X-ray-absorption sum rules in *jj*-coupled operators and ground-state moments of actinide ions

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Sum rules for magnetic x-ray dichroism, relating the signals of the spin-orbit split core level absorption edges to the ground-state spin and orbital operators, are expressed in jj-coupled operators. These sum rules can be used in the region of intermediate coupling by taking into account the cross term between the $j=l\pm 1/2$ ground-state levels and are, therefore, particularly useful in the study of actinides. The calculated expectation values for the ground-state moments of the actinide ions in intermediate coupling show that the spin-orbit-induced operators, such as the magnetic-dipole term, differ strongly from their Hund's rule ground-state values. We also prove the general rule that, when there is a perturbing interaction which is weak compared to the spin-orbit interaction, the ratio of operators with the same total moment remains constant. This condition is usually fulfilled for the crystal-field interaction in the lanthanides and actinides. The values of the ground-state moments as a function of f count give rise to an interesting trend in the dichroism of the spin-orbit split-core edges. The branching ratio of the $3d$ and $4d$ circular dichroism signal gradually increases from nearly zero for $5f^1$ to $\sim$0.4 for $5f^5$ and is close to unity for a more than half-filled shell. The unusual behavior of the branching ratio can be related to the higher (lower) value of the magnetic dipole term, T_z, for a less (more) than half-filled shell of the actinides in the presence of spin-orbit interaction. Uranium compounds will have a much larger value of T_z than the corresponding $4f$ compounds. Its precise value can be used as a measure for the f count. [S0163-1829(96)02521-0]

I. INTRODUCTION

The basic properties of magnetism depend strongly on the spin and orbital components of the magnetization. These moments are determined by the interplay of the hybridization, exchange, and Coulomb interactions, crystal-field and spin-orbit coupling. Actinides are characterized by a strong spin-orbit interaction and a variable degree of localization of the $5f$ electrons which induces a wide variety of magnetic behavior, such as Pauli paramagnetism, itinerant magnetism, heavy fermions, quadrupolar Kondo effect, and exotic superconductivity.[1–6] Not only in ionic compounds but also in dilute alloys the $5f$ electrons are relatively localized.[7,8] The magnetic ordering is often caused by an indirect coupling of the $5f$ moments through the valence electrons in the compound, such as in the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling.[9] The electrostatic interactions in the $5f$ configuration for the actinide ions are comparable to those in the $4f$ configuration for the rare-earth ions. However, the $5f$ spin-orbit interaction is about twice as large as the $4f$ spin-orbit interaction. Therefore, a jj-coupled ground state is better approximated by the actinides than by the rare earths, which have an almost LS-coupled ground state. But since the electrostatic interactions cannot be neglected the ground state should in reality be expressed in intermediate coupling.

Actinide compounds display large white lines at the threshold for $3d$ and $4d$ core excitation in x-ray-absorption spectroscopy (XAS). These lines originate from the dipole transitions $5f^n \rightarrow d^9 5f^{n+1}$, where the core hole spin-orbit interaction splits the final states into two parts which are well separated in energy. Kalkowski *et al.*[10] measured the isotropic $3d$ and $4d$ absorption structures for a number of U systems and a few Th compounds, and observed very strong white lines with hardly any fine structure within each line, in agreement with calculated results.[11] The interest in dichroic core-level spectroscopy of magnetic actinide compounds was prompted by the observation of 5–6 orders of magnitude enhancement in magnetic x-ray diffraction at the $3d$ edges of uranium arsenide,[12] resulting in intensities of about 1% of the charge scattering. As in the case of XAS the resonance enhancement at the U $3d$ edge is due to the electric-dipole transitions from the spin-orbit split core levels into the narrow $5f$ band. More recently strong magnetic x-ray dichroism (MXD) was observed in the U $3d$ edge of uranium monosulphide[13] and $USb_{0.5}Te_{0.5}$ and UFe_2.[14] Whereas the dichroism signal is very strong at the U $3d_{3/2}$, there is only a small signal observed at the U $3d_{5/2}$ edge.

The information about the magnetic moments can be extracted by using the sum rules,[15] which relate the integrated intensities of the spin-orbit split core levels to the one-electron operators of the ground state. The spectral distribution further contains information about the correlation between the electrons,[16] but if, as in the sum rules, we integrate over all final states these effects are averaged out. For a core level which is split into two well-defined spin-orbit split j levels the relative intensities give information about spin-dependent quantities, such as S_z and T_z. When core-valence electrostatic interactions are of the order of the core spin-orbit interactions, they transfer spectral weight between the two spin-orbit split levels. However, this effect is small in the $4d \rightarrow 5f$ transitions, and even smaller in the $3d \rightarrow 5f$ transitions.

TABLE I. The relation between some of the tensor operators w^{xyz} and the common operators for the ground-state magnetic moments.

Significance	w^{xyz}	d shell	f shell
Number operator	$w^{000}=n$	n	n
Spin-orbit coupling	$w^{110}=(ls)^{-1}\Sigma_i l_i\cdot s_i$	$l\cdot s$	$\frac{2}{3}\ l\cdot s$
Spin moment	$w_\eta^{011}=-s^{-1}S_\eta$	$-2S_\eta$	$-2S_\eta$
Orbital magnetic moment	$w_\xi^{101}=-l^{-1}L_\xi$	$-\frac{1}{2}\ L_\zeta$	$-\frac{1}{3}\ L_\zeta$
Magnetic dipole term	$w_\zeta^{211}=-(2l+3)l^{-1}T_\zeta$	$-\frac{7}{2}\ T_\zeta$	$-3T_\zeta$
Quadrupole moment	$w_0^{202}=3[l(2l-1)]^{-1}Q_{zz}$	$\frac{1}{2}\ Q_{zz}$	$\frac{1}{5}\ Q_{zz}$

Previously, the sum rules have been expressed in LS-coupled operators. In this paper we will express them in jj-coupled operators, which helps in understanding the *unusual* branching ratios which have been measured in actinides. It also provides new insights in the way spin-orbit coupling influences the spectral distribution. We will compare the jj-coupled properties with those obtained in LS coupling. By taking into account the cross terms between the two ground-state levels $j_{1,2}=l\pm 1/2$ the formalism can be used in any region of the intermediate-coupling scheme.

This paper serves a dual purpose. It introduces the sum rules for jj-coupled operators and it treats the properties of the f-shell ground-state operators. The outline is as follows. In Sec. II the tensor operators in LS and jj coupling are defined and in Sec. III they are expressed in terms of each other. In Sec. IV the expressions for the sum rules are given. In Sec. V we present a general rule relating operators that couple to the same total moment. This rule remains valid in the presence of a small perturbing interaction. In Sec. VI we discuss the ground-state moments for the f shell coupled in the different schemes. As an illustration we discuss in Sec. VII the trends in the XAS spectra and the dichroic branching ratio over the actinide series. Conclusions are drawn in Sec. VIII.

II. TENSOR OPERATORS

To treat any moment of a shell l containing one or more holes one can define the LS-coupled double tensors[16]

$$w_\zeta^{xyz}\equiv\sum_{m_1m_2\sigma_1\sigma_2\xi\eta} l^\dagger_{m_1\sigma_1}l_{m_2\sigma_2}(-)^{l-m_1}\begin{pmatrix} l & x & l\\ -m_1 & \xi & m_2\end{pmatrix}$$
$$\times(-)^{s-\sigma_1}\begin{pmatrix} s & y & s\\ -\sigma_1 & \eta & \sigma_2\end{pmatrix}$$
$$\times(-)^{x-\xi+y-\eta}\begin{pmatrix} x & y & z\\ -\xi & -\eta & \zeta\end{pmatrix} n_{lx}^{-1}n_{sy}^{-1}\underline{n}_{xyz}^{-1}, \qquad (1)$$

where the operator $l^\dagger_{m\sigma}$ ($l_{m\sigma}$) creates (annihilates) an l-shell electron with orbital component m and spin component σ. The normalizations n, which remove the square roots, are defined as

$$n_{lx}=\frac{(2l)!}{\sqrt{(2l-x)!(2l+1+x)!}}, \qquad (2)$$

$$n_{abc}\equiv\begin{pmatrix} a & b & c\\ 0 & 0 & 0\end{pmatrix}, \qquad (3)$$

$$\underline{n}_{abx}=i^g\left(\frac{(g-2a)!(g-2b)!(g-2x)!}{(g+1)!}\right)^{1/2}$$
$$\times\frac{g!!}{(g-2a)!!(g-2b)!!(g-2x)!!}, \qquad (4)$$

with $g=a+b+x$. When g is even and a, b, and c are integers we have $\underline{n}_{abx}=n_{abx}$ but when g is odd $n_{abx}=0$. The $\underline{n}_{abx}$ can also be used for half-integer arguments.

The coupled tensors w^{xyz} are the one-particle operators for the orbital ($x=0,...,2l$) and spin ($y=0,1$) moment of the shell coupled to a total moment (z). The systematic notation which denotes the moments with xyz is useful to derive general equations for XAS,[16] (resonant) photoemission,[17–20] and Raman scattering.[21] The relation between some of the tensor operators w^{xyz} and the more common operators, such as L_ζ and S_η, is given in Table I. The moments with $x+y+z$ odd describe axial couplings between spin and orbit, such as $w^{111}=-2l^{-1}(l\times s)$. The w^{z0z} with z even describe the shape (the 2^z pole) of the charge distribution and the w^{x1z} describe spin-orbit correlations.

Similar to the operators w for electrons, which contain $l_1^\dagger l_2$ in Eq. (1), we can define operators $\underline{w}$ for holes, containing $l_1l_2^\dagger$. The difference between these operators is a factor of -1 except for the number operator for which we have $\underline{w}^{000}=4l+2-w^{000}$, stating that the number of electrons plus holes is $4l+2$. For the ground-state moments we will use the electron operators w. However, in spectroscopies, such as XAS, where a core electron is excited into an unoccupied state, the hole operators $\underline{w}$ appear naturally.

Alternatively, we can define jj-coupled tensors for the shell l with angular quantum numbers $j_1=l-1/2$ and $j_2=l+1/2$:

$$v_\zeta^{j_1j_2z}\equiv\sum_{m_1m_2} a^\dagger_{j_1m_1}a_{j_2m_2}(-)^{j_1-m_1}\begin{pmatrix} j_1 & z & j_2\\ -m_1 & \zeta & m_2\end{pmatrix}\tilde{n}^{-1}_{j_1j_2z}, \qquad (5)$$

with the normalization

$$\tilde{n}_{j_1j_2z}=\Delta(j_1j_2z)\begin{pmatrix} j_1+j_2\\ z\end{pmatrix}, \qquad (6)$$

$$\Delta(l_1l_2l_3)=\left(\frac{(L-2l_1)!(L-2l_2)!(L-2l_3)!}{(L+1)!}\right)^{1/2}, \qquad (7)$$

where $L=l_1+l_2+l_3$ and the last coefficient in Eq. (6) is Newton's binomial. Note also that $\tilde{n}_{jjz}=n_{jz}$.

Using $a^\dagger_{jm}a_{jm}=n_{jm}$, Eq. (5) gives in the case of electrons in a single j level

$$\nu^{jj0}=\sum_{m_j} n_{jm}\equiv n_j\,, \tag{8}$$

$$\nu_0^{jj1}=j^{-1}\sum_{m_j} n_{m_j}m_j\equiv j^{-1}J_0^j\,, \tag{9}$$

$$\nu_0^{jj2}=[j(2j-1)]^{-1}\sum_{m_j} n_{m_j}[3m_j^2-j(j+1)], \tag{10}$$

where Eqs. (8) and (9) give the number operator and total angular momentum, respectively.

III. TRANSFORMS

The tensor operators can be converted into each other using the transformations

$$w^{xyz}=\sum_{j_1j_2} C^{j_1j_2xyz}\nu^{j_1j_2z}\equiv\sum_{j_1j_2} \nu^{j_1j_2z}[j_1j_2]^{1/2}\tilde{n}_{j_1j_2z}n_{lx}^{-1}n_{sy}^{-1}\underline{n}_{xyz}^{-1}(-)^{j_2-j_1}\begin{Bmatrix} l & x & l\\ s & y & s\\ j_1 & z & j_2\end{Bmatrix}, \tag{11}$$

$$\nu^{j_1j_2z}=\sum_{xy} C^{xyz}w^{xyz}\equiv\sum_{xy} w^{xyz}[xy][j_1j_2]^{1/2}\tilde{n}^{-1}_{j_1j_2z}n_{lx}n_{sy}\underline{n}_{xyz}(-)^{j_2-j_1}\begin{Bmatrix} l & x & l\\ s & y & s\\ j_1 & z & j_2\end{Bmatrix}. \tag{12}$$

Table II expresses the LS-coupled operators w^{xyz} as linear combinations of the jj-coupled operators $\nu^{j_1j_2z}$. The number operator w^{000} and the spin-orbit operator w^{110} are diagonal in j, so that

$$\langle w^{000}\rangle=\langle n\rangle=\langle n^{j_1}\rangle+\langle n^{j_2}\rangle, \tag{13}$$

$$\begin{aligned}\langle w^{110}\rangle&=(ls)^{-1}\langle l\cdot s\rangle\\ &=\frac{1}{2}\,(ls)^{-1}\sum_{j=j_\pm}\langle n^j\rangle[j(j+1)-l(l+1)-s(s+1)]\\ &=-\frac{l+1}{l}\,\langle n^{j_1}\rangle+\langle n^{j_2}\rangle.\end{aligned} \tag{14}$$

TABLE II. The values of the coefficients $C^{j_1j_2xyz}$ in the transformations $w^{xyz}=\Sigma_{j_1j_2}C^{j_1j_2xyz}\nu^{j_1j_2z}$ for the f shell operators. $C^{(7/2)(5/2)xyz}=-C^{(5/2)(7/2)xyz}$.

w^{xyz}	$C^{(5/2)(5/2)xyz}$	$C^{(5/2)(7/2)xzy}$	$C^{(7/2)(7/2)xyz}$
w^{000}	1	0	1
w^{110}	−4/3	0	1
w^{101}	−20/21	2/7	−1
w^{011}	5/7	−12/7	−1
w^{211}	12/7	9/7	−1
w^{202}	6/7	−3/7	1
w^{112}	−10/21	15/14	1
w^{312}	−15/7	−10/7	1
w^{303}	−5/7	4/7	−1
w^{213}	2/7	−16/21	−1
w^{413}	55/21	11/7	−1
w^{404}	11/21	−5/7	1
w^{314}	−1/7	15/28	1
w^{514}	−22/7	−12/7	1
w^{505}	−2/7	6/7	−1
w^{415}	1/21	−12/35	−1
w^{615}	26/7	13/7	−1
w^{606}	0	−1	1
w^{516}	0	1/6	1
w^{617}	0	0	−1

Other operators generally contain crossterms $j_1\neq j_2$. The cross operators are non-Hermitian: $\nu^{j_1j_2z}=(-)^{j_2-j_1}\nu^{j_2j_1z}$. Therefore, Hermitian operators w^{xyz} with $x+y+z$ even, which have real coefficients, contain the difference $\nu^{j_1j_2z}-\nu^{j_2j_1z}$. Since

$$C^{j_1j_2xyz}=-C^{j_2j_1xyz}, \tag{15}$$

only the values of $C^{(5/2)(7/2)xyz}$ have been tabulated, but the $C^{(7/2)(5/2)xzy}$ are of course also present in the transformations given by Eq. (11). The coefficient $C^{(7/2)(7/2)xyz}$ is $(-1)^z$. For axially coupled tensors w^{z1z}, which are not included in Table II, the coefficients C of the crossterms are imaginary:

$$w^{z1z}=-i\,\frac{2l+2}{2l+1}\,(\nu^{j_1j_2z}+\nu^{j_2j_1z}). \tag{16}$$

Some examples will make the use of Table II clear. Combined with Table I for f shells

$$\begin{aligned}\langle L_\zeta\rangle=-3\langle w^{101}\rangle&=\frac{20}{7}\,\langle\nu^{(5/2)(5/2)1}\rangle-\frac{12}{7}\,\langle\nu^{(5/2)(7/2)1}\rangle\\ &\quad+3\langle\nu^{(7/2)(7/2)1}\rangle,\end{aligned}$$

$$\langle S_\zeta \rangle = -\frac{1}{2}\langle w^{011}\rangle = -\frac{5}{14}\langle \nu^{(5/2)(5/2)1}\rangle + \frac{12}{7}\langle \nu^{(5/2)(7/2)1}\rangle + \frac{12}{7}\langle \nu^{(7/2)(7/2)1}\rangle,$$

$$\langle T_\zeta \rangle = -\frac{1}{3}\langle w^{211}\rangle = -\frac{4}{7}\langle \nu^{(5/2)(5/2)1}\rangle - \frac{6}{7}\langle \nu^{(5/2)(7/2)1}\rangle + \frac{3}{7}\langle \nu^{(7/2)(7/2)1}\rangle, \quad (17)$$

we can obtain other operators which contain no cross operators $j_1 \neq j_2$:

$$\langle L_\zeta\rangle + \langle S_\zeta\rangle = \langle J_\zeta^{5/2}\rangle + \langle J_\zeta^{7/2}\rangle = \langle J_\zeta\rangle,$$

$$\langle L_\zeta\rangle - 2\langle T_\zeta\rangle = \frac{8}{5}\langle J_\zeta^{5/2}\rangle + \frac{2}{3}\langle J_\zeta^{7/2}\rangle,$$

$$\langle S_\zeta\rangle + 2\langle T_\zeta\rangle = -\frac{3}{5}\langle J_\zeta^{5/2}\rangle + \frac{1}{3}\langle J_\zeta^{7/2}\rangle. \quad (18)$$

Table III expresses the jj-coupled operators $\nu^{j_1j_2z}$ as linear combinations of the LS-coupled operators w^{xyz}, which gives the reverse relations of Eq. (17),

$$\langle J_\zeta^{5/2}\rangle = \frac{5}{14}\langle L_\zeta\rangle - \frac{5}{7}\langle S_\zeta\rangle - \frac{15}{7}\langle T_\zeta\rangle,$$

$$\langle J_\zeta^{7/2}\rangle = \frac{9}{14}\langle L_\zeta\rangle + \frac{12}{7}\langle S_\zeta\rangle + \frac{15}{7}\langle T_\zeta\rangle, \quad (19)$$

where J^j has been defined in Eq. (9).

TABLE III. The values of the coefficients C^{xyz} in the transforms $\nu^{j_1j_2z} = \Sigma_{xy} C^{xyz} w^{xyz}$ for the f-shell operators.

$\nu^{j_1j_2z}$	C^{z0z}	$C^{(z-1)1z}$	$C^{(z+1)1z}$
$\nu^{(5/2)(5/2)0}$	3/7	0	−3/7
$\nu^{(7/2)(7/2)0}$	4/7	0	3/7
$\nu^{(5/2)(5/2)1}$	−3/7	1/7	2/7
$\nu^{(5/2)(7/2)1}$	1/14	−4/21	5/42
$\nu^{(7/2)(7/2)1}$	−27/49	−12/49	−10/49
$\nu^{(5/2)(5/2)2}$	3/7	−6/35	−9/35
$\nu^{(5/2)(7/2)2}$	−1/7	9/35	−4/35
$\nu^{(7/2)(7/2)2}$	25/49	18/49	6/49
$\nu^{(5/2)(5/2)3}$	−3/7	9/49	12/49
$\nu^{(5/2)(7/2)3}$	3/14	−15/49	9/98
$\nu^{(7/2)(7/2)3}$	−22/49	−165/343	−24/343
$\nu^{(5/2)(5/2)4}$	3/7	−4/21	−5/21
$\nu^{(5/2)(7/2)4}$	−2/7	22/63	−4/63
$\nu^{(7/2)(7/2)4}$	18/49	88/147	5/147
$\nu^{(5/2)(5/2)5}$	−3/7	15/77	18/77
$\nu^{(5/2)(7/2)5}$	5/14	−30/77	5/154
$\nu^{(7/2)(7/2)5}$	−13/49	−390/539	−6/539
$\nu^{(5/2)(7/2)6}$	−3/7	3/7	0
$\nu^{(7/2)(7/2)6}$	1/7	6/7	0
$\nu^{(7/2)(7/2)7}$	0	−1	0

IV. SUM RULES

We abstain here from giving a derivation and present directly results for the general sum rules in LS- and jj-coupled operators. For the Q-pole excitation from a core level $j = \{j_\pm = c \pm 1/2\}$ to the empty levels $j_{1,2} = l \pm 1/2$ we obtain the signal of the z spectra integrated over the j edge as

$$\begin{aligned} I_j^z &= \sum_{xy} (-)^{z+y+j+s}[xyclj] \begin{Bmatrix} s & y & s \\ c & j & c \end{Bmatrix} \begin{Bmatrix} l & x & l \\ c & y & c \\ Q & z & Q \end{Bmatrix} n_{Qz}^{-1} n_{lx} n_{sy} n_{xyz} \langle \underline{w}^{xyz}\rangle \\ &= \sum_{j_1j_2} (-)^{j_1-j}[clj][j_1j_2]^{1/2} \begin{Bmatrix} j_2 & z & j_1 \\ Q & j & Q \end{Bmatrix} \begin{Bmatrix} j & Q & j_1 \\ l & s & c \end{Bmatrix} \begin{Bmatrix} j & Q & j_2 \\ l & s & c \end{Bmatrix} n_{Qz}^{-1} \tilde{n}_{j_1j_2z} \langle \underline{\nu}^{j_1j_2z}\rangle, \end{aligned} \quad (20)$$

where the z spectra are connected to the spectra I_q measured with q polarized light in a collinear geometry[19]

$$I^z = I_q n_{Qz}^{-1} (-)^{Q-q} \begin{pmatrix} Q & z & Q \\ -q & 0 & q \end{pmatrix}. \quad (21)$$

Thus, e.g., for dipole transitions with left ($q=1$), right ($q=-1$) circularly polarized and Z perpendicularly polarized ($q=0$) light we have the isotropic spectrum $I^0 = I_1 + I_0 + I_{-1}$, the circular dichroism $I^1 = I_1 - I_{-1}$, and the linear dichroism $I^2 = I_1 + I_{-1} - 2I_0$.

A. LS-coupled operators

From Eq. (20) we can obtain the well-known sum rules in LS-coupled operators. In particular for $l = c+1$, which includes the most common transitions $p \to d$ and $d \to f$, we obtain a simple expression for the integrated signal over the two edges

$$\rho^z = [c]\langle \underline{w}^{z0z}\rangle, \quad (22)$$

and for the weighted difference over the spin-orbit split core-levels

$$\delta^z \equiv -\frac{c+1}{c} I^z(j_-) + I^z(j_+), \quad (23)$$

we obtain

$$\delta^0 = [c]\langle \underline{w}^{110}\rangle, \quad (24)$$

TABLE IV. Sum rules in LS-coupled operators for $d \to f$ transitions.

I^z	$\sum_{xy} C_{3/2}^{xyz} \langle \underline{w}^{xyz} \rangle$	$\sum_{xy} C_{5/2}^{xyz} \langle \underline{w}^{xyz} \rangle$
I^0	$2\langle \underline{w}^{000} \rangle - 2\langle \underline{w}^{110} \rangle$	$3\langle \underline{w}^{000} \rangle + 2\langle \underline{w}^{110} \rangle$
I^1	$2\langle \underline{w}^{101} \rangle - \frac{2}{3}\langle \underline{w}^{011} \rangle - \frac{4}{3}\langle \underline{w}^{211} \rangle$	$3\langle \underline{w}^{101} \rangle + \frac{2}{3}\langle \underline{w}^{011} \rangle + \frac{4}{3}\langle \underline{w}^{211} \rangle$
I^2	$2\langle \underline{w}^{202} \rangle - \frac{4}{5}\langle \underline{w}^{112} \rangle - \frac{6}{5}\langle \underline{w}^{312} \rangle$	$3\langle \underline{w}^{202} \rangle + \frac{4}{5}\langle \underline{w}^{112} \rangle + \frac{6}{5}\langle \underline{w}^{312} \rangle$

$$\delta^1 = [c]\left\{ \frac{1}{3} \langle \underline{w}^{011} \rangle + \frac{2}{3} \langle \underline{w}^{211} \rangle \right\}, \tag{25}$$

$$\delta^2 = [c]\left\{ \frac{2}{5} \langle \underline{w}^{112} \rangle + \frac{3}{5} \langle \underline{w}^{312} \rangle \right\}. \tag{26}$$

Table IV gives the separate integrated signals for the $j_- = 3/2$ and $j_+ = 5/2$ core edges as a sum over $C_j^{xyz} \langle \underline{w}^{xyz} \rangle$ where the C are coefficients for the $d \to f$ transition.

B. jj-coupled operators

Table V gives the integrated signals for the $j = 3/2$ and 5/2 core edges as a sum over $C_j^{j_1 j_2 xyz} \langle \underline{v}^{j_1 j_2 z} \rangle$ for the $d \to f$ transition, where using Eq. (15) the crossterms have been collected into a single term. For $z = 0$ there are no crossterms between the two ground-state j levels, because the number operator w^{000} and the spin-orbit operator w^{110} are diagonal in j:

$$\rho^0 = [c] \sum_{j = j_\pm} \langle n_h^j \rangle, \tag{27}$$

$$\delta^0 = [c]\left\{ -\frac{l+1}{l} \langle n_h^{j_1} \rangle + \langle n_h^{j_2} \rangle \right\}, \tag{28}$$

where n_h is the number operator for holes.

Combining Tables IV and V we obtain the useful equations

$$\frac{\delta^0}{\rho^0} = \frac{\langle \underline{w}^{110} \rangle}{\langle \underline{w}^{000} \rangle} = \frac{-4\langle n_h^{5/2} \rangle + 3\langle n_h^{7/2} \rangle}{3\langle n_h \rangle}, \tag{29}$$

$$\frac{\delta^1}{\rho^1} = \frac{\langle w^{011} \rangle + 2\langle w^{211} \rangle}{3\langle w^{101} \rangle} = \frac{29\langle \nu^{(5/2)(5/2)1} \rangle + 12\langle \nu^{(5/2)(7/2)1} \rangle - 21\langle \nu^{(7/2)(7/2)1} \rangle}{-20\langle \nu^{(5/2)(5/2)1} \rangle + 12\langle \nu^{(5/2)(7/2)1} \rangle - 21\langle \nu^{(7/2)(7/2)1} \rangle}, \tag{30}$$

$$\frac{\delta^2}{\rho^2} = \frac{2\langle w^{112} \rangle + 3\langle w^{312} \rangle}{5\langle w^{202} \rangle} = \frac{-155\langle \nu^{(5/2)(5/2)2} \rangle + 105\langle \nu^{(5/2)(7/2)2} \rangle - 102\langle \nu^{(7/2)(7/2)2} \rangle}{90\langle \nu^{(5/2)(5/2)2} \rangle + 105\langle \nu^{(5/2)(7/2)2} \rangle - 90\langle \nu^{(7/2)(7/2)2} \rangle}, \tag{31}$$

where the first part of the equalities is valid generally for $l = c+1$ and the second part only for f shells. In Eqs. (30) and (31) we have chosen electron operators in order to simplify the analysis given in the following sections.

V. PROPORTIONALITY RULE

We will give a general rule which deals with the influence of a small perturbation on an αJ level. Assume that, e.g., a crystal or magnetic field splits the level producing a ground state $|\alpha J \gamma\rangle = \Sigma_M c_M |\alpha JM\rangle$. Then

TABLE V. Sum rules in jj-coupled operators for $d \to f$ transitions.

I^z	$\sum_{j_1 j_2} C_{3/2}^{j_1 j_2 xyz} \langle \underline{\nu}^{j_1 j_2 z} \rangle$	$\sum_{j_1 j_2} C_{5/2}^{j_1 j_2 xyz} \langle \underline{\nu}^{j_1 j_2 z} \rangle$
I^0	$\frac{14}{3} \langle \underline{\nu}^{(5/2)\,(5/2)\,0} \rangle$	$\frac{1}{3} \langle \underline{\nu}^{(5/2)\,(5/2)\,0} \rangle + 5\langle \underline{\nu}^{(7/2)\,(7/2)\,0} \rangle$
I^1	$-\frac{14}{3} \langle \underline{\nu}^{(5/2)\,(5/2)\,1} \rangle$	$-\frac{2}{21} \langle \underline{\nu}^{(5/2)\,(5/2)\,1} \rangle + \frac{20}{7} \langle \underline{\nu}^{(5/2)\,(7/2)\,1} \rangle - 5\langle \underline{\nu}^{(7/2)\,(7/2)\,1} \rangle$
I^2	$\frac{14}{3} \langle \underline{\nu}^{(5/2)\,(5/2)\,2} \rangle$	$-\frac{8}{21} \langle \underline{\nu}^{(5/2)\,(5/2)\,2} \rangle - \frac{30}{7} \langle \underline{\nu}^{(5/2)\,(7/2)\,2} \rangle + 5\langle \underline{\nu}^{(7/2)\,(7/2)\,2} \rangle$

$$\begin{aligned}\langle \alpha J\gamma|O^z_\zeta|\alpha J\gamma\rangle &= \sum_{MM'} c_M c_{M'}\langle \alpha JM|O^z_\zeta|\alpha JM'\rangle \\ &= \langle \alpha J\|O^z\|\alpha J\rangle \sum_{MM'} c_M c_{M'} \\ &\quad\times(-)^{J-M}\begin{pmatrix} J & z & J \\ -M & \zeta & M'\end{pmatrix} \\ &\equiv \langle \alpha J\|O^z\|\alpha J\rangle U^z_\zeta, \end{aligned} \tag{32}$$

where we used the Wigner-Eckart theorem. Equation (32) shows that different operators O with the same rank z are all proportional to a tensor U^z_ζ. The proportionality factor is the reduced matrix element which is different for each operator. For example, for $z=1$ we may take $O=L,S$, or T. These vectors are always parallel and have a constant ratio, independent of the c_M, i.e., of the crystal field. They are only no longer proportional when the crystal field becomes of the order of the spin-orbit coupling and so mixes in other αJ levels. Similarly, the operators with $z=2$ are proportional to a single tensor.

The rule implies that also in intermediate coupling the ratios of the moments with the same z is fixed, as long as the crystal field is smaller than the electrostatic and spin-orbit interactions. Relating the moments to integrated intensities by the sum rules we get that for changing crystal field the integrated intensity of the dichroism changes, while the branching ratios in both the isotropic and the dichroism spectrum have to remain the same. The exact ratio of the moments is determined by the Coulomb and spin-orbit interactions. This works nicely for the actinides and rare earths but breaks down for the d transition metals, which have typical crystal fields of a few eV and a spin-orbit coupling of a few hundredths of an eV. The moments are then not necessarily parallel, except when the magnetization is along a high-symmetry direction of the crystal lattice, and they can be pulled apart by a sufficiently strong magnetic field.[22]

VI. *f*-SHELL GROUND-STATE MOMENTS

In Fig. 1 we compare the moments w^{xyz} for the Hund's rule state (Table VI), the jj-coupled ground state (Table VII), and the actinide ground state in intermediate coupling (Table VIII). The latter were calculated using the atomic Hartree-Fock code of Cowan[23] where the Slater integrals were reduced to 80% to account for intra-atomic relaxation. The Hartree-Fock values for the parameters have been tabulated in Ref. 11. The Hund's rule state is expected to be a reasonable approximation in the case of rare earths.

The atomic moments were obtained for an infinitely small magnetic field and without crystal-field interaction. Independent of the coupling this always yields a total moment

$$\begin{aligned} M=J_z=L_z+S_z &= -3\langle w^{101}\rangle - \frac{1}{2}\langle w^{011}\rangle \\ &= \frac{5}{2}\langle \nu^{(5/2)(5/2)1}\rangle + \frac{7}{2}\langle \nu^{(7/2)(7/2)1}\rangle. \end{aligned} \tag{33}$$

A. Hund's rule ground state

Table VI gives the expectation values of the LS-coupled operators with $z=0,1,2$ for the Hund's rule state (short-dashed lines in Fig. 1). All $\underline{w}^{xyz}$ values are unity for l^{4n+1} $LSJ(M=J)$, thus apart from the number operator, $w^{xyz}=-1$. For $M=-J$, the sign changes when z is odd. Note also that the columns w^{xyz} in Table VI for f^1 (one $f_{5/2}$ electron) and f^{13} (one $f_{7/2}$ hole) with $M=J$ are equal to the rows $C^{5/2,5/5xyz}$ and $C^{7/2,7/2xyz}$ respectively, in Table II.

For a more than half-filled shell the ground state has $J=L+S$, and for $M=\pm J$, the wave function is a single Slater determinant. The expectation values of the operators can then be simply obtained from $L_z=\Sigma m$, $S_z=\Sigma\sigma$, $Q_{zz}=\Sigma m^2-1/3\, l(l+1)$. Because for all holes σ is the same, operators w^{xyz} with the same x are equal in this state except for a factor $(-1)^z$, and so, e.g., $T_z=3(2l-1)^{-1}(2l+3)^{-1}Q_{zz}$. For a less than half-filled shell, $J=L-S$, and the wave function is a linear combination of Slater determinants, so that the expectation values include crossterms between determinants, and are not expressible in only occupation numbers. Although operators with the same x are not equal anymore, the sign relationship is still as it was for more than half-filled shells.

We will now discuss the trends of the specific operators. The expectation value of $\langle w^{110}\rangle$ is always negative because the spin-orbit interaction couples l and s antiparallel. The value of $\langle w^{101}\rangle$ is always positive whereas $\langle w^{011}\rangle$ is negative (positive) for a less (more) than half-filled shell. This is because we take a negative value of M in Eq. (33) for the magnetic ground state. For $n\leqslant 5$, the orbital contribution is larger than the spin contribution, so that the antiparallel coupling of their moments results in a positive value for $\langle w^{101}\rangle$ and a negative value for $\langle w^{011}\rangle$. The configuration f^6, where only $\langle w^{110}\rangle$ is nonzero, has no net magnetic moment. The configuration f^7 has no orbital moment, so that $\langle w^{011}\rangle$ is positive. For $n\geqslant 8$ the parallel coupling of spin and orbit makes $\langle w^{101}\rangle$ and $\langle w^{011}\rangle$ both positive.

The quadrupole moment $\langle w^{202}\rangle$ changes sign for quarter-filled shells. A positive value is obtained when high values of $|m|$ are occupied which makes the ion flat in the XY plane. A negative value is obtained when predominantly low values of $|m|$ are occupied which corresponds to an elongation along the Z axis. The values in Table VI are for spherical symmetry and give the quadrupole moment induced by a small magnetic field and spin-orbit coupling. In the presence of an anisotropic electrostatic field larger than the magnetic interaction these values will be different.

B. *jj*-coupled ground state

The expectation values of the jj-coupled operators of the f shell with $z=0,1,2$ for the jj-coupled ground state can be found from Eqs. (8)–(10), where first all $j=5/2$ levels are filled with $m_j=-5/2,-3/2,...,5/2$, respectively, and then the $j=7/2$ levels. In the limit of jj coupling the cross operators are all zero. Note that by this procedure the J value obtained for the ground state is the same as the Hund's rule J value in LS coupling. In practice the ground state has always this same J value also in intermediate coupling [cf. Eq. (33)].

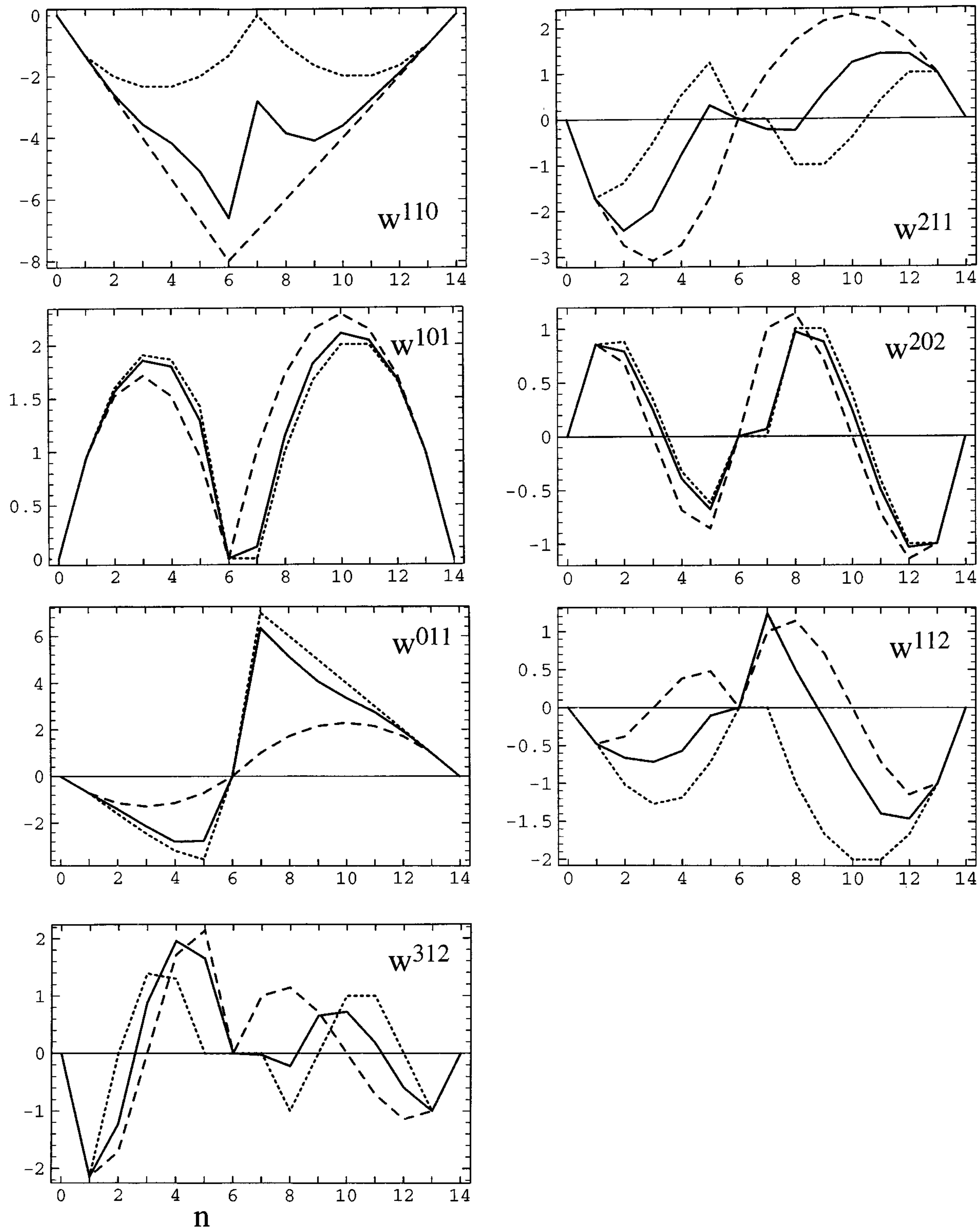

FIG. 1. The f-shell moments $\langle w^{xyz}\rangle$ for the Hund's rule state (short dashes), the jj-coupled ground state (long dashes), and the actinide ground state calculated in intermediate coupling (drawn line).

Table VII gives the values of w^{xyz} for the jj-coupled ground state (long-dashed lines in Fig. 1). The linear behavior of w^{110} can be understood by combining Eqs. (24) and (28) where we obtain

$$\langle w^{110}\rangle = \frac{l+1}{l}\,\langle n_h^{j_1}\rangle - \langle n_h^{j_2}\rangle. \tag{34}$$

The values for operators with $z=1$ ($z=2$) are symmetric (antisymmetric) around f^3 and around f^{10}. For $n\geqslant 6$ all operators with the same z have the same value. For $n\leqslant 6$ they have a ratio different from unity. Because we keep J_z constant ($=-J$), Eq. (33) shows that the difference in w^{101} between the jj-coupled and Hund's rule ground state has to be compensated by a six times larger opposite change in w^{011}.

TABLE VI. Expectation values $\langle w^{xyz}\rangle$ for the Hund's rule states $LSJ(M=-J)$ of the configuration f^n.

	$\langle w^{000}\rangle$	$\langle w^{110}\rangle$	$\langle w^{101}\rangle$	$\langle w^{011}\rangle$	$\langle w^{211}\rangle$	$\langle w^{202}\rangle$	$\langle w^{112}\rangle$	$\langle w^{312}\rangle$
$f^1\ {}^2F_{5/2}$	1	−4/3	20/21	−5/7	−12/7	6/7	−10/21	−15/7
$f^2\ {}^3H_4$	2	−2	8/5	−8/5	−104/75	728/825	−56/55	0
$f^3\ {}^4I_{9/2}$	3	−7/3	21/11	−27/11	−63/121	42/121	−14/11	168/121
$f^4\ {}^5I_4$	4	−7/3	28/15	−16/5	28/55	−196/605	−196/165	784/605
$f^5\ {}^6H_{5/2}$	5	−2	10/7	−25/7	26/21	−13/21	−5/7	0
$f^6\ {}^7F_0$	6	−4/3	0	0	0	0	0	0
$f^7\ {}^8S_{7/2}$	7	0	0	7	0	0	0	0
$f^8\ {}^7F_6$	8	−1	1	6	−1	1	−1	−1
$f^9\ {}^6H_{15/2}$	9	−5/3	5/3	5	−1	1	−5/3	0
$f^{10}\ {}^5I_8$	10	−2	2	4	−2/5	2/5	−2	1
$f^{11}\ {}^4I_{15/2}$	11	−2	2	3	2/5	−2/5	−2	1
$f^{12}\ {}^3H_6$	12	−5/3	5/3	2	1	−1	−5/3	0
$f^{13}\ {}^2F_{7/2}$	13	−1	1	1	1	−1	−1	−1

C. Actinides in intermediate coupling

Table VIII give the expectation values of the ground-state operators calculated in intermediate coupling (continuous lines in Fig. 1). The operators with either $x=0$ or $y=0$ only change in second order and their values remain close to the LS-coupling values. In intermediate coupling for less (more) than half-filled shells $\langle w^{101}\rangle$ is slightly lower (higher) and $\langle w^{011}\rangle$ is slightly higher (lower), of course obeying Eq. (33).

The expectation value of the operators with $x\neq 0$, $y=1$ change in first order and their values are about midway between LS and jj coupling. The negative value of $\langle w^{110}\rangle$ in the Hund's rule state becomes more negative in intermediate coupling due to the increasing $5f$ spin-orbit interaction. The value of $\langle w^{211}\rangle$ in intermediate coupling is much lower (higher) for less (more) than half-filled shells. The value of $\langle w^{112}\rangle$ is always higher. One way to understand why operators with $y=1$ have to change strongly is that in LS coupling, as a function of n, w^{xyz} changes like w^{x0x} while in jj coupling it behaves like w^{z0z}.

The strong difference in behavior between spin-orbit-dependent and independent operators can also be understood as follows. Consider the intermediate-coupling states as LSJ-coupled states perturbed by the spin-orbit coupling, which mixes in other LSJ states. A first-order change in the expectation value of an operator w is only possible when there are excited states which are coupled to the ground state both by w and by the spin-orbit coupling. The spin-orbit coupling only interacts with states of $\Delta L,\Delta S=0,\pm 1$ and $\Delta J=0$. S_z and L_z only have matrix elements $\Delta L,\Delta S=0$ and $\Delta J=0,\pm 1$. Therefore, these operators only change in first order if there are other states with $\Delta L,\Delta S,\Delta J=0$. For the Hund's rule state there are no such states and S_z and L_z can only change in second order. We can even make a slightly stronger statement for the Hund's rule state. Inspection of the possible LS terms shows that for the Hund's rule state there are no terms with $\Delta S=0$ and $\Delta L=0,\pm 1$. Only $\Delta S=-1$ is possible. Because w^{xyz} obeys $\Delta L=-x\cdots x$, $\Delta S=-y\cdots y$, and $\Delta J=-z\cdots z$, only $\langle w^{z1z}\rangle$ can change in first order and $\langle w^{x0x}\rangle$ can only change in second order. Note that, as an exception to the general ones for w^{xyz}, the selection rules for $L(w^{101})$ and $S(w^{011})$ are stricter. We may say that in the Hund's rule state the spin and orbit operators have extreme values (either maximum or minimum) such that spin-orbit coupling cannot change them directly, but can only turn on a correlation of their movement.

TABLE VII. Expectation values $\langle w^{xyz}\rangle$ for the jj-coupled ground state.

$\langle w^{000}\rangle$	$\langle w^{110}\rangle$	$\langle w^{101}\rangle$	$\langle w^{011}\rangle$	$\langle w^{211}\rangle$	$\langle w^{202}\rangle$	$\langle w^{112}\rangle$	$\langle w^{312}\rangle$
1	−4/3	20/21	−5/7	−12/7	6/7	−10/21	−15/7
2	−8/3	32/21	−8/7	−96/35	24/35	−8/21	−12/7
3	−4	12/7	−9/7	−108/35	0	0	0
4	−16/3	32/21	−8/7	−96/35	−24/35	8/21	12/7
5	−20/3	20/21	−5/7	−12/7	−6/7	10/21	15/7
6	−8	0	0	0	0	0	0
7	−7	1	1	1	1	1	1
8	−6	12/7	12/7	12/7	8/7	8/7	8/7
9	−5	15/7	15/7	15/7	5/7	5/7	5/7
10	−4	16/7	16/7	16/7	0	0	0
11	−3	15/7	15/7	15/7	−5/7	−5/7	−5/7
12	−2	12/7	12/7	12/7	−8/7	−8/7	−8/7
13	−1	1	1	1	−1	−1	−1

TABLE VIII. Expectation values $\langle w^{xyz}\rangle$ for the $5f^n$ ground state in intermediate coupling.

$\langle w^{000}\rangle$	$\langle w^{110}\rangle$	$\langle w^{101}\rangle$	$\langle w^{011}\rangle$	$\langle w^{211}\rangle$	$\langle w^{202}\rangle$	$\langle w^{112}\rangle$	$\langle w^{312}\rangle$
1	−1.333	0.952	−0.714	−1.714	0.857	−0.476	−2.143
2	−2.588	1.566	−1.397	−2.428	0.792	−0.662	−1.227
3	−3.562	1.857	−2.140	−1.978	0.250	−0.716	0.880
4	−4.170	1.802	−2.810	−0.781	−0.392	−0.569	1.957
5	−5.104	1.295	−2.767	0.302	−0.679	−0.105	1.650
6	−6.604	0	0	0	0	0	0
7	−2.812	0.110	6.343	−0.225	0.067	1.240	−0.030
8	−3.865	1.147	5.119	−0.251	0.971	0.490	−0.225
9	−4.106	1.822	4.065	0.559	0.876	−0.147	0.654
10	−3.612	2.107	3.358	1.228	0.248	−0.815	0.722
11	−2.754	2.041	2.752	1.421	−0.492	−1.394	0.178
12	−1.906	1.678	1.932	1.411	−1.034	−1.461	−0.593
13	−1	1	1	1	−1	−1	−1

VII. ILLUSTRATION

Figures 2 and 3 show the $4d$ absorption spectra for the different $5f^n$ configurations calculated in intermediate coupling using Cowan's code.[23] To see specifically the differences as a function of n, all spectra in Fig. 2 are given for ^{92}U and those in Fig. 3 for ^{100}Fm. The other elements in the actinide series have similar shapes as in Figs. 2 and 3 depending on their value of n. Also the shapes of the $3d$ spectra are similar to those in Figs. 2 and 3, despite the fact that the ratios of core-valence interaction to core spin-orbit interaction are different, e.g., for the U $3d$ and $4d$ edge $F^2(df\,)/\zeta(d)$ is 0.035 and 0.29, respectively. This shows that in the first instance the ground state is governing the overall spectral shape, whereas the fine structure is specific to the final-state parameters. Since for both core levels the intrinsic lifetime broadening is about $\Gamma=2$ eV,[10] the fine structure is not resolved. The sign of the spectra is defined by Eq. (21): in the I^1 spectrum the signal is positive (negative) for transitions $q=+1$ (-1) and in the I^2 spectrum the signal is positive (negative) for transitions $q=\pm1$ (0).

The branching ratio B^z of the spin-orbit split core levels, which is the fraction of the spectral weight of the j_+ signal, is related to σ^z/ρ^z as

$$B^z\equiv\frac{I^z(j_+)}{I^z(j_-)+I^z(j_+)}=\frac{1}{[c]}\left(c+1+c\,\frac{\delta^z}{\rho^z}\right). \qquad (35)$$

For a transition into an $f_{7/2}$ hole Eqs. (29)–(31) give $B^z=\delta^z/\rho^z=1$, which are the values found for f^{13}, i.e., $I^z(j_-)=0$ (cf. Figs. 2 and 3). For an $f_{5/2}$ hole $\delta^z/\rho^z=-4/3$, $-29/20$, $-31/18$, so that $B^z=1/15$, 1/50, $-8/90$ for $z=0,1,2$, respectively.

These unusual branching ratios find their origin in the Δj selection rules. The angular dependent part of the dipole transition probability $|j\rangle\rightarrow|j_i\rangle$ is

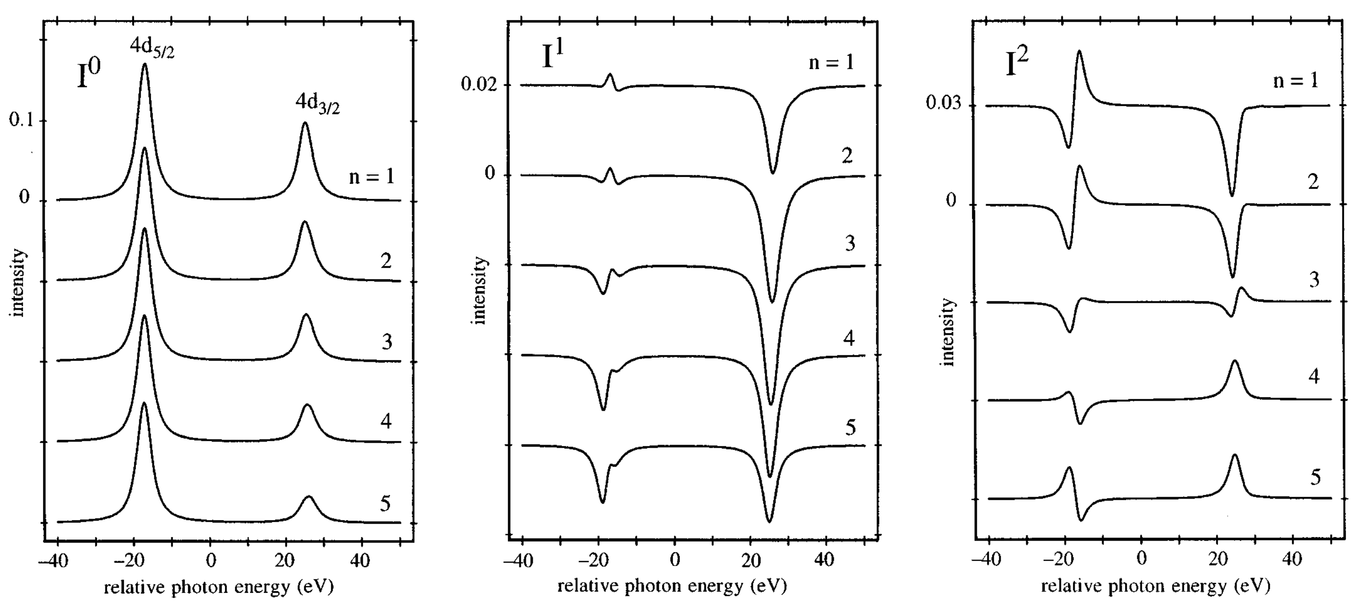

FIG. 2. Isotropic spectrum I^0, circular dichroism I^1, and linear dichroism I^2, calculated in intermediate coupling for the $4d$ absorption edges of ^{92}U $5f^1$ to f^5. Convolution by $\Gamma=2$ eV and $\sigma=0.2$ eV.

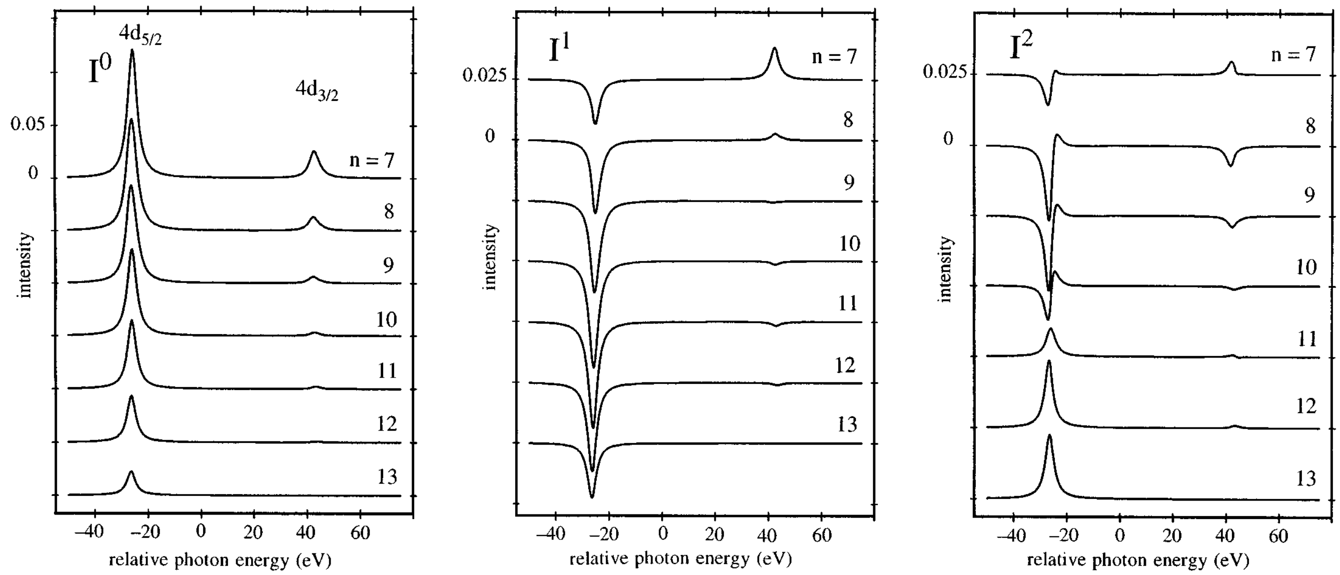

FIG. 3. Isotropic spectrum I^0, circular dichroism I^1, and linear dichroism I^2, calculated in intermediate coupling for the $4d$ absorption edges of ^{100}Fm $5f^7$ to f^{13}. Convolution by $\Gamma=2$ eV and $\sigma=0.2$ eV.

$$I(j\rightarrow j_i)=[jcl]\begin{Bmatrix} j & 1 & j_i \\ l & \frac{1}{2} & c \end{Bmatrix}^2 . \tag{36}$$

For $l=c+1$ we have the allowed dipole transitions to $j_1=j-1/2$ and $j_2=j+1/2$

$$\Delta j=0: \quad I(j_+\rightarrow j_1)=1/l,$$

$$\Delta j=1: \quad I(j_-\rightarrow j_1)=(2l+1)(l-1)/l,$$

$$\Delta j=1: \quad I(j_+\rightarrow j_2)=2l-1. \tag{37}$$

The transition $j_-\rightarrow j_2$ is forbidden, and Eq. (37) shows that the transition probability for $j_+\rightarrow j_1$ is much smaller than the transitions $j_-\rightarrow j_1$ and $j_+\rightarrow j_2$ which are governed by $\Delta j=1$. Therefore, the j_- edge only probes the j_1 level, and the j_+ edge probes mainly the j_2 level. Since the signal from the j_- edge contains no terms with j_2 (Table V), we obtain the simple expression

$$\frac{I^z(j_-)}{I^0(j_-)}=(-)^z\,\frac{\langle \underline{\nu}^{j_1j_1z}\rangle}{\langle n_h^{j_1}\rangle}, \tag{38}$$

which generalizes the result for $z=1$ given by Strange and Gyorffy.[24] From Table V it is evident that such a simple relation does not exist between the j_+ signal and the j_2 moments. The complication is not so much due to the transition probability $j_+\rightarrow j_1$, which is weak, but primarily to the large crossterm.

The intensity integrated over each edge can be obtained from the sum rules given in Table IV. Without $5f$ spin-orbit coupling the isotropic branching ratio has the statistical value 3/5. The relative weight transferred between the edges is measured by δ^0/ρ^0, which by Eq. (29) is related to the spin-orbit interaction per hole. Therefore, the isotropic branching ratio increases strongly with n, as is seen in Figs. 2 and 3. The sum rule does not take into account the mixing of the j levels between both edges due to electrostatic interactions.[25] This effect is small as long as the core d spin-orbit interaction is much larger than the df electrostatic interactions.

The integrated signal of the I^1 spectrum is $\rho^1=5L_z/3$, which will be statistically distributed over the edges in the absence of other $z=1$ moments. The relative weight transferred between the edges is proportional to $\delta^1/\rho^1=[2S_z+(2/3)T_z]/L_z$. Therefore, the dichorism is strong in the $d_{5/2}$ edge when T_z and S_z are parallel to L_z, and strong in the $d_{3/2}$ edge when T_z and S_z are antiparallel to L_z. Similarly, the branching ratio in the I^2 spectrum depends on the relative values of w^{112} and w^{312} with respect to w^{202}. Since the quadrupole moment reverses for the quarter-filled shell also the integrated intensity has to reverse.

Table V expresses the edge signals in terms of jj-coupled operators. The I^1 signal of the $d_{3/2}$ edge is proportional to $\langle \nu^{(5/2),(5/2)1}\rangle$, which is only large for less than half-filled shells, reaching its extreme value at $n=3$. Note that $\langle \nu^{(5/2),(5/2)1}\rangle$ becomes positive for $n=7$ and 8 (Fig. 3). The $d_{5/2}$ signal is mainly related to $\langle \nu^{(7/2)(7/2)1}\rangle$ but with crossterms that cannot be neglected. The $d_{5/2}$ signal increases with n up to the point that the $f_{7/2}$ shell is half-filled, after which it reduces. In the I^2 spectra the edge signals reverse in sign for quarter-filled shells just as the value of $\langle \nu^{jj2}\rangle$.

Figure 4 shows the values of δ^1/ρ^1 for the Hund's rule, jj- and intermediate-coupled ground states of the actinides. In the jj-coupled ground state a partly filled $f_{5/2}$ level ($n>6$) results mainly in a large positive dichroism for the $d_{3/2}$ edge ($B^1=0.02$ or $\delta^1/\rho^1=-29/20$). A partly filled $f_{7/2}$ level ($n<6$) gives a large positive dichroism in the $d_{5/2}$ edge ($B^1=\delta^1/\rho^1=1$). In the other coupling schemes also holes with the other j value are present, making the branching ratio less extreme. The change in δ^1/ρ^1 between the different coupling schemes can be understood from the change in $\langle w^{xyz}\rangle$ due to the $5f$ spin-orbit interaction. Since $\langle w^{101}\rangle$ and $\langle w^{011}\rangle$ do not vary much as a function of the spin-orbit interaction, the variation in δ^1/ρ^1 is proportional to $\langle w^{211}\rangle$. For a less than half-filled shell the value of $\langle w^{211}\rangle$ becomes more negative if

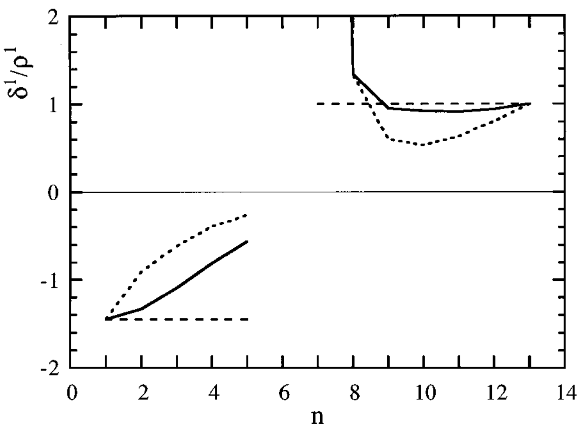

FIG. 4. The values of δ^1/ρ^1 for the Hund's rule state (short dashes), the jj-coupled ground state (long dashes), and the actinide ground state calculated in intermediate coupling (drawn line).

the spin-orbit interaction is increased (Fig. 1), thus δ^1/ρ^1 will be lower than in the Hund's rule state (cf. Fig. 4). For $n>7$ the value of $\langle w^{211}\rangle$ becomes more positive, so that δ^1/ρ^1 will be higher than in the Hund's rule state. An exception is $n=7$ where the small value of $\langle w^{101}\rangle$ makes $\delta^1/\rho^1=18$.

From Fig. 1 we saw that for $5f^2$, f^3 and f^4 in intermediate coupling T_z is strongly enhanced compared to the Hund's rule state (as for rare earths $4f^n$) so that it will be the dominant factor in δ^1. Due to the proportionality rule this will also be the case in a weak crystal field. From the experimental results of Collins *et al.*[13] on US it was found that in this cubic compound the moments L_z, S_z, and T_z are about equally reduced to 50% of their ground-state values in intermediate coupling. Moreover, since the value of T_z changes strongly between $n=2$ and 5, it can be used as an indicator for the f count to reveal the mixed valent character of the uranium compounds. In the case of US,[26] T_z suggests an f count of around 2.5.

VIII. CONCLUSIONS

We have presented sum rules in jj-coupled one-electron operators which relate the core level spin-orbit split signals of the magnetic x-ray dichroism to the ground-state operators. These jj-coupled operators also include a crossterm between the two one-electron ground-state levels $j_{1,2}=l\pm 1/2$ which cannot be neglected. Inclusion of the crossterms allows us to use the sum rules for jj-coupled operators in the region of intermediate coupling on an equal footing with the LS-coupled operators. We have presented conversion tables between both kinds of coupled operators.

In the case of an f shell, transitions from a $d_{3/2}$ core level are only allowed to the $f_{5/2}$ level, so that the dichroism signal over this edge is directly proportional to the magnetic moment of this level. The transition probability from the $d_{5/2}$ core level to the $f_{7/2}$ level is much larger than to the $f_{5/2}$ level, but the dichroism is strongly influenced by the crossterms.

The ground-state moments of the actinides have been calculated in intermediate coupling and compared to the values obtained for the Hund's rule states. Although the spin moment, orbital moment, and quadrupole moment are not much different, those ground-state moments $\langle w^{xyz}\rangle$ for the actinides which are directly induced by spin-orbit interaction ($x\neq 0$, $y=1$) differ considerably from the Hund's rule state values. For instance, in uranium compounds the value of T_z is strongly increased in intermediate coupling.

The weak crystal-field interaction in the lanthanides and actinides can be included by using our rule which states that the ratio between moments with the same z remains constant in the presence of a perturbation which is small compared to the spin-orbit interaction.

The unusual branching ratios which have been observed in the magnetic dichroism and magnetic scattering of the actinides find their origin in the strong $5f$ spin-orbit interaction. The branching ratio of the dichroism is near zero for a less than half-filled shell, and near unity for a more than half-filled shell, as expected for $f_{5/2}$ and $f_{7/2}$ holes, respectively. Since $\langle L_z\rangle$ and $\langle S_z\rangle$ do not change much when the spin-orbit interaction is increased, the change in the branching ratio of the dichroic signal is mainly due to $\langle T_z\rangle$. Since this operator changes strongly as a function of f count this branching ratio can be used as a probe for the covalency of the actinides.

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