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Abstract. We present the main steps governing the theory of resonant x-ray diffraction (RXD). We focus on the derivation of the anomalous scattering amplitude from perturbation theory and starting from the low-energy expansion of the Dirac Hamiltonian. We give the main ingredients of the multipolar expansion in term of electric and magnetic transitions. We also show the expansion in terms of scattering tensors of the material. We end by giving the RXD formula necessary to simulate in practice this spectroscopy.

1 Introduction

The abrupt variation with energy of the diffracted peak intensities around the absorption edges is known from the 1920th. Nevertheless, the first measurement of a complete spectra, by Yvette Cauchois, had to wait untill 1956 [1]. She recorded the (002) peak around the Al K edge in mica. Such a reflection shew an important variation in intensity, thus revealing the potentialities of the so-called anomalous diffraction. From this moment on, the close relation between X-ray absorption fine structures (XAFS) spectra and RXD spectra has often been noticed. The last three decades have seen important advances in the technique both on the theoretical and experimental sides. The first breqkthrough was the finding, in 1982 by David and Liselotte Templeton, of the polarization dependence of anomalous scattering [2]. One year later V. E. Dmitrienko explained the occurence of the forbidden reflections, with zero (or extremely weak) intensity far from the edges but which are clearly detectable around the edges [3]. Such phenomena have been extensively used since then. The year 1988 was characterized by the discovery of the magnetic resonant x-ray diffraction. Gibbs and co-workers measured magnetic peaks in Holmium with a clear resonant effect at the Ho L_3 absorption edge [5]. The next paper in the same journal, by Hannon *et al.* [6] contained the theoretical interpretation, separating the scattering amplitude in a scalar anomalous ("Thomson") part, a vectori part directly proportional to the magnetic moment and a third anisotropic part which for cubic system is directly

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related through the spin-orbit to a term quadratic in the magnetic moment components. Even more surprising was the measurement in 1992 by K. Finkelstein *et al.* [7] of a reflection in haematite that was not only forbidden for the classical non-resonant diffraction term but also for the usually dominating dipole resonant amplitude. The resulting spectra is non zero only in a 3 eV range at an energy corresponding to the pre-edge in the absorption spectra, where the $3d$ unoccupied states of the iron atom are situated. More work on processes involving non simple dipole transitions were performed again by Templeton and Templeton [8] demonstrating a specific anisotropy occuring in tetrahedral sites.

Our paper is organised as follows: section 2 aims at being a continuation of the pioneering work by M. Blume [9] in the proceedings of the Malente conference in 1992. We complete the derivation, from the Dirac hamiltonian, of the low-energy matter-radiation interaction that is at the basis of the x-ray scattering amplitude, both off-resonance (Thomson scattering, magnetic scattering) and at resonance. Then we specialize to those terms responsible of the resonant x-ray scattering and provide an extended analysis of transition matrix elements also including electric octupole (E3) and magnetic dipole (M1) and quadrupole (M2) events, not inserted in the paper of 1994. Some analogies with absorption spectroscopies are highlighted. In section 3 we review briefly the cartesian-tensor approach and the multipole expansion in matter as an interpretation of RXD. Section 4 is devoted to the way wave functions for transition matrix elements are numerically evaluated and section 5 gives some introduction on the monoelectronic approach allowing the simulations of RXD when the probed states are delocalized.

2 Matter-radiation interaction and resonant process

2.1 Process

Third generation synchrotrons are characterized by a very high brilliance, which is typically 10^{19} photons/s/mrad^2/mm^2/0.1% bandwidth, corresponding, from an undulator, to 10^{13} up to 10^{16} photons/s on the target. Even with such high values we are still in the linear interaction regime: each electron of the sample interacts with one photon at a time. This means that processes involving the simultaneous interaction of two (or more) incoming photons with the sample electrons are negligible. Notice that this condition might be no more valid with future experiments at free electron laser sources. In this paper, however, we limit ourselves to the linear case.

The central process of RXD is the virtual absorption of the incoming photon, provoking a transition of a core electron up to some unoccupied levels. The process is elastic, coherent and the electron immediately ($\sim 10^{-15}$ s) decays back to its initial core state, emitting thus a new photon, with the same energy than the incoming one, but eventually with another polarization and wave vector. The virtual process can also be inelastic, leading to Resonant Inelastic X-ray Spectroscopy (RIXS), an incoherent resonant spectroscopy out of the scope of the present paper. Actually, even for the resonant process of RXD, the energy of the photon is not necessarily identical with the difference in energy between the intermediate and initial state. This difference is related by the Heisenberg principle $\Delta E \Delta t \geq \hbar/2$ to the inverse lifetime of the intermediate state. This is why the real part of the anomalous scattering amplitude is not zero bellow the Fermi energy. Consequently the intensity of Bragg peaks can vary until several tenths of eV bellow the edge.

It should be reminded that the transition process is a fundamentally multielectronic phenomena. Around the *driving* electron, promoted from a core state g to some intermidiate state n, all the other electrons react. The main effect is the screening of the core-hole potential by the electrons belonging to the absorbing atom and also (to a less extent) to the surrounding ligands. Often, especially at K-edges, these secondary effects can be seen as passive, ie, we can consider only the transition of the *driving* electron, the effect of the other ones being just an extra energy ΔE_a such that at the resonance $\hbar\omega = E_n - E_g + \Delta E_a$. Here E_n and E_g are the eigenvalues of the corresponding electronic states and $\hbar\omega$ the incoming photon energy. We can consider the phenomena as describable by a *monoelectronic* scheme when ΔE_a is a simple constant along the spectra. Then, *ad hoc* procedures are used to take into account the core hole, as for instance considering the absorbing atom in its excited state as an atom with a screened core-hole having one extra electron in the first non occupied valence orbital. This approach fails at edges where the intermediate states are localized. This is often the case at the L_{23} edge of the $3d$ transition elements, where multiplet structures usually need to be introduced using the ligand field calculation methods. Amongst these, the first and most popular is the method introduced by Thole *et al.* [10], in the framework established by Cowan [11] and Butler [12]. This calculation method is atomic-like and disregards the band structure of the solid, i.e. only transition towards localized states are being accounted for. In this approch, the absorbing ion is described by a parametrized hamiltonian that includes terms describing the spin-orbit coupling, the electron-electron and the Zeeman interaction. The crystal field effect is included *via* a term describing the geometrical environement of the absorbing atom. In general, this situation occurs if the shape of the absorption spectrum falls very close to zero immediately after the rising edge, within a few eV. In the opposite case, when the edge is step like, as in most K-edges of all elements and in the L_{23} of heavy elements, monoelectronic approach must be sufficient. The simulations in this situations uses then most often the Density Functional Theory (DFT) in its Local (Spin) Density Approximation (L(S)DA).

2.2 Interaction Hamiltonian

We now formally consider the interaction of a photon with a single bound electron in an atom. RXD scattering amplitude is usually written by means of perturbation theory in the matter-radiation interaction, from Schrödinger Hamiltonian, or, if one is interested in magnetic-dipole interaction, from Schrödinger-Pauli Hamiltonian (ie, with the addition of the scalar magnetic energy $\sigma \cdot \mathbf{B}$). These approaches are sufficient to get all the terms that contribute at resonance, but do not allow obtaining magnetic scattering far from resonance correctly. Therefore, in the spirit of Ref. [9], where the total cross-section was derived (ie, including non-resonant magnetic scattering) we shall first describe here what is the low-energy limit of the Dirac Hamiltonian through a Foldy-Wouthuysen (FW) transformation [13]. Due to relativistic-invariance constraints, Dirac Hamiltonian H_D is linear in the matter-radiation coupling (ie, it is linear in the vector potentials $\mathbf{A}(\mathbf{r}, t)$):

$$H_D = \beta mc^2 + eV(\mathbf{r}) + c\alpha \cdot (\mathbf{p} - e\mathbf{A}(\mathbf{r}, t)) \quad (1)$$

This Hamiltonian is a 4x4 matrix, determined by β and α matrices in standard notations (see, eg, [14]). $V(\mathbf{r})$ and $\mathbf{A}(\mathbf{r}, t)$ are the scalar and vector potential, respectively. As atomic edges, where resonant phenomena appear, are far lower than the electron rest-energy ($mc^2 \simeq 511$ keV), except maybe for K-edges of actinides, only the low-energy limit of H_D is of interest to us. The usual procedure to obtain the low-energy limit of H_D is through the solution of the set of two coupled differential equations for the 'lower' and 'upper' bispinor in the stationary case (see, eg, relativistic corrections to hydrogen atom in [14]). This leads to the appearence of the $\mathbf{s} \cdot \mathbf{B}$ term with the correct gyromagnetic ratio and to the 'usual' quadratic dependence

$(\mathbf{p} - e\mathbf{A}(\mathbf{r}))^2$ in the vector potential. However, such a procedure cannot be applied in the case of a time-dependent vector potential $\mathbf{A}(\mathbf{r}, t)$, because it needs stationary states. The alternative procedure to keep the time-dependence of the vector potential is through the use of a FW transformation of the original Dirac Hamiltonian and then work with the transformed FW low-energy Hamiltonian, that reads:

$$H_{FW} = \beta mc^2 + eV(\mathbf{r}) + \frac{\beta}{2m}(\mathbf{p} - e\mathbf{A}(\mathbf{r}, t))^2 - \frac{\beta e\hbar}{2m}\sigma \cdot \mathbf{B} \qquad (2)$$
$$+ \frac{e\hbar}{8m^2c^2}\sigma \cdot ((\mathbf{p} - e\mathbf{A}(\mathbf{r}, t)) \times \mathbf{E} - \mathbf{E} \times (\mathbf{p} - e\mathbf{A}(\mathbf{r}, t))) - \frac{e\hbar^2}{8m^2c^2}\nabla \cdot \mathbf{E}$$

Here σ represent the Pauli matrices (not the spin $\mathbf{s} = \hbar\sigma/2$). This gives the correct gyromagnetic prefactor to the fourth term. The first term just splits the rest-energy of electrons and positrons, the last is the Darwin term: both can be lumped in the matter hamiltonian. Notice that the electric field is $\mathbf{E}(\mathbf{r}, t) = -\nabla V(\mathbf{r}) - \partial_t \mathbf{A}(\mathbf{r}, t)$: with the usual (stationary) procedure, only the "$-\nabla V(\mathbf{r})$" term would have appeared (spin-orbit correction), thereby missing the interaction energy given by Eq. 4 below. The explicit unitary transformation leading to Eq. 3 is too involved to be reported here and we refer to [15], Eq. (7), that corrects the version previously given in [13], Eq. (14). Actually, also in Eq. (7) of Ref. [15] a term of the same order of magnitude is missing, the relativistic correction to the kinetic energy ($\propto \frac{p^4}{m^2c^3}$), but, as for the first and last terms, it is of no concern to us, as it can be lumped in the matter hamiltonian.

From Eq. (2) we get the following terms for the matter-radiation Hamiltonian that are important for x-ray scattering:

$$H_1 = \sum_i \frac{e^2}{2m} \left[\mathbf{A}(\mathbf{r}_i, t)\right]^2 \qquad (3)$$

$$H_2 = -\sum_i \frac{e^2\hbar}{2m^2c^2} \mathbf{s}_i \left[\partial_t \mathbf{A}(\mathbf{r}_i, t) \times \mathbf{A}(\mathbf{r}_i, t)\right] \qquad (4)$$

$$H_3 = -\sum_i \frac{e}{m} \left[\mathbf{A}(\mathbf{r}_i, t) \cdot \mathbf{p}_i\right] \qquad (5)$$

$$H_4 = -\sum_i \frac{e}{m} \mathbf{s}_i \cdot \left[\nabla \times \mathbf{A}(\mathbf{r}_i, t)\right] \qquad (6)$$

where i labels the electrons. The first two terms, quadratic in the vector potential, describe usual Thomson scattering and non-resonant magnetic scattering, respectively. Indeed, in a plane-wave representation, the vector potential can be associated to the absorption or the emission of a photon with a given wave-vector; therefore the product of the vector potential with itself represents an absorption followed by emission of a photon, ie, a scattering. Such a scattering is formally expressed by the two Eqs. 8 and 9. The last two equations, 5 and 6, are instead linear in the vector potential and in order to get a scattering process, we should consider second order pertubation theory, as in Eq. 10 below.

2.3 Resonant X-ray Diffraction formula

The total diffraction intensity is given, up to the second-order in absorption/emission photon processes, by the expression:

$$I(\omega) \propto \left| \sum_j e^{i\mathbf{Q}\cdot\mathbf{R}_j} \left(f_j^{(0)} + f_j^{(0m)} + f_j'(\omega) + i f_j''(\omega) \right) \right|^2 \tag{7}$$

where the sum is over all atoms j, $\mathbf{Q} \equiv \mathbf{k}_s - \mathbf{k}_i$ is the exchanged wave-vector and $\hbar\omega$ the photon energy. The three atomic scattering amplitudes are given by:

$$f_j^{(0)} = \langle \varphi_g^{(j)} | \hat{H}_1 | \varphi_g^{(j)} \rangle \tag{8}$$

$$f_j^{(0m)} = \langle \varphi_g^{(j)} | \hat{H}_2 | \varphi_g^{(j)} \rangle \tag{9}$$

$$f_j'(\omega) + i f_j''(\omega) = \sum_{n,g} \frac{\langle \varphi_g^{(j)} | \hat{H}_3^* + \hat{H}_4^* | \varphi_n \rangle \langle \varphi_n | \hat{H}_3 + \hat{H}_4 | \varphi_g^{(j)} \rangle}{\hbar\omega - (E_n - E_g) + i\frac{\Gamma}{2}} \tag{10}$$

where $\varphi_g^{(j)}$ is the core-state centered at site j and φ_n are all possible intermediate states that can be reached by the virtual absorption/emission process, characterized by an energy E_n and a lifetime $\simeq \hbar/\Gamma$. It should be noted that two processes are possible: either the incoming photon is absorbed before that the outgoing photon is emitted, or the outgoing photon is emitted before that the incoming photon is absorbed. Only in the first case we have resonance and $E_n = E_n(\text{matter})$, whereas in the second the intermediate energy $E_n = E_n(\text{matter}) + 2\hbar\omega$ and the imaginary term $i\frac{\Gamma}{2}$ can be dropped out. It should be noted that the imaginary part f_j'' of the forward scattering amplitude of an atom at site j is proportional to the absorption cross-section at the same site: $\sigma_j(\omega) = \sum_{n,g} \left| \langle \varphi_n | \hat{H}_3 + \hat{H}_4 | \varphi_g^{(j)} \rangle \right|^2 \delta(\hbar\omega - (E_n - E_g))$.

There is therefore a strict link between these two spectroscopies and all what will be said below concerning the symmetry properties of transition-matrix elements and calculation of wave functions is valid as well for absorption spectroscopies. What makes REXS (RXD) peculiar compared to other spectroscopies (X-ray absorption, RIXS) is that all atomic scattering process coherently interfere, as shown in Eq. 7, and this is not the case for X-ray absorption or RIXS, where all terms are added incoherently: $\sigma(\omega) = \sum_j \sigma_j(\omega)$. In what follows we drop out all non-resonant terms and just focus on the resonant part of Eq. 7.

2.4 Transition matrix

In order to obtain absorption or emission cross-sections or the resonant scattering amplitude, matrix elements of the form $\langle \varphi_n | \hat{O} | \varphi_g \rangle$ have to be evaluated. The operator $\hat{O}$ corresponds either to Eq. 5 or to Eq. 6. Both cases are characterized by a linear dependence on the vector potential, which can be written in a plane wave expansion as proportional to $\mathbf{A}(\mathbf{r}, t) = \sum_{\mathbf{k}} (a_{\mathbf{k}} \epsilon_{\mathbf{k}} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} + c.c.)$, where $\epsilon_{\mathbf{k}}$ is the polarization vector (we shall drop the label $\mathbf{k}$ in the following), $\mathbf{k}$ the wave vector and $\hbar\omega$ the energy of the mode determined by the amplitude $a_{\mathbf{k}}$ (equivalent to the destruction operator in a second-quantization form). In turn, the plane-wave exponent in the operator can be expanded in terms of $\mathbf{k} \cdot \mathbf{r}$ and reads, apart from some normalization factors, at second order:

$$\hat{O}_A = \epsilon \cdot \mathbf{P} e^{i\mathbf{k}\cdot\mathbf{r}} = \epsilon \cdot \mathbf{P}\left(1 + i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2 + \dots\right) , \tag{11}$$

$$\hat{O}_B = i\mathbf{S}\cdot(\mathbf{k}\times\epsilon)e^{i\mathbf{k}\cdot\mathbf{r}} = i\mathbf{S}\cdot(\mathbf{k}\times\epsilon)(1 + i\mathbf{k}\cdot\mathbf{r} - \dots) . \tag{12}$$

The expansion for $\hat{O}_B$ was stopped at terms linear in $\mathbf{k}\cdot\mathbf{r}$ for reasons that will be clear below. In previous expressions, $\hat{O}_A$ and $\hat{O}_B$ represent, respectively, Eq. 5 and Eq. 6. The operators associated to these terms can be rewritten in order to switch the linear momentum operator $\mathbf{p}$ to the coordinate $\mathbf{r}$-form. The first term, in $\hat{O}_A$, called electric dipole (E1) reads:

$$M_{ng,E1} = \langle\varphi_n|\epsilon\cdot\mathbf{P}|\varphi_g\rangle = \left\langle\varphi_n\left|\frac{m}{i\hbar}[\epsilon\cdot\mathbf{r}, H_0]\right|\varphi_g\right\rangle = i\frac{m}{\hbar}(E_n - E_g)\langle\varphi_n|\epsilon\cdot\mathbf{r}|\varphi_g\rangle , \tag{13}$$

where the second equality was obtained through the Heisenberg equation of motion for $\mathbf{p} = \frac{1}{m}\frac{d\mathbf{r}}{dt}$. A similar procedure, though slightly more involved due to the presence of multiple-commutators can be used for all the other terms. For example, a typical term from $\epsilon\cdot\mathbf{P}\mathbf{k}\cdot\mathbf{r}$ in $\hat{O}_A$ would read as:

$$\begin{aligned}\frac{m}{2\hbar}[zy, H_0] &= \frac{m}{2\hbar}([z, H_0]y + z[y, H_0]) = \frac{i}{2}(P_z y + zP_y) \\ &= \frac{i}{2}(2P_z y - P_z y + zP_y) = iP_z y - \frac{i}{2}L_x ,\end{aligned} \tag{14}$$

where L_x is the x component of the angular moment $\mathbf{L}$. For any direction we thus get:

$$i\mathbf{P}\cdot\epsilon\mathbf{k}\cdot\mathbf{r} = \frac{m}{2\hbar}[\epsilon\cdot\mathbf{r}\mathbf{k}\cdot\mathbf{r}, H_0] + \frac{i}{2}\mathbf{k}\times\epsilon\cdot\mathbf{L} . \tag{15}$$

The first term of the second member of this expression gives the electric quadrupole (E2) contribution:

$$M_{ng,E2} = i\frac{m}{\hbar}(E_n - E_g)\frac{i}{2}\langle\varphi_n|\epsilon\cdot\mathbf{r}\mathbf{k}\cdot\mathbf{r}|\varphi_g\rangle , \tag{16}$$

The second term of the second member of Eq. 15, depending on orbital moment $\mathbf{L}$, is magnetic in origin. Consequently it is grouped with the zeroth order of the expansion coming from the spin contribution. The two terms lumped together are known as *magnetic dipole* (M1):

$$M_{ng,M1} = \frac{1}{2}\langle\varphi_n|\mathbf{k}\times\epsilon\cdot(\mathbf{L} + 2\mathbf{S})|\varphi_g\rangle . \tag{17}$$

as $\mathbf{m} \equiv \mu_B(\mathbf{L} + 2\mathbf{S})$ is the magnetic moment.

Proceeding further, we can collect the second-order term in $\hat{O}_A$ with the first-order term in $\hat{O}_B$, to get the electric octupole (E3), the magnetic quadrupole (M2) and the toroidal dipole (T1). For example, we have for the transition-matrix element:

$$\begin{aligned}\left[zy^2, H_0\right] &= \left([z, H_0]y^2 + z[y, H_0]y + zy[y, H_0]\right) \\ &= \frac{i\hbar}{m}\left(zyP_y + zP_y y + P_z y^2\right) = \frac{i\hbar}{m}\left(2zP_y y + i\hbar z + P_z y^2\right) \\ &= \frac{i\hbar}{m}\left(2(zP_y - P_z y + P_z y)y + i\hbar z + P_z y^2\right) \\ &= \frac{i\hbar}{m}\left(-2L_x y + i\hbar z + 3P_z y^2\right) ,\end{aligned} \tag{18}$$

This leads to the following expression for the second-order term in Eq. 11:

$$\mathbf{P}\cdot\epsilon(\mathbf{k}\cdot\mathbf{r})^2 = \frac{m}{3i\hbar}\left[\epsilon\cdot\mathbf{r}(\mathbf{k}\cdot\mathbf{r})^2, H_0\right] - \frac{i\hbar k^2}{3}\epsilon\cdot\mathbf{r} + \frac{2}{3}(\mathbf{k}\times\epsilon)\cdot\mathbf{L}\mathbf{k}\cdot\mathbf{r}\ , \tag{19}$$

The first term represents the electric octupole. The second is a correction to the electric dipole, which can however be usually neglected due to the prefactor that makes it less than 1% of the E1 term. Finally, the third term is magnetic and can be lumped together with the second term of Eq. 12. It is therefore clear that the reason why we developed Eq. 12 just up to the first order is that magnetic terms of order n combine with electric terms of order n+1. It should be noted that the third, magnetic, term of Eq. 19 can be written as the scalar product of two 3 by 3 matrices, one representing the radiation $((\mathbf{k}\times\epsilon)_\alpha(\mathbf{k})_\beta)$ and another representing the matter $((\mathbf{L})_\alpha(\mathbf{r})_\beta)$. The latter can be further decomposed in the irreducible terms under rotation, ie, a scalar part (the trace of the matrix), an antisymmetric part $((\mathbf{L})_\alpha(\mathbf{r})_\beta - (\mathbf{L})_\beta(\mathbf{r})_\alpha)$ and a symmetric traceless part. The latter corresponds to the magnetic quadrupole (M2), whereas the antisymmetric part is the polar toroidal dipole (T1) part of the matter-radiation interaction, not to be confused with the toroidal moments of the matter, as we shall clarify in the next section. As a final step, we can collect together all prefactor to write down the final expression for the transition matrix element to include all terms (E1, E2, E3, M1, M2, T1) calculated up to now. The total amplitude, M_{ng}, reads (the fourth term is the dipolar correction of Eq. 19) :

$$\begin{aligned} M_{ng} = C(&\langle\varphi_n|\epsilon\cdot\mathbf{r}|\varphi_g\rangle + \frac{i}{2}\langle\varphi_n|\epsilon\cdot\mathbf{r}\mathbf{k}\cdot\mathbf{r}|\varphi_g\rangle - \frac{1}{6}\left\langle\varphi_n\left|\epsilon\cdot\mathbf{r}(\mathbf{k}\cdot\mathbf{r})^2\right|\varphi_g\right\rangle \\ &+\frac{\hbar^2k^2}{6m(E_n-E_g)}\langle\varphi_n|\epsilon\cdot\mathbf{r}|\varphi_g\rangle + C_M\langle\varphi_n|\mathbf{k}\times\epsilon\cdot(\mathbf{L}+2\mathbf{S})|\varphi_g\rangle \\ &+iC_M\langle\varphi_n|(\mathbf{k}\times\epsilon)\cdot\left(\frac{2}{3}\mathbf{L}+2\mathbf{S}\right)\mathbf{k}\cdot\mathbf{r}|\varphi_g\rangle)\ , \end{aligned} \tag{20}$$

where $C = q\mathcal{E}_0\frac{E_n-E_g}{\hbar\omega}e^{-i\omega t}$, $C_M = \frac{\hbar}{2m(E_n-E_g)}$ and finally $\mathcal{E}_0$ is the amplitude of the electric field of the incoming photon at the position of the electron.

Finally, and more important, we should evaluate the order of magnitude of each of the terms treated here in order to check the possibility to detect them experimentally. The M1 contribution is usually very small in the x-ray energy range, though there have been recent claims of its detection. The reason is that the radial part of the matrix elements corresponds to the initial and intermediate wave-functions overlap (the corresponding selection rules gives $\Delta\ell = 0$) and the two are nearly orthogonal. Usual estimates of this term are of the order of 10^{-3} for L-edges of transition-metal oxides. Paradoxically, the M2 term is of the same order of magnitude and could be even bigger at L-edges of actinides, because in this case the selection rule allows $\Delta\ell = 1$ as an electric dipole E1 and only the prefactor of $\frac{\hbar\omega}{2mc^2}$ strongly depletes it. At Cu L-edges this terms is about 10^{-3} and can be $2\cdot 10^{-2}$ at U L-edges. In what follows we shall neglect E3, M1, M2 and T1 terms.

3 Multipole analysis

In the last part of the previous section we have used the so-called multipole expansion of the vector potential, based on the series expansion of its phase factor $e^{i\mathbf{k}\cdot\mathbf{r}}$. We may call the terms obtained (E1, E2, E3, M1, M2, T1) as "interaction multipoles" in order to distinguish them from the "matter multipoles" that we treat in this section. The latters can be obtained from an expansion of the total energy for matter and physically represent the matter reaction to an external field. For example, whereas the M1 term in the previous section is related to the magnetic dipole interaction of the external electromagnetic field and the electron at position $\mathbf{r}$, this is not the same as the magnetic moment of the sample under analysis, that is instead related to the quantity summarized in Table 1, as we shall see below.

The access to any particular component of such "matter multipoles" by spectroscopical means can be obtained by playing with the polarization and taking into account the symmetry of the material, both at the level of the (magnetic) point group and of the (Schubnikov) space group [19]. The consequence is that the measurement under specific conditions can give information on the space-group of the material, including the magnetic group. A complete calculation of these symmetries, limited to the E1-E1 case for all cubic (non magnetic) space-groups was provided by Dmitrienko [4].

For E1 and E2 terms, the matrix elements can be expanded into dipole and quadrupole components :

$$\langle \varphi_n | \hat{o}_i | \varphi_g \rangle = D_i^n + i\frac{k}{2} Q_i^n + \ldots \; . \tag{21}$$

and signal amplitude can be written as:

$$\langle \varphi_g | \hat{o}_s^* | \varphi_n \rangle \langle \varphi_n | \hat{o}_i | \varphi_g \rangle \cong D_o^{n*} D_i^n + i\frac{k}{2}\left(D_o^{n*} Q_i^n - Q_o^{n*} D_i^n\right) + \frac{k^2}{4} Q_o^{n*} Q_i^n \; . \tag{22}$$

where $\hat{o}_i$ and $\hat{o}_s$ refer to incoming and scattered beams, respectively. We can then introduce three cartesian tensors. The dipole-dipole or E1-E1 rank-2 tensor, the dipole-quadrupole or E1-E2 rank-3 tensor and the quadrupole-quadrupole or E2-E2 rank-4 tensor:

$$D_{\alpha\beta} = \sum_n \langle \varphi_g | r_\alpha | \varphi_n \rangle \langle \varphi_n | r_\beta | \varphi_g \rangle \;\; , \tag{23}$$

$$I_{\alpha\beta\gamma} = \sum_n \langle \varphi_g | r_\alpha r_\beta | \varphi_n \rangle \langle \varphi_n | r_\gamma | \varphi_g \rangle \;\; , \tag{24}$$

$$Q_{\alpha\beta\gamma} = \sum_n \langle \varphi_g | r_\alpha r_\beta | \varphi_n \rangle \langle \varphi_n | r_\gamma r_\delta | \varphi_g \rangle \;\; . \tag{25}$$

where α, β, γ and δ label the three Cartesian coordinates x, y and z.

With this, the signal amplitude (except for the multiplicative factor in the absorption cross-section and the denominator in RXD) is given by:

$$A = \sum_{\alpha,\beta} \epsilon_\alpha^{s*} \epsilon_\beta^i D_{\alpha\beta} + \frac{i}{2} \sum_{\alpha,\beta,\gamma} \epsilon_\alpha^{s*} \epsilon_\beta^i \left(k_\gamma^i I_{\alpha\beta\gamma} - k_\gamma^s I_{\alpha\beta\gamma}^*\right) + \frac{1}{4} \sum_{\alpha,\beta,\gamma,\delta} \epsilon_\alpha^{s*} \epsilon_\beta^i k_\gamma^s k_\delta^i Q_{\alpha\beta\gamma\delta} \; . \tag{26}$$

To fix the idea the E1-E1 amplitude is given by:

$$A_{E1E1} = \left(\epsilon_x^{s*}, \epsilon_y^{s*}, \epsilon_z^{s*}\right) \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \begin{pmatrix} \epsilon_x^i \\ \epsilon_y^i \\ \epsilon_z^i \end{pmatrix} \; . \tag{27}$$

Off-diagonal elements are complex when the material is magnetic.

The E1-E2 terms in RXD can be observed only for atoms whose point-symmetry does not contain inversion (whereas for absorption spectroscopies the constraint of inversion-breaking moves to the global space-symmetry group, because of the incoherent sum). Indeed, due to the different selection rules of E1 and E2 matrix elements ($\Delta\ell$ odd for the first and $\Delta\ell$ even for the second), intermediate states φ_n must have both odd-ℓ and even-ℓ components. Of course, only for those reflections such that the Bragg factor is opposite on two equivalent atoms related by inversion symmetry, a pure E1-E2 term appears, the E1-E1 and E2-E2 contributions being zero.

The importance of the point group can be illustrated by a simple example limited to the E1-E1 case.

$m3m$ symmetry (O_h) This cubic symmetry is for instance the case of an atom surrounded by a regular octahedron. Due to the symmetry plane perpendicular to Ox, Oy and Oz, the off-diagonal components of the E1-E1 cartesian tensor are zero, because of the three-fold axis its diagonal elements are equal. The amplitudes of the signal is in this case:

$$A_{E1E1} = \epsilon^+ \begin{pmatrix} D_{zz} & 0 & 0 \\ 0 & D_{zz} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} \epsilon = \frac{1}{3}\epsilon \cdot \epsilon Tr\left(D\right) = D_{zz} \tag{28}$$

The E1-E1 signal amplitude is isotropic. It does not depend on the polarization orientation. This is however not the case for E1-E2 and E2-E2 [18]. It is useful to emphasize that this property of E1-E1 amplitude does not depend on the edge, ie, it is valid independently of the kind of intermediate states (p, d, f) that are probed. This means that investigating the same d states by E2-E2 transitions (at K-edges) or by E1-E1 transitions (at $L_{2,3}$-edges) leads to different information.

$4/mmm$ symmetry (D_{4h}) This symmetry can be obtained for instance by the elongation of a regular octahedron along the z-axis. The three-fold axes of cubic symmetry are lost and the four-fold axis around z makes $D_{xx} = D_{yy}$. One thus gets:

$$A_{E1E1} = \epsilon^+ \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{xx} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} \epsilon = \frac{1}{3}\left(2D_{xx} + D_{zz}\right) + \frac{1}{3}\left(D_{zz} - D_{xx}\right)\left(3\left|\epsilon_z\right|^2 - 1\right) \tag{29}$$

When using the spherical coordinates for the linear polarization :

$$\epsilon = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} , \tag{30}$$

we see that one gets a polarization orientation dependence equivalent to the spherical harmonics $Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$. The atomic signal is no more isotropic, not even in the E1-E1 channel.

$4/m'm'm$ symmetry If we add a magnetic moment along the z-axis to the previous case, then the symmetry planes perpendicular to Ox and Oy must be multiplied by time reversal, and one gets the $4/m'm'm$ symmetry. Therefore the Cartesian tensor contains off-diagonal imaginary terms of the kind:

$$\begin{aligned} A_{E1E1} &= \epsilon^+ \begin{pmatrix} D_{xx} & iD_{xy}^i & 0 \\ -iD_{xy}^i & D_{xx} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} \epsilon \\ &= \frac{1}{3}\left(2D_{xx} + D_{zz}\right) - \frac{i}{\sqrt{2}}\epsilon^* \times \epsilon \cdot \mathbf{m} + \frac{1}{3}\left(D_{zz} - D_{xx}\right)\left(3\left|\epsilon_z\right|^2 - 1\right) . \end{aligned} \tag{31}$$

Table 1. List of the electric and magnetic multipoles in matter. The couples $++$, $+-$, $-+$ and $--$ represent the change in sign under time reversal and spatial inversion respectively. Magnetic terms are odd by time reversal. E1-E2 components are odd by spatial inversion. The electric monopole term measures the charge density $ch_{\ell+1}$ in E1-E1 and $ch_{\ell+2}$ for E2-E2. The magnetic dipole terms measure the magnetic density $m_{\ell+1}$ in E1-E1 and a part of $m_{\ell+2}$ for E2-E2. The time-reversal odd dipole in E1-E2 measures the toroidal moment (or anapole) t, the even one measures the electric moment μ. The time-reversal even quadrupole in E1-E2 measures the axial toroidal quadrupole (t_q)[20]. Other components measure higher-order multipoles.

ℓ		E1-E1	E1-E2 elec.	E1-E2 magn.	E2-E2
0	monopole	$++$ $ch_{\ell+1}$			$++$ $\approx ch_{\ell+2}$
1	dipole	$-+$ $m_{\ell+1}$	$+-$ μ	$--$ t	$-+$ $\approx m_{\ell+2}$
2	quadrupole	$++$	$+-$ t_q	$--$	$++$
3	octupole		$+-$	$--$	$-+$
4	hexadecapole				$++$

We get a new term compared to Eq. 29 which is related to the magnetic moment $\mathbf{m}$.

The use of cartesian tensor is rather natural. Nevertheless there exist a linear basis transformation to the set of spherical coordinates that allows a direct relation of each term in this basis with specific observable physical quantities like, for example, the orbital anisotropy, the magnetic moment or the toroidal moment. These tensors can be related to the multipole expansion of the studied material and are also separated in the E1-E1, E1-E2 and E2-E2 contributions. In this case the scattering amplitude, Eq. 26, can be written as:

$$A = \sum_{\substack{0\leq\ell\leq 2\\ -\ell\leq m\leq\ell}} (-1)^{\ell+m} T_\ell^m D_\ell^m + i \sum_{\substack{1\leq\ell\leq 3\\ -\ell\leq m\leq\ell}} (-1)^{\ell+m} U_\ell^m I_\ell^m + \sum_{\substack{0\leq\ell\leq 4\\ -\ell\leq m\leq\ell}} (-1)^{\ell+m} V_\ell^m Q_\ell^m, \quad (32)$$

where D_ℓ^m, I_ℓ^m and Q_ℓ^m are the E1-E1, E1-E2 and E2-E2 components, respectively, of the matter tensors and T_ℓ^m, U_ℓ^m and V_ℓ^m those of the polarization - wave vector tensors. More details on their transformations can be found in Ref. [17]. Their physical meaning is instead illustrated in Table 1. E1-E2 terms are all inversion-odd and those that change sign with time reversal are magnetic. This allows peculiar measurements on specific reflections or/and with specific polarization and/or wave-vector conditions that allows to measure separately the various multipoles, as detailed, eg, in Refs. [19–21].

4 Description of core and photo-electron states: the RXD evaluation in practice

4.1 Anomalous scattering amplitude

Starting from Eq. 10 one usually makes the summation on the intermediate states n in two steps. We first group, the states of same energy E, that we still sum in a discrete form. The sum over the states of different energies is performed in a second step through an integral spreading from the Fermi level up to infinity. In the elastic case where we are supposed to have $E - E_g + \Delta E_a \cong \hbar\omega$ the resonant or anomalous scattering amplitude is given by:

$$f' - if'' \cong m\omega^2 \int_{E_F}^{\infty} \frac{\sum_{n,g} \frac{1}{\pi} \langle\varphi_g| \hat{o}_s^* |\bar{\varphi}_n\rangle \langle\bar{\varphi}_n| \hat{o}_i |\varphi_g\rangle}{\hbar\omega - (E - E_g + \Delta E_a) + i\frac{\Gamma}{2}} dE\ , \quad (33)$$

where E_F is the Fermi energy and Γ is the broadening. Note the minus sign in front of the imaginary part of the scattering amplitude to get the conventional way where f' is negative and f'' positive[1]. When the incoming and outgoing polarizations are parallel, the absorption cross-section is nearly proportional to $\hbar\omega \times f''$.

The density of states $\delta(E)$ does not appear explicitly because it is included in the atomic amplitudes and in the normalization of the radial wave functions. This one is built by continuity with an outer sphere where the potential is constant. The solutions are there, the Bessel and Hankel functions normalized by the square root of the density of states in vacuum, that is by $\sqrt{k/\pi}$ where k is the photo-electron wave-vector expressed in atomic unit. One thus gets the normalized radial solutions $\bar{b}_\ell(E,r)$ instead of the $b_\ell(E,r)$ which are normalized to one. Thus one replaces in the formulas $\langle\varphi_g|\hat{o}_s^*|\varphi_n\rangle\langle\varphi_n|\hat{o}_i|\varphi_g\rangle\,\delta(E)$ by $\langle\varphi_g|\hat{o}_s^*|\bar{\varphi}_n\rangle\langle\bar{\varphi}_n|\hat{o}_i|\varphi_g\rangle$.

We have to calculate:

$$\langle\varphi_n|\hat{o}|\varphi_g\rangle_\sigma = \int \varphi_n^*(\mathbf{r},\sigma)\,\hat{o}(\mathbf{r})\,\varphi_g(\mathbf{r},\sigma)\,d^3\mathbf{r} \; . \tag{34}$$

When considering only the E1 and E2 transitions, there is no possibility of spin-flip during the transition. Here the operator just contains the terms inside the matrix of eq. 13 for E1 and eq. 16 for E2, that is:

$$\hat{o} = \epsilon\cdot\mathbf{r}\left(1+\frac{1}{2}i\mathbf{k}\cdot\mathbf{r}\right) \; . \tag{35}$$

The core state g is localized, thus the integral has to be performed only inside the absorbing atom. The expansion of φ_n, $\hat{o}$ and φ_g in spherical harmonics is consequently very convenient because it singles out the angular momentum quantum numbers explicitly, and separates the radial and angular dependances.

4.2 Final states

In the non magnetic case, the final (or intermediate) state can be written as:

$$\bar{\varphi}_n(\mathbf{r}) = \sum_{\ell,m} a_{\ell,m}^n(E)\,\bar{b}_\ell(E,r)\,Y_\ell^m(\Omega) \;, \tag{36}$$

where $\mathbf{r}=(r,\Omega)$ is expressed in spherical coordinates, $\bar{b}_\ell(E,r)$ is the radial component of the wave function inside the atom. It is obtained by solving the radial Schrödinger equation in the atom. It weakly depends on the photo electron energy E. The $a_{\ell,m}^f(E)$ are the amplitudes[2].

In the magnetic case, if one neglects the spin-orbit, a single sum over σ is to be include:

$$\bar{\varphi}_n(\mathbf{r}) = \sum_{\ell,m,\sigma} a_{\ell,m,\sigma}^n(E)\,\bar{b}_{\ell,\sigma}(E,r)\,Y_\ell^m(\Omega)\,\chi_\sigma \;, \tag{37}$$

[1] This sign as well as the plus sign in the exponent of the Bragg factor comes from a different convention in the time arrow between the crystallograph community and the theorists of quantum mechanics.

[2] When using the monoelectronic approach, the $a_{\ell,m}^f(E)$ contain the main dependence on the energy E. They are obtained using the continuity of the wave function and its derivative between the atom and its surrounding. In the other approaches, they are just normalization coefficients, and the dependence in function of energy is put outside of the transition matrix. At this stage, whatever is the method, our demonstration is general

where the spin state is given by:

$$\chi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \ , \quad \chi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \ . \tag{38}$$

When one considers the spin-orbit, the intermediate state is written as:

$$\bar{\varphi}_n(\mathbf{r}) = \sum_{\ell,m,s} a^n_{\ell,m+\frac{1}{2}-s,s}(E)\, \bar{b}^{\sigma}_{\ell,m+\frac{1}{2}-\sigma,s}(E,r)\, Y_\ell^{m+\frac{1}{2}-\sigma}(\Omega)\, \chi_\sigma \ . \tag{39}$$

Note that in this case, the spherical harmonics are necessarily the complex ones. This expression comes from the solution in the atom of the Dirac equation. σ is not anymore a good quantum number. We replace it by the index s. Due to the spin-orbit the $\left(\ell, m, \frac{1}{2}\right)$ and $\left(\ell, m+1, -\frac{1}{2}\right)$ components are part of the same state. This is what gives the eventual spin-flip during the photo electron scattering.

4.3 Initial states

Now let us look at the initial states. They are localized and the expansion seen in the previous expression is limited to one or two components. For example at the K-edge, one has $\ell = 0$ and two initial states:

$$\left|\frac{1}{2}, -\frac{1}{2}\right\rangle = b_{0\frac{1}{2}}(r)\, Y_0^0 \chi_{-\frac{1}{2}} \ , \tag{40}$$

$$\left|\frac{1}{2}, \frac{1}{2}\right\rangle = b_{0\frac{1}{2}}(r)\, Y_0^0 \chi_{\frac{1}{2}} \ . \tag{41}$$

At the L_2-edge; one has $\ell = 1$, $j = 1/2$ and two initial states:

$$\begin{aligned} \left|\frac{1}{2}, -\frac{1}{2}\right\rangle &= b_{1\frac{1}{2}}(r) \left(-\sqrt{\frac{2}{3}} Y_1^{-1} \chi_{\frac{1}{2}} + \sqrt{\frac{1}{3}} Y_1^0 \chi_{-\frac{1}{2}} \right) \ , \\ \left|\frac{1}{2}, \frac{1}{2}\right\rangle &= b_{1\frac{1}{2}}(r) \left(-\sqrt{\frac{1}{3}} Y_1^0 \chi_{\frac{1}{2}} + \sqrt{\frac{2}{3}} Y_1^1 \chi_{-\frac{1}{2}} \right) \ . \end{aligned} \tag{42}$$

At the L_3-edge; one has $\ell = 1$, $j = 3/2$ and four initial states:

$$\begin{aligned} \left|\frac{3}{2}, -\frac{3}{2}\right\rangle &= b_{1\frac{3}{2}}(r)\, Y_1^{-1} \chi_{-\frac{1}{2}} \ , \\ \left|\frac{3}{2}, -\frac{1}{2}\right\rangle &= b_{1\frac{3}{2}}(r) \left(\sqrt{\frac{1}{3}} Y_1^{-1} \chi_{\frac{1}{2}} + \sqrt{\frac{2}{3}} Y_1^0 \chi_{-\frac{1}{2}} \right) \ , \\ \left|\frac{3}{2}, \frac{1}{2}\right\rangle &= b_{1\frac{3}{2}}(r) \left(\sqrt{\frac{2}{3}} Y_1^0 \chi_{\frac{1}{2}} + \sqrt{\frac{1}{3}} Y_1^1 \chi_{-\frac{1}{2}} \right) \ , \\ \left|\frac{3}{2}, \frac{3}{2}\right\rangle &= b_{1\frac{3}{2}}(r)\, Y_1^1 \chi_{\frac{1}{2}} \ . \end{aligned} \tag{43}$$

In general when using complex harmonics one can just write:

$$\varphi_g = \sum_\sigma G_g^\sigma b_g(r) Y_{\ell_g}^{m_g+\frac{1}{2}-\sigma} \chi_\sigma \ . \tag{44}$$

4.4 Operator

The operator can also be expanded in spherical harmonics:

$$\hat{o} = \epsilon \cdot \mathbf{r} \left(1 + \frac{1}{2} i \mathbf{k} \cdot \mathbf{r} \right) = \sum_{\ell_o, m_o} \left(\frac{i}{2} k \right)^{\ell_o - 1} c_{\ell_o, m_o} r^{\ell_o} Y_{\ell_o}^{m_o} (\Omega) \tag{45}$$

where the c_{ℓ_o,m_o} are specific coefficients with their operator quantum numbers (ℓ_o, m_o). For example for a polarization along z and a wave vector along x one gets:

$$\epsilon \cdot \mathbf{r} = z = r \cos\theta = \sqrt{\frac{4\pi}{3}} r Y_1^0 \ , \tag{46}$$

$$\frac{i}{2} \epsilon \cdot \mathbf{r} \mathbf{k} \cdot \mathbf{r} = \frac{i}{2} kzx = \frac{i}{2} kr^2 \sin\theta \cos\varphi = \frac{i}{2} k \sqrt{\frac{2\pi}{15}} r^2 \left(Y_2^1 - Y_2^{-1} \right) \ , \tag{47}$$

where we have used the complex spherical harmonics.

4.5 The transition matrix

We can now gather the equations 39, 44 and 45. The transition matrix for each spin σ is then:

$$\begin{aligned} \langle \varphi_n | \hat{o} | \varphi_g \rangle_\sigma = & \sum_o \left(\frac{i}{2} k \right)^{\ell_o - 1} c_{\ell_o, m_o} \sum_{\ell, m} \Gamma_{\ell, m + \frac{1}{2} - \sigma}^{\ell_g, m_g + \frac{1}{2} - \sigma, \ell_o, m_o} \\ & \times \sum_s \mathcal{R}_{\ell, m + \frac{1}{2} - \sigma, s}^{g, \ell_o, \sigma} (E) \, a_{\ell, m + \frac{1}{2} - s, s}^n (E) \ , \end{aligned} \tag{48}$$

where

$$\mathcal{R}_{\ell, m + \frac{1}{2} - \sigma, s}^{g, \ell_o, \sigma} (E) = \int_0^R \bar{b}_{\ell, m + \frac{1}{2} - s, s}^{\sigma *} (E, r) \, b_g (r) \, r^{2 + \ell_o} dr \ , \tag{49}$$

is the radial integral performed up to the atom radius R, and

$$\Gamma_{\ell, m}^{\ell_g, m_g, \ell_o, m_o} = G_g^\sigma \int_{sphere} Y_\ell^{m*} (\Omega) \, Y_{\ell_o}^{m_o} (\Omega) \, Y_{\ell_g}^{m_g} (\Omega) \, d\Omega \ , \tag{50}$$

is the angular integral or Gaunt coefficient multiplied by the factor G_g^σ coming from the initial state. It is usually expressed in terms of Clebsch-Gordon coefficients. The angular integral is not zero only for peculiar value of ℓ, m:

- ℓ must have the same parity than $\ell_g + \ell_o$,
- $|\ell_g - \ell_o| \leq \ell \leq |\ell_g + \ell_o|$,
- $m = m_o + m_g$.

The last condition on m is when using complex spherical harmonics.

For the dipole and quadrupole components, we have respectively $\ell_o = 1$ and $\ell_o = 2$. Thus, the difference on ℓ between the initial and the final state is

- dipole: $\Delta\ell = \pm 1$,
- quadrupole: $\Delta\ell = 0, \pm 2$.

The orbitals probed at the different edges are summarized in Table 2.

Table 2. Probed states for the E1 and E2 transition for the different edges

Edge	E1 probed state	E2 probed state
K, L_1, M_1, N_1, O_1	p	s - d
L_2, L_3, M_2, M_3, N_2, N_3, O_2, O_3	s - d	p - f
M_4, M_5, N_4, N_5, O_4, O_5	p - f	s - d - g

4.6 Complete form

With this simplification we can use the matrix product which appears in the RXD formula:

$$A = \sum_{f,g} \langle \varphi_g | \hat{o}_s^* | \bar{\varphi}_n \rangle \langle \bar{\varphi}_n | \hat{o}_i | \varphi_g \rangle \ . \tag{51}$$

In the absorption case one just has to impose $\hat{o}_s = \hat{o}_i$. Using moreover eq. 49 which express the transition matrix in terms of the radial and angular integrals and of the atomic amplitudes, one gets:

$$A = \sum_{o_i,o_s} c_{\ell_{o_i},m_{o_i}} c_{\ell_{o_s},m_{o_s}} \sum_{\sigma,g} \sum_{\ell,m,\ell',m'} \mathit{\Gamma}^{\ell_g,m_g+\frac{1}{2}-\sigma,\ell_{o_i},m_{o_i}}_{\ell,m+\frac{1}{2}-\sigma} \mathit{\Gamma}^{\ell_g,m'_g+\frac{1}{2}-\sigma,\ell_{o_s},m_{o_s}}_{\ell,m'+\frac{1}{2}-\sigma} \tag{52}$$
$$\times \sum_{s,s'} \mathcal{R}^{g,\ell_{o_i},\sigma}_{\ell,m+\frac{1}{2}-\sigma,s}(E)\, \mathcal{R}^{g,\ell_{o_s},\sigma}_{\ell,m+\frac{1}{2}-\sigma,s'}(E) \sum_f a^n_{\ell,m,s}(E)\, a^{n*}_{\ell',m',s'}(E) \ .$$

5 Mono Electronic Simulations

As stated above simulations can be very helpful in the interpretation of the experiments. Moreover, in order to quantitatively access to parameters such as atom positions, charges or magnetic moments, they can be absolutely necessary. We have seen that in some cases ligand field multiplet theory is necessary. Here we focus on the mono electronic simulations. They often gives satisfactory results for the K-edges and the $L_{2,3}$ edges of heavy elements.

The mono electronic simulations uses the local spin density approximation (LSDA) of the density functional theory (DFT). There are two groups of calculation method: one solving the Schrödinger (or Dyson, or Dirac) equation in a cluster centered around the absorbing atom and the one, usually derived from band structure calculations, using the 3D periodicity of the material. The calculations can be performed with or without self-consistency.

Whatever the method, the first thing we need is a potential. It is seen briefly in the next section. About the different methods of calculation (Linear augmented plane wave (LAPW) [24], tight-banding, linear combination of atomic orbital (LCAO), pseudo-potential [26], linear muffin-tin orbital (LMTO), KKR [27], finite difference method [30]...) the most used for practical purposes is the multiple scattering theory (MST) that is discussed a bit more in Sec. 5.2.

5.1 The potential

It is often said that all the methods are equivalent, at the end. Although it might be true, in fact, they give different results... This is due to the fact that, inside each method, approximations are done. Expansion in spherical harmonic or in plane waves are limited, there are interpolations in the building of the potential, calculations are in single or double precision, but in particular, there are the potential problems. The first one comes from the approximation done on the potential shape. The second is related to the choice of the exchange correlation potential.

The multiple scattering theory, as LMTO, usually makes an approximation on the potential shape. To have the calculation simpler, the potential is taken as spherically symmetric in the atoms and constant between them, in the interstitial region. This is the so-called muffin-tin approximation. The radius of the atoms (of the spherical part) is thus a technical difficulty, each code author having its own recipe. Most often a small overlap is authorized because, pragmatically, this improves the agreement with the experiments. Nevertheless from a mathematical point of view this trick is not justified. Now, using the finite difference method, pseudo potential or FLAPW technique for example, it is possible to have free-shape (or full) potential. The price to pay is that calculations are heavier. Nevertheless when the structures are sparse, when there are few symmetry elements or when the absorbing atom is relatively light, important differences are observed due to the muffin-tin approximation [30]. A recent work has nevertheless shown that the multiple scattering theory, up to now always using the muffin-tin approximation, can also be applied with a full potential shape [28].

In the LSDA the exchange-correlation problem is treated with a local potential which depends only on the local density of electrons (that is, on the point where one calculates the potential). In the magnetic case it depends as well on the local difference between the spin-up and spin-down density. This one can have different forms. Presently the most used ones are the Hedin and Lundqvist [29] and the Perdew and Wang [32]. Globally they give an attractive potential of increasing amplitude with increasing electron density. It is important to consider the energy dependence of this potential, as proposed by Von Bart and Hedin [33]. Indeed the amplitude of the potential decreases with increasing electron kinetic energy. In a relatively narrow energy range around the plasmon energy, that is between 10 and 30 eV, this potential changes by several eV. Without considering this phenomena one gets structures in the spectra shifted by the same amount. Because the position of the oscillations are related to the inter atomic distances, this could lead to false agreement with wrong fit of the corresponding parameters.

5.2 The multiple scattering theory

Explain this theory in a single paragraph is difficult. Readers can find detailed description by Natoli and coworkers [31] or Brouder [25]. It is the main theory used in many codes as FEFF [16], MXAN [22] or KXQX [23] and one of the two used in FDMNES [30].

First, one considers just one atom. We build a complete basis in the surrounding vacuum. There, the potential is constant and the solutions of the radial Schrödinger equation are the Bessel, j_ℓ, Neuman and Hankel functions. Using the phase shift theory one looks how the atom scatters all the Bessel functions. One uses the continuity of the wave function and its derivative at the border. For simplicity we keep the non magnetic case, and we can write:

$$a_\ell b_\ell \left(R\right) Y_\ell^m = \sqrt{\frac{k}{\pi}} \left(j_\ell \left(r\right) - i t_\ell h_\ell^+ \left(R\right)\right) Y_\ell^m \ , \tag{53}$$

for the wave function at the muffin-tin radius R. $h_\ell^+ \left(r\right)$ is the Hankel outgoing function, t_ℓ is the atomic scattering amplitude, b_ℓ the solution of the radial Schrödinger equation in the atom, k the electron wave vector and a_ℓ the amplitude inside the atom. All these terms depend on the kinetic electron energy. We have introduced the normalization by the square root of the density of states in vacuum $\sqrt{\frac{k}{\pi}}$. By continuity, the theorem of asymptotic completenees for differential equation, makes the density of states included in the atomic amplitudes. Using the two equations of continuity (function and derivative), one gets a_ℓ and t_ℓ.

Now the atom is embedded in a cluster. Thus the incoming wave is not anymore included in a simple Bessel function, but the superposition of this Bessel function and all the other waves of Hankel type, backscattered by the other atoms. The problem is thus not anymore spherical, and the scattering and atomic amplitudes will also depend on the quantum number m (and eventually on the spin index). One has to consider all the scattering processes from one atom to any other atom. To do that, one fills a (big) multiple scattering matrix, containing, for all the atoms, all their individual expansion in spherical harmonics. Its diagonal contains the atomic scattering amplitudes. The off-diagonal part contain the propagation terms connecting the scattering from the (ℓ, m) of an atom a, to the (ℓ', m') of another atom a'. The inversion of this matrix gives the multiple scattering amplitudes, $\tau_{\ell,m,a}^{\ell',m',a'}$, by the relation:

$$\tau_{\ell,m,a}^{\ell',m',a'} = \left[\frac{1}{1-TH}T\right]_{\ell,m,a}^{\ell',m',a'} . \tag{54}$$

T is a diagonal matrix (when there is no spin-orbit) containing the atomic scattering amplitudes. H is the matrix containing the propagation terms.

Using $a = a'$ and skipping the atom index, the optical theorem gives:

$$-\Im\left(\tau_{\ell,m}^{\ell',m'}\right) = \left|\sum_n a_{\ell,m}^{n*} a_{\ell',m'}^{n}\right| . \tag{55}$$

when the potential is real. Introducing this in the XANES formula, one gets :

$$\sigma = -4\pi^2\alpha\hbar\omega \sum_g \sum_{\ell,m,\ell',m'} \Im\left(\left\langle\varphi_g\left|\hat{o}^*\right|\bar{b}_\ell Y_\ell^m\right\rangle \tau_{\ell,m}^{\ell',m'} \left\langle\bar{b}_{\ell'} Y_{\ell'}^{m'}\left|\hat{o}\right|\varphi_g\right\rangle\right) . \tag{56}$$

The central term $\left|\bar{b}_\ell Y_\ell^m\right\rangle \tau_{\ell,m}^{\ell',m'} \left\langle\bar{b}_{\ell'} Y_{\ell'}^{m'}\right|$ is the Green's function.

One can do the same for the RXD case. To be more complete, we have written the equation in the spin-orbit case:

$$\begin{aligned} f' - if'' = {} & \frac{\pi}{2}\frac{2m}{\hbar^2}(\hbar\omega)^2 \\ & \times \sum_{g,\sigma,\sigma'} \sum_{\substack{\ell,m,s \\ \ell',m',s'}} \left\langle\varphi_g^\sigma\left|o_s^*\right|\bar{b}_{\ell,m+\frac{1}{2}-\sigma,s}^\sigma Y_\ell^m\right\rangle \tau_{\ell,m+\frac{1}{2}-s,s}^{\ell',m'+\frac{1}{2}-s',s'} \left\langle\bar{b}_{\ell',m'+\frac{1}{2}-\sigma',s'}^\sigma\left|o_i\right|\varphi_g^{\sigma'}\right\rangle . \end{aligned} \tag{57}$$

When the potential is complex, the expression contains more terms because the irregular solutions of the radial Schrödinger equation have to be considered, as well.

6 Conclusion

We have reviewed the different phenomena governing the resonant x-ray spectroscopies related to the transition of an electron from a core level up to some other level. The number of applications of these processes is huge. Because the process of transition is complex, the interpretation is not always direct. Some of them need multiplet calculations. Some others can use mono electronic simulations as presented here. The following years will see the development of new simulation techniques permitting the taking into account of both difficulties, the multi-electronic phenomena and the partially delocalize intermediate state effects occuring in many low energy L_{23} edges. Good candidates for this purposes are the Time-Dependent DFT [34,35], but with a sophisticated kernel, the multi-channel approach [36] or the Bethe Salpeter equation techniques. On the RXD itself, at this date, we think that all main processes are understood. What remain to be done is the building of a relatively easy tool able to give quantitative pieces of informations on the probed samples.

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