}{5}}$</td></tr>
<tr><td>$(^5I\|W^{(1,1)}\|^5I)$</td><td>$-\frac{3}{2}\sqrt{\frac{65}{2}}$</td><td>$(^5I_4\|W^{(1,1)2}\|^5I_4)$</td><td>$7\sqrt{\frac{1}{165}}$</td></tr>
<tr><td>$(^5I\|W^{(1,3)}\|^5I)$</td><td>$\sqrt{\frac{455}{22}}$</td><td>$(^5I_4\|W^{(1,3)2}\|^5I_4)$</td><td>$\frac{4}{11}\sqrt{\frac{21}{55}}$</td></tr>
<tr><td>$(^5I\|W^{(1,2)}\|^5I)$</td><td>$-\frac{5}{2}\sqrt{\frac{13}{22}}$</td><td>$(^5I_4\|W^{(1,2)3}\|^5I_4)$</td><td>$\frac{7}{22}\sqrt{\frac{3}{55}}$</td></tr>
<tr><td>$(^5I\|W^{(1,4)}\|^5I)$</td><td>$\frac{1}{11}\sqrt{\frac{3315}{2}}$</td><td>$(^5I_4\|W^{(1,4)3}\|^5I_4)$</td><td>$\frac{476}{1089}\sqrt{\frac{2}{15}}$</td></tr>
<tr><td>$(^5I\|W^{(1,3)}\|^5I)$</td><td>$\sqrt{\frac{455}{22}}$</td><td>$(^5I_4\|W^{(1,3)4}\|^5I_4)$</td><td>$-\frac{4}{11}\sqrt{\frac{14}{143}}$</td></tr>
<tr><td>$(^5I\|W^{(1,5)}\|^5I)$</td><td>$-\frac{1}{2}\sqrt{\frac{1105}{11}}$</td><td>$(^5I_4\|W^{(1,5)4}\|^5I_4)$</td><td>$-\frac{119}{121}\sqrt{\frac{5}{143}}$</td></tr>
</table>

to exploit the result

$$\begin{Bmatrix} \bar{l} & \bar{l} & 1 \\ l & l & 2 \\ t & t & 1 \end{Bmatrix} = \frac{1}{2}\left(\frac{1}{30}\right)^{1/2}\left[(l\|l\|l)(\bar{l}\|\bar{l}\|\bar{l})\sqrt{(2l-1)(2l+3)t(t+1)(2t+1)}\right]^{-1}$$
$$\times\left[l(l+1)\{l(l+1)+2\bar{l}(\bar{l}+1)+2t(t+1)\}-3\{t(t+1)-\bar{l}(\bar{l}+1)\}^2\right].$$

(4.4)

Higher-rank $T(K\colon \bar{J})$s can contain reduced matrix elements of $W^{(a,b)}$ found in lower-rank tensors, e.g. $T(2\colon \bar{J})$ contains $W^{(1,1)}$, which we encountered in $T(0\colon \bar{J})$, and $W^{(1,3)}$. By and large, there is not too much that can be usefully added in the way of physical intuition to the meaning of the higher-order $W^{(a,b)}$s. Relations analogous to (4.1) and (4.3) can be found, using a little ingenuity, but they seem to have little value in extending our understanding about the physical properties of the valence electrons, simply because the relations involve complex combinations of electron operators. Instead, we refer the reader to table 1 which contains the reduced matrix elements $(\theta J\|W^{(1,b)K}\|\theta J)$ for the d$^n$ and f$^n$ configuration and values of $\theta = \nu SL$ and $J$ determined by Hund's rules. Table A1 contains all the 9$j$-symbols that accompany these reduced matrix elements in $(\theta J\|T(K\colon \bar{J})\|\theta J)$.

**Table 1.** (Continued)

| $Sm^{3+}$   $f^5$   $n_h = 9$ | | | |
|---|---|---|---|
| $(^6H\|\|W^{(0,1)}\|\|^6H)$ | $3\sqrt{\dfrac{55}{14}}$ | $(^6H_{5/2}\|\|W^{(0,1)1}\|\|^6H_{5/2})$ | $\dfrac{3}{7}\sqrt{5}$ |
| $(^6H\|\|W^{(0,2)}\|\|^6H)$ | $\sqrt{\dfrac{715}{42}}$ | $(^6H_{5/2}\|\|W^{(0,2)2}\|\|^6H_{5/2})$ | $\dfrac{13}{21}\sqrt{\dfrac{1}{2}}$ |
| $(^6H\|\|W^{(0,3)}\|\|^6H)$ | $0$ | $(^6H_{5/2}\|\|W^{(0,3)3}\|\|^6H_{5/2})$ | $0$ |
| $(^6H\|\|W^{(0,4)}\|\|^6H)$ | $-2\sqrt{\dfrac{39}{7}}$ | $(^6H_{5/2}\|\|W^{(0,4)4}\|\|^6H_{5/2})$ | $-\dfrac{13}{21}\sqrt{\dfrac{1}{11}}$ |
| $(^6H\|\|W^{(1,1)}\|\|^6H)$ | $-3\sqrt{\dfrac{11}{2}}$ | $(^6H_{5/2}\|\|W^{(1,1)0}\|\|^6H_{5/2})$ | $-\sqrt{\dfrac{1}{7}}$ |
| $(^6H\|\|W^{(1,0)}\|\|^6H)$ | $\sqrt{165}$ | $(^6H_{5/2}\|\|W^{(1,0)1}\|\|^6H_{5/2})$ | $-\dfrac{5}{7}\sqrt{5}$ |
| $(^6H\|\|W^{(1,2)}\|\|^6H)$ | $-\sqrt{\dfrac{143}{6}}$ | $(^6H_{5/2}\|\|W^{(1,2)1}\|\|^6H_{5/2})$ | $-\dfrac{13}{21}\sqrt{\dfrac{2}{15}}$ |
| $(^6H\|\|W^{(1,1)}\|\|^6H)$ | $-3\sqrt{\dfrac{11}{2}}$ | $(^6H_{5/2}\|\|W^{(1,1)2}\|\|^6H_{5/2})$ | $\dfrac{1}{7}\sqrt{5}$ |
| $(^6H\|\|W^{(1,3)}\|\|^6H)$ | $0$ | $(^6H_{5/2}\|\|W^{(1,3)2}\|\|^6H_{5/2})$ | $0$ |
| $(^6H\|\|W^{(1,2)}\|\|^6H)$ | $-\sqrt{\dfrac{143}{6}}$ | $(^6H_{5/2}\|\|W^{(1,2)3}\|\|^6H_{5/2})$ | $\dfrac{13}{21}\sqrt{\dfrac{1}{30}}$ |
| $(^6H\|\|W^{(1,4)}\|\|^6H)$ | $2\sqrt{\dfrac{39}{5}}$ | $(^6H_{5/2}\|\|W^{(1,4)3}\|\|^6H_{5/2})$ | $\dfrac{26}{63}\sqrt{\dfrac{5}{33}}$ |
| $(^6H\|\|W^{(1,3)}\|\|^6H)$ | $0$ | $(^6H_{5/2}\|\|W^{(1,3)4}\|\|^6H_{5/2})$ | $0$ |
| $(^6H\|\|W^{(1,5)}\|\|^6H)$ | $\sqrt{\dfrac{429}{5}}$ | $(^6H_{5/2}\|\|W^{(1,5)4}\|\|^6H_{5/2})$ | $\dfrac{13}{231}\sqrt{10}$ |
| $Eu^{3+}$   $f^6$   $n_h = 8$ | | | |
| $(^7F\|\|W^{(1,1)}\|\|^7F)$ | $-\sqrt{14}$ | $(^7F_0\|\|W^{(1,1)0}\|\|^7F_0)$ | $-\dfrac{1}{3}\sqrt{\dfrac{2}{21}}$ |
| $Gd^{3+}$   $f^7$   $n_h = 7$ | | | |
| $(^8S\|\|W^{(1,0)}\|\|^8S)$ | $6$ | $(^8S_{7/2}\|\|W^{(1,0)1}\|\|^8S_{7/2})$ | $2\sqrt{3}$ |

## 5. Dichroic signals

By way of illustrations, we report two examples of the use of (3.4) to calculate the circular dichroic signal. First, we consider E1 events and give a general expression for the signal in terms of atomic variables, and, secondly, we report the value of the signal for E2 events and a valence shell $f^9$ with a pure Hund-rules ground state.

The dichroic signal is defined to be the difference in the attenuation coefficient evaluated for two values of the mean helicity of the primary beam of equal magnitude and opposite sign. In the notation of Lovesey and Collins (1996), which is used here, the mean helicity is $P_2$, the second parameter in the Stokes vector that describes the states of polarization in a beam of x-rays. A look at equation (2.4) for the attenuation coefficient reveals that it is sufficient to study the quantity

$$\Delta Z = \langle Z(P_2)\rangle_0 - \langle Z(-P_2)\rangle_0. \tag{5.1}$$

For E1 absorption events $\langle Z\rangle_0$ contains $\varepsilon' \times \varepsilon$ averaged with respect to states of polarization in the primary beam and evaluated for the forward-scattering geometry. The result is given

**Table 1.** (Continued)

| | $Tb^{3+}$ $f^8$ $n_h = 6$ | | |
|---|---|---|---|
| $(^7F||W^{(0,1)}||^7F)$ | $\sqrt{\dfrac{21}{2}}$ | $(^7F_6||W^{(0,1)1}||^7F_6)$ | $\dfrac{1}{4}\sqrt{13}$ |
| $(^7F||W^{(0,2)}||^7F)$ | $-\sqrt{\dfrac{35}{2}}$ | $(^7F_6||W^{(0,2)2}||^7F_6)$ | $-\dfrac{5}{4}\sqrt{\dfrac{13}{33}}$ |
| $(^7F||W^{(0,3)}||^7F)$ | $7\sqrt{\dfrac{1}{2}}$ | $(^7F_6||W^{(0,3)3}||^7F_6)$ | $\sqrt{\dfrac{13}{33}}$ |
| $(^7F||W^{(0,4)}||^7F)$ | $-3\sqrt{\dfrac{7}{2}}$ | $(^7F_6||W^{(0,4)4}||^7F_6)$ | $-\dfrac{1}{33}\sqrt{221}$ |
| $(^7F||W^{(1,1)}||^7F)$ | $\sqrt{14}$ | $(^7F_6||W^{(1,1)0}||^7F_6)$ | $-\dfrac{1}{2}\sqrt{\dfrac{13}{42}}$ |
| $(^7F||W^{(1,0)}||^7F)$ | $2\sqrt{42}$ | $(^7F_6||W^{(1,0)1}||^7F_6)$ | $\sqrt{13}$ |
| $(^7F||W^{(1,2)}||^7F)$ | $-\sqrt{\dfrac{70}{3}}$ | $(^7F_6||W^{(1,2)1}||^7F_6)$ | $\dfrac{1}{6}\sqrt{\dfrac{13}{6}}$ |
| $(^7F||W^{(1,1)}||^7F)$ | $\sqrt{14}$ | $(^7F_6||W^{(1,1)2}||^7F_6)$ | $\dfrac{1}{2}\sqrt{\dfrac{65}{66}}$ |
| $(^7F||W^{(1,3)}||^7F)$ | $7\sqrt{\dfrac{2}{3}}$ | $(^7F_6||W^{(1,3)2}||^7F_6)$ | $-\dfrac{1}{2}\sqrt{\dfrac{65}{462}}$ |
| $(^7F||W^{(1,2)}||^7F)$ | $-\sqrt{\dfrac{70}{3}}$ | $(^7F_6||W^{(1,2)3}||^7F_6)$ | $-\sqrt{\dfrac{13}{66}}$ |
| $(^7F||W^{(1,4)}||^7F)$ | $-\sqrt{42}$ | $(^7F_6||W^{(1,4)3}||^7F_6)$ | $\dfrac{2}{33}\sqrt{\dfrac{13}{3}}$ |
| $(^7F||W^{(1,3)}||^7F)$ | $7\sqrt{\dfrac{2}{3}}$ | $(^7F_6||W^{(1,3)4}||^7F_6)$ | $\dfrac{2}{9}\sqrt{\dfrac{221}{77}}$ |
| $(^7F||W^{(1,5)}||^7F)$ | $\sqrt{\dfrac{154}{3}}$ | $(^7F_6||W^{(1,5)4}||^7F_6)$ | $-\dfrac{1}{99}\sqrt{\dfrac{1105}{22}}$ |

in paper I, and it is $iP_2\hat{q}$ where $\hat{q}$ is a unit vector in the direction of propagation of the primary beam. Using this result, and (3.4) to evaluate the matrix element (3.1), we arrive at

$$\Delta Z = \frac{-\langle l|R|l-1\rangle^2}{2(4l^2-1)} P_2\hat{q} \cdot \langle J\rangle \Bigg\{ (2-g)(2\bar{J}+1) \pm \frac{4}{3}(l-1)$$
$$\times \left[ l(g-1) + \frac{(2l+3)}{(J||J||J)}(\theta J||\mathbf{T}||\theta J) \right] \Bigg\}. \tag{5.2}$$

Here, $\bar{J} = \bar{l} \pm \frac{1}{2}$, and the reduced matrix element of $\mathbf{T}$ is defined in (4.3). In arriving at (5.2) we have assumed that the wave functions used to calculate the mean value of $Z$ are drawn from one $J$-manifold, which then permits the use of an operator equivalent. Note that the result (5.2) comes solely from the tensor of rank one, and the temperature dependence is that of the magnetic moment.

The coefficients of $\langle L\rangle$, $\langle S\rangle$ and the magnetic dipole operator inside curly brackets in (5.2) agree with the values reported by Carra *et al* (1993); see, also, Ankudinov and Rehr (1995). This finding implies that the physical picture behind our scattering length is the same as that in the calculation, specific to the dichroic sum rule, performed by Carra *et al*. In this connection, also note that our idealized scattering length reproduces the sum rule for dichroic signals due to Thole *et al* (1992).

As a final topic, we consider the E2 dichroic signal for the valence shell configuration

**Table 1.** (Continued)

| | | | |
|---|---|---|---|
| | | $Dy^{3+}$   $f^9$   $n_h = 5$ | |
| $(^6H\|\|W^{(0,1)}\|\|^6H)$ | $3\sqrt{\dfrac{55}{14}}$ | $(^6H_{15/2}\|\|W^{(0,1)1}\|\|^6H_{15/2})$ | $\dfrac{1}{3}\sqrt{\dfrac{170}{7}}$ |
| $(^6H\|\|W^{(0,2)}\|\|^6H)$ | $-\sqrt{\dfrac{715}{42}}$ | $(^6H_{15/2}\|\|W^{(0,2)2}\|\|^6H_{15/2})$ | $-\dfrac{1}{7}\sqrt{34}$ |
| $(^6H\|\|W^{(0,3)}\|\|^6H)$ | $0$ | $(^6H_{15/2}\|\|W^{(0,3)3}\|\|^6H_{15/2})$ | $0$ |
| $(^6H\|\|W^{(0,4)}\|\|^6H)$ | $2\sqrt{\dfrac{39}{7}}$ | $(^6H_{15/2}\|\|W^{(0,4)4}\|\|^6H_{15/2})$ | $\dfrac{8}{21}\sqrt{\dfrac{323}{143}}$ |
| $(^6H\|\|W^{(1,1)}\|\|^6H)$ | $3\sqrt{\dfrac{11}{2}}$ | $(^6H_{15/2}\|\|W^{(1,1)0}\|\|^6H_{15/2})$ | $-\dfrac{5}{3}\sqrt{\dfrac{2}{21}}$ |
| $(^6H\|\|W^{(1,0)}\|\|^6H)$ | $\sqrt{165}$ | $(^6H_{15/2}\|\|W^{(1,0)1}\|\|^6H_{15/2})$ | $\dfrac{2}{3}\sqrt{\dfrac{170}{7}}$ |
| $(^6H\|\|W^{(1,2)}\|\|^6H)$ | $-\sqrt{\dfrac{143}{6}}$ | $(^6H_{15/2}\|\|W^{(1,2)1}\|\|^6H_{15/2})$ | $\dfrac{2}{3}\sqrt{\dfrac{17}{105}}$ |
| $(^6H\|\|W^{(1,1)}\|\|^6H)$ | $3\sqrt{\dfrac{11}{2}}$ | $(^6H_{15/2}\|\|W^{(1,1)2}\|\|^6H_{15/2})$ | $\dfrac{2}{21}\sqrt{85}$ |
| $(^6H\|\|W^{(1,3)}\|\|^6H)$ | $0$ | $(^6H_{15/2}\|\|W^{(1,3)2}\|\|^6H_{15/2})$ | $0$ |
| $(^6H\|\|W^{(1,2)}\|\|^6H)$ | $-\sqrt{\dfrac{143}{6}}$ | $(^6H_{15/2}\|\|W^{(1,2)3}\|\|^6H_{15/2})$ | $-\dfrac{1}{7}\sqrt{\dfrac{646}{65}}$ |
| $(^6H\|\|W^{(1,4)}\|\|^6H)$ | $2\sqrt{\dfrac{39}{5}}$ | $(^6H_{15/2}\|\|W^{(1,4)3}\|\|^6H_{15/2})$ | $-\dfrac{16}{63}\sqrt{\dfrac{323}{715}}$ |
| $(^6H\|\|W^{(1,3)}\|\|^6H)$ | $0$ | $(^6H_{15/2}\|\|W^{(1,3)4}\|\|^6H_{15/2})$ | $0$ |
| $(^6H\|\|W^{(1,5)}\|\|^6H)$ | $-\sqrt{\dfrac{429}{5}}$ | $(^6H_{15/2}\|\|W^{(1,5)4}\|\|^6H_{15/2})$ | $\dfrac{1}{77}\sqrt{\dfrac{3230}{13}}$ |

$f^9$, $^6H_{15/2}$, for which $g = 4/3$, and $\bar{l} = l - t = 1$. This configuration is appropriate for $Dy^{3+}$, and the E2 dichroic signal of dysprosium has been measured by Lang *et al* (1995).

The appropriate expression for the matrix element of $Z$ in terms of the reduced matrix element of $T(K: \bar{J})$ is found in paper II. For the case in hand,

$$\Phi = \frac{3}{10}\{q\langle l|R^2|l-2\rangle\}^2$$

and we use entries in tables 1 and A1 to evaluate the right-hand side of (3.4). The rank-one contribution to $\Delta Z$ is ($K = 1$)

$$\Delta Z = -(\Phi P_2 \hat{q} \cdot \langle J\rangle/945)\left\{2\bar{J} + 1 \pm \frac{6}{5}\right\}$$

where the $\pm$ sign prefaces the contribution made by the spin-dependent part of the scattering length, and the choice of sign goes with $\bar{J} = \bar{l} \pm 1/2 = 3/2$ or $1/2$. Evidently, the rank-one contribution to the dichroic signal is largest at the edge with $\bar{J} = \frac{3}{2}$. The term in the rank-three contribution with $a = 0$ is zero. (This result is found for $f^n$ with $n = 2, 5, 9$ and $12$.) In consequence, the rank-three contribution to the dichroic signal for $Dy^{3+}$, in the ground state determined by Hund's rules, arises solely from the spin-dependent contribution to the matrix element of $Z$. We find ($K = 3$)

$$\Delta Z = \pm 0.059\Phi\mathbf{H}^{(3)} \cdot \langle \mathbf{I}^{(3)}\rangle.$$

The seven spherical components of $\mathbf{H}^{(3)}$ are given in paper II, and $\mathbf{I}^{(3)}$ has components

**Table 1.** (Continued)

| Ho$^{3+}$  f$^{10}$  $n_h = 4$ | | | |
|---|---|---|---|
| $(^5\text{I}\|W^{(0,1)}\|^5\text{I})$ | $\frac{1}{2}\sqrt{195}$ | $(^5\text{I}_8\|W^{(0,1)1}\|^5\text{I}_8)$ | $\frac{3}{4}\sqrt{\frac{51}{7}}$ |
| $(^5\text{I}\|W^{(0,2)}\|^5\text{I})$ | $-\frac{5}{2}\sqrt{\frac{13}{33}}$ | $(^5\text{I}_8\|W^{(0,2)2}\|^5\text{I}_8)$ | $-\frac{1}{20}\sqrt{\frac{323}{7}}$ |
| $(^5\text{I}\|W^{(0,3)}\|^5\text{I})$ | $-\sqrt{\frac{455}{33}}$ | $(^5\text{I}_8\|W^{(0,3)3}\|^5\text{I}_8)$ | $-\frac{1}{28}\sqrt{323}$ |
| $(^5\text{I}\|W^{(0,4)}\|^5\text{I})$ | $\frac{1}{11}\sqrt{1105}$ | $(^5\text{I}_8\|W^{(0,4)4}\|^5\text{I}_8)$ | $\frac{3}{4}\sqrt{\frac{323}{1001}}$ |
| $(^5\text{I}\|W^{(1,1)}\|^5\text{I})$ | $\frac{3}{2}\sqrt{\frac{65}{2}}$ | $(^5\text{I}_8\|W^{(1,1)0}\|^5\text{I}_8)$ | $-\sqrt{\frac{17}{42}}$ |
| $(^5\text{I}\|W^{(1,0)}\|^5\text{I})$ | $2\sqrt{\frac{195}{7}}$ | $(^5\text{I}_8\|W^{(1,0)1}\|^5\text{I}_8)$ | $\sqrt{\frac{51}{7}}$ |
| $(^5\text{I}\|W^{(1,2)}\|^5\text{I})$ | $-\frac{5}{2}\sqrt{\frac{13}{22}}$ | $(^5\text{I}_8\|W^{(1,2)1}\|^5\text{I}_8)$ | $\frac{1}{10}\sqrt{\frac{17}{14}}$ |
| $(^5\text{I}\|W^{(1,1)}\|^5\text{I})$ | $\frac{3}{2}\sqrt{\frac{65}{2}}$ | $(^5\text{I}_8\|W^{(1,1)2}\|^5\text{I}_8)$ | $\frac{1}{2}\sqrt{\frac{323}{70}}$ |
| $(^5\text{I}\|W^{(1,3)}\|^5\text{I})$ | $-\sqrt{\frac{455}{22}}$ | $(^5\text{I}_8\|W^{(1,3)2}\|^5\text{I}_8)$ | $\frac{1}{28}\sqrt{\frac{323}{10}}$ |
| $(^5\text{I}\|W^{(1,2)}\|^5\text{I})$ | $-\frac{5}{2}\sqrt{\frac{13}{22}}$ | $(^5\text{I}_8\|W^{(1,2)3}\|^5\text{I}_8)$ | $-\frac{1}{70}\sqrt{\frac{323}{2}}$ |
| $(^5\text{I}\|W^{(1,4)}\|^5\text{I})$ | $\frac{1}{11}\sqrt{\frac{3315}{2}}$ | $(^5\text{I}_8\|W^{(1,4)3}\|^5\text{I}_8)$ | $-\frac{1}{42}\sqrt{\frac{323}{11}}$ |
| $(^5\text{I}\|W^{(1,3)}\|^5\text{I})$ | $-\sqrt{\frac{455}{22}}$ | $(^5\text{I}_8\|W^{(1,3)4}\|^5\text{I}_8)$ | $-\frac{1}{14}\sqrt{\frac{323}{13}}$ |
| $(^5\text{I}\|W^{(1,5)}\|^5\text{I})$ | $\frac{1}{2}\sqrt{\frac{1105}{11}}$ | $(^5\text{I}_8\|W^{(1,5)4}\|^5\text{I}_8)$ | $-\frac{1}{22}\sqrt{\frac{1615}{182}}$ |

defined by

$$I_{m_0}^{(3)} = (-1)^{J-M}\begin{pmatrix} J & 3 & J \\ -M & m_0 & M' \end{pmatrix}.$$

For the special case in which the wave function of the electrons in the valence shell has a spatial symmetry so high that mean values of $\mathbf{I}^{(3)}$ with $m_0 = M - M' \neq 0$ are zero it is convenient to use for $\langle I_0^{(3)}\rangle$ the octupole operator equivalent given in paper II. Continuing the calculation for this special case, the total E2 dichroic signal for Dy$^{3+}$ is then ($K = 1$ and 3)

$$\Delta Z = -(\Phi P_2 \hat{q}_c/945)\left\{\langle J_c\rangle\left(2\bar{J} + 1 \pm \frac{6}{5}\right) \mp \left\langle J_c\left\{5J_c^2 - \frac{761}{4}\right\}\right\rangle [(5\hat{q}_c^2 - 3)/455]\right\}. \quad (5.3)$$

Here, the magnetic quantization axis is labelled by $c$ and $\hat{q}_c$ is the projection of the unit vector $\hat{q}$ on this axis. Note that for a saturated magnetic atom the octupole moment has the value

$$\left(\frac{1}{455}\right)\left\langle J_c\left\{5J_c^2 - \frac{761}{4}\right\}\right\rangle = 3/2$$

and this is to be compared to the corresponding value of the magnetic moment $\langle J_c\rangle = 15/2$.

**Table 1.** (Continued)

|  | Er$^{3+}$  f$^{11}$  $n_h = 3$ |  |  |
|---|---|---|---|
| $(^4I||W^{(0,1)}||^4I)$ | $\sqrt{39}$ | $(^4I_{15/2}||W^{(0,1)1}||^4I_{15/2})$ | $2\sqrt{\dfrac{34}{35}}$ |
| $(^4I||W^{(0,2)}||^4I)$ | $\sqrt{\dfrac{65}{33}}$ | $(^4I_{15/2}||W^{(0,2)2}||^4I_{15/2})$ | $\dfrac{2}{35}\sqrt{34}$ |
| $(^4I||W^{(0,3)}||^4I)$ | $-2\sqrt{\dfrac{91}{33}}$ | $(^4I_{15/2}||W^{(0,3)3}||^4I_{15/2})$ | $-\dfrac{2}{7}\sqrt{\dfrac{323}{65}}$ |
| $(^4I||W^{(0,4)}||^4I)$ | $-\dfrac{2}{11}\sqrt{221}$ | $(^4I_{15/2}||W^{(0,4)4}||^4I_{15/2})$ | $-\dfrac{2}{7}\sqrt{\dfrac{323}{143}}$ |
| $(^4I||W^{(1,1)}||^4I)$ | $\sqrt{65}$ | $(^4I_{15/2}||W^{(1,1)0}||^4I_{15/2})$ | $-2\sqrt{\dfrac{2}{21}}$ |
| $(^4I||W^{(1,0)}||^4I)$ | $\sqrt{\dfrac{390}{7}}$ | $(^4I_{15/2}||W^{(1,0)1}||^4I_{15/2})$ | $2\sqrt{\dfrac{34}{35}}$ |
| $(^4I||W^{(1,2)}||^4I)$ | $\dfrac{5}{3}\sqrt{\dfrac{13}{11}}$ | $(^4I_{15/2}||W^{(1,2)1}||^4I_{15/2})$ | $-\dfrac{4}{15}\sqrt{\dfrac{17}{105}}$ |
| $(^4I||W^{(1,1)}||^4I)$ | $\sqrt{65}$ | $(^4I_{15/2}||W^{(1,1)2}||^4I_{15/2})$ | $\dfrac{4}{7}\sqrt{\dfrac{17}{5}}$ |
| $(^4I||W^{(1,3)}||^4I)$ | $-\dfrac{2}{3}\sqrt{\dfrac{455}{11}}$ | $(^4I_{15/2}||W^{(1,3)2}||^4I_{15/2})$ | $\dfrac{2}{7}\sqrt{\dfrac{17}{35}}$ |
| $(^4I||W^{(1,2)}||^4I)$ | $\dfrac{5}{3}\sqrt{\dfrac{13}{11}}$ | $(^4I_{15/2}||W^{(1,2)3}||^4I_{15/2})$ | $\dfrac{2}{35}\sqrt{\dfrac{646}{65}}$ |
| $(^4I||W^{(1,4)}||^4I)$ | $-\dfrac{2}{11}\sqrt{\dfrac{1105}{3}}$ | $(^4I_{15/2}||W^{(1,4)3}||^4I_{15/2})$ | $\dfrac{4}{21}\sqrt{\dfrac{323}{715}}$ |
| $(^4I||W^{(1,3)}||^4I)$ | $-\dfrac{2}{3}\sqrt{\dfrac{455}{11}}$ | $(^4I_{15/2}||W^{(1,3)4}||^4I_{15/2})$ | $-\dfrac{4}{21}\sqrt{\dfrac{323}{91}}$ |
| $(^4I||W^{(1,5)}||^4I)$ | $\dfrac{1}{3}\sqrt{\dfrac{2210}{11}}$ | $(^4I_{15/2}||W^{(1,5)4}||^4I_{15/2})$ | $-\dfrac{2}{231}\sqrt{\dfrac{3230}{13}}$ |

## 6. Comments

It has been demonstrated that the information in the proposed resonant scattering length not present in the idealized scattering length is related to the spins of the electrons in the valence shell of the magnetic atom. The idealized scattering length provides information on the number of holes in the shell and its orbital properties. However, in these matters it should be borne in mind that the difference between spin and orbital contributions to the resonant scattering length depends on the representation of the atomic variables, e.g. for a simple atomic wave function the thermodynamic quantities are magnetic multipoles and one uses relations like $\langle S \rangle = (g-1)\langle J \rangle$ and $\langle L \rangle = (2-g)\langle J \rangle$ to convey the physical origin of contributions to the scattering length. We have illustrated this point in section 5 in a treatment of the E2 circular dichroic signal for Dy$^{3+}$. The result, (5.3), contains two multipoles, of ranks one and three, created with $J$ and there are no explicit references to spin or orbital operators.

The formulation presented here, and in papers I and II, provides a framework for the interpretation of measured signals. In applying it to a particular measurement, on a magnetic material, the first step is to create a realistic wave function for the electrons in the valence shell, often a major task and the source of the input of much of the information on the chemical and physical properties of the target sample. Atomic states derived from the

**Table 1.** (Continued)

|  | Tm$^{3+}$  f$^{12}$  $n_h = 2$ |  |  |
|---|---|---|---|
| $({}^3H||W^{(0,1)}||{}^3H)$ | $\dfrac{3}{2}\sqrt{\dfrac{55}{7}}$ | $({}^3H_6||W^{(0,1)1}||{}^3H_6)$ | $\dfrac{5}{12}\sqrt{13}$ |
| $({}^3H||W^{(0,2)}||{}^3H)$ | $\dfrac{1}{2}\sqrt{\dfrac{715}{21}}$ | $({}^3H_6||W^{(0,2)2}||{}^3H_6)$ | $\dfrac{5}{4}\sqrt{\dfrac{13}{33}}$ |
| $({}^3H||W^{(0,3)}||{}^3H)$ | $0$ | $({}^3H_6||W^{(0,3)3}||{}^3H_6)$ | $0$ |
| $({}^3H||W^{(0,4)}||{}^3H)$ | $-\sqrt{\dfrac{78}{7}}$ | $({}^3H_6||W^{(0,4)4}||{}^3H_6)$ | $-\dfrac{4}{99}\sqrt{221}$ |
| $({}^3H||W^{(1,1)}||{}^3H)$ | $3\sqrt{\dfrac{55}{14}}$ | $({}^3H_6||W^{(1,1)0}||{}^3H_6)$ | $-\dfrac{5}{6}\sqrt{\dfrac{13}{42}}$ |
| $({}^3H||W^{(1,0)}||{}^3H)$ | $2\sqrt{\dfrac{33}{7}}$ | $({}^3H_6||W^{(1,0)1}||{}^3H_6)$ | $\dfrac{1}{3}\sqrt{13}$ |
| $({}^3H||W^{(1,2)}||{}^3H)$ | $\sqrt{\dfrac{715}{42}}$ | $({}^3H_6||W^{(1,2)1}||{}^3H_6)$ | $-\dfrac{1}{6}\sqrt{\dfrac{13}{6}}$ |
| $({}^3H||W^{(1,1)}||{}^3H)$ | $3\sqrt{\dfrac{55}{14}}$ | $({}^3H_6||W^{(1,1)2}||{}^3H_6)$ | $\dfrac{5}{6}\sqrt{\dfrac{65}{66}}$ |
| $({}^3H||W^{(1,3)}||{}^3H)$ | $0$ | $({}^3H_6||W^{(1,3)2}||{}^3H_6)$ | $0$ |
| $({}^3H||W^{(1,2)}||{}^3H)$ | $\sqrt{\dfrac{715}{42}}$ | $({}^3H_6||W^{(1,2)3}||{}^3H_6)$ | $\sqrt{\dfrac{13}{66}}$ |
| $({}^3H||W^{(1,4)}||{}^3H)$ | $-2\sqrt{\dfrac{39}{7}}$ | $({}^3H_6||W^{(1,4)3}||{}^3H_6)$ | $\dfrac{8}{99}\sqrt{\dfrac{13}{3}}$ |
| $({}^3H||W^{(1,3)}||{}^3H)$ | $0$ | $({}^3H_6||W^{(1,3)4}||{}^3H_6)$ | $0$ |
| $({}^3H||W^{(1,5)}||{}^3H)$ | $-\sqrt{\dfrac{429}{7}}$ | $({}^3H_6||W^{(1,5)4}||{}^3H_6)$ | $\dfrac{1}{33}\sqrt{\dfrac{1105}{22}}$ |

application of Hund's rules are likely to be a guide, at best, to observed features.

There is an analogue to resonance-enhanced x-ray scattering in the scattering of a beam of neutrons by a sample of condensed matter. In this instance, the resonance process is provided by compound states of nuclei, and the information obtained from an interpretation of the scattered signal relates to the structures and motions of molecules in the sample (Trammell 1984).

## Acknowledgments

## Appendix

Here we bring together some information on the reduced matrix element $(\theta J||W^{(a,b)K}||\theta' J')$ that appears in $(\theta J||T(K:\bar{J})||\theta' J')$ from which our matrix element of the resonant scattering length is constructed. The label $\theta = \nu SL$ where $\nu$ is the seniority quantum number. We adopt the definition of the reduced matrix element proposed by Judd (1963); in this case, $(\theta J||W^{(a,b)K}||\theta' J')$ is proportional to a second reduced matrix element, $(\theta||W^{(a,b)}||\theta')$, that is of the type studied by Racah (1943). The proportionality constant carries the dependence

**Table 1.** (Continued)

| | Yb$^{3+}$   f$^{13}$   $n_h = 1$ | |
|---|---|---|
| $(^2\text{F}||W^{(0,1)}||^2\text{F})$ | $\sqrt{3}$ | $(^2\text{F}_{7/2}||W^{(0,1)1}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(0,2)}||^2\text{F})$ | $\sqrt{5}$ | $(^2\text{F}_{7/2}||W^{(0,2)2}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(0,3)}||^2\text{F})$ | $\sqrt{7}$ | $(^2\text{F}_{7/2}||W^{(0,3)3}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(0,4)}||^2\text{F})$ | $3$ | $(^2\text{F}_{7/2}||W^{(0,4)4}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,1)}||^2\text{F})$ | $3$ | $(^2\text{F}_{7/2}||W^{(1,1)0}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,0)}||^2\text{F})$ | $\sqrt{3}$ | $(^2\text{F}_{7/2}||W^{(1,0)1}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,2)}||^2\text{F})$ | $\sqrt{15}$ | $(^2\text{F}_{7/2}||W^{(1,2)1}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,1)}||^2\text{F})$ | $3$ | $(^2\text{F}_{7/2}||W^{(1,1)2}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,3)}||^2\text{F})$ | $\sqrt{21}$ | $(^2\text{F}_{7/2}||W^{(1,3)2}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,2)}||^2\text{F})$ | $\sqrt{15}$ | $(^2\text{F}_{7/2}||W^{(1,2)3}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,4)}||^2\text{F})$ | $3\sqrt{3}$ | $(^2\text{F}_{7/2}||W^{(1,4)3}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,3)}||^2\text{F})$ | $\sqrt{21}$ | $(^2\text{F}_{7/2}||W^{(1,3)4}||^2\text{F}_{7/2})$ |
| $(^2\text{F}||W^{(1,5)}||^2\text{F})$ | $\sqrt{33}$ | $(^2\text{F}_{7/2}||W^{(1,5)4}||^2\text{F}_{7/2})$ |

Values in right column:
$\frac{3}{7}\sqrt{3}$;
$\frac{5}{7}$;
$\frac{1}{7}\sqrt{22}$;
$\frac{3}{7}\sqrt{2}$;
$-\sqrt{\frac{1}{21}}$;
$\frac{2}{7}\sqrt{3}$;
$-\frac{1}{7}\sqrt{2}$;
$\frac{1}{7}\sqrt{10}$;
$-\frac{1}{7}\sqrt{\frac{10}{7}}$;
$\frac{1}{7}\sqrt{11}$;
$-\frac{2}{21}\sqrt{2}$;
$\frac{2}{7}\sqrt{\frac{22}{7}}$;
$-\frac{1}{7}\sqrt{\frac{5}{11}}$

of $(\theta J||W^{(a,b)K}||\theta' J')$ on $J$ and $J'$. The indices $a$ and $b$ refer to different atomic variables, and with Judd's notation and phase convention the index $a$ is the rank of the spin variable and $b$ is the rank of the orbital variable. The second type of reduced matrix element is built from fractional parentage coefficients. In one sense, the $(\theta||W^{(a,b)}||\theta')$ are quantities characteristic of the $n$-electron configuration $l^n$, and they satisfy useful symmetry relations (Racah 1943). The symmetry with respect to a state and its conjugate (both states have the same quantum numbers) is grouped according to whether $a + b$ is an even or odd integer, and it is summarized in paper I.

In the following material we use the angular momentum coupling scheme of Russell and Saunders. Papers I and II contain results for this scheme and the $jj$-coupling scheme. Applications of the latter to properties of the dichroic signal are also explored by van der Laan and Thole (1996).

First of all,

$$(\theta J||W^{(a,b)K}||\theta' J') = \left\{ \frac{(2J + 1)(2K + 1)(2J' + 1)}{(2a + 1)(2b + 1)} \right\}^{1/2} \begin{Bmatrix} S & S' & a \\ L & L' & b \\ J & J' & K \end{Bmatrix} (\theta||W^{(a,b)}||\theta').$$

(A.1)

For $a = 0$ or $b = 0$ the $9j$-symbol is proportional to a $6j$-symbol. Properties of $nj$-symbols are reviewed by Rotenberg *et al* (1959), Edmonds (1960) and Judd (1963), among others.

**Table A1.** Values of the $9j$-symbols needed in the reduced matrix element (3.4) are listed for $d^n$ and $f^n$ configurations, and E1 and E2 absorption events.

$$\left\{ \begin{array}{ccc} \bar{l} & l & t \\ \bar{l} & l & t \\ a & b & K \end{array} \right\}$$

$$\bar{l} = 1, l = 2, t = 1$$

| $a$ | $b$ | $K$ | | $9j$-symbol |
|---|---|---|---|---|
| 1 | 1 | 0 | <u>221</u> | $\dfrac{1}{6}\sqrt{\dfrac{1}{5}}$ |
| 1 | 0 | 1 | *<u>231</u> | $-\dfrac{1}{6}\sqrt{\dfrac{1}{15}}$ |
| 1 | 2 | 1 | <u>2321</u> | $\dfrac{1}{30}\sqrt{\dfrac{7}{3}}$ |
| 1 | 1 | 2 | *<u>223</u> | $-\dfrac{1}{30}\sqrt{\dfrac{1}{5}}$ |
| 1 | 3 | 2 | <u>113</u> | $\dfrac{1}{5}\sqrt{\dfrac{1}{30}}$ |

For example, if $a = 0$ then $b = K$ and $S = S'$, and

$$(\theta J || W^{(0,K)K} || \theta' J') = \delta_{s,s'}(-1)^{L'+J+S+K} \left[ \frac{(2J+1)(2J'+1)}{(2S+1)(2K+1)} \right]^{1/2} \left\{ \begin{array}{ccc} J' & L' & S \\ L & J & K \end{array} \right\}$$
$$\times (\theta || W^{(0,K)} || \theta').$$

A key relation in our work is

$$(\theta J || T(K) || \theta' J') = 2^{1/2}(\theta J || W^{(0,K)K} || \theta' J')$$
$$= \delta_{s,s'}(-1)^{L'+J+S+K} \left\{ \frac{(2J+1)(2J'+1)}{(2K+1)} \right\}^{1/2} \left\{ \begin{array}{ccc} J' & L' & S \\ L & J & K \end{array} \right\} (\theta || V(K) || \theta')$$

$$\text{(A.2)}$$

in which we have used

$$(\theta || W^{(0,K)} || \theta') = \left\{ \frac{1}{2}(2S+1) \right\}^{1/2} (\theta || V(K) || \theta'). \tag{A.3}$$

Values of $(\theta || V(K) || \theta')$ for $p^n$, $d^n$ and $f^n$ configurations are given by Nielson and Koster (1963), and the values required in the study of rare-earth atoms are listed by us in papers I and II. For $K = 0$, $(\theta || V(K) || \theta')$ is diagonal with respect to $\theta$ and proportional to the number of holes, $n_h$, in the configuration. This and several more results are found in paper I. Other results used here are

$$(\theta || W^{(1,0)} || \theta') = \delta_{\theta,\theta'} \left\{ \frac{2(2L+1)}{(2l+1)} \right\}^{1/2} (S||S||S) \tag{A.4}$$

and

$$(\theta || W^{(0,1)} || \theta') = \delta_{\theta,\theta'} \left\{ \frac{3(2S+1)}{2} \right\}^{1/2} \frac{(L||L||L)}{(l||l||l)}. \tag{A.5}$$

In these expressions, the reduced matrix elements of $S$, $L$ and $l$ are $\{S(S+1)(2S+1)\}^{1/2}$ and similar results for $L$ and $l$. (If both expressions are written in terms of spin and orbital

**Table A1.** (Continued)

$$
\begin{Bmatrix}
\bar{l} & l & t \\
\bar{l} & l & t \\
a & b & K
\end{Bmatrix}
$$

$$\bar{l} = 2, l = 3, t = 1$$

| $a$ | $b$ | $K$ | | $9j$-symbol |
|---|---|---|---|---|
| 1 | 1 | 0 | 3$\underline{41}$1 | $\dfrac{2}{9}\sqrt{\dfrac{2}{35}}$ |
| 1 | 0 | 1 | *0$\underline{31}$1 | $-\dfrac{1}{3}\sqrt{\dfrac{1}{105}}$ |
| 1 | 2 | 1 | 3$\underline{23}$1 | $\dfrac{2}{15}\sqrt{\dfrac{2}{35}}$ |
| 1 | 1 | 2 | *3$\underline{43}$1 | $-\dfrac{2}{45}\sqrt{\dfrac{2}{35}}$ |
| 1 | 3 | 2 | 10$\underline{32}$ | $\dfrac{1}{35}\sqrt{\dfrac{2}{5}}$ |

$$\bar{l} = 1, l = 3, t = 2$$

| $a$ | $b$ | $K$ | | $9j$-symbol |
|---|---|---|---|---|
| 1 | 1 | 0 | 1$\underline{31}$1 | $\dfrac{1}{3}\sqrt{\dfrac{2}{105}}$ |
| 1 | 0 | 1 | *0$\underline{31}$1 | $-\dfrac{1}{3}\sqrt{\dfrac{1}{105}}$ |
| 1 | 2 | 1 | 3$\underline{23}$1 | $\dfrac{2}{15}\sqrt{\dfrac{2}{35}}$ |
| 1 | 1 | 2 | *3$\underline{32}$2 | $-\dfrac{2}{105}\sqrt{\dfrac{2}{3}}$ |
| 1 | 3 | 2 | 11$\underline{23}$ | $\dfrac{1}{35}\sqrt{\dfrac{6}{7}}$ |
| 1 | 2 | 3 | *01$\underline{33}$ | $-\dfrac{1}{35}\sqrt{\dfrac{3}{35}}$ |
| 1 | 4 | 3 | 1$\underline{31}$3, 1 | $\dfrac{1}{21}\sqrt{\dfrac{22}{105}}$ |
| 1 | 3 | 4 | *1$\underline{41}$3 | $-\dfrac{1}{63}\sqrt{\dfrac{2}{35}}$ |
| 1 | 5 | 4 | 0$\underline{40}$2 | $\dfrac{1}{63}$ |

variables they are symmetric in the variables, and we have chosen to write them down using the explicit values $2s + 1 = 2$ and $(s||s||s) = \sqrt{(3/2)}$.) From

$$
(\theta J||W^{(K,0)K}||\theta' J') = \delta_{L,L'}(-1)^{J'+S+L+K} \left\{ \frac{(2J+1)(2J'+1)}{(2K+1)(2L+1)} \right\}^{1/2} \begin{Bmatrix} J' & S' & L \\ S & J & K \end{Bmatrix}
$$
$$
\times (\theta||W^{(K,0)}||\theta') \tag{A.6}
$$

and from (A.4)

$$
(\theta J||W^{(1,0)1}||\theta' J') = \delta_{\theta,\theta'}(-1)^{J'+S+L+1} \left\{ \frac{2(2J+1)(2J'+1)}{3(2l+1)} \right\}^{1/2} (S||S||S) \begin{Bmatrix} S & J' & L \\ J & S & 1 \end{Bmatrix}. \tag{A.7}
$$

An important special case for the last expression is its value for $J = J'$:

$$(\theta J||W^{(1,0)1}||\theta' J) = \delta_{\theta,\theta'} \left\{ \frac{2}{3(2l+1)} \right\}^{1/2} (J||J||J)(g-1) \tag{A.8}$$

where $g$ is the Landé factor. The corresponding result for $(\theta J||W^{(0,1)1}||\theta' J)$ is proportional to $2 - g$. We recall that within a $J$-manifold, $\langle S \rangle = (g-1)\langle J \rangle$ and $\langle L \rangle = (2-g)\langle J \rangle$.

For $a = 1$ and $K = 1$, the next in line of the reduced matrix elements is the one with $b = 2$ (matrix elements with $a + b + K = $ odd integer do not appear in $T(K: \bar{J})$). A standard exercise reveals (see, e.g., Edmonds 1960)

$$\langle \theta JM| \sum_j \{3\hat{R}(\hat{R} \cdot s) - s\}_j |\theta JM \rangle = \frac{M(l||l||l)}{(J||J||J)} \left\{ \frac{15}{(2l-1)(2l+3)} \right\}^{1/2} (\theta J||W^{(1,2)1}||\theta J) \tag{A.9}$$

where $\hat{R}$ and $s$ are, respectively, the unit position vector and spin operators of electrons labelled by $j$ in the $l^n$-configuration. For a saturated magnetic atom, $M = J$, and on adapting a result given by Carra *et al* (1993), the value of the right-hand side of (A.9) is found to be ($n \leqslant 2l + 1$)

$$\left( l - n + \frac{1}{2} \right) \{L(L+1)[L(L+1) + 2S(S+1) + 2J(J+1)] - 3(S-J)^2(S+J+1)^2\}$$

$$\times [2(2l+3)(2l-1)(2L-1)S(J+1)]^{-1}. \tag{A.10}$$

The odd tensor $(\theta||W^{(1,2)}||\theta)$ has the property that its values for $n$ electrons and $n_h$ holes with $n = n_h$ are the same. Hence, for $n > 2l + 1$ the appropriate value of (A.10) is found by replacing $n$ by $n_h = 2(2l+1) - n$.

A little ingenuity enables one to go beyond (A.9) and construct other operators to represent higher-order reduced matrix elements. Since they become quite complicated, and so have only a modest physical appeal, we shall not go further than the result (A.9).

We conclude with a special case for $W^{(1,1)}$ that has a simple expression. The reduced matrix element of $W^{(1,1)}$ evaluated for a $\theta$ given by Hund's rules is

$$(\theta||W^{(1,1)}||\theta) = \pm \left( \frac{3}{2} \right)^{1/2} \left( \frac{1}{S} \right) \frac{(S||S||S)(L||L||L)}{(l||l||l)} \tag{A.11}$$

where the upper (lower) sign is correct for $n_h \leqslant 2l + 1$ ($n_h > 2l + 1$). From (A.11) we get

$$(\theta J||W^{(1,1)0}||\theta J) = \pm \left\{ \frac{1}{2}(2J+1) \right\}^{1/2} \frac{[L(L+1) + S(S+1) - J(J+1)]}{6S(l||l||l)}. \tag{A.12}$$

This expression is used to calculate the mean value of the spin–orbit interaction in a Hund-rules ground state, and it leads to the Landé rule of intervals. Using (A.11) and (4.4) one can obtain an analytic expression for $(\theta J||W^{(1,1)2}||\theta J)$.

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