Angular momentum sum rules for x-ray absorption

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The sum rules for circular and linear x-ray dichroism, which relate the signals of the core absorption edges to the expectation values of the valence spin and orbital operators, are expressed in jj-coupled operators. By including the cross terms between the $j=l\pm 1/2$ ground-state levels these sum rules are no longer restricted to jj coupling but are equally valid in intermediate coupling. The physical significance of these—usually very large—cross terms is discussed. [S0163-1829(98)02902-6]

Magnetic circular x-ray dichroism has become increasingly important as an element-specific tool to separate the orbital and spin contributions to the magnetic moments. The understanding of magnetic dichroism in both localized[1] and itinerant systems.[2] has made significant progress. Thole and van der Laan[3] developed a sum rule relating the integrated signals over the spin-orbit split core edges of the unpolarized x-ray-absorption spectrum to the expectation value of the ground-state spin-orbit operator. More recently, Thole *et al.*[4] and Carra *et al.*[5] derived sum rules to relate the integrated signals over the spin-orbit split core edges of the circular dichroism to ground-state orbital and spin magnetic moments. These rules were later extended to include electric quadrupole transitions.[6] All sum rules are based on the assumption that it is possible to integrate over the signal of a core level which can be assigned good quantum numbers, such as its total angular momentum. However, core-valence electrostatic interactions can induce a transfer of spectral weight between the two absorption edges, invalidating both the spin-orbit[3] and the spin sum rule.[7] Furthermore, for metallic magnets there persists an ambiguity in the choice of the energy cutoff for the integration range as well as in the determination of the number of holes. This has been studied in detail by Wu, Wang, and Freeman,[8,9] who found the orbital magnetic sum rule to be valid within 10%, whereas Guo *et al.*[10] report much larger discrepancies, of up to 35%. Ankudinov and Rehr[11] rederived the sum rules using the independent electron approximation. Ebert and co-workers[12–14] widely used first-principles spin-polarized relativistic multiple-scattering calculations, which are considered to be accurate for metallic magnets. Van der Laan and Thole[15] used x-ray-absorption sum rules in jj-coupled operators to explain the anomalous branching ratios observed in actinides. Strange and Gyorffy[16] derived a simple sum rule relating the dichroism signal at the $j_c=c-1/2$ absorption edge to the expectation value of the $j=l-1/2$ total angular momentum of the valence band. However, it is less straightforward to find a similar rule for excitations from the $j_c=c+1/2$ edge. In this paper we will derive general sum rules for jj-coupled operators which are valid in intermediate coupling. This is of interest to gain understanding in relativistic band-structure calculations where j appears as a quantum number, but which are often considered as black box calculations. We show that omission of the matrix elements between different jm components results in large errors in the branching ratios of the polarized spectra.[17]

For an electron with orbital momentum l and spin $s=1/2$ we can couple the angular momenta $j=l\pm s$ with magnetic components m to a total moment z with components ζ along a quantization axis Z. We define the jj-coupled tensor operators as

$$\nu_{\zeta}^{jj'z} \equiv \sum_{mm'} a_{jm}^{\dagger} a_{j'm'} (-)^{j-m} \begin{pmatrix} j & z & j' \\ -m & \zeta & m' \end{pmatrix} \tilde{n}_{jj'z}^{-1}, \quad (1)$$

where $a_{jm}^{\dagger}(a_{jm})$ is a creation (annihilation) operator of an electron with quantum numbers jm, and the normalization is

$$\tilde{n}_{l_1 l_2 l_3} = \left(\frac{(L-2l_1)!(L-2l_2)!(L-2l_3)!}{(L+1)!} \right)^{1/2} \binom{l_1+l_2}{l_3}, \quad (2)$$

where $L=l_1+l_2+l_3$ and the last coefficient in Eq. (2) is Newton's binomial.

Using $a_{jm}^{\dagger} a_{jm} = n_{jm}$, Eq. (1) gives in the case of electrons in a single j level

$$\langle \nu^{jj0} \rangle = \sum_m \langle m \rangle \equiv \langle n_j \rangle, \quad (3)$$

$$\langle \nu_0^{jj1} \rangle = j^{-1} \sum_m \langle m \rangle m \equiv j^{-1} \langle J_0 \rangle, \quad (4)$$

$$\langle \nu_0^{jj2} \rangle = \sum_m \langle m \rangle \frac{3m^2 - j(j+1)}{j(2j-1)} \equiv \frac{\langle 3J_0^2 - J^2 \rangle}{j(2j-1)}, \quad (5)$$

which give the expectation values of the number operator, angular moment, and quadrupole moment of the j level, respectively. Similar to the tensor operators ν for electrons, which contain the product of a creation and annihilation operator, $a_{jm}^{\dagger} a_{jm}$, we can define operators $\underline{\nu}$ for holes, containing $a_{jm} a_{jm}^{\dagger}$. Hole and electron operators differ by a factor of -1, except for the number operator, for which $\langle \nu^{000} \rangle + \langle \underline{\nu}^{000} \rangle = 2j+1$. Cross operators with $j \neq j'$ occur in intermediate coupling for $z \neq 0$ and determine the matrix elements between different j levels.

We will now derive sum rules which relate the integrated signal over the x-ray absorption edges to the jj-coupled hole operators of the ground state. For a spin-orbit split core level

$j_c \in \{j_c^{\pm} = c \pm s\}$ the one-electron transition probability into the empty valence level $j \in \{j^{\pm} = l \pm s\}$, using q-polarized electric 2^Q-pole radiation, is given by an operator

$$T_q = (-)^{j-j_c}[clj_c]^{1/2} \begin{Bmatrix} j_c & Q & j \\ l & s & c \end{Bmatrix} \times \sum_{mm_c} \begin{pmatrix} j_c & Q & j \\ m_c & q & m \end{pmatrix} a_{jm}^{\dagger} a_{j_c m_c} P_{lj_c}, \tag{6}$$

where $a_{j_c m_c}$ is the annihilation operator of a core electron and $a_{jm}^{\dagger}$ is the creation operator of a valence electron. P_{lj_c} represents the reduced matrix element, $[cl\cdots]$ is shorthand for $(2c+1)(2l+1)\cdots$. The $3jm$ coefficient gives the dependence on the magnetic quantum numbers. From a many-electron ground state $|g\rangle$ with polarized radiation characterized by q and q', the x-ray-absorption signal summed over the final states $|f\rangle$ is

$$I_{qq'} = \sum_f \langle g|T_q^{\dagger}|f\rangle\langle f|T_{q'}|g\rangle. \tag{7}$$

Removing the core-hole operator $a_{j_c m_c}^{\dagger} a_{j_c m_c}$ using the completeness relation,[5] the $3jm$ coefficients can be recoupled to remove the m_c dependence of the core hole by using

$$\sum_{m_c} \begin{pmatrix} j & Q & j_c \\ -m & q & m_c \end{pmatrix} \begin{pmatrix} j' & Q & j_c \\ -m' & q' & m_c \end{pmatrix} = \sum_{z\zeta} [z] \begin{Bmatrix} j' & z & j \\ Q & j_c & Q \end{Bmatrix} \begin{pmatrix} j & z & j' \\ -m & \zeta & m' \end{pmatrix} \begin{pmatrix} Q & z & Q \\ -q' & \zeta & q \end{pmatrix}. \tag{8}$$

We can define z spectra as linear combinations of the spectra $I_{qq'}$ measured with polarized radiation along the direction $\mathbf{P}$,[18]

$$I^z(\mathbf{P}) = \sum_{qq'\zeta} I_{qq'} n_{Qz}^{-1} (-)^{Q-q} \begin{pmatrix} Q & z & Q \\ -q' & \zeta & q \end{pmatrix} C_{\zeta}^z(\mathbf{P}), \tag{9}$$

where the normalization is $n_{Qz} \equiv \left(\begin{smallmatrix} Q & z & Q \\ -Q & 0 & Q \end{smallmatrix}\right)$, and $C_{\zeta}^z(\mathbf{P})$ is a reduced spherical harmonic. Choosing a collinear geometry with $\mathbf{P}$ along $\mathbf{Z}$ in cylindrical symmetry, $\zeta = 0$, so that $q' = q$, and, e.g., for electric 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 $I^2 = I_1 + I_{-1} - 2I_0$.

Combining Eqs. (6)–(9) and using the definition of $\langle \underline{\nu}^{jj'z} \rangle$ in Eq. (1) we obtain the signal integrated over the j edge of the z spectrum in collinear geometry as

$$I_{j_c}^z = \sum_{jj'} (-)^{j-j_c+Q-1}[clj_c][jj']^{1/2} \begin{Bmatrix} j_c & Q & j \\ l & s & c \end{Bmatrix} \times \begin{Bmatrix} j_c & Q & j' \\ l & s & c \end{Bmatrix} \begin{Bmatrix} j' & z & j \\ Q & j_c & Q \end{Bmatrix} n_{Qz}^{-1} \tilde{n}_{jj'z} \langle \underline{\nu}^{jj'z} \rangle |P_{lj_c}|^2. \tag{10}$$

The triangle relation of the last $6j$ symbol gives for $z=0$ that $j'=j$, which means that the isotropic signal contains no cross operators.

In the case of jj coupling in the ground state, j is a good quantum number, so that the expectation values of the cross operators will vanish. Generalizing the results of Strange and Gyorffy[16] for a transition $cj_c \to lj$ with $l = c+Q$ and $j = j_c + Q$, Eq. (10) yields

$$\frac{I_{j_c}^z}{I_{j_c}^0} = \begin{Bmatrix} j & z & j \\ Q & j_c & Q \end{Bmatrix} \begin{Bmatrix} j & 0 & j \\ Q & j_c & Q \end{Bmatrix}^{-1} \frac{\langle \underline{\nu}_0^{jjz} \rangle}{\langle \underline{n}_j \rangle}, \tag{11}$$

where for $Q=1$ the ratio of the $6j$ symbols simplifies to $(-1)^z$. Although we assume that j_c is a good quantum number, this will generally not be true for j. In intermediate coupling there will be cross operators for $z \neq 0$, and Eq. (11) is insufficient. For the *special* case of $l = c+Q$, which includes dipole transitions, such as $s \to p$, $p \to d$ and $d \to f$, and quadrupole transitions, such as $s \to d$ and $p \to f$, the triad (lQc) is *stretched* and the integrated signals in Eq. (10) can be simplified to

$$I_{j_c^-}^z = (-)^z[l](l-Q)l^{-1}\langle \underline{\nu}^{j^-j^-z} \rangle |P_{lj_c^-}|^2, \tag{12}$$

$$I_{j_c^+}^0 = \{Ql^{-1}\langle \underline{\nu}^{j^-j^-0} \rangle + (2l+1-2Q)\langle \underline{\nu}^{j^+j^+0} \rangle\}|P_{lj_c^+}|^2, \tag{13}$$

$$\begin{aligned} I_{j_c^+}^1 = \{&(2l+1-3Q-2Ql)l^{-1}[l]^{-1}\langle \underline{\nu}^{j^-j^-1} \rangle \\ &+ 2(2l+1-2Q)[l]^{-1}[\langle \underline{\nu}^{j^-j^+1} \rangle - \langle \underline{\nu}^{j^+j^-1} \rangle] \\ &- (2l+1-2Q)\langle \underline{\nu}^{j^+j^+1} \rangle\}|P_{lj_c^+}|^2, \end{aligned} \tag{14}$$

$$\begin{aligned} I_{j_c^+}^2 = \{&-(6l+3-7Q-2Ql)l^{-1}[l]^{-1}\langle \underline{\nu}^{j^-j^-2} \rangle \\ &- 3(2l+1-2Q)[l]^{-1}[\langle \underline{\nu}^{j^-j^+2} \rangle - \langle \underline{\nu}^{j^+j^-2} \rangle] \\ &+ (2l+1-2Q)\langle \underline{\nu}^{j^+j^+2} \rangle\}|P_{lj_c^+}|^2. \end{aligned} \tag{15}$$

In order to give a physical meaning to the cross terms and to allow a quantitative analysis, we will give the conversion to LS-coupled tensor operators w_{ζ}^{xyz}, where the orbital moment x and the spin moment y are coupled to a total moment z. The w^{z0z} with z even describe the shape (2^z pole) of the charge distribution and the w^{x1z} describe spin-orbit correlations.[19] Table I gives the relation between these tensor operators and standard atomic operators, such as L_z and S_z. Moments with $x+y+z$ odd, which describe axial couplings between spin and orbit, have been omitted. The LS-coupled tensor operators can be written as linear combinations of the jj-coupled operators $\nu^{jj'z}$ using

TABLE I. Relations between LS-coupled tensor operators w^{xyz} and standard ground-state operators, $S_z=\Sigma_i s_{z,i}$, $L_z=\Sigma_i l_{z,i}$, $T_z=\frac{1}{4}(3[l_z(l\cdot s)]_+-2l^2 s_z)_i$, $Q_{zz}=\Sigma_i(l_z^2-\frac{1}{3}l^2)_i$, $P_{zz}=\Sigma_i(l_z s_z-\frac{1}{3}l\cdot s)_i$, and $R_{zz}=\frac{1}{3}\Sigma_i[5l_z(l\cdot s)l_z-(l^2-2)l\cdot s-(2l^2+1)l_z s_z]_i$.

	w^{xyz}	p shell	d shell	f shell
Number operator	$w^{000}=n$	n	n	n
Spin-orbit coupling	$w^{110}=(ls)^{-1}\Sigma_i l_i\cdot s_i$	$2l\cdot s$	$l\cdot s$	$\frac{2}{3}l\cdot s$
Spin moment	$w_0^{011}=-s^{-1}S_z$	$-2S_z$	$-2S_z$	$-2S_z$
Orbital moment	$w_0^{101}=-l^{-1}L_z$	$-L_z$	$-\frac{1}{2}L_z$	$-\frac{1}{3}L_z$
Magnetic dipole term	$w_0^{211}=-(2l+3)l^{-1}T_z$	$-5T_z$	$-\frac{7}{2}T_z$	$-3T_z$
Quadrupole moments	$w_0^{202}=3[l(2l-1)]^{-1}Q_{zz}$	$3Q_{zz}$	$\frac{1}{2}Q_{zz}$	$\frac{1}{5}Q_{zz}$
	$w_0^{112}=3l^{-1}P_{zz}$	$3P_{zz}$	$\frac{3}{2}P_{zz}$	P_{zz}
	$w_0^{312}=3[(l-1)(2l-1)]^{-1}R_{zz}$		R_{zz}	$\frac{3}{10}R_{zz}$

$$w_\zeta^{xyz}=\sum_{jj'}(-)^{j'-j}[jj']^{1/2}\tilde{n}_{jj'z}n_{lx}^{-1}n_{sy}^{-1}\underline{n}_{xyz}^{-1}\times\begin{Bmatrix} l & x & l\\ s & y & s\\ j & z & j'\end{Bmatrix}\nu_\zeta^{jj'z}\equiv\sum_{jj'}C^{jj'xyz}\nu_\zeta^{jj'z},\qquad(16)$$

with the normalization $\underline{n}_{xyz}$ given in Ref. 19. Compact expressions for the coefficients with $z\leqslant 2$ are given in Table II. The coefficients $C^{j^+j^+xyz}$ are always $(-1)^z$. The cross operators of nonaxial coupled tensors are non-Hermitian, $\nu^{j^+j^-z}=(-)^{j^+-j^-}\nu^{j^+j^-z}$. Therefore, Hermitian operators w^{xyz} with $x+y+z$ even, which have real coefficients, must contain the difference $\nu^{j^-j^+z}-\nu^{j^+j^-z}$. Since

$$C^{j^+j^-xyz}=-C^{j^-j^+xyz},\qquad(17)$$

only the values of $C^{j^-j^+xyz}$ have been tabulated. Using Eq. (17) the cross terms between the two ground-state j levels in Eqs. (14), (15) can be collected into a single term. Although the cross terms have usually been ignored in the analysis,[17,20] they are by no means small. For instance, for a hard ferromagnet with typical moments $\langle S_z\rangle=-0.5$, $\langle L_z\rangle=-0.05$, and $\langle T_z\rangle\approx 0$ per hole, omission of the cross term increases the $I^1_{j_c^+}$ signal by more than a factor of 2.

TABLE II. Values of the coefficients $C^{jj'xyz}$ in the transform $w^{xyz}=\Sigma_{jj'}C^{jj'xyz}\nu^{jj'z}$ for the l shell operators up to $z=2$, assuming that $2l\geqslant z$ and $\Sigma_i j^i\geqslant z$. $C^{j^+j^-xyz}=-C^{j^-j^+xyz}$.

w^{xyz}	$C^{j^-j^-xyz}$	$C^{j^-j^+xyz}$	$C^{j^+j^+xyz}$
w^{000}	1	0	1
w^{110}	$-(l+1)l^{-1}$	0	1
w^{101}	$-(l+1)(2l-1)l^{-1}[l]^{-1}$	$2[l]^{-1}$	-1
w^{011}	$(2l-1)[l]^{-1}$	$-4l[l]^{-1}$	-1
w^{211}	$(l+1)(2l+3)l^{-1}[l]^{-1}$	$(2l+3)[l]^{-1}$	-1
w^{202}	$(l-1)(2l+3)l^{-1}[l]^{-1}$	$-3[l]^{-1}$	1
w^{112}	$-(l-1)(2l-1)l^{-1}[l]^{-1}$	$3(2l-1)2^{-1}[l]^{-1}$	1
w^{312}	$-(l+2)(2l+3)l^{-1}[l]^{-1}$	$-2(l+2)[l]^{-1}$	1

Furthermore, from Table II it is clear that operators for the magnetic moment ($z=1$) which have no cross terms must be linear combinations of

$$J_z\equiv L_z+S_z=-lw^{101}-\frac{1}{2}w^{011}=\frac{2l-1}{2}\nu^{j^-j^-1}+\frac{2l+1}{2}\nu^{j^+j^+1},\qquad(18)$$

$$S_z+2T_z=-\frac{1}{2}w^{011}-\frac{2l}{2l+3}w^{211}=-\frac{3}{2}\nu^{j^-j^-1}+\frac{3(2l+1)}{2(2l+3)}\nu^{j^+j^+1}.\qquad(19)$$

Thus accurate expectation values of these operators can be obtained, even if cross terms are neglected, but for all other operators cross terms need to be included.

By using the conversions given in Table II we can retrieve the well-known sum rules for LS-coupled operators[3–6] from the sum rules for jj-coupled operators in Eqs. (12)–(15):

$$I^z_{j_c^\pm}=\left\{\frac{[j_c^\pm]}{2}\langle\underline{w}^{z0z}\rangle\pm\frac{cz}{[z]}\langle\underline{w}^{(z-1)1z}\rangle\pm\frac{c(z+1)}{[z]}\langle\underline{w}^{(z+1)1z}\rangle\right\}|P_{lj_c^\pm}|^2,\qquad(20)$$

where, assuming that $|P_{lj_c^-}|^2=|P_{lj_c^+}|^2$, the integrated signals of the sum, $\rho^z\equiv I^z_{j_c^+}+I^z_{j_c^-}$, and the weighed difference, $\delta^z\equiv I^z_{jc}-(c+1)c^{-1}I^z_{j_c^-}$, are related to spin-independent ($y=0$) and spin-dependent ($y=1$) ground-state moments, respectively.

Summarizing, we derived sum rules in jj-coupled operators which relate the core-level spin-orbit split signals of polarized x-ray-absorption spectra to ground-state angular momenta. An operator has been included describing the cross terms between the ground–state levels $j=l\pm 1/2$. The sum rules which take into account these cross terms are valid in intermediate coupling. The isotropic signals of the absorption edges are related to the number of $j=l\pm 1/2$ holes in the ground state, however, polarized signals also depend on the matrix elements between the jm levels. Therefore, jj-coupled operators give more complicated expressions than LS-coupled operators.

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