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.

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

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,