A multiple-scattering theory of circular and linear dichroism for photoemission and photoabsorption

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A unified treatment of circular dichroism, both natural and magnetic, in (spin-resolved) photoemission and photoabsorption from core levels is given, valid in the many-body case and for extended systems, together with an extension of the formalism to treat linear dichroism. The reduction of this scheme to a one-electron picture in the framework of multiple-scattering theory is briefly discussed and shows the intimate connection of the two spectroscopies *via* a generalized optical theorem. Plausibility arguments are given that in correlated *d*-band systems screening and relaxation effects are not so drastic as in other cases, due to the autoscreening action of the excited photoelectron, so that the final density of states is much like the initial unperturbed one. It is shown how to exploit this point of view to obtain in favorable cases separated orbital and spin moment radial (surface) distribution maps from dichroic magnetic EXAFS spectra (photoelectron diffraction patterns) related to the ground state. Dichroic natural spectra, both in photoemission and absorption, are shown to be sensitive only to atoms in chiral geometry.

Keywords: circular and linear dichroism; multiple scattering theory; sum rules.

1. Introduction

In recent years, circular and linear dichroism in core-level excitations have received increasing attention due to the availability of polarized synchrotron radiation in the soft X-ray regime and the realization that dichroic spectroscopies have the power to increase our selectivity on the physical quantities we want to study. Therefore it would be useful to have a theoretical scheme to use as a guidance in planning the experiment, all the more that the same scheme can provide the necessary tools for analyzing the experimental results and extracting the maximum of information there contained. In the following we shall show that this framework is provided by the multiple-scattering (MS) theory as a unifying language to interpret the various spectroscopies.

2. The multiple-scattering basis

Since we want to derive expressions for the cross sections for circular (natural and magnetic) and linear dichroic spectroscopies valid for the many-body case and in extended systems, we work in the second quantization scheme. Our one particle basis will comprise spin–orbit coupled core states of the form

$$\Phi^{c}_{c\gamma;l_c}(\mathbf{r}) = R_c(r)|c\gamma; l_c) = R_c(r)\sum_{m_c\boldsymbol{\sigma}} Y_{l_c m_c}\boldsymbol{\chi}_{\boldsymbol{\sigma}}\,(l_c m_c 1/2\boldsymbol{\sigma}|c\gamma)\,, \quad (1)$$

(where χ_σ are the usual spin functions) and valence occupied and excited states which are MS solutions of the Schrödinger equation, obtained from the Dirac equation by working with the upper component of the wave-function after eliminating the lower one (Wood & Boring, 1978). This will ensure that the singularity of the potential at the origin will be of the centrifugal type ($\sim r^{-2}$) even for the spin–orbit potential. Allowing for spin-polarized potential the equation reads, in a.u.,

$$\left\{\nabla^2 + k_e^2 - V_0(\mathbf{r}) - V_1(\mathbf{r})s_z - 2V_2(\mathbf{r})\vec{\ell}\cdot\vec{s}\right\}\psi_{\mathbf{k}_e,s}(\mathbf{r}) = 0,$$

supplemented by scattering wave boundary conditions

$$\psi_{\mathbf{k}_e,s}(\mathbf{r}) = e^{i\mathbf{k}_e\cdot\mathbf{r}}\boldsymbol{\chi}_s - f(\hat{\mathbf{k}}_e, s; \hat{\mathbf{r}}, s')\frac{e^{k_e r}}{r}\boldsymbol{\chi}_{s'}$$

describing an incoming electron plane wave along the direction $\hat{\mathbf{k}}_e$ with spin projection $s = (\pm 1/2)$ along the quantization axis and a scattered spherical wave along direction $\hat{\mathbf{r}}$ with spin projection s' and scattering amplitude $f(\hat{\mathbf{k}}_e, s; \hat{\mathbf{r}}, s')$. Here $V_0(\mathbf{r}) = [V_\uparrow(\mathbf{r}) + V_\downarrow(\mathbf{r})]/2$ is the average of the spin up and spin down potential, $V_1(\mathbf{r})$ their semi-difference and $V_2(\mathbf{r})$ the usual spin orbit potential corrected by relativistic effects.

In the MS approach the solution inside the *i*th atomic muffin-tin sphere can be written as

$$\psi_{\mathbf{k}_e,s}(\mathbf{r}_i) = \sum_{L\boldsymbol{\sigma}} B^i_{L\boldsymbol{\sigma}}(\mathbf{k}_e, s)R_{L\boldsymbol{\sigma}}(r_i)Y_L(\hat{\mathbf{r}}_i)\boldsymbol{\chi}_{\boldsymbol{\sigma}}\,, \quad (2)$$

writing for brevity $L \equiv l, m$. With a proper normalization of the radial functions $R_{L\sigma}(r_i)$ to one state per Rydberg, the scattering amplitudes $B^i_{L\sigma}(\mathbf{k}_e, s)$ obey the MS equations (Gunnella *et al*, 1998),

$$\sum_j \sum_{L'\sigma'} M^{ij}_{L\sigma,L'\sigma'} B^j_{L'\sigma'}(\mathbf{k}_e, s) = \boldsymbol{\delta}_{s\boldsymbol{\sigma}}\, i^l Y_L(\hat{\mathbf{k}}_e)e^{i\mathbf{k}_e\cdot\mathbf{R}_i},$$

where

$$M^{ij}_{L\sigma,L'\sigma'} = \left(t^{-1}_{lm\sigma,l'm'\sigma'}\delta_{ij}\delta_{ll'}\delta_{m+\sigma,m'+\sigma'} + G^{ij}_{L,L'}\delta_{\sigma,\sigma'}\right)$$

is the usual MS matrix generalized to spin variables and $\mathbf{R}_i$ denotes the position of the *i*th atom in the cluster with respect to the origin of the coordinates.

By introducing as usual the scattering path operator $\tau^{ij}_{L\sigma,L'\sigma'}$ as the inverse of $M^{ij}_{L\sigma,L'\sigma'}$, the solution for the scattering amplitudes $B^i_{L\sigma}$ is given by

$$B^i_{L\sigma}(\mathbf{k}_e, s) = \sum_j \sum_{L'} \boldsymbol{\tau}^{ij}_{L\boldsymbol{\sigma},L's} i^{l'} Y_{L'}(\hat{\mathbf{k}}_e)e^{i\mathbf{k}_e\cdot\mathbf{R}_j}. \quad (3)$$

As is well known, $\tau^{ij}_{L\sigma,L's}$ is the probability amplitude for the excited photoelectron to propagate from site *i*, starting with angular momentum *L* around site *i* and spin σ, to arrive at site *j* with angular momentum L' and spin σ'. It is the obvious generalization of the corresponding spin-independent quantity (Natoli, 1995).

Also it is worth noting that the scattering amplitute $B^i_{L\sigma}$ satisfies a generalized optical theorem (Natoli *et al.*, 1986),

$$\sum_s \int d\hat{\mathbf{k}}_e B^i_{L\sigma}(\mathbf{k}_e, s)B^j_{L'\boldsymbol{\sigma}'}(\mathbf{k}_e, s) = \mathrm{Im}\ \boldsymbol{\tau}^{\mathrm{ij}}_{\mathrm{L}\boldsymbol{\sigma},\mathrm{L}'\boldsymbol{\sigma}'} \quad (4)$$

which can be used to relate averages of operators in the final state to a density of states in case of absorption.

Since we shall be concerned with transition from localized core states which project the properties of the final state onto an atomic site, we shall consider for convenience the following fermionic field,

$$\Psi(\mathbf{r}) = \sum_{lm\boldsymbol{\sigma}} R_{lm\boldsymbol{\sigma}}(r)Y_{lm}(\hat{\mathbf{r}})\boldsymbol{\chi}_{\boldsymbol{\sigma}}a_{lm\boldsymbol{\sigma}} + \sum_{\boldsymbol{\gamma}} \boldsymbol{\Phi}^{c}_{c\boldsymbol{\gamma};l_c}(\mathbf{r})a_{c\boldsymbol{\gamma}}\,, \quad (5)$$

where the operators $a_{lm\sigma}$ annihilates an electron in the extended valence states and $a_{c\gamma}$ annihilates an electron in the core states. In this representation the independent particle basis for excited states is given by

$$|\Psi_{\mathbf{k}_e,s}> = \sum_{lm\sigma} B^i_{lm\sigma}(\mathbf{k}_e,s)a^\dagger_{lm\boldsymbol{\sigma}}a_{c\boldsymbol{\gamma}}|0> \tag{6}$$

where $|0>$ is the Slater determinant of the occupied states.

3. The expression for the magnetic dichroic signal

In the dipole approximation the transition operator is

$$\boldsymbol{\pi}\cdot\mathbf{r} = (4\boldsymbol{\pi}/3)r\sum_{\boldsymbol{\lambda}} Y^*_{1\boldsymbol{\lambda}}(\boldsymbol{\pi})Y_{1\boldsymbol{\lambda}}(\hat{\mathbf{r}}), \tag{7}$$

where $\boldsymbol{\pi}$ is the complex polarization of the incident light. The cross-section for the ejection of an electron along the $\hat{\mathbf{k}}_e$ direction with spin s is given by

$$\frac{d\sigma_s}{d\mathbf{k}_e}(\omega,\boldsymbol{\pi}) = 4\boldsymbol{\pi}^2\boldsymbol{\alpha}\hbar\boldsymbol{\omega}\sum_{\boldsymbol{\mu\nu}} Y^*_{1\boldsymbol{\mu}}(\boldsymbol{\pi})Y^*_{1\boldsymbol{\nu}}(\boldsymbol{\pi}^*)\boldsymbol{\sigma}_{\boldsymbol{\mu\nu}}(\boldsymbol{\omega};s), \tag{8}$$

where $\hbar\omega$ is the energy of the incident photon and, by definition,

$$\sigma_{\mu\nu}(\omega;s) = \left(\frac{4\pi}{3}\right)^2 <g|\sum_n r_n Y_{1\mu}(\hat{\mathbf{r}}_n)|\overline{f}_{\mathbf{k}_e,s}> \times <\overline{f}_{\mathbf{k}_e,s}|\sum_m r_n Y_{1\nu}(\hat{\mathbf{r}}_m)|g> . \tag{9}$$

Here the sums over n, m run over all the electrons in the system and $|\overline{f}_{\mathbf{k}_e,s}>$ is the many-body time-reversed scattering state, normalized to one state per Rydberg, as appropriate for photoemission so that, if Θ is the time reversal operator, then $|\overline{f}_{\mathbf{k}_e,s}> = \Theta|f_{\mathbf{k}_e,s}>$. Note that the total cross section is obtained by summing over all states $|\overline{f}_{\mathbf{k}_e,s}>$ with the same final energy (elastic and inelastic channels), integrating over all escape directions and summing over the photoelectron spin variables. In the independent particle approach the final state is $\Theta|\Psi_{\mathbf{k}_e,s}>$ so that to obtain the total cross section it is sufficient to integrate over the directions of the ejected photoelectron and sum over the final spin. This is the one-particle description of the photoemission process.

From Eq. (8) one immediately derives for the magnetic circular dichroic (MCD) signal the expression

$$\frac{d\sigma_{MCD}}{d\mathbf{k}_e} = 4\pi^2\alpha\hbar\omega\sum_{\mu\nu}\left[Y^*_{1\mu}(\boldsymbol{\pi})Y^*_{1\boldsymbol{\nu}}(\boldsymbol{\pi}^*) - Y^*_{1\boldsymbol{\mu}}(\boldsymbol{\pi}^*)Y^*_{1\boldsymbol{\nu}}(\boldsymbol{\pi})\right]\sigma_{\mu\nu}(\omega) \tag{10}$$

as the difference of the cross section with different helicity $\boldsymbol{\pi}$ and $\boldsymbol{\pi}^*$. Using the relation (see Varshalovich *et al.*, 1988, p. 66)

$$Y_{1\mu}(\boldsymbol{\pi})Y_{1\boldsymbol{\nu}}(\boldsymbol{\pi}^*) - Y_{1\boldsymbol{\mu}}(\boldsymbol{\pi}^*)Y_{1\boldsymbol{\nu}}(\boldsymbol{\pi}) = (8\pi)^{1/2}\sum_{\boldsymbol{\lambda}}(-1)^{\boldsymbol{\lambda}}\begin{pmatrix} 1 & 1 & 1 \\ \mu & \nu & -\boldsymbol{\lambda}\end{pmatrix}Y_{1\boldsymbol{\lambda}}(\hat{\mathbf{k}}_{ph}), \tag{11}$$

where $\hat{\mathbf{k}}_{ph}$ is the direction of the incident photon, we easily find for the MCD signal

$$\frac{d\sigma_{MCD}}{d\mathbf{k}_e}(\omega) = -C(\omega)\sum_{\lambda\mu\nu}\begin{pmatrix} 1 & 1 & 1 \\ \mu & \nu & \lambda\end{pmatrix}Y_{1\lambda}(\hat{\mathbf{k}}_{ph})\sigma_{\mu\nu}(\omega), \tag{12}$$

putting for brevity $C(\omega) = 4\pi^2\alpha\hbar\omega(8\pi)^{1/2}$.

Writing the transition operators in Eq. (9) in second quantized form [*e.g.* $T_\mu = (4\pi/3)\int d\mathbf{r}\ \boldsymbol{\Psi}^\dagger(\mathbf{r})Y_{1\boldsymbol{\mu}}(\mathbf{r})\boldsymbol{\Psi}(\mathbf{r})$] and picking out only the matrix elements related to the physical process of interest we find, after some tedious angular-momentum algebra,

$$T_\mu = \sum_{lm\sigma}(l_c\|1\|l)'(-1)^\mu(2c+1)^{1/2}D^c_{lm\sigma}\sum_{jj_z}(2j+1) \times\begin{Bmatrix} l & 1 & l_c \\ c & 1/2 & j\end{Bmatrix}\begin{pmatrix} c & 1 & j \\ \gamma & -\mu & j_z\end{pmatrix}\begin{pmatrix} l & 1/2 & j \\ m & \sigma & j_z\end{pmatrix} \times a^\dagger_{c\gamma}a_{lm\sigma}, \tag{13}$$

where

$$(l_c\|1\|l)' = (-1)^{l_c}[(2l_c+1)(2l+1)]^{1/2}\begin{pmatrix} l_c & 1 & l \\ 0 & 0 & 0\end{pmatrix}(4\pi/3)$$

and $D^c_{lm\sigma} = \int drr^3R_c(r)R_{lm\sigma}(r)$ is the dipole radial matrix element of the transition. Notice that in the recoupling of the 3-j symbols to derive the above equation, the sum over m is never used, so that we can retain for the moment the m and σ dependence of $D^c_{lm\sigma}$. A similar expression is found for T_ν except for the replacement of $\mu\rightarrow-\nu$ and the disappearance of the factor $(-1)^\mu$, as appropriate for the complex conjugate matrix element.

Inserting these espressions in Eq. (12) and using Eq. (6.2.8) of Edmond (1974) we finally find

$$\frac{d\sigma_{MCD}}{d\mathbf{k}_e}(\omega) = C(\omega)\sum_{\lambda}Y^*_{1\lambda}(\mathbf{k}_{ph})\sum_{ll'}\sum_{jj'}f(1;jj';ll')\sum_{j_zj'_z}(-1)^{j_z} \times\sum_{m\sigma}\sum_{m'\sigma'}\begin{pmatrix} l & 1/2 & j \\ m & \sigma & -j_z\end{pmatrix}\begin{pmatrix} l' & 1/2 & j' \\ m' & \sigma' & -j'_z\end{pmatrix} \times\begin{pmatrix} 1 & j' & j \\ \lambda & -j'_z & j_z\end{pmatrix}D^c_{lm\sigma}D^c_{l'm'\sigma'} <g|a^\dagger_c a_{lm\sigma}|\overline{f}_{\mathbf{k}_e,s}> \times <\overline{f}_{\mathbf{k}_e,s}|a^\dagger_{l'm'\sigma'}a_c|g>, \tag{14}$$

where $f(q;jj';ll')$ is a symmetric expression in jj' and ll' given by

$$f(q;jj';ll') = (l_c\|1\|l)'\left(l_c\|1\|l'\right)'(2c+1)(2j+1)(2j'+1)\times \begin{Bmatrix} l & 1 & l_c \\ c & 1/2 & j\end{Bmatrix}\begin{Bmatrix} l' & 1 & l_c \\ c & 1/2 & j'\end{Bmatrix}\begin{Bmatrix} 1 & j' & j \\ c & q & 1\end{Bmatrix}(-1)^{c+j+j'}.$$

In deriving Eq. (14) we have assumed that the matrix element $<\overline{f}_{\mathbf{k}_e,s}|a^\dagger_{l'm'\sigma'}a_{c\gamma}|g>$ does not depend crucially on the magnetic quantum number γ, so that we could recouple the 3-j symbols with the help of the appropriate 6-j symbol. In keeping with this we have dropped in the formula the index γ of the annihilation operator of the core hole. This assumption is obviously valid when the interaction of the core hole with the photoelectron in the final state can be neglected, but can remain equally valid in the presence of such interaction. This is the case, for example, if the interaction reduces to a static spherical Coulomb potential felt by the photoelectron or if one can perform an average over the two spin–orbit split edges of the multiplet structure between the photoelectron and the core hole.

4. The MCD signal in photoelectron diffraction

Eq. (14) is the general many-body result for the MCD photoemission cross section we wanted to arrive at, valid for extended systems and general direction of the incoming photon with respect to the quantization axis. Its content is best illustrated in the case of the one-particle

picture. Indeed, if we take the photon direction parallel to the quantization axis, so that $\lambda = 0$, evaluate the various three and six j symbols and use Eq. (6) for the final state, assuming only transitions to $l = l_c + 1$ orbital angular momenta, we obtain, writing for short $A_{lm\sigma} = D^c_{lm\sigma} B_{lm\sigma}(\mathbf{k}_e, s)$

- for transitions from the $J_c = l_c + 1/2$ edge

$$\frac{d\sigma_{MCD}}{d\mathbf{k}_e}(\omega, s) = \frac{C(\omega)}{2(2l_c+1)(2l_c+3)} \times \sum_m \left[G_3(m) \left(A^*_{lm\uparrow} A_{lm\uparrow} - A^*_{l-m\downarrow} A_{l-m\downarrow} \right) + G_1(m) \left(A^*_{lm+1\downarrow} A_{lm\uparrow} - A^*_{l-m-1\uparrow} A_{l-m\downarrow} \right) \right], \quad (15)$$

- for transitions from the $J_c = l_c - 1/2$ edge

$$\frac{d\sigma_{MCD}}{d\mathbf{k}_e}(\omega, s) = \frac{C(\omega)}{2(2l_c+1)(2l_c+3)} \times \sum_m \left[G_2(m) \left(A^*_{lm\uparrow} A_{lm\uparrow} - A^*_{l-m\downarrow} A_{l-m\downarrow} \right) - G_1(m) \left(A^*_{lm+1\downarrow} A_{lm\uparrow} - A^*_{l-m-1\uparrow} A_{l-m\downarrow} \right) \right], \quad (16)$$

where

$$G_3(m) = 2\left\{ m(2l_c+1)(l_c+1) - l_c(l_c+1) + 2l_c m^2 \right\}$$
$$G_2(m) = 2\left\{ m(2l_c+1) l_c + l_c(l_c+1) - 2l_c m^2 \right\}$$
$$G_1(m) = -[l_c(l_c+1) - 2 - m(m+3)]^{1/2}(l_c - m)[(l_c-m)^2 - 1]^{1/2} + [l_c(l_c+1) - m(m-1)]^{1/2}(l_c + m + 1)[(l_c+m)(l_c+m+2)]^{1/2}.$$

If one can neglect the m dependence of the radial dipole matrix elements $D^c_{lm\sigma}$, Eq.s (15, 16) show that the photoemission cross section is proportional to the ℓ-projected average in the final state $|\psi_{\mathbf{k}_e,s}>$ (Eq. 6) of the operators

$$\sum_{lm} \{ G_3(m) \left(a^*_{lm\uparrow} a_{lm\uparrow} - a^*_{l-m\downarrow} a_{l-m\downarrow} \right) + G_1(m) \left(a^*_{lm+1\downarrow} a_{lm\uparrow} - a^*_{l-m-1\uparrow} a_{l-m\downarrow} \right) \},$$

that is to say to a linear combination of the averages of the operators ℓ_z, s_z and $t_z = s_z - 3\left\{ \vec{s}\cdot\vec{\ell}, \ell_z \right\}_+ / [2l(2l+1)]$. This latter is better known under the form $t_z = s_z - 3(\vec{s}\cdot\hat{r})\, r_z/r$ to which it is proportional by use of the Wigner–Eckart theorem.

By way of example,

$$\sum_{lm} m \left(a^*_{lm\uparrow} a_{lm\uparrow} - a^*_{l-m\downarrow} a_{l-m\downarrow} \right) = \sum_{lm\sigma} m a^*_{lm\sigma} a_{lm\sigma} \propto \int d\mathbf{r}\ \mathbf{\Psi}^\dagger(\mathbf{r}) \ell_z \mathbf{\Psi}(\mathbf{r}),$$

and similarly for s and t.

In the many-particle case the same property still holds since each operator $a_{lm\sigma}$ ($a^\dagger_{lm\sigma}$) picks out in the respective matrix element that particular amplitude of the final state wave function as appropriate to its character. Then such amplitudes are multiplied and combined in the way dictated by the various three j symbols appearing in the expression for the cross section, which do not depend on the particular approximation for the final state.

Of particular importance in photoemission is the elastic channel in which the ejected photoelectron is scattered coherently by the atoms surrounding the photoemitter. In the normal (non-magnetic) case it is known that the diffraction patterns of the photoemitted current, as a function of the escape direction of the photoelectron, allows a sort of holographic reconstruction of the environment of the photoemitter. Such an interpretation is based on the expression (3) for the scattering amplitude as a function of the scattering path operator τ (Gunnella *et al*., 1998, and references therein), where the reduction from the many-channel case to the picture of one particle moving in an effective optical potential for the elastic channel has been described. As apparent from the above derivation and in analogy with the use of photoelectron diffraction for surface structural analysis (Gunnella *et al*., 1998), magnetic circular dichroic photoelectron diffraction would allow for a sort of holographic surface reconstruction of the spatial density of the spin and orbital moment. As for the MCD sum rules one can take particular combinations of the spin–orbit split edge spectra in order to isolate one particular operator. For dichroism at the K edge, one has to deal only with the average of the angular momentum operator $<\psi_{\mathbf{k}_e,s}|\ell_z|\psi_{\mathbf{k}_e,s}>$, but for $L_{\rm II}, L_{\rm III}$ edges, for example, it is necessary to separate the contributions from the two levels at energies above the $L_{\rm II}$ edge. This separation is possible if the two edges are so separated in energy that the dichroic signal of the $L_{\rm III}$ has died out at energies above the $L_{\rm II}$ edge. Alternatively, one can use an interplay of theory and experiment in order to carry out such separation.

5. Photoabsorption and sum rules

Photoabsorption is obtained by integrating the many-body photoemission cross section over all event at a given excitation energy. In the effective one particle picture this is obtained by integrating Eqs. (15, 16) over $d\hat{\mathbf{k}}_e$ and summing over the spin s. Use of the generalized optical theorem in Eq. (4) leads to the following expression in the case of a transitions from the $J_c = l_c + 1/2$ edge,

$$\sigma_{MCD}(\omega) = \frac{C(\omega)}{2(2l_c+1)(2l_c+3)} \times \mathrm{Im} \sum_m \{ G_3(m) \left(\rho^{oo}_{lm\uparrow,lm\uparrow} - \rho^{oo}_{l-m\downarrow,l-m\downarrow} \right) + G_1(m) \left(\rho^{oo}_{lm+1\downarrow,lm\uparrow} - \rho^{oo}_{l-m-1\uparrow,l-m\downarrow} \right) \}, \quad (17)$$

defining

$$\rho^{oo}_{lm\sigma,l'm'\sigma'} = D^c_{lm\sigma} \tau^{oo}_{lm\sigma,l'm'\sigma'} D^c_{l'm'\sigma'}$$

and assuming that the absorber is located at site o. A similar expression, *mutatis mutandis*, holds for the $J_c = l_c - 1/2$ edge. Since Im $\tau^{oo}_{lm\sigma,lm\sigma}$ is proportional to the local projected density of states we see that the MCD signal in absorption is proportional to the local density of the various operators $\vec{\ell}$, $\vec{s}$ and $\vec{t}$ in the final state, again neglecting the m and σ dependence of $D^c_{lm\sigma}$. By developing the scattering path operator in terms of multiple scattering paths in the EXAFS region one can perform the same analysis as for the more conventional EXAFS. In particular, in favorable cases one can now access radial distribution functions either of the density of orbital or spin moment by performing the same combinations of the spectra, as discussed above for photoemission (see Natoli, 1995, for more details) and with the same limitations. With respect to this latter spectroscopy there is obviously a loss of information, since we have integrated out two of the three degrees of freedom of photoelectron diffraction spectra (energy and polar angles of $\hat{\mathbf{k}}_e$).

Up to now we have deliberately avoided the question of whether the local density of the operators probed by MCD spectroscopy (*i.e.* $\vec{\ell}$, $\vec{s}$ and $\vec{t}$) has anything to do with the properties of the ground state, which we are interested in. At first sight the presence of the core hole in the final state would prone to give a negative answer to this question.

There exist sum rules involving all possible transitions that relate them to averages of operators over the ground state. One of them is the generalized f sum rule (*i.e.* for oscillator strengths) for circularly polarized light (Smith, 1976, Eq. 70). Defining

$$\sum_\beta f^{\pm}_{\alpha\beta} = \sum_\beta (E_\beta - E_\alpha)\ |<\Phi_\beta|R^{\pm}|\Phi_\alpha>|^2,$$

where $R^{\pm} = X \pm Y$ is the many electron dipole operator for circularly polarized light, one can show that

$$\sum_\beta (f^{+}_{\alpha\beta} - f^{-}_{\alpha\beta}) = \frac{2}{\hbar}(<\Phi_\alpha|L_z|\Phi_\alpha> + (1/2mc^2)\ <\Phi_\alpha|S_z(X\nabla_x + Y\nabla_y)V|\Phi_\alpha>)$$

where V is the spin orbit potential. Another one is the so called Kuhn sum rule stating that the net transition rate for right- and left-hand light are equal (Smith, 1976, Eq. 66), which is here rederived for later use. From the definition of the absorption cross section in the many-body case for opposite photon helicity,

$$\sigma^-(\omega) \propto \omega \sum_f <g|R^+|f><f|R^-|g> \delta(\hbar\omega - E_f + E_g),$$
$$\sigma^+(\omega) \propto \omega \sum_f <g|R^-|f><f|R^+|g> \delta(\hbar\omega - E_f + E_g),$$

(where *e.g.* $R^{\pm} = \sum_n r^{\pm}_n$), one easily obtains

$$\int_0^\infty d\omega\ \frac{\sigma^-(\omega)}{\omega} = <g|R^+R^-|g> - <g|R^+|g><g|R^-|g>,$$
$$\int_0^\infty d\omega\ \frac{\sigma^+(\omega)}{\omega} = <g|R^-R^+|g> - <g|R^-|g><g|R^+|g>,$$

so that

$$\int_0^\infty d\omega\ \frac{\sigma^-(\omega) - \sigma^+(\omega)}{\omega} = 0. \qquad (18)$$

However they obviously cannot be used at particular edges to help in the analysis.

At a particular edge the integration over energy of MCD spectra (Carra *et al.*, 1993) has been devised as a means to cope with this problem, in the hope of obtaining averages of magnetic operators related to the ground state. As a matter of fact, if one eliminates the intermediate states in Eq. (14) by dividing by ω and integrating over all $\mathbf{k}_e$ and energies one would formally obtain the average of the magnetic operators over the ground state *for the particular edge considered*. However, underlying such a result is the implicit assumption that different edges do not interfere, since we have arbitrarily neglected in the transition operator T_μ all other transitions not coming from the particular edge of interest. This fact might affect the spin sum rules in the presence of the exchange interaction of the core hole with the valence electrons which mixes the two core j_c levels (Thole & van der Laan, 1988) and affects their statistical branching ratio. By summing over the spin–orbit split edges it is possible to derive an orbital sum rule valid in the presence of such interaction, as done by Thole *et al.* (1992) in the framework of an ion model in a crystal field of arbitrary symmetry.

In the derivation of these edge-specific sum rules, what one actually obtain is the average of certain combinations of the magnetic operators O_m over the state $|g'> = \ a_c|g>: <g'|O_m|g'>$. For a deep core transition, this is a highly excited state that can be expanded in terms of the stationary states Ψ_n of the Hamiltonian of the system: $|g'> = \sum_n \alpha_n\Psi_n$ so that, assuming that the cross terms $<\Psi_n|O_m|\Psi_{n'}>$ with $n \neq n'$ are negligible, one obtains

$$<g'|O_m|g'> = \sum_n \alpha_n^2 <\Psi_n|O_m|\Psi_n>\ .$$

In this sum one expects that the terms having the most important overlap with the state $|g'>$ are those describing an excited state relaxed around the core hole and that α_n^2 should be identified with the many-body reduction factor S_n^2. It is hoped that the sum over all these configurations will cancel the effects of the perturbation of the core hole and restore the properties of the ground state. However, a direct proof to our knowledge has not been given. An alternative possibility might be to assume that this perturbation is not so drastic.

From this point of view, whenever sum rules *à la* Thole *et al.* work (in the sense that one obtains ground state values for the averages of the various magnetic operators as checked against independent experimental findings), we should assume that the perturbation of the core hole in the final state is negligible so that the final density of states is much like the initial unperturbed one. This assumption should not be far from reality since in correlated electronic systems presenting magnetic phenomena the processes of screening and relaxation in response to the sudden creation of the core hole might not be so drastic as in other cases (see *e.g.* the π^* resonance in diatomic molecules!) due to the autoscreening action of the excited photoelectron. Looking for instance at the $L_{\rm II}, L_{\rm III}$ absorption edge of Ni with its sharp white line just at the edge, it is apparent that the excited photoelectron is seeing a final 3*d* hole (there are only 0.6 holes in the 3*d* band), since its screening by the other electrons would cost too much energy to the system and this energy is not available near the edge. On the other hand, studies by some authors (Nesvizhskii & Rehr, 1999) on the $L_{\rm II}, L_{\rm III}$ edges of Cu and Cr show that the use of a self-consistent ground state potential gives much better agreement with experiments than the one with the core hole. It is clear that in the case of correlated systems the $Z+1$ final state rule, which in any case was based on simple metals (von Barth & Grossman, 1982), has to be revised and more investigation is needed on this problem.

This alternative point of view allows to relate integrated spectra to ground-state properties in a different way. Making the reduction from the many-body case to the one-particle model moving in an effective optical potential we can again use Eq. (18). However, now the integration is over transitions to all states, either unoccupied or occupied. Since the Pauli principle forbids these latter, we have

$$\int_{E_f}^\infty d\omega\ \frac{\sigma^-(\omega) - \sigma^+(\omega)}{\omega} = -\int_0^{E_f} d\omega\ \frac{\sigma^-(\omega) - \sigma^+(\omega)}{\omega}, \qquad (19)$$

where E_f is the Fermi level. In an independent electron model the average of the magnetic operators over the states lying below the Fermi level is nothing else that their value on the ground state. If this point of view is correct far-reaching consequences can be derived for the analysis of magnetic EXAFS and photoelectron diffraction in all those cases where a separation of the dichoic signal from the two spin–orbit split edge is possible, as discussed at the end of the previous section. Indeed, these spectroscopies might then be used to obtain density maps of the various magnetic operators referring to properties of the ground state.

6. Natural circular dichroism in photoemission and absorption

For non-magnetic materials the differential absorption of right- and left-handed circular polarization is called natural circular dichroism (NCD). It can be shown that in the case of absorption the only way to observe a dichroic effect is *via* an interference between electric dipole and magnetic dipole and/or electric quadrupole matrix elements. In fact, in the absence of magnetic fields one has

$$\sum_{\beta}(E_\beta - E_\alpha)\,|<\Phi_\beta|R^+|\Phi_\alpha>|^2 = \sum_{\beta}(E_\beta - E_\alpha)\,|<\Phi_\beta|R^-|\Phi_\alpha>|^2,$$

since the intermediate states can be taken to be real. While in the optical regime E1–M1 interfence is preponderant, in the X-ray regime this effect is depressed by two or three order of magnitude with respect to E1–E2 (Alagna *et al.*, 1998). This effect has been recently measured at the Nd $L_{\rm III}$ of an hexagonal crystal of $Na_3[Nd(digly)_3]\cdot 2NaBF_4\cdot 6H_2O$ (digly = the dianion of diglycolic acid) (D_3 symmetry) (Alagna *et al.*, 1998) and at the $L_{\rm I}, L_{\rm II}, L_{\rm III}$ edges of a non-linear crystal $LiIO_3$ (Natoli *et al.*, 1998). The effect is small ($\Delta\sigma/\sigma \approx 10^{-2}-10^{-3}$) but definitely measurable on third-generation synchrotron radiation rings and insertion devices. We give here only the final result, referring the reader to Natoli *et al.* (1998) for details of the derivation. One finds

$$\sigma_{ND}(\mathbf{k}_{ph}) = i16\pi^3(\hbar\omega)^2\alpha^2\left(\frac{2}{15}\right)^{1/2}\sum_{ll'} f(ll')\sum_{\gamma} Y^*_{2\gamma}(\mathbf{k}_{ph})\boldsymbol{\sigma}^{\gamma}_{ll'}(\boldsymbol{\omega}),$$

where

$$f(ll') = (l_c\|1\|l)\,\left(l_c\|1\|l'\right)\left\{\begin{array}{ccc} 2 & l' & l \\ l_c & 1 & 2\end{array}\right\}$$

and

$$\sigma^{\gamma}_{ll'}(\omega) = -\sum_{mm'}\left(\begin{array}{ccc} l & l' & 2 \\ m & -m' & \gamma\end{array}\right) \times \sum_f D^c_l Q^c_{l'} <g|a^\dagger_{l_c lm}|f><f|a^\dagger_{l'm'}a_{l_c}|g>,$$

where D^c_l ($Q^c_{l'}$) are dipole (quadrupole) radial matrix elements and, as before, the sum is only over states $|f>$ at the same final energy in the many-body case or should be replaced by an integration over $\mathbf{k}_e$ in the one-electron case. Specializing to this latter case and taking $\mathbf{k}_{ph}$ along the direction of quantization, remembering Eq. (4) and calculating the relevant three j symbol, we obtain

$$\sigma_{ND}(\mathbf{k}_{ph}\parallel z;\boldsymbol{\omega}) \propto \sum_{m=1}^{l_<} m\left[3(l_>^2 - m^2)\right]^{1/2}\,{\rm Im}(\boldsymbol{\tau}^{oo}_{lm,l'm'} - \boldsymbol{\tau}^{oo}_{l-m,l'-m'})$$

where $l_<$ ($l_>$) is the lesser (the greater) of l and l'. This expression lends itself to a MS path analysis of the signal. Examination of the various ingredients entering into the above equations shows that the signal is zero if the system under study has a local symmetry point group containing an inversion center and, for particular incidence geometries, a reflection plane or a roto-reflexion axis, so that a mixing of both dipole and quadrupole allowed wave function components is not allowed. Stated in more physical terms, one observes that an absorption experiment conserves parity, therefore in particular is invariant to a mirror reflection containing the incident photon direction. Since this operation interchanges the hands of circular polarization the absorption does not depend on the helicity of the photon if the system is invariant under the same operation, hence there is no dichroism. If instead the system as a whole is not invariant, it may well happen that a subset of MS paths transforms into itself under the reflection. In this case the set does not contribute to the dichroic signal. This is easily seen in the case of single scattering paths. Hence the dichroic absorption reflects only higher-order MS processes and only those processes that involve subsets of atoms in chiral geometry. Therefore, in a path analysis the dichroic effect brings about a drastic simplification that can be exploited to the benefit of structural analysis. This aspect is in fact common to all dichroic spectroscopies.

As in the case of MCD, a sum rule can be established that measures the degree of mixing of even and odd parity compoments of the wave function of the system. The relevant operator is easily seen to be

$$G^{\gamma}_{ll'} = -\sum_{mm'}(-1)^{l'+m'}\left(\begin{array}{ccc} l & l' & 2 \\ m & -m' & \gamma\end{array}\right)a^\dagger_{l'm'}a_{lm} + h.c.$$

where l and l' differ by 1. Its expression in configuration space has been given by Carra & Benoist (2000) for $\gamma = 0$ in their Eq. (12):

$$-i(A - A^\dagger)_0 L_z \qquad (20)$$

where A_0 in polar coordinates is given by $A_0 = (l\cos\theta - \sin\theta\frac{\partial}{\partial\theta})$ and is such that $A_0 Y_{lm} = (l^2 - m^2)^{1/2}Y_{l-1,m}$. There is no guarantee in this case that its average refers to the ground state of the system, due to the core hole and the fact that we might deal with non-correlated systems. However, since the mixing of odd and even components in the wavefunction is not a local property of the system, one might hope to access ground state information.

Natural dichroism in photoemission introduces a new degree of freedom into the effect, namely the escape direction of the photoelectron. Considering also the incident photon direction and a third direction describing the orientation of the system under study (a molecular axis in case of oriented molecules on a surface, the normal to a surface *etc*.), the combined system of photon plus target can exhibit a definite handedness. More important, since the final-state wave function is a scattering state and therefore complex, the argument used in the case of photoabsorption does not apply here, so that one can observe CD in the angular dependence of photoemission with the sole dipole operator. Obviously the angle-integrated signal averages to zero. The relevant formula is

$$\frac{d\sigma_{MCD}}{d\mathbf{k}_e}(\omega) = 4\pi^2\alpha\hbar\omega\sum_{ll'} g(ll')\sum_{\gamma} Y^*_{1\gamma}(\mathbf{k}_{ph})\boldsymbol{\sigma}^{\gamma}_{ll'}(\boldsymbol{\omega}),$$

where

$$g(ll') = (l_c\|1\|l)\,\left(l_c\|1\|l'\right)\left\{\begin{array}{ccc} 1 & l' & l \\ l_c & 1 & 1\end{array}\right\}$$

and

$$\sigma^{\gamma}_{ll'}(\omega) = \sum_{mm'}\left(\begin{array}{ccc} l & l' & 1 \\ m & -m' & \gamma\end{array}\right) \times D^c_l D^c_{l'} <g|a^\dagger_{l_c lm}|\overline{f}_{\mathbf{k}_e,s}><\overline{f}_{\mathbf{k}_e,s}|a^\dagger_{l'm'}a_{l_c}|g>\,.$$

Putting $\gamma = 0$ and specializing to the one-particle case, one sees from this last formula that in this spectroscopy one measures the average of L_z in the final state. This is the exact analog of the MCD case if one eliminates the spin.

7. The expression for linear dichroism (LD)

Within the same framework used for MCD and NCD, we can also study the linear dichroism, in both dipole–dipole and dipole–quadrupole channels, in order to derive the expressions of the physical observables that are measured in these processes. We limit ourselves to the case of absorption and photoemission, neglect the spin and do not treat the quadrupole–quadrupole (QQ) channel. The extension of this formalism to the case of diffraction up to the QQ channel including the spin variables will be treated in a forthcoming publication.

Let us start from the dipole–dipole channel. In principle, to treat the LD we could follow the same procedure already described in the case of MCD up to Eqs. (7), (8) and (9) and then adapt Eqs. (10) and (11) to the case of two linear polarizations. But we prefer to choose an alternative more general method, which unifies the treatment of circular and linear dichroism and can be extended to treat resonant diffraction. The idea is to recouple the two polarizations $\boldsymbol{\pi}$ and $\boldsymbol{\pi}^*$ to a rank-2 tensor after Eq. (8), as done by Luo *et al.* (1993) and write this tensor in terms of its irreducible components. In this way the MCD is expressed by the antisymmetric time-reversal odd part of the tensor while the LD is given by its symmetric time-reversal even part.

The absorption signal for a given polarization is expressed through Eq. (8), which can be rewritten, by recoupling the two spherical harmonics, to give

$$\frac{d\sigma}{d\mathbf{k_e}}(\omega,\boldsymbol{\pi}) = 4\pi^2\alpha\hbar\omega \sum_{\mu,\nu,q,\lambda} \begin{pmatrix} 1 & 1 & q \\ \mu & \nu & \lambda \end{pmatrix} T_\lambda^{(q)}(\boldsymbol{\pi},\boldsymbol{\pi}^*)\sigma_{\mu\nu}, \tag{21}$$

where the irreducible tensor of rank q, $T_\lambda^{(q)}(\boldsymbol{\pi},\boldsymbol{\pi}^*)$, is defined as

$$T_\lambda^{(q)}(\boldsymbol{\pi},\boldsymbol{\pi}^*) \equiv \sum_{\boldsymbol{\mu},\boldsymbol{\nu}} C^{q\boldsymbol{\lambda}}_{1\boldsymbol{\nu},1\boldsymbol{\mu}} Y_{1\boldsymbol{\mu}}(\boldsymbol{\pi}) Y_{1\boldsymbol{\nu}}(\boldsymbol{\pi}^*). \tag{22}$$

Moreover, we can introduce another tensor of rank q representing the properties of the system through the recoupling,

$$M_\lambda^{(q)} \equiv \sum_{\mu,\nu} C^{q\lambda}_{1\nu,1\mu}\sigma_{\mu\nu}. \tag{23}$$

Using the relation between 3-j symbols and Clebsch–Gordan coefficients,

$$\begin{pmatrix} 1 & 1 & q \\ \mu & \nu & \lambda \end{pmatrix} \equiv \frac{(-)^\lambda}{(2q+1)^{1/2}} C^{q-\lambda}_{1\nu,1\mu}, \tag{24}$$

we find that Eq. (21) can be interpreted as a scalar product between two irreducible tensors, one representing the properties of the light, $T_\lambda^{(q)}(\boldsymbol{\pi},\boldsymbol{\pi}^*)$, and the other showing the response of the system, $M_\lambda^{(q)}$,

$$\frac{d\sigma}{dk_e}(\omega,\boldsymbol{\pi}) = 4\pi^2\alpha\hbar\omega \sum_{q,\lambda} \frac{(-)^\lambda}{(2q+1)^{1/2}} T_\lambda^{(q)}(\boldsymbol{\pi},\boldsymbol{\pi}^*) M_{-\lambda}^{(q)}. \tag{25}$$

If we write down the first tensor explicitly, we have, for the three possible values of q,

- $T_0^{(0)}(\boldsymbol{\pi},\boldsymbol{\pi}^*) = -(1/\sqrt{3})(3/4\pi)\boldsymbol{\pi}^*\cdot\boldsymbol{\pi}$: being a scalar product between the two polarizations, this term cannot give rise to any kind of dichroism.
- $T_\lambda^{(1)}(\boldsymbol{\pi},\boldsymbol{\pi}^*) = (i/\sqrt{2})(3/4\pi)(\boldsymbol{\pi}^*\times\boldsymbol{\pi})_{\boldsymbol{\lambda}}$: this is the axial vector responsible for MCD, as seen before. This tensor is sensitive to time-reversal odd observables.
- The rank-2 time-reversal even irreducible tensor is responsible for LD, as shown below, and its components, apart from a common factor $\frac{3}{4\pi}$, are given by

$$\begin{aligned} T_{\pm2}^{(2)} &= \pi_{\pm1}^*\pi_{\pm1}, \\ T_{\pm1}^{(2)} &= \frac{1}{\sqrt{2}}(\pi_1^*\pi_0 + \pi_0^*\pi_1), \\ T_0^{(2)} &= \frac{1}{\sqrt{6}}(\pi_1^*\pi_{-1} + 2\pi_0^*\pi_0 + \pi_{-1}^*\pi_1) \\ &= 3\pi_0^*\pi_0 - \boldsymbol{\pi}^*\cdot\boldsymbol{\pi}. \end{aligned}$$

The linear dichroism is defined as the differential absorption of two different linear polarizations that are real and conventionally chosen orthogonal to each other, say $\boldsymbol{\pi}_{\boldsymbol{\alpha}}$ and $\boldsymbol{\pi}_{\boldsymbol{\beta}}$. From the definition we obtain

$$\frac{d\sigma_{LD}}{d\mathbf{k}_e} \equiv \left[\frac{d\sigma}{d\mathbf{k}_e}(\omega,\boldsymbol{\pi}_{\boldsymbol{\alpha}}) - \frac{d\boldsymbol{\sigma}}{d\mathbf{k}_e}(\boldsymbol{\omega},\boldsymbol{\pi}_{\boldsymbol{\beta}})\right]. \tag{26}$$

Note that it is convenient to choose at this point a reference frame for the irreducible tensors where the quantization axis coincides with the direction of propagation of the light. We can choose, for simplicity, $\boldsymbol{\pi}_{\boldsymbol{\alpha}} \equiv (1,0,0)$ and $\boldsymbol{\pi}_{\boldsymbol{\beta}} \equiv (0,1,0)$ in the frame where $\mathbf{k} \equiv (0,0,1)$. In this case only $T_{\pm2}^{(2)}$ and $T_0^{(2)}$ survive and this latter cannot be responsible for LD as it reduces to a scalar product due to the fact that $\pi_0 = 0$ for both polarizations

Using this reference frame, we obtain, from Eqs. (25) and (26),

$$\frac{d\sigma_{LD}}{d\mathbf{k_e}}(\omega) = 4\pi^2\alpha\hbar\omega\frac{1}{\sqrt{5}}\frac{3}{4\pi}\left[M_2^{(2)} + M_{-2}^{(2)}\right], \tag{27}$$

where the expression for $M_{\pm2}^{(2)}$ can be obtained from Eqs. (13) and (14), substituting 2 to 1 and ±2 to λ in the last 3-j symbol of Eq. (14). Explicitly,

$$\begin{aligned} M_{\pm2}^{(2)} = \sum_{ll'}\sum_{jj'} f(2;jj';ll') \sum_{j_z j_z'}(-1)^{j_z} \\ \times \sum_{m\sigma}\sum_{m'\sigma'} \begin{pmatrix} l & 1/2 & j \\ m & \sigma & -j_z \end{pmatrix} \begin{pmatrix} l' & 1/2 & j' \\ m' & \sigma' & -j_z' \end{pmatrix} \\ \times \begin{pmatrix} 2 & j' & j \\ \pm2 & -j_z' & j_z \end{pmatrix} D^c_{lm\sigma} D^c_{l'm'\sigma'} <g|a_c^\dagger a_{lm\sigma}|\overline{f}_{\mathbf{k}_e,s}> \\ \times <\overline{f}_{\mathbf{k}_e,s}|a^\dagger_{l'm'\sigma'}a_c|g> . \end{aligned} \tag{28}$$

At this point we can follow the same steps made in section 4, to obtain the expression for LD in terms of an effective operator acting on the final states. We give, as an example, just the case where we sum up over the two partner functions $J_c \pm 1/2$, thus eliminating the spin variable. The final result is

$$\sum_{lm}(2l+1)\begin{Bmatrix} 1 & l_c & l \\ l & 2 & 1 \end{Bmatrix}(-)^{m+l}\begin{pmatrix} l & l & 2 \\ m+2 & -m & -2 \end{pmatrix} \times \left(a^\dagger_{lm}a_{lm+2} + a^\dagger_{l-m}a_{l-m-2}\right) \propto \int d\mathbf{r}\ \boldsymbol{\Psi}^\dagger(\mathbf{r})(\ell_x^2 - \ell_y^2)\boldsymbol{\Psi}(\mathbf{r}),$$

and the signal is proportional to the average in the final state of the operator $\ell_x^2 - \ell_y^2$. The directions x and y appear explicitly because we already chose a specific reference frame. The general result must be read as follows: the LD in the dipole–dipole channel allows to see the

difference of the projections of the square of the magnetic moments along the directions of the two polarizations. In the reference frame chosen, z has no particular meaning for the crystal, that can be oriented with its symmetry axes (if it has any) along the direction of z or not. What is important for detecting a signal is that the point group associated to the crystal space group be sufficiently low to admit as a totally symmetric representation the combination $\langle M_2^{(2)} + M_{-2}^{(2)} \rangle$.

The same procedure can be followed in the case of the dipole–quadrupole channel. We report only the final results omitting the rather tedious details of the derivation. As in Eq. (21), the signal is given by the scalar product between a tensor representing the light properties and one that is related to the properties of the system. In this case the irreducible tensors involved are of rank 1, 2 and 3. If we choose the same reference frame used previously, *i.e.* with the z axis in the direction of the wave vector, then some of the components of these tensors are zero and the only different from zero are

$$\begin{aligned}
\tilde{T}_0^{(1)} &= \frac{1}{\sqrt{2}} k_0 (\pi_1^* \pi_{-1} + \pi_{-1}^* \pi_1), \\
\tilde{T}_0^{(2)} &= \frac{1}{\sqrt{2}} k_0 (\pi_1^* \pi_{-1} - \pi_{-1}^* \pi_1), \\
\tilde{T}_{\pm 2}^{(2)} &= \pm \frac{1}{\sqrt{2}} k_0 (\pi_{\pm 1}^* \pi_{\pm 1}), \\
\tilde{T}_0^{(3)} &= \frac{1}{\sqrt{2}} k_0 (\pi_1^* \pi_{-1} + \pi_{-1}^* \pi_1), \\
\tilde{T}_{\pm 2}^{(3)} &= k_0 (\pi_{\pm 1}^* \pi_{\pm 1}).
\end{aligned}$$

From these formulae it is simple to derive the conditions under which it is possible to detect a dichroic signal: the irreducible tensors $T_0^{(1)}$ and $T_0^{(3)}$ cannot give rise to any dichroism as they are symmetric in the exchange $\boldsymbol{\pi}^* \leftrightarrow \boldsymbol{\pi}$ (this prevents from having circular dichroism) and they go into themselves by interchanging two linear polarizations $\boldsymbol{\pi}_\alpha$ and $\boldsymbol{\pi}_\beta$ (this forbids linear dichroism). The time-even $T_0^{(2)}$ is responsible for NCD as already analyzed in the previous paragraph and the time-odd tensors $T_{\pm 2}^{(2)}$ and $T_{\pm 2}^{(3)}$ are those responsible for LD in the dipole–quadrupole channel. Again, starting from definition (26), we obtain that the signal in this case is proportional to

$$\frac{d\sigma_{LD}}{d\mathbf{k}_e} \propto ik \left\{ \left[\tilde{M}_2^{(3)} + \tilde{M}_{-2}^{(3)} - h.c. \right] + \frac{1}{\sqrt{2}} \left[\tilde{M}_2^{(2)} - \tilde{M}_{-2}^{(2)} - h.c. \right] \right\}. \quad (29)$$

The expression for the $\tilde{M}$ can be derived in the same way as done previously for the dipole–dipole channel. We limit ourselves here to give, as an example, the expression for the effective operators that are seen in LD spectroscopy at the K-edge.

Summing again over the spin variables, the expression in second quantization is (omitting the imaginary unit)

$$\begin{aligned}
G_{ll'} \propto & \sum_m (-1)^{l+m} \left[\begin{pmatrix} l & l' & 3 \\ m+2 & -m & -2 \end{pmatrix} \right. \\
& \left. + \frac{1}{\sqrt{2}} \begin{pmatrix} l & l' & 2 \\ m+2 & -m & -2 \end{pmatrix} \right] \\
& \times (a_{l'm}^\dagger a_{lm+2} + a_{l',-m}^\dagger a_{l,-m-2}) - h.c.
\end{aligned}$$

where $l' = l \pm 1$.

In terms of configuration space operators its expression reads:

$$\int d\mathbf{r}\ \boldsymbol{\Psi}^\dagger(\mathbf{r}) \left[(\ell_x^2 - \ell_y^2) A_0 - h.c. \right] \boldsymbol{\Psi}(\mathbf{r}) \quad (30)$$

in striking similarity with the analogous equation for natural dichroism (Eq. (20), with the obvious difference that now the tensor is time-reversal odd.

A similar result was found by Carra *et al.* (2001), but apparently without the contribution of the rank-two time-odd orbital tensor $T_{\pm 2}^{(2)}$. This contribution is essential to obtain the simple form of the operator in Eq. (30) and also provides an exception to the usual statement that odd-rank irreducible tensors are time-reversal odd and even-rank irreducible tensors are time-reversal even.

Eq. (30) constitutes the basis for the analysis of the tranverse X-ray linear dichroism at the V K-edge of V_2O_3 observed by Goulon *et al.* (2000), measuring non-reciprocal gyrotropy in this system. A more detailed investigation will be given elsewhere.

8. Conclusions

We have presented a unified approach for calculating magnetic and natural dichroism (both circular and linear) in (spin resolved) photoemission and absorption as well as linear dichroism valid for extended systems and the many-body case. The reduction of this scheme to a one-particle model in the framework of multiple-scattering theory shows their intimate relation *via* the generalized optical theorem Eq. (4). In photoemission the circular dichroic cross section is proportional to linear combinations of the averages of the various operators $\vec{\ell}$, $\vec{s}$ and $\vec{t}$ in the final state $\Psi_{\mathbf{k}_e,s}(\mathbf{r})$ selected by the experimenter, with simple coefficients that depend on the initial spin–orbit split edge. By suitable linear combination of the two edges one can select one or the other of such operators. Under the assumption that the final state optical potential is similar to that of the ground state due to correlation effects, this spectroscopy as a surface technique provides the maximum of selectivity to explore the properties of the ground state of the system under study. On the other hand, what is observed in photoabsorption is substantially an average of the same expression over all photoelectron directions. There is a loss of information with respect to photoemission since we have at our disposal only the photon energy. We can now access bulk properties and in principle radial distribution functions. Integrating over energy there is a further loss of information and we probe the average of the same operators over the ground state, under the assumptions discussed above. For LD we have shown what type of operators are observed both in dipole–dipole and in dipole–quadrupole transitions. More investigation is needed to understand their role in the description of the various physical systems. The above spectroscopies constitute a powerful new class of techniques that exploit the availability of tunable circularly polarized X-rays with high brilliance coming from third-generation synchrotron radiation sources. Combined with elemental selectivity they have the potentiality to probe element-specific magnetic moments, exchange and spin–orbit splitting and atomic-scale magnetic structure especially in the study of nanoscale materials.

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