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Rapid Note

Band structure and atomic sum rules for X-ray dichroism

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Abstract. Corrections to the atomic orbital sum rule for circular magnetic X-ray dichroism in solids are derived using orthonormal LMTOs as a single-particle basis for electron band states.

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Atomic physics affords a theory of X-ray dichroism by providing a set of sum rules which relate dichroic intensities, integrated over a finite energy interval, to the ground-state expectation value of effective one-electron operators [1–3]. For circular magnetic X-ray dichroism, that is the difference in absorption between right- and left-circularly polarised photons in a system with a net magnetisation, the effective operators coincide with spin and orbital multipoles [3,4].

The spherical symmetry and the discreteness of the spectrum governing the atomic results do not hold for an atom in a solid, where the spin and angular-momentum character selected by a specific X-ray transition is spread out over a band of final states. This difference has hindered the identification of a well-defined connection between the atomic sum rules and band-structure calculations of magnetic X-ray dichroism [5]. Except in cases of strong electronic correlations, such calculations have been very successful in simulating experimental absorption spectra [6,7]. It therefore seems desirable to derive a band-structure formalism which exhibits the atomic sum rules as the dominant term. This should be important not only for the interpretation of X-ray dichroism in cases where current density-functional band theory works, but also as a prerequisite for understanding dichroism in strongly correlated materials. The current paper is an attempt in this direction.

By leaving a localised hole, inner-shell photo absorption selects a specific site in the solid, which we shall label by $R = 0$. A local process is thus expected to control the excitation, to leading order. Additional contributions should emerge when the remaining sites in the lattice are taken into account, that is, when electron delocalisation is included. In this case, a minimal set of orthonormal linear muffin-tin orbitals (LMTOs) provides a suitable single-particle basis [8–10].

The macroscopic quantity of interest is the polarisation and energy dependent extinction coefficient, $\kappa^{\boldsymbol{\epsilon}}(\omega)$ [12]. In a microscopic description, this is given by

$$\kappa^{\boldsymbol{\epsilon}}(\omega) = 2\pi\,(c/\omega)^2\,\mathcal{N}\,\mathrm{Im}f^{\boldsymbol{\epsilon}}(\omega)\,,$$

where $f^{\boldsymbol{\epsilon}}(\omega)$ stands for the forward scattering amplitude, as determined by the $\mathbf{p}\cdot\mathbf{A}$ coupling between X-rays and electrons. Photon energy (in units of $\hbar$) and polarisation are identified by ω and $\boldsymbol{\epsilon}$, respectively; $\mathcal{N}$ denotes the number of excitable core electrons per unit volume. Only electric-dipole transitions will be retained between spin-orbit coupled inner orbitals, $\varphi_{\bar{n}\bar{l}\,\bar{j}\bar{m}_j}(\mathbf{r},\mathbf{s})$, localized around site $R = 0$, and spin-polarized, spin-orbit coupled band states, $\psi_k(\mathbf{r},\mathbf{s})$ [13]. We consider only magnetic circular dichroism integrated over the two partners $\left(\bar{j} = \bar{l} \pm \frac{1}{2}\right)$ of a given spin-orbit split inner shell $\left(\bar{n}\bar{l}\right)$. For this, we have

$$\int_{\sim\,\varepsilon_{\mathrm{F}}-\varepsilon_{\bar{n}\,\bar{l}\,\bar{l}+\frac{1}{2}}}^{\sim\,\varepsilon_{\mathrm{c}}-\varepsilon_{\bar{n}\,\bar{l}\,\bar{l}-\frac{1}{2}}} \left[\kappa^{+}(\omega)-\kappa^{-}(\omega)\right]\,\mathrm{d}\omega = \frac{(2\pi)^3}{3}\mathcal{N}\cos\theta\sum_k \langle\Psi_0|a_k\,a_k^{\dagger}|\Psi_0\rangle \sum_{\bar{j}=\bar{l}\pm\frac{1}{2}}\ \sum_{\bar{m}_j=-\bar{j}}^{\bar{j}} \left[\left|\left\langle\psi_k\left|Q_{1\,1}\right|\varphi_{\bar{n}\bar{l}\bar{j}\bar{m}_j}\right\rangle\right|^2 - \left|\left\langle\psi_k\left|Q_{1\,-1}\right|\varphi_{\bar{n}\bar{l}\bar{j}\bar{m}_j}\right\rangle\right|^2\right]. \quad (1)$$

Here, $\varepsilon_{\mathrm{F}} - \varepsilon_{\bar{n}\,\bar{l}\,\bar{l}\pm\frac{1}{2}}$ are the two threshold energies and ε_{c} is a cut-off, positioned far above the top of the valence band so that nothing would change if ε_{c} were increased by the spin-orbit splitting, $\varepsilon_{\bar{n}\,\bar{l}\,\bar{l}+\frac{1}{2}} - \varepsilon_{\bar{n}\,\bar{l}\,\bar{l}-\frac{1}{2}}$ of the inner level. The superscripts ± identify circular polarisations,

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and $Q_{1M} = eY_{1M}(\hat{\mathbf{r}})\, r$ is the electric dipole moment; θ is the angle between photon wave vector and magnetization direction (orbital quantisation), which we take along the z axis; Ψ_0 denotes the ground state of the system, and $a_k^\dagger$ is a fermionic creation operator for band states.

To evaluate $\left\langle \psi_k \left| Q_{1M} \right| \varphi_{\bar{n}\bar{l}\bar{j}\bar{m}_j} \right\rangle$, we use

$$\varphi_{\bar{n}\bar{l}\bar{j}\bar{m}_j}(\mathbf{r},\mathbf{s}) = \sum_{\bar{m}\,\bar{m}_s} C^{\bar{j}\,\bar{m}_j}_{\bar{l}\,\bar{m};\frac{1}{2}\,\bar{m}_s} \varphi_{\bar{n}\bar{l}}(r) Y_{\bar{l}\bar{m}}(\hat{\mathbf{r}}) \xi_{\bar{m}_s}(\mathbf{s})\,, \tag{2}$$

for the inner orbitals, that is a two-component function with the *same* radial dependence, $\varphi_{\bar{n}\bar{l}}(r)$, for $\bar{j} = \bar{l} - \frac{1}{2}$ and $\bar{l} + \frac{1}{2}$. Notice that this is an excellent approximation as the radial probability densities, $4\pi r^2 [f_\kappa(\varepsilon,r)^2 + g_\kappa(\varepsilon,r)^2]$, for $\kappa{=}l$ and $\kappa{=} -l-1$ differ appreciably only close to the nucleus where they are small [14]; here $f_\kappa(\varepsilon,r)$ and $g_\kappa(\varepsilon,r)$ are the solutions of the radial Dirac equations with $\kappa{=}l$, $\varepsilon{=}\varepsilon_{\bar{n}\,\bar{l}\,\bar{l}-\frac{1}{2}}$ and $\kappa{=} -l-1$, $\varepsilon{=}\varepsilon_{\bar{n}\,\bar{l}\,\bar{l}+\frac{1}{2}}$ for the two partners, respectively. For ψ_k we use an expansion in spin functions times spherical harmonics centered at the absorption site

$$\psi_k(\mathbf{r},\mathbf{s}) = \sum_{l\,m\,m_s} u^i_{lmm_s,k}\, \phi_l(r)\, Y_{lm}(\hat{\mathbf{r}})\, \xi_{m_s}(\mathbf{s})\,. \tag{3}$$

The inner orbitals are so localized that, in the region relevant to the integral $\left\langle \psi_k \left| Q_{1M} \right| \varphi_{\bar{n}\bar{l}\bar{j}\bar{m}_j} \right\rangle$, the self-consistent field for a band electron is dominated by the Hartree contribution, which is centrally symmetric and independent of k. As a consequence, the coefficients in expansion (3) factorise into normalization constants, $u^i_{lmm_s,k}$, and radial functions, $\phi_l(r)$, which depend *only* on the magnitude of angular momentum about the absorption site. Regarding relativistic effects, the argument given above for neglecting the $j = l \pm \frac{1}{2}$ dependence of the inner radial function holds also for the radial functions of the band states. The exchange-correlation potential *does* depend on the spin and possibly the orbital character but, in the inner region, it amounts to m_s- and possibly lm-dependent shifts, which are *small* compared with the radial kinetic energy, $\varepsilon_k - v(r) - l(l+1)/r^2$, in that region. Compared with that kinetic energy, the band-energy range, $\varepsilon_c - \varepsilon_F$, is also small.

We now write the difference between the squared matrix elements for right- and left-circularly polarized light as

$$\sqrt{2} \sum_{M=\pm 1} C^{1M}_{1M;10} \left\langle \psi_k \left| Q_{1M} \right| \varphi_{\bar{n}\bar{l}\bar{j}\bar{m}_j} \right\rangle \left\langle \varphi_{\bar{n}\bar{l}\bar{j}\bar{m}_j} \left| Q^*_{1M} \right| \psi_k \right\rangle,$$

insert expressions (2) and (3), and apply the Wigner-Eckart theorem. Notice that, owing to the sum over $\bar{j}$ in (1), the resulting expression is spin independent. The angular part is then recoupled with use of the transformation [15]

$$\frac{(-1)^{M+l-\bar{l}}}{2\bar{l}+1} \sum_{\bar{m}} C^{\bar{l}\bar{m}}_{l\,m;1\,-M}\, C^{\bar{l}\,\bar{m}}_{l'm';1\,-M'} = \sum_{l''\,m''} (-1)^{l''-m''+l-m}\, C^{l''\,-m''}_{1\,M;\,1\,-M'}\, C^{l''\,m''}_{l'\,m';\,l\,-m} \begin{Bmatrix} l & 1 & \bar{l} \\ 1 & l' & l'' \end{Bmatrix},$$

with $l'' = 0,1,2$, corresponding to isotropic absorption, circular, and linear dichroism, respectively. Hence, we obtain the result

$$\int_{\sim\varepsilon_F-\varepsilon_{\bar{n}\,\bar{l}\,\bar{l}+\frac{1}{2}}}^{\sim\varepsilon_c-\varepsilon_{\bar{n}\,\bar{l}\,\bar{l}-\frac{1}{2}}} \left[\kappa^+(\omega) - \kappa^-(\omega)\right] \mathrm{d}\omega = \pi^2 e^2 \mathcal{N} \cos\theta \sum_{l=\bar{l}\pm 1} \frac{l-\bar{l}}{2l+1} R_{l1\bar{l}} \left\langle \Psi_0 \left| L^l_z \right| \Psi_0 \right\rangle, \tag{4}$$

with the radial integral over the inner region defined as

$$R_{l1\bar{l}} \equiv \left(\int_0^\infty \varphi_{\bar{n}\bar{l}}(r)\; r\, \phi_l(r)\; r^2 \mathrm{d}r \right)^2, \tag{5}$$

and $\int_0^\infty \varphi_{\bar{n}\bar{l}}(r)^2\, r^2 \mathrm{d}r \equiv 1$. The operator L^l_z is given by

$$L^l_z = \sum_k a_k a_k^\dagger \sum_m m \sum_{m_s} \left| u^i_{lmm_s,k} \right|^2. \tag{6}$$

The individual normalisations of (5) and (6) are irrelevant when simulating the integrated dichroism (4). This is because normalization of the band states to unity in the solid merely fixes the normalization of the product $u^i_{lmm_s,k}\, \phi_l(r)$ in (3). The usefulness of atomic sum-rules, however, stems from a separation into an atomic factor which is independent of the magnetisation direction, and a remainder which, for circular dichroism, is approximately the ground-state orbital angular momentum of the excited atom. Suppose normalisations could be defined such that $u^i_{lmm_s,k}$ were equal to the $R = 0$ component of the eigenvectors, $u^\perp_{Rlmm_s,k}$, for the states

$$\psi_k(\mathbf{r},\mathbf{s}) = \sum_{Rlmm_s} \chi^\perp_{Rlm}(\mathbf{r}-\mathbf{R})\, \xi_{m_s}(\mathbf{s})\, u^\perp_{Rlmm_s,k}\,, \tag{7}$$

in a representation of *orthonormal orbitals*. Then, from (4) and (6), $\left\langle \Psi_0 \left| L^l_z \right| \Psi_0 \right\rangle$ would be the expectation value of the orbital angular momentum in the ground state, and the atomic sum rule would also hold in the solid.

Our use of LMTOs is motivated by the following features: they constitute a minimal basis whose orthonormal representation and spherical-harmonic expansions about neighboring sites are well known; their use in practical computations is well established [8–11], even for systems with appreciable electronic correlations [16], and for systems with spin-orbit coupling and spin-polarization [17]; the simple formalism for the orthonormal set, which we shall use below, was recently re-derived without resort to the approximations of taking the interstitial kinetic energy equal to zero and of dividing space into atomic spheres [9–11]. Moreover, the LMTOs have recently been generalized to Nth-order MTOs spanning the states in a broad energy range, the accuracy and range increasing with N, for a fixed basis-set size [11].

MTOs are derived from an MT-potential, *i.e.* a superposition of atom-centered spherically symmetric potential wells with ranges limited to about 0.7 times the distance to the nearest neighbour [10]. In accordance with (7), we shall use MTOs derived from a spin- and orbital-independent potential: $V(\mathbf{r}) \equiv \sum_R v_R(|\mathbf{r}-\mathbf{R}|)$. To construct an LMTO, one first solves the appropriate radial Schrödinger or scalar-relativistic Dirac equation for various energies in the band region, thus obtaining the radial functions $\phi_{Rl}(\varepsilon, r)$. Each of these is then multiplied by $Y_{lm}(\widehat{\mathbf{r}})$ and, if we are using the atomic-spheres approximation (ASA), truncated outside the atomic sphere. If not, they are augmented continuously with tails; these are localized (screened) solutions of the wave equation with the correct energies and are excluded from any inner region [9–11]. As a result, we obtain the so-called truncated or kinked partial waves, $\phi_{Rlm}(\varepsilon, \mathbf{r}-\mathbf{R})$. Now, the LMTO,

$$\begin{aligned}&\chi_{Rlm}(\mathbf{r}-\mathbf{R}) \equiv \\ &\phi_{Rlm}(\mathbf{r}-\mathbf{R}) + \sum_{R'l'm'} \dot{\phi}_{R'l'm'}(\mathbf{r}-\mathbf{R}')\ h_{R'l'm',Rlm}\,, \end{aligned} \tag{8}$$

centered at site R and with spherical-harmonic character lm, is defined as the corresponding partial wave, taken at energy ε_ν at the centre of interest, plus a *smoothing cloud* of the first energy derivatives, $\dot{\phi}_{R'l'm'}(\mathbf{r}-\mathbf{R}') \equiv \partial \phi_{R'l'm'}(\varepsilon, \mathbf{r}-\mathbf{R}')/\partial\varepsilon\big|_{\varepsilon_\nu}$, of partial waves at their own and at neighboring sites. (Here, and in the following, an omitted energy argument implies that $\varepsilon \equiv \varepsilon_\nu$.) In (8), the expansion coefficients, h, form a Hermitian matrix which is approximately the *band Hamiltonian* with respect to ε_ν, for the MT-potential used to generate the LMTO set. Specifically, since the LMTO is smooth, we may operate with $(-\Delta + V - \varepsilon_\nu)$ on each term in (8) to obtain $(-\Delta + V - \varepsilon)|\phi(\varepsilon)\rangle = 0$. Energy differentiation then yields $(-\Delta + V - \varepsilon)|\dot{\phi}(\varepsilon)\rangle = |\phi(\varepsilon)\rangle$ and, as a result,

$$\begin{aligned}&(-\Delta + V(\mathbf{r}) - \varepsilon_\nu)\,\chi_{Rlm}(\mathbf{r}-\mathbf{R}) = \\ &\sum_{R'l'm'} \phi_{R'l'm'}(\mathbf{r}-\mathbf{R}')\ h_{R'l'm',Rlm}\,. \end{aligned} \tag{9}$$

As $\partial\phi(\varepsilon,\mathbf{r})T(\varepsilon)/\partial\varepsilon = \dot{\phi}(\mathbf{r})\,T + \phi(\mathbf{r})\,\dot{T}$, with T=1, changing the energy-dependent normalization of a partial wave changes the shape of its energy derivative function by adding some amount of $\phi(\mathbf{r})$ to it. This in turn changes the shape of the LMTOs *via* equation (8), but not the Hilbert space spanned by them. If each partial wave is normalized to one, we obtain a *nearly orthonormal* set since, in that case, the corresponding $\dot{\phi}_{Rlm}(\mathbf{r})$ is orthogonal to $\phi_{Rlm}(\mathbf{r})$, as energy differentiation will reveal. Neglecting the overlap between partial waves at different sites (ASA), or using Löwdin orthogonalisation [9–11], one obtains

$$\langle \phi_{Rlm} \mid \phi_{R'l'm'} \rangle = \delta_{RR'}\delta_{ll'}\delta_{mm'}, \left\langle \phi_{Rlm} \mid \dot{\phi}_{R'l'm'} \right\rangle = 0.$$

Insertion into (9) and (8) finally shows that, in the nearly orthonormal representation, the LMTO Hamiltonian and the overlap matrices are given by $\langle\chi| - \Delta + V - \varepsilon_\nu|\chi\rangle = h$ and $\langle\chi \mid \chi\rangle = 1 + hph$, respectively. (The off-diagonal elements of the matrix $p \equiv \langle\dot{\phi} \mid \dot{\phi}\rangle$ may be neglected.) The *truly orthonormal* set is therefore

$$\begin{aligned}\left|\chi^{\perp}\right\rangle &= \left|\phi^{\perp}\right\rangle + \left|\dot{\phi}^{\perp}\right\rangle h^{\perp} = \left|\chi^{\perp}\right\rangle (1+hph)^{-\frac{1}{2}} \\ &= \left(|\phi\rangle + \left|\dot{\phi}\right\rangle h\right)(1+hph)^{-\frac{1}{2}}\,, \end{aligned} \tag{10}$$

where the expansion matrix,

$$h^{\perp} \equiv (1+hph)^{-\frac{1}{2}}\ h\ (1+hph)^{-\frac{1}{2}}\,, \tag{11}$$

is the band Hamiltonian without spin polarization and spin-orbit coupling, and where $\left|\phi^{\perp}\right\rangle = |\phi\rangle\,(1+hph)^{\frac{1}{2}}$ and $\left|\dot{\phi}^{\perp}\right\rangle = \left(\left|\dot{\phi}\right\rangle - |\phi\rangle\,hp\right)(1+hph)^{\frac{1}{2}}$.

Next, we may work out the matrix elements of the exchange splitting and spin-orbit coupling in the orthonormal representation (10), add them to $\varepsilon_\nu + h^{\perp}$, and diagonalize to find the eigenvalues, ε_k, eigenvectors, $u^{\perp}_{Rlmm_s,k}$, and band states (7). Expanding the latter in spherical harmonics about the excited site using (10), we are finally able to identify the coefficients $u^i_{lmm_s,k}$ in (3). (As usual, an omitted subscript R implies that R=0.) At first glance, it seems as if *two* radial integrals in (5) are needed: one involving $\phi_l(r)$, as contributed by the head of the LMTO, and the other involving $\dot{\phi}_l(r)$, as contributed mainly by the tails of neighboring LMTOs. However we observe that, when integrating the radial equation for the l-channel outwards we may use the *same initial condition* for all energies. Hence, we obtain an energy-derivative function, $\dot{\phi}^i_l(r)$, which is essentially excluded from the inner region, and whose contribution to the integral (5) may therefore be neglected [18]. Since this procedure amounts to choosing a particular energy-dependent normalisation of the corresponding radial function, $\phi^i_l(\varepsilon, r)$, the energy derivative function, $\dot{\phi}^i_l(r)$, must be a particular linear combination of the Y_{lm} projections of $\phi_{lm}(\mathbf{r})$ and $\dot{\phi}_{lm}(\mathbf{r})$. These projections are independent of m in the ASA, where $\phi_{lm}(\varepsilon, \mathbf{r}) = \phi_l(\varepsilon, r)\,Y_{lm}(\hat{\mathbf{r}})$, but only approximately independent when $\phi_{lm}(\varepsilon, \mathbf{r})$ is a Löwdin orthonormalized kinked partial wave. In the latter case, the m-dependence may be minimized through adjustment of the screening [10,11]; this dependence will be neglected in the present paper. Choosing to normalize $\phi^i_{lm}(\varepsilon, \mathbf{r})$ to one at ε_ν, we can express the linear combination which does not contribute to the radial integral (5) as a projection onto the orthonormal $\left(\phi, \dot{\phi}\right)$ set

$$\left|\dot{\phi}^i\right\rangle = \left|\dot{\phi}\right\rangle + |\phi\rangle \left\langle \phi \mid \dot{\phi}^i \right\rangle \equiv \left|\dot{\phi}\right\rangle + |\phi\rangle\, o^i. \tag{12}$$

Here, $\langle \phi \mid \dot{\phi}^i \rangle \equiv o^i$ is a matrix whose elements vanish unless R=R'=0 and l=$l' = \bar{l} \pm 1$, and whose off-diagonal elements are neglected together with any m-dependence. We thus eliminate $\dot{\phi}_{lm}(\mathbf{r})$ from (10) and find

$$\left|\chi^{\perp}\right\rangle = \left[|\phi\rangle\,(1 - o^i h) + \left|\dot{\phi}^i\right\rangle h\right](1+hph)^{-\frac{1}{2}}\,.$$

(One should keep in mind that $|\dot{\phi}^i\rangle = |\dot{\phi}\rangle$ unless $R = 0$ and $l = \bar{l} \pm 1$.) Identification of (7) with (3) yields

$$\begin{aligned} u_k^i &= (1 - o^i h)(1 + hph)^{-\frac{1}{2}} u_k^{\perp} \\ &= (1 - o^i h^{\perp} - \frac{1}{2} h^{\perp} p h^{\perp} + ...) u_k^{\perp}. \end{aligned} \tag{13}$$

and, hence, the final result for use in (6) is

$$\begin{aligned} &\left|u_{lmm_s,k}^i\right|^2 = \left|u_{lmm_s,k}^{\perp}\right|^2 \\ &-2\,\mathrm{Re}\left\{u_{lmm_s,k}^{\perp *}\, o_l^i \sum_{R'l'm'} h_{lm,R'l'm'}^{\perp} u_{R'l'm'm_s,k}^{\perp}\right\} \\ &+\left|o_l^i \sum_{R'l'm'} h_{lm,R'l'm'}^{\perp}\, u_{R'l'm'm_s,k}^{\perp}\right|^2 \\ &-\mathrm{Re}\left\{u_{lmm_s,k}^{\perp *} \sum_{R'l'm'} \left(h^{\perp} p h^{\perp}\right)_{lm,R'l'm'}\, u_{R'l'm'm_s,k}^{\perp}\right\} + ... \end{aligned} \tag{14}$$

The first term is contributed by LMTO heads only and gives the atomic sum rule. Of the terms with $R' \neq 0$, the ones on the second line are LMTO head-tail contributions, and those on the remaining lines are tail-tail contributions. However, the sum of the terms on the second and third lines may also contribute to the atomic sum rule, as they depend on ε_ν. (This dependence is cancelled by the ε_ν dependence of the radial integral brought about by $\phi_l\,(\varepsilon_\nu, r)$ in (5). Notice that to be able to neglect the m-dependence of the valence orbital in the radial integral, we have chosen this orbital as a partial wave rather than an LMTO, which has longer range.) To clarify this point, let us assume that the spin-orbit interaction is smaller than the exchange splitting and that the latter is fairly independent of k. In this case,

$$\sum_{R'l'm'} h_{lm,R'l'm'}^{\perp} u_{R'l'm'm_s,k}^{\perp} \approx \left(\epsilon_k - \varepsilon_\nu\right) u_{lmm_s,k}^{\perp},$$

where ϵ_k is the (doubly degenerate) band without spin-orbit and exchange couplings, and (14) reduces to

$$\begin{aligned} &\left|u_{lmm_s,k}^i\right|^2 \approx \left[1 - \left(\epsilon_k - \varepsilon_\nu\right) o_l^i\right]^2 \left|u_{lmm_s,k}^{\perp}\right|^2 \\ &-\mathrm{Re}\left\{u_{lmm_s,k}^{\perp *} \left(\epsilon_k - \varepsilon_\nu\right) \sum_{R'l'm'} \left(h^{\perp} p\right)_{lm,R'l'm'}\, u_{R'l'm',k}^{\perp}\right\}. \end{aligned}$$

We now realize that the *deviation* from the atomic sum rule is the contribution to the integrated dichroism (4) stemming from the second and further lines of (14), *after* they have been *minimized* with respect to ε_ν, that is, when ε_ν is chosen as the centre of gravity of the unoccupied part of the l-projected density of band states

$$\varepsilon_{\nu l} = \frac{\sum_k \epsilon_k N_k^l}{\sum_k N_k^l}, \quad N_k^l \equiv \left\langle \Psi_0 \left| a_k a_k^{\dagger} \right| \Psi_0 \right\rangle \sum_{m\, m_s} \left|u_{lmm_s,k}^{\perp}\right|^2.$$

This choice of ε_ν is the one which also minimizes the errors of the LMTO method. (When an l-independent ε_ν is used, the $o_l^i R_{l1\bar{l}}/(2l+1)$-weighted average should be chosen).

To summarise: to estimate the accuracy of atomic sum rules for X-ray dichroism in solids, we have examined the problem of X-ray absorption by band electrons, with emphasis on the interpretation of the total intensity of spectra obtainable with circular polarisation in magnetic systems. Using an orthonormal set of LMTOs, we have found corrections to the atomic results in the form of energy moments of the band. Applications of the approach to unpolarised and linear-dichroic spectra, together with a numerical determination of the actual size of the corrections in specific cases will be reported elsewhere.

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12. Another macroscopic quantity of interest, the absorption coefficient $\mu^{\boldsymbol{\epsilon}}(\omega)$, is defined by $\mu^{\boldsymbol{\epsilon}}(\omega) = (2\omega/c)\kappa^{\boldsymbol{\epsilon}}(\omega)$.
13. Translational symmetry is no prerequisite for our formalism. For states with translational symmetry, k is a joint label for the band index and the Bloch vector.
14. This approximation causes errors smaller than 1% for the $L_{2,3}$ edges of $3d$ transition metals and the $M_{4,5}$ edges of rare earths [2].
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