1.11.5. Non-resonant magnetic scattering

Far from resonance ($\hbar\omega \gg E_c - E_a$), the non-resonant parts of the scattering factor, f_0 and $f_{ij}^{\rm mag}$, described by the first two terms in (1.11.4.3) are the most important. In the classical approximation (Brunel & de Bergevin, 1981), there are four physical mechanisms (electric or magnetic, dipolar or quadrupolar) describing the interaction of an electron and its magnetic moment with an electromagnetic wave, causing the re-emission of radiation. The non-resonant magnetic term $f^{\rm magn}$ is small compared to the charge (Thomson) scattering owing (a) to small numbers of unpaired (magnetic) electrons and (b) to the factor $\hbar\omega/mc^2$ of about 0.02 for a typical X-ray energy $\hbar\omega = 10$ keV. This is the reason why it is so difficult to observe non-resonant magnetic scattering with conventional X-ray sources (de Bergevin & Brunel, 1972, 1981; Brunel & de Bergevin, 1981), in contrast to the nowadays normal use of synchrotron radiation.

Non-resonant magnetic scattering yields polarization properties quite different from those obtained from charge scattering. Moreover, it can be divided into two parts, which are associated with the spin and orbital moments. In contrast to the case of neutron magnetic scattering, the polarization properties of these two parts are different, as described by the tensors (Blume, 1994)

$$A_{ijk} = -2(1 - \mathbf{k}\cdot\mathbf{k}'/k^2)\epsilon_{ijk}, \tag{1.11.5.1}$$

$$\begin{aligned} B_{ijk} = \epsilon_{ijk} - \big[&\epsilon_{ilk}k'_l k'_j - \epsilon_{jlk}k_l k_i + \tfrac{1}{2}\epsilon_{ijl}(k'_l k_k + k_l k'_k) \\ &- \tfrac{1}{2}[\mathbf{k}\times\mathbf{k}']_i\delta_{jk} - \tfrac{1}{2}[\mathbf{k}\times\mathbf{k}']_j\delta_{ik}\big]/k^2, \end{aligned} \tag{1.11.5.2}$$

where ϵ_{ijk} is a completely antisymmetric unit tensor (the Levi-Civita symbol).

Being convoluted with polarization vectors (Blume, 1985; Lovesey & Collins, 1996; Paolasini, 2012), the non-resonant magnetic term can be rewritten as

$$\begin{aligned} &f_{\rm nonres}^{\rm magn}(\mathbf{G}) \\ &= -i\frac{\hbar\omega}{mc^2}\big\langle a\big|\sum_p(\mathbf{A}\cdot[\mathbf{G}\times\mathbf{P}_p]/\hbar k^2 + \mathbf{B}\cdot\mathbf{s}_p)\exp(i\mathbf{G}\cdot\mathbf{r}_p)\big|a\big\rangle, \end{aligned} \tag{1.11.5.3}$$

with vectors $\mathbf{A}$ and $\mathbf{B}$ given by

$$\mathbf{A} = [\mathbf{e}'^{*}\times\mathbf{e}], \tag{1.11.5.4}$$

$$\begin{aligned} \mathbf{B} = [\mathbf{e}'^{*}\times\mathbf{e}] - \{&[\mathbf{k}\times\mathbf{e}](\mathbf{k}\cdot\mathbf{e}'^{*}) - [\mathbf{k}'\times\mathbf{e}'^{*}](\mathbf{k}'\cdot\mathbf{e}) \\ &+ [\mathbf{k}'\times\mathbf{e}'^{*}]\times[\mathbf{k}\times\mathbf{e}]\}/k^2. \end{aligned} \tag{1.11.5.5}$$

According to (1.11.5.4) and (1.11.5.5), the polarization dependences of the spin and orbit contributions to the atomic scattering factor are significantly different. Consequently, the two contributions can be separated by analysing the polarization of the scattered radiation with the help of an analyser crystal (Gibbs *et al.*, 1988). Usually the incident (synchrotron) radiation is σ-polarized, *i.e.* the polarization vector is perpendicular to the scattering plane. If due to the orientation of the analysing crystal only the σ-polarized part of the scattered radiation is recorded, we can see from (1.11.5.4) that the orbital contribution to the scattering atomic factor vanishes, whereas it differs from zero considering the $\sigma \rightarrow \pi$ scattering channel.

1.11.6. Resonant atomic factors: multipole expansion

Strong enhancement of resonant scattering occurs when the energy of the incident radiation gets close to the energy of an electron transition from an inner shell to an empty state (be it localized or not) above the Fermi level. There are two widely used approaches for calculating resonant atomic amplitudes. One uses Cartesian, the other spherical (polar) coordinates, and both have their own advantages and disadvantages. Supposing in (1.11.4.3)

$$\exp(i\mathbf{k}\cdot\mathbf{r}_p) \approx 1 + i\mathbf{k}\cdot\mathbf{r}_p + \tfrac{1}{2}(i\mathbf{k}\cdot\mathbf{r}_p)^2 + \ldots \tag{1.11.6.1}$$

and using the expression for the velocity matrix element v_{ac} (Berestetskii *et al.*, 1982) $v_{ac} = i\omega_{ac}r_{ac}$, it is possible to present the resonant part of the atomic factor (1.11.4.3) as

$$\begin{aligned} f_{jk}^{\rm res} = \sum_c p_a \frac{m\omega_{ca}^3}{\omega}\Bigg\{ &\frac{\langle a|R_j|c\rangle\langle c|R_k|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} \\ &+ \frac{i}{2}\left[\frac{\langle a|R_j|c\rangle\langle c|R_k R_l k_l|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} - \frac{\langle a|R_j R_l k'_l|c\rangle\langle c|R_k|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2}\right] \\ &+ \frac{1}{4}\frac{\langle a|R_j R_l k'_l|c\rangle\langle c|R_k R_m k_m|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2}\Bigg\} \end{aligned} \tag{1.11.6.2}$$

$$= D_{jk} + \frac{i}{2}I_{jkl}k_l - \frac{i}{2}I_{kjl}k'_l + \frac{1}{4}Q_{jlkm}k_m k'_l, \tag{1.11.6.3}$$

where $\hbar\omega_{ca} = E_c - E_a$, D_{jk} is a dimensionless tensor corresponding to the dipole–dipole ($E1E1$) contribution, I_{jkl} is the dipole–quadrupole ($E1E2$) contribution and Q_{jklm} is the quadrupole–quadrupole ($E2E2$) term. All the tensors are complex and depend on the energy and the local properties of the medium. The expansion (1.11.6.1) over the wavevectors is possible near X-ray absorption edges because the products $\mathbf{k}\cdot\mathbf{r}_p$ are small for the typical sizes of the inner shells involved. In resonant X-ray absorption and scattering, the contribution of the magnetic multipole ML transitions is usually much less than that of the electric multipole EL transitions. Nevertheless, the scattering amplitude corresponding to $E1M1$ events has also been considered (Collins *et al.*, 2007). The tensors I_{jkl} and Q_{jklm} describe the spatial dispersion effects similar to those in visible optics.

1.11.6.1. *Tensor atomic factors: internal symmetry*

Different types of tensors transform under the action of the extended orthogonal group (Sirotin & Shaskolskaya, 1982) as

$$A_{i'_1\ldots i'_n} = \gamma r_{i'_1 k_1}\ldots r_{i'_n k_n}A_{k_1\ldots k_n}, \tag{1.11.6.4}$$

where the coefficients $\gamma = \pm 1$ depend on the kind of tensor (see Table 1.11.6.1) and $r_{i'_1 k_1}$ are coefficients describing proper rotations.

Various parts of the resonant scattering factor (1.11.6.3) possess different kinds of symmetry with respect to: (1) space inversion $\bar{1}$ or parity, (2) rotations R and (3) time reversal $1'$. Both dipole–dipole and quadrupole–quadrupole terms are parity-even, whereas the dipole–quadrupole term is parity-odd. Thus,

Table 1.11.6.1. *Coefficients γ corresponding to various kinds of tensor symmetry with respect to space inversion $\bar{1}$, rotations R, and time reversal $1'$*

Tensor type	Example	Transformation type			
		R	$\bar{1}R$	$1'R$	$\bar{1}'R$
Even	Strain	1	1	1	1
Electric	Electric field	1	−1	1	−1
Magnetic	Magnetic field	1	1	−1	−1
Magnetoelectric	Toroidal moment	1	−1	−1	1

dipole–quadrupole events can exist only for atoms at positions without inversion symmetry.

It is convenient to separate the time-reversible and time-non-reversible terms in the contributions to the atomic tensor factor (1.11.6.3). The dipole–dipole contribution to the resonant atomic factor can be represented as a sum of an isotropic, a symmetric and an antisymmetric part, written as (Blume, 1994)

$$D_{jk} = D_0^{\rm res}\delta_{jk} + D_{jk}^{+} + D_{jk}^{-}, \tag{1.11.6.5}$$

where $D_0^{\rm res} = (1/3)({\rm Tr}D)$,

$$\begin{aligned} D_{jk}^{+} &= \frac{1}{2}(D_{jk} + D_{kj}) - \frac{1}{3}({\rm Tr}D)\delta_{jk} \\ &= \frac{1}{4}\sum_{a,c}\frac{m\omega_{ca}^3}{\hbar\omega}(p'_a + p'_{\bar a})(\langle a|R_j|c\rangle\langle c|R_k|a\rangle + \langle a|R_k|c\rangle\langle c|R_j|a\rangle \end{aligned} \tag{1.11.6.6}$$

and

$$\begin{aligned} D_{jk}^{-} &= \frac{1}{2}(D_{jk}^{-} - D_{kj}^{-}) \\ &= \frac{1}{4}\sum_{a,c}\frac{m\omega_{ca}^3}{\hbar\omega}(p'_a - p'_{\bar a})(\langle a|R_j|c\rangle\langle c|R_k|a\rangle - \langle a|R_k|c\rangle\langle c|R_j|a\rangle, \end{aligned} \tag{1.11.6.7}$$

$p'_a = p_a/[\omega - \omega_{ca} - i\Gamma/(2\hbar)]$ and $p'_{\bar a} = p_{\bar a}/[\omega - \omega_{c\bar a} - i\Gamma/(2\hbar)]$; $p_{\bar a}$ means the probability of the time-reversed state $|\bar a\rangle$. If, for example, $|a\rangle$ has a magnetic quantum number m, then $|\bar a\rangle$ has a magnetic quantum number $-m$.

In non-magnetic crystals, the probability of states with $\pm m$ is the same, so that $p_{\bar a} = p_a$ and $\langle\bar a|R_j^s|\bar c\rangle = \langle c|R_k^s|a\rangle$; in this case D_{jk} is symmetric under permutation of the the indices.

Similarly, the dipole–quadrupole atomic factor can be represented as (Blume, 1994)

$$\begin{aligned} f_{jk}^{dq} &= \frac{i}{2}\sum_{ac} p_a\frac{m\omega_{ca}^3}{\hbar\omega}\times\{\langle a|R_j|c\rangle\langle c|R_kR_l|a\rangle k_l \\ &\quad - \langle a|R_jR_l|c\rangle\langle c|R_k|a\rangle k'_l\} \qquad (1.11.6.8) \\ &= \frac{i}{8}\sum_{ac}\frac{m\omega_{ca}^3}{\hbar\omega}\{I_{jkl}^{++}(k_l - k'_l) + I_{jkl}^{--}(k_l - k'_l) \\ &\quad + I_{jkl}^{-+}(k_l + k'_l) + I_{jkl}^{+-}(k_l + k'_l)\}, \qquad (1.11.6.9) \end{aligned}$$

where

$$\begin{aligned} I_{jkl}^{\mu\nu} &= \sum_{ac}(p'_a + \mu p'_{\bar a})\{\langle a|R_j|c\rangle\langle c|R_kR_l|a\rangle k_l \\ &\quad + \nu\langle a|R_jR_l|c\rangle\langle c|R_k|a\rangle k'_l\} \end{aligned} \tag{1.11.6.10}$$

with $\mu, \nu = \pm 1$. In (1.11.6.10) the first plus ($\mu = 1$) corresponds to the non-magnetic case (time reversal) and the minus ($\mu = -1$) corresponds to the time-non-reversal magnetic term, while the second $\pm$ corresponds to the symmetric and antisymmetric parts of the atomic factor. We see that $I_{jkl}^{--}(k_l - k'_l)$ can contribute only to scattering, while $I_{jkl}^{-+}(k_l + k'_l)$ can contribute to both resonant scattering and resonant X-ray propagation. The latter term is a source of the so-called magnetochiral dichroism, first observed in Cr_2O_3 (Goulon *et al.*, 2002, 2003), and it can be associated with a toroidal moment in a medium possessing magnetoelectric properties. The symmetry properties of magnetoelectic tensors are described well by Sirotin & Shaskolskaya (1982), Nye (1985) and Cracknell (1975). Which magnetoelectric properties can be studied using X-ray scattering are widely discussed by Marri & Carra (2004), Matsubara *et al.* (2005), Arima *et al.* (2005) and Lovesey *et al.* (2007).

It follows from (1.11.6.8) and (1.11.6.10) that $I_{jkl} = I_{jlk}$ and the dipole–quadrupole term can be represented as a sum of the symmetric $I_{jkl}^{+} = I_{kjl}^{+}$ and antisymmetric $I_{jkl}^{-} = -I_{kjl}^{-}$ parts. From the physical point of view, it is useful to separate the dipole–quadrupole term into I_{jkl}^{+} and I_{jkl}^{-}, because only I_{jkl}^{-} works in conventional optics where $\mathbf{k}' = \mathbf{k}$. The dipole–quadrupole terms are due to the hybridization of excited electronic states with different spacial parities, *i.e.* only for atomic sites without an inversion centre.

The pure quadrupole–quadrupole term in the tensor atomic factor is equal to

$$f_{jk}^{qq} = \tfrac{1}{4}Q_{jlkm}k'_lk_m \tag{1.11.6.11}$$

with the fourth-rank tensor Q_{jklm} given by

$$Q_{jlkm} = \sum_{ac} p_a\frac{m\omega_{ca}^3}{\hbar\omega}\frac{\langle a|R_jR_l|c\rangle\langle c|R_kR_m|a\rangle}{\omega - \omega_{ca} - i(\Gamma/2\hbar)}. \tag{1.11.6.12}$$

This fourth-rank tensor Q_{ijkm} has the following symmetries:

$$Q_{jlkm} = Q_{ljkm} = Q_{jlmk}. \tag{1.11.6.13}$$

We can define

$$Q_{jlkm} = Q_{jlkm}^{+} + Q_{jlkm}^{-} \tag{1.11.6.14}$$

with $Q_{jlkm}^{\pm} = \pm Q_{kmjl}$, where

$$\begin{aligned} Q_{jlkm}^{\pm} &= \tfrac{1}{4}\sum_a(p'_a \pm p'_{\bar a})(\langle a|R_jR_l|c\rangle\langle c|R_kR_m|a\rangle \\ &\quad \pm \langle a|R_kR_m|c\rangle\langle c|R_jR_l|a\rangle). \end{aligned} \tag{1.11.6.15}$$

We see that Q_{jlkm}^{-} vanishes in time-reversal invariant systems, which is true for non-magnetic structures.

1.11.6.2. *Tensor atomic factors (non-magnetic case)*

In time-reversal invariant systems, equation (1.11.6.3) can be rewritten as

$$f_{jk}^{\rm res} = D_{jk}^{+} + iI_{jkl}^{+}(k'_l - k_l) + iI_{jkl}^{-}(k'_l + k_l) + Q_{jlkm}^{+}k'_lk_m + \ldots, \tag{1.11.6.16}$$

where D_{jk}^{+} corresponds to the symmetric part of the dipole–dipole contribution, I_{jkl}^{+} and I_{jkl}^{-} mean the symmetric and antisymmetric parts of the third-rank tensor describing the dipole–quadrupole term, and Q_{jlkm}^{+} denotes a symmetric quadrupole–quadrupole contribution. From the physical point of view, it is useful to separate the dipole–quadrupole term into I_{jkl}^{+} and I_{jkl}^{-}, because in conventional optics, where $\mathbf{k}' = \mathbf{k}$, only I_{jkl}^{-} is relevant.

The tensors contributing to the atomic factor in (1.11.6.16), D_{jk}, I_{jkl}^{+}, I_{jkl}^{-}, Q_{jlkm}, are of different ranks and must obey the site symmetry of the atomic position. Generally, the tensors can be different, even for crystallographically equivalent positions, but all tensors of the same rank can be related to one of them, because all are connected through the symmetry operations of the crystal space group. In contrast, the scattering amplitude tensor $f_{jm}^{\rm res}$ does not necessarily comply with the point symmetry of the atomic position, because this symmetry is usually violated considering the arbitrary directions of the radiation wavevectors $\mathbf{k}$ and $\mathbf{k}'$.

Equation (1.11.6.16) is also frequently considered as a phenomenological expression of the tensor atomic factor where