Chapter 3
Theoretical Basis of Photon Spectroscopies

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Abstract The theoretical basis of x-ray spectroscopies most commonly used in the investigation of magnetic systems is reviewed. A systematic derivation of the cross sections of the different processes (elastic and inelastic, resonant and non-resonant scattering, absorption spectroscopies and dichroism) is attempted, emphasizing the conceptual common aspects of these techniques and, at the same time, the variety of information that they deliver.

3.1 Introduction

The purpose of this article is to review the basic aspects of photon spectroscopies, with special emphasis on the techniques that find widespread application to magnetic systems. Our aim is to give a pedagogical presentation, by providing a step-by-step guide through the sometimes elaborate calculations of the relevant scattering amplitudes and cross sections.

Crystallographers have used x-ray diffraction for almost one hundred years, as a tool for the determination of crystal structures. A particularly important development of more recent years was the realization that the scattering of polarized x-rays can deliver information not only on the electron

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E. Beaurepaire et al. (eds.), *Magnetism and Synchrotron Radiation: Towards the Fourth Generation Light Sources*, Springer Proceedings in Physics 151,
DOI: 10.1007/978-3-319-03032-6_3,

density distribution, but also on the distribution of magnetic moments. Although the application of magnetic x-ray scattering has only recently become popular, thanks to the development of modern synchrotron light sources, the coupling between photons and magnetic moments is predicted by quantum electrodynamics, and in fact it was described as early as 1954 by Low [1] and Gell-Mann and Goldberger [2] in their derivations of the low-energy limit of the Compton cross section. Later, Platzman and Tzoar [3] pointed out the possibility to use this effect to investigate magnetic structures.

Due to the very small cross section, it was not until 1981, however, that the first magnetic scattering experiment was carried out by de Bergevin and Brunel [4] on NiO, demonstrating the basic features of non-resonant scattering. The truly heroic apects of this first experiment performed with an x-ray tube were later alleviated by the advent of synchrotron sources, and experiments were performed to take advantage of the attractive features of x-ray magnetic scattering, as compared to neutron scattering, i.e. the very high momentum resolution and the possibility of a separate determination of the spin and of the orbital contributions to the magnetic moment by the different polarization dependence.

A further important step forward was the discovery that in the anomalous or resonant region (when the x-ray photon energy is close to an absorption edge of one of the atomic species of the sample), the scattering amplitude often displays a strong dependence on the polarization of the incoming and scattered beams. This is formally translated in the description of the atomic scattering amplitude as a *tensor* (rather than as a *scalar*) quantity, with important consequences for the selection rules for the diffracted beams [5, 6].

The particular significance of the resonant scattering for magnetism studies was realized in 1988, with the discovery by Gibbs et al. [7] of resonant magnetic scattering (also called resonant exchange scattering), i.e. of an enhancement of several orders of magnitude of the magnetic scattering intensity when the photon energy is close to an absorption edge of the material. A very large number of studies in rare earth, actinide and transition metal systems followed. Although the price to pay for the resonant enhancement is the loss of a direct interpretation of the scattering intensity in terms of spin and orbital magnetic structure factors, many experiments followed, and contributed to clarify many issues on the electronic structure of magnetic materials: as we shall see, the selection rules for optical transitions make the resonant process sensitive to electronic states with specific orbital character, and enhance their contribution to the magnetic properties.

This last remark leads naturally to another recent development, the exploitation of the sensitivity of resonant scattering not only to charge and magnetic order, but also to orbital order, because the atomic scattering amplitude can vary substantially depending on the occupation of selected spin or orbital states and therefore on their availability to serve as intermediate states in the second order scattering process.

Modern x-ray sources, providing high brilliance and controlled polarization, allowed two more techniques to acquire paramount importance: on the one hand the use of the polarization dependence of absorption cross sections (circular or linear dichroism); on the other, the resonant enhancement of the scattering amplitude for inelastic scattering, which has a cross section much smaller than the corresponding elastic process. The study of electronic, including magnetic, excitations by resonant inelastic x-ray scattering (RIXS) is becoming an increasingly popular technique, and great progress in energy resolution, on the one hand, and in the interpretation of the resulting spectra, on the other, is taking place.

The structure of the article is the following: in Section 3.2 we recall the formalism necessary to set up the Hamiltonian for the interaction between radiation and matter, and to develop a perturbation description of scattering processes (in the range of radiation intensities where the perturbation approach is justifiable). In Section 3.3 the cross section for the non-resonant case is obtained and discussed, while the resonant elastic case is treated in Section 3.4. Section 3.5 is devoted to absorption spectroscopy, showing how the relevant quantities are related to those for resonant scattering by the "optical theorem" of scattering theory, and how their dependence on polarization in anisotropic and magnetic systems can be derived. Finally, Section 3.6 is devoted to a discussion of resonant inelastic scattering and of some recent applications to the study of electronic and magnetic excitations and properties.

3.2 Interaction of Radiation with Electronic Matter

A microscopic discussion of the electronic properties of matter must necessarily be formulated in the language of quantum mechanics. We also need to consider relativistic effects, if we want to consider magnetic x-ray scattering, because quantities such as the magnetic moment associated to the electron spin appear only in a relativistic theory, and relativistic effects such as the spin-orbit interaction play an essential role in determining the coupling between radiation and magnetic moments, as we shall see.

We therefore expect the reader to be familiar with basic quantum mechanics and its general formalism, including some aspects of advanced topics such as relativistic quantum mechanics and the second quantization formalism.

In discussing the scattering of electromagnetic waves on a material system composed of electrons and nuclei, we shall follow the usual approach and consider the Hamiltonian for the material system, plus the Hamiltonian for the free electromagnetic field, plus an interaction term between the two systems. As it will be clear soon, the scattering from electrons is much more intense than the scattering from nuclei, and we shall therefore consider matter as a system of electrons, interacting with one another and with a set of nuclei in fixed positions, through a potential energy which can be written

$$V(\mathbf{r}_1,...,\mathbf{r}_N) = \sum_{i=1}^{N} V_{nuc}(\mathbf{r}_i) + \sum_{i>j} V_C\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) \tag{3.1}$$

where the first term represents the interaction with the nuclei, and in the second the Coulomb interaction is $V_C(r) = e^2/r$. The system of electrons and nuclei is a many-body system and, in general, not much progress is possible without suitable approximations. Although it is not indispensable for our derivations, a *self-consistent field* approximation, in which the dependence of (3.1) on the positions of all electrons is replaced by a one-electron average

$$V(\mathbf{r}_1,...,\mathbf{r}_N) \simeq \sum_{i=1}^{N} V(\mathbf{r}_i) \tag{3.2}$$

is convenient to simplify the notations and the developments. The potential energy is the key ingredient that allows to write the Hamiltonian for the i-th electron, which, in relativistic quantum mechanics, is the Dirac Hamiltonian [8, 9]

$$H_{el} = \sum_{i=1}^{N} (c\alpha \cdot \mathbf{p_i} + \beta mc^2 + V(\mathbf{r}_i)) \tag{3.3}$$

where α and β are the 4×4 Dirac matrices

$$\alpha_{(x,y,z)} = \begin{pmatrix} 0 & \sigma_{(x,y,z)} \\ \sigma_{(x,y,z)} & 0 \end{pmatrix}$$
$$\beta = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}, \tag{3.4}$$

where $\sigma_(x,y,z)$ denotes the 2×2 Pauli matrices and **1** the 2×2 unit matrix; in addition, $\mathbf{p}_i$ is the momentum of the i-th electron. We now consider that the processes we are interested in (scattering and energy exchanges of x-ray photons with energies at most in the $\sim 10\,\text{keV}$ range), always involve energies much smaller than the electron rest energy, $mc^2 \simeq 511\,\text{keV}$, an energy scale that is indeed bigger than any binding energies of core levels that we want to investigate. This authorizes us to adopt the weakly relativistic limit of (3.3), which is considered and derived in great detail in Section 15 of [9]. To see the basic idea, we separate the four-component Dirac spinor into an upper and a lower two-component spinors Ψ_a and Ψ_b, so that the Dirac equation in the stationary case

$$H_{el}\Psi = \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = E\Psi \tag{3.5}$$

can be written as

$$c(\sigma\cdot\mathbf{p})\Psi_b = (E - mc^2 - V(\mathbf{r}))\Psi_a = (E^{nr} - V(\mathbf{r}))\Psi_a\,, \tag{3.6}$$
$$c(\sigma\cdot\mathbf{p})\Psi_a = (E + mc^2 - V(\mathbf{r}))\Psi_b = (2mc^2 + E^{nr} - V(\mathbf{r}))\Psi_b \tag{3.7}$$

where we defined the non-relativistic energy $E^{nr} = E - mc^2 \ll mc^2$. From this inequality and the structure of the two equations, one can already guess that Ψ_a is much larger than Ψ_b. Upon substituting Ψ_b from the second equation into the first

$$(\sigma\cdot\mathbf{p})\frac{c^2}{2mc^2 + E^{nr} - V(\mathbf{r})}(\sigma\cdot\mathbf{p})\Psi_a = [E^{nr} - V(\mathbf{r})]\Psi_a \tag{3.8}$$

we can expand

$$\frac{c^2}{2mc^2 + E^{nr} - V(\mathbf{r})} \simeq \frac{1}{2m}(1 - \frac{E^{nr} - V(\mathbf{r})}{2mc^2} + \ldots) \tag{3.9}$$

If we retain only the first term in the expansion, we recover the non-relativistic kinetic energy expression; including also the second gives the leading relativistic correction, of order v^2/c^2. In order to obtain the equation for the two-component spinor Ψ_a, we must carefully handle the commutation of the

p operators with the functions of **r**, and obtain, after dropping the a index (for details, see [9, 10])

$$\left[\frac{p^2}{2m} - \frac{p^4}{8m^3c^2} - \frac{e\hbar\mathbf{s}\cdot(\mathbf{E}\times\mathbf{p})}{2m^2c^2} - \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\mathbf{E}\right]\Psi = E^{nr}\Psi\ , \tag{3.10}$$

where the vector $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$, and the spin operator **s** appearing in the third term (representing the spin-orbit interaction) is defined as $\mathbf{s} = (1/2)\sigma$, and the electric field **E** is the gradient of the potential energy V, divided by the (negative) electron charge.The second term in this equation represents the relativistic mass correction, and the last one is the so-called Darwin term, that is different from zero where the electric field has a non-vanishing divergence. Let us now come to the radiation field, that, on the other hand, is described by the electric and magnetic fields $\mathbf{E}, \mathbf{B}$, which obey Maxwell's equations [11], and which can also be described by introducing a scalar and a vector potential, $\Phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r},t)$

$$\begin{aligned} \mathbf{B} &= \nabla\times\mathbf{A} \\ \mathbf{E} &= -\nabla\Phi - (1/c)\frac{\partial\mathbf{A}}{\partial t}\ . \end{aligned} \tag{3.11}$$

For given $\mathbf{E}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$, the definition of the vector and scalar potentials is not unique; when describing the fields of electromagnetic waves in vacuum, we can use this freedom to chose the *gauge* in such a way that the scalar potential vanishes, and the vector potential **A** is divergence free ($\nabla\cdot\mathbf{A} = 0$) [12]. This will turn out to be a convenient choice later. An arbitrary space- and time-dependent vector potential can be expanded in terms of plane waves, which are characterized by a wavevector **k** and by one of the two polarization modes labeled by λ. Let us write this expansion in the following form

$$\begin{aligned} \mathbf{A}(\mathbf{r},t) = \textstyle\sum_{\mathbf{k},\lambda} \left(\frac{hc^2}{\Omega\omega_{\mathbf{k}}}\right)^{1/2} \Big[&\mathbf{e}_\lambda(\mathbf{k})a(\mathbf{k},\lambda)\mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} \\ &+ \mathbf{e}^*_\lambda(\mathbf{k})a^\dagger(\mathbf{k},\lambda)\mathrm{e}^{-\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}\Big]\ . \end{aligned} \tag{3.12}$$

In this equation, Ω is the volume of the quantization box, and does not appear in any physically meaningful quantity in the following, $\omega_{\mathbf{k}}$ is just $c|\mathbf{k}|$, $\mathbf{e}_\lambda$ is the polarization vector associated to the mode λ, i.e. one of two orthogonal unit vectors in the plane normal to **k**. Furthermore, in a classical description of the field, $a(\mathbf{k},\lambda)$ and $a^\dagger(\mathbf{k},\lambda)$ are the amplitude of the corresponding mode of the field and its complex conjugate. However, in the language of the second quantization formalism a and $a^\dagger$ are *operators*, respectively the annihilation and creation operators of a photon with quantum numbers $(\mathbf{k}, \lambda)$. In this formalism the Hamiltonian of the field takes a very simple and appealing form

$$H_{rad} = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}} \left(a^\dagger(\mathbf{k},\lambda) a(\mathbf{k},\lambda) + 1/2 \right) . \tag{3.13}$$

Turning now to the modifications of H_{el} in presence of the electromagnetic field, we follow the usual prescription to write the Hamiltonian for the motion of a charged particle in external electric and magnetic fields, that reproduces the equations of motion in the electric force and in the Lorentz force: we insert the $\mathbf{A}(\mathbf{r}_i)$ in the Dirac Hamiltonian as an additional term to the momentum operator [8, 9]

$$H'_{el} = \sum_{i=1}^{N} \left(c\alpha \cdot [\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i)] + \beta mc^2 + V(\mathbf{r}_i) \right) , \tag{3.14}$$

and follow the previous line of reasoning to obtain the non-relativistic limit of (3.14), which is considered and derived in great detail in Section 15 of [9]. The resulting Hamiltonian, to order $(v/c)^2$ is

$$\begin{aligned} H'_{el} = \sum_{i=1}^{N} \Big[\; & [\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i)]^2/(2m) \\ & -\mathbf{p}_i{}^4/8m^3c^2 \\ & +V(\mathbf{r}_i) - (e\hbar/mc)\mathbf{s}_i \cdot \mathbf{B} \\ & -(e\hbar/2m^2c^2)\mathbf{s}_i \cdot (\mathbf{E} \times [\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i)]) \\ & +(e\hbar^2/8m^2c^2)\nabla \cdot \mathbf{E} \Big] . \end{aligned} \tag{3.15}$$

In this equation, the first term on the r.h.s. is the usual modification of the kinetic energy in presence of a field, the second (the relativistic mass correction) does not involve the field and is therefore not relevant to our discussion; the fourth term is the interaction of the electron spin $\mathbf{s} = (1/2)\sigma$ with the magnetic field of the radiation, $\mathbf{B} = \nabla \times \mathbf{A}$, confirming that the Dirac equation implies that electrons have spin and a magnetic moment associated to it; the fifth is the spin-orbit interaction term, with the usual modification of the momentum in presence of the field; and the last, the Darwin correction, is again independent of the radiation field, because the transversality of electromagnetic waves ($\mathbf{k}\cdot\mathbf{E}=0$) implies $\nabla\cdot\mathbf{E}=0$, so that there is no contribution to this term from the radiation electric field. After removing all the relativistic corrections to H'_{el} which are not affected by the radiation field, we are left with the following Hamiltonian $H=H'_{el}+H_{rad}$ for the system of electrons and the radiation field:

$$\begin{aligned} H = \sum_{i=1}^{N} \Bigg[& \frac{[\mathbf{p}_i-(e/c)\mathbf{A}(\mathbf{r}_i)]^2}{2m} + V(\mathbf{r}_i) - (e\hbar/mc)\mathbf{s}_i\cdot\mathbf{B} \\ & -(e\hbar/2m^2c^2)\mathbf{s}_i\cdot(\mathbf{E}\times[\mathbf{p}_i-(e/c)\mathbf{A}(\mathbf{r}_i)])\Bigg] \\ & + \sum_{\mathbf{k},\lambda}\hbar\omega_{\mathbf{k}}\left(a^\dagger(\mathbf{k},\lambda)a(\mathbf{k},\lambda)+1/2\right) . \end{aligned} \tag{3.16}$$

We are then in a position to separate all the terms mixing electron and photon variables, that constitute the *interaction Hamiltonian*, H_{int}

$$H = H_{el}+H_{rad}+H_{int} \ , \tag{3.17}$$

$$H_{el} = \sum_{i=1}^{N}\left[\frac{\mathbf{p}_i^{\,2}}{2m}+V(\mathbf{r}_i)+(e\hbar/2m^2c^2)\mathbf{s}_i\cdot(\nabla V(\mathbf{r}_i)\times\mathbf{p}_i)\right] , \tag{3.18}$$

$$H_{rad} = \sum_{\mathbf{k},\lambda}\hbar\omega_{\mathbf{k}}\left(a^\dagger(\mathbf{k},\lambda)a(\mathbf{k},\lambda)+1/2\right) , \tag{3.19}$$

$$\begin{aligned} H_{int} &= \sum_{i=1}^{N}\big[(e^2/2mc^2)\mathbf{A}^2(\mathbf{r}_i)-(e/mc)\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i \\ &\quad -(e\hbar/mc)\mathbf{s}_i\cdot(\nabla\times\mathbf{A}(\mathbf{r}_i)) \\ &\quad +(e\hbar/2m^2c^3)\mathbf{s}_i\cdot[(\partial\mathbf{A}(\mathbf{r}_i)/\partial t)\times(\mathbf{p}_i-(e/c)\mathbf{A}(\mathbf{r}_i))]\big] \\ &\equiv H'_1+H'_2+H'_3+H'_4 . \end{aligned} \tag{3.20}$$

The total Hamiltonian, to the required order of relativistic corrections, is thus split into the Hamiltonian for electronic matter, (3.18), for the radiation field, (3.19) and the Hamiltonian describing the interaction between matter and radiation, (3.20). In the next section, scattering processes will be described as transitions between the eigenstates of H_{el} and H_{rad} induced by the perturbation H_{int}. This can be done by regarding the $\mathbf{A}$ field as a classical quantity, or alternatively and more elegantly, by considering it as an operator, according to the expansion (3.12) in terms of annihilation and creation operators. Before proceeding to the implementation of this program, one should briefly explore the range of validity of the perturbation expansion. One way to approach this question is to ask under which conditions the interaction with the radiation fields leaves the structure of electronic energy levels and wavefunctions essentially unchanged. To this aim, we can compare the size of the electric field experienced by an electron inside an atom with the size of the radiation electric field. The magnitude of the atomic field has the order of magnitude of the hydrogen atom field, that is, in atomic units, simply $\sim e/a_B$ where a_B is the Bohr radius. This gives $E_{atom} \sim 5 \cdot 10^9$ V/cm . To compare this with the field of radiation, let us remember that if denote by I the intensity of radiation, i.e. the energy deposited on the unit surface in the unit time, the energy density (energy per unit volume) is I/c and it equals $(1/4\pi)E^2_{rms}$ [11]. So for a typical situation at a modern synchrotron beamline, where, say $10^{11} \times 1$ keV photons per second are delivered in a 1 μm^2 spot, even if we consider the peak intensity during one of $\sim 10^7$ pulses per second, each with a duration of ~ 10 ps, the peak electric field is of order of $\sim 10^5$ V/cm at most. We are therefore several order of magnitudes below the atomic field, the structure of the electronic energy levels is hardly affected and we are in a position to describe the effect of radiation as the occurrence of transitions of the electronic system from one unperturbed eigenstate to another, that we can compute by perturbation methods. However, as it has been the case for the IR and visible region, lasers can deliver a much higher intensity than other sources. Similarly, X-ray Free-Electron Lasers [13, 14, 15] are capable of delivering 10^{11} photons in one 10 fs pulse, with the same 1 μm^2 focus. The corresponding increase by ten orders of magnitude of the energy density leads to peak fields of order 10^{10} V/cm, quite comparable or exceeding atomic fields!

In this case, which we shall however not consider any further, perturbation theory is in trouble, and strong non-linear effects can be anticipated (for evidence of such behavior in absorption experiments, see [16, 17] for the theoretical investigation of possible effects in scattering experiments).

3.3 Cross Section for Non-Resonant Elastic Scattering

In developing the expressions for the scattering cross section, we closely follow the lucid discussion by Blume [18], warning the reader that this important paper unfortunately contains many misprints.

In this Section, our discussion is restricted to *elastic* scattering, i.e. to processes in which the sample (the system of electrons) is in the same state (for simplicity, let us say the ground state) before and after the scattering event. If we consider the scattering of an incoming photon with polarization $\mathbf{e}$ and wavevector $\mathbf{k}$ into an outgoing photon with polarization $\mathbf{e}'$ and wavevector $\mathbf{k}'$ (conservation of energy implies $|\mathbf{k}| = |\mathbf{k}'|$), we can describe the initial and final state of the system (sample plus radiation field) as

$$\begin{aligned} |i\rangle &= |0;\ldots,(\mathbf{e},\mathbf{k}),\ldots\rangle \\ |f\rangle &= |0;\ldots,(\mathbf{e}',\mathbf{k}'),\ldots\rangle \ , \end{aligned} \tag{3.21}$$

with an obvious notation labelling the ground state of the electronic system with $|0\rangle$, and the radiation field state with the quantum numbers of the photons present in that state.

It is then clear that the transition consists in the *annihilation* of one photon $(\mathbf{e},\mathbf{k})$, and in the *creation* of one photon $(\mathbf{e}',\mathbf{k}')$. This means that the operator $\mathbf{A}$, which is linear in the creation and annihilation operators, must operate twice. Therefore the lowest order contributing processes will come from applying second order perturbation theory to H_2' and H_3', which contain one $\mathbf{A}$ operator, and by first order perturbation theory applied to H_1' and H_4', which contain two $\mathbf{A}$ operators. As a matter of fact, H_4' contains two terms, respectively proportional to $\partial\mathbf{A}/\partial t\cdot\mathbf{p}$ and to $\partial\mathbf{A}/\partial t\cdot(e/c)\mathbf{A}$. However, we shall later see that the first one produces a negligible effect, so we will drop it and retain the second term only.

According to Fermi's Golden Rule of time-dependent perturbation theory, the number of transitions per unit time is proportional to

$$\begin{aligned} w = \left(\frac{2\pi}{\hbar}\right) \Bigg| & \langle f|H_1'+H_4'|i\rangle \\ & + \sum_n \frac{\langle f|H_2'+H_3'|n\rangle\langle n|H_2'+H_3'|i\rangle}{E_0-E_n+\hbar\omega_{\mathbf{k}}} \Bigg|^2 \delta(\hbar(\omega_{\mathbf{k}}-\omega_{\mathbf{k}'})) \ . \end{aligned} \tag{3.22}$$

In the second term, the sum over the complete set of eigenstates $|n\rangle$ of the unperturbed Hamiltonian, $H_{el}+H_{rad}$ appears, referred to as the sum over the intermediate states. The calculation of the matrix elements involve both electron and photon operators and is tedious, but straightforward. For example

$$\begin{aligned}\langle f|H_1'|i\rangle &= \left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)\left(\frac{e^2}{mc^2}\right)\\ &\quad \sum_i \langle 0;(\mathbf{e}',\mathbf{k}')|(\mathbf{e}'^*\cdot\mathbf{e})a^\dagger(\mathbf{k}',\mathbf{e}')a(\mathbf{k},\mathbf{e})\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i}|0;(\mathbf{e},\mathbf{k})\rangle\\ &= \left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)\left(\frac{e^2}{mc^2}\right)(\mathbf{e}'^*\cdot\mathbf{e})\sum_i\langle 0|\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i}|0\rangle\,, \end{aligned} \tag{3.23}$$

after taking the photon annihilation and destruction operator matrix elements according to the usual rules. In this matrix element we recognize the *Thomson scattering* amplitude, with the dot product polarization dependence and the structure factor, expressed by the ground state expectation value of $\sum_i \mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i}$. Notice also that the matrix element magnitude per electron is controlled by the quantity $r_0 \equiv e^2/mc^2$ which has the dimensions of length and is the *Thomson radius*, $r_0 = 2.818\cdot 10^{-13}\,\mathrm{cm}$.

We are now in a position to confirm that the scattering from the nuclei is negligible. In fact, to obtain the corresponding matrix element for nuclear scattering, we should simply replace the electronic positions with the atomic ones, and also replace e^2/mc^2, with Z^2e^2/Mc^2 , where Z and M are the nuclear charge and mass. However, M is roughly equal to $2Zm_n$, where m_n is the nucleon mass, and the mass ratio m_n/m is about 1850. Therefore, the scattering matrix element for a nucleus is $\sim Z/(2\times 1850)$ times smaller than that for an electron, and can be neglected because Z never exceeds 92. In addition, one should also note that there are Z times more electrons than nuclei!).

3.3.1 Thomson Scattering and Crystallography

Before proceeding to the evaluation of the matrix elements deriving from the other pieces of the interaction Hamiltonian, we briefly consider the implications of the H_1' matrix elements. As a matter of fact, we shall later show that, as long as the photon energy $\hbar\omega_{\mathbf{k}}$ is not close to any of the absorption edges of the atoms in the system, this is the dominant matrix element for the photon scattering process. Consider for example the radiation from a Mo x-ray tube, which allows to exploit the K_α line, with an energy of 17.4 keV. This is well above all edges of light atoms such as Al, Si, Ca or Ti, which are below 5 keV, and contributions other than H_1' are negligible. In this approximation,(3.22) simplifies to

$$w = \left(\frac{2\pi}{\hbar}\right) \left|\langle f|H_1'|i\rangle\right|^2 \delta\left(\hbar\left(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'}\right)\right) \ . \tag{3.24}$$

We are now ready to replace (3.23) into (3.24). However, this gives a number of transitions per unit time which depends on the normalization volume. We would rather have a physically meaningful quantity, i. e. a *cross section*, defined as: the number of transitions per unit time, into photon states with energy $\hbar\omega_{\mathbf{k}'} < E < \hbar\omega_{\mathbf{k}'} + \mathrm{d}E$, with wavevector $\mathbf{k}'$ in the solid angle $\mathrm{d}O'$, divided by the number of incident photons per unit time and area. That is, in differential form

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}E\mathrm{d}O'}\right) = \frac{w\rho(E)}{c/\Omega} \tag{3.25}$$

where ρ is the density of photon states (with specified polarization), i.e. the number of wavevectors within dO’ satisfying periodic boundary conditions in a box of volume Ω and $\hbar\omega_{\mathbf{k}} \leq \hbar\omega_{\mathbf{k}'} \leq \hbar\omega_{\mathbf{k}} + \mathrm{d}E$, i.e.

$$\rho(E)\mathrm{d}E\mathrm{d}O' = \left(\frac{\Omega}{(2\pi)^3}\right)\left(\frac{E^2}{\hbar^3c^3}\right)\mathrm{d}E\mathrm{d}O' \tag{3.26}$$

Finally, by putting Eqs. (3.22), (3.23), and (3.25) together, and upon multiplying (3.25) by $\mathrm{d}E$ and integrating (remember the Dirac δ in (3.22)) we obtain the important result

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}O'}\right) = r_0^2 \left|\sum_j \langle 0|\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}|0\rangle\right|^2 (\mathbf{e}'^* \cdot \mathbf{e})^2 \tag{3.27}$$

after defining $(\mathbf{k} - \mathbf{k}') \equiv \mathbf{q}$, the *scattering vector*.

With reference to Fig. 3.1, define the *scattering plane* as that identified by $\mathbf{k}, \mathbf{k}'$, and introduce a specific basis for the polarization vectors, $\mathbf{e}_\pi$ *parallel* to the scattering plane, and $\mathbf{e}_\sigma$ *perpendicular* to the scattering plane. Define further the *scattering angle* 2θ (the factor 2 is a mere convention !) as the angle between $\mathbf{k}, \mathbf{k}'$. It is easy to see that the polarization factor $(\mathbf{e}'^* \cdot \mathbf{e})^2$ forbids σ to π transitions and viceversa, and in other cases is worth

$$\begin{aligned} (\mathbf{e}'^* \cdot \mathbf{e})^2 &= \quad 1 \qquad (\sigma \to \sigma) \\ (\mathbf{e}'^* \cdot \mathbf{e})^2 &= \cos^2(2\theta) \ \ (\pi \to \pi') \ . \end{aligned} \tag{3.28}$$

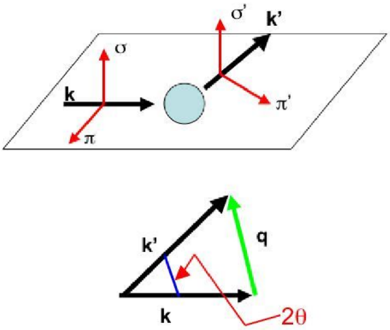


Fig. 3.1 Scattering and polarization geometry

For example, if the photon source is unpolarized, we have to average over the incoming polarizations, and we obtain

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}O'}\right) = \frac{1}{2}r_0^2\left(1+\cos^2(2\theta)\right)|F(\mathbf{q})|^2 \;, \tag{3.29}$$

where we defined

$$F(\mathbf{q}) = \sum_j \langle 0|\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}|0\rangle \;. \tag{3.30}$$

In full generality, let the scattering object be a system with N electrons, with its ground state $|0\rangle$ described by an antisymmetric wavefunction $\Psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)$, from which an electron density is derived as:

$$\rho(\mathbf{r}) = N\int \mathrm{d}\mathbf{r}_2\mathrm{d}\mathbf{r}_3\ldots\mathrm{d}\mathbf{r}_N\,|\Psi(\mathbf{r},\mathbf{r}_2,....,\mathbf{r}_N)|^2 \;. \tag{3.31}$$

It is then easy to see that

$$F(\mathbf{q}) = \int \mathrm{d}\mathbf{r}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\rho(\mathbf{r}) \;, \tag{3.32}$$

so that the scattering cross section with scattering vector **q**, (3.27), is proportional to the absolute square of the Fourier transform of the electron density at momentum **q**. A knowledge of the Fourier transform at all wavevectors is of course equivalent to the knowledge of the electron density. However, much to the crystallographers' sorrow, we see that x-ray scattering only delivers the *absolute value* of the Fourier transform. To reconstruct the electron density one should also know the *phase* of each reflection, which, however, is a much more elusive quantity.

3.3.2 Non-resonant Magnetic Scattering

We now resume the systematic exploration of (3.22), and, after dealing with the matrix elements of H'_1, we consider the remaining terms, which contribute exclusively to *magnetic* scattering.

The next task is the evaluation of $\langle f|H'_4|i\rangle$. Remember that H'_4 contains two terms, respectively proportional to $\partial\mathbf{A}/\partial t\cdot\mathbf{p}$ and to $\partial\mathbf{A}/\partial t\cdot(e/c)\mathbf{A}$. However, we shall soon verify that the second order perturbation on the first term produces a contribution to the cross section which is a factor $(\hbar\omega/mc^2)^2$ smaller than the first order contribution of the second, so we will drop it and retain the second term only. We must first of all determine an expression for the operator $\partial\mathbf{A}/\partial t$ from (3.12). For one mode only, i.e. omitting for simplicity the sum over all $\mathbf{k},\lambda$,

$$\partial\mathbf{A}/\partial t=\left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)^{1/2}\Big[-\mathrm{i}\quad\omega_{\mathbf{k}}\mathbf{e}_\lambda(\mathbf{k})a(\mathbf{k},\lambda)\mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}$$
$$+\mathrm{i}\quad\omega_{\mathbf{k}}\mathbf{e}^*_\lambda(\mathbf{k})a^\dagger(\mathbf{k},\lambda)\mathrm{e}^{-\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}\Big]\ . \qquad (3.33)$$

Inserting this expression, the H'_4 matrix element is readily evaluated:

$$\langle f|H'_4|i\rangle=-\mathrm{i}\left(\frac{e^2}{mc^2}\right)\left(\frac{\hbar\omega_{\mathbf{k}}}{mc^2}\right)\left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)$$
$$\sum_j\langle 0|\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j}\mathbf{s}_j\cdot(\mathbf{e}'^*(\mathbf{k}')\times\mathbf{e}(\mathbf{k}))|0\rangle\ . \qquad (3.34)$$

One therefore sees immediately that a term containing the spin operators, i.e. a genuine *magnetic* scattering term appears, and that its magnitude compared to the Thompson term is reduced by the factor $(\hbar\omega_{\mathbf{k}}/mc^2)$. This is a small number, because typically in the x-ray region $\hbar\omega_{\mathbf{k}} \sim 10\,\mathrm{keV}$, while $mc^2 = 511\,\mathrm{keV}$. Additional magnetic information is hidden in the second term in (3.22), which we now proceed to evaluate. The accessible intermediate states have either no photons, or two photons, and their energy is

$$|n\rangle = |\Psi_n\,;0,0\rangle; E_n = E(\Psi_n) \tag{3.35}$$

$$|n\rangle = |\Psi_n\,;(\mathbf{e},\mathbf{k}),(\mathbf{e}',\mathbf{k}')\rangle; E_n = E(\Psi_n) + 2\hbar\omega_{\mathbf{k}}\,. \tag{3.36}$$

The first set of terms (let us call them terms (a)) is reached by the action of the annihilation part of the **A** operator on the initial state; the second (terms (b)) by the action of the creation operator part. There is also an additional, important difference between the two kinds of terms: in case (a) the energy denominator can vanish, and give rise to a resonance, when $E_0 - E_n + \hbar\omega_{\mathbf{k}} = 0$; in case (b) it cannot, because $E_0 - E(\Psi n) - \hbar\omega_{\mathbf{k}} < 0$ always. To prevent an unphysical divergence of the scattering cross section, we must take into account that the intermediate states $|n\rangle$ are not really stationary, but have a finite lifetime, which is represented by adding a small imaginary part to the eigenvalue, which becomes important only near the resonance condition; i.e. $E(\Psi_n)$ is replaced by $E(\Psi_n) - \mathrm{i}\Gamma_n/2$. We want to examine the non-resonant case first, i.e. the case in which $\hbar\omega_{\mathbf{k}} \gg E(\Psi_n) - E_0$ for all states, or, more precisely, for all states $|n\rangle$ which give an appreciable contribution to the sum in (3.22). Using the following simple identities for the energy denominators:

$$\begin{aligned}\frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2} &= \frac{1}{\hbar\omega_{\mathbf{k}}} \\ &\quad + \frac{E(\Psi_n) - E_0 - \mathrm{i}\Gamma_n/2}{\hbar\omega_{\mathbf{k}}} \frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2} \\ \frac{1}{E_0 - E(\Psi_n) - \hbar\omega_{\mathbf{k}}} &= -\frac{1}{\hbar\omega_{\mathbf{k}}} + \frac{E_0 - E(\Psi_n)}{\hbar\omega_{\mathbf{k}}} \frac{1}{E_0 - E(\Psi_n) - \hbar\omega_{\mathbf{k}}}\,,\end{aligned} \tag{3.37}$$

it is easy to see that in this case the denominators are well approximated by $\pm\hbar\omega_{\mathbf{k}}$. As a matter of fact, as discussed in a recent work [19], the same conclusions hold even in the case in which $\hbar\omega_{\mathbf{k}}$ is much bigger than $E(\Psi_n) - E_0$ for some n, and much smaller for others, i.e. as long as it is far away from possible resonances. Substituting (3.12) into $H_2' + H_3'$, and paying due attention to the action of photon creation and annihilation operators on the two kinds of intermediate states, we find for type (a) intermediate states

$$\begin{aligned}\langle f|H_2'+H_3'|n\rangle\;\;\langle n|H_2'+H_3'|i\rangle = &\\ \left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)\left(\frac{e}{mc}\right)^2 &\langle 0|\sum_{j=1}^{N}\left[\mathbf{e}'^{*}\cdot\mathbf{p}_j-\mathrm{i}\hbar(\mathbf{k}'\times\mathbf{e}'^{*})\cdot\mathbf{s}_j\right]\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}_j}|n\rangle\\ &\langle n|\sum_{j'=1}^{N}\left[\mathbf{e}\cdot\mathbf{p}_{j'}+\mathrm{i}\hbar(\mathbf{k}\times\mathbf{e})\cdot\mathbf{s}_{j'}\right]\mathrm{e}^{\mathbf{ik}\cdot\mathbf{r}_{j'}}|0\rangle \qquad (3.38)\end{aligned}$$

while for type (b) intermediate states we obtain an expression differing only in that the operators acting between $\langle 0|$ and $|n\rangle$ and between $\langle n|$ and $|0\rangle$ are interchanged. This, together with the fact that the energy denominators, in the non-resonant approximation defined above, are independent of $|n\rangle$ and change sign for the two types of intermediate states, and with the *closure* relationship

$$\sum_n |n\rangle\langle n| = \mathbf{1} \qquad (3.39)$$

where **1** denotes the unit operator, allows to write the second term in (3.22) as the expectation value of a commutator

$$\sum_n \frac{\langle f|H_2'+H_3'|n\rangle\langle n|H_2'+H_3'|i\rangle}{E_0-E_n+\hbar\omega_{\mathbf{k}}} \simeq \left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)\left(\frac{e}{mc}\right)^2\langle 0|\left[C',C\right]|0\rangle\,, \qquad (3.40)$$

where

$$C' = \left[\mathbf{e}'^{*}_{\lambda'}\cdot\mathbf{p}_j-\mathrm{i}\hbar(\mathbf{k}'\times\mathbf{e}'^{*}_{\lambda'})\cdot\mathbf{s}_j\right]\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}_j} \qquad (3.41)$$

$$C = \left[\mathbf{e}_{\lambda}\cdot\mathbf{p}_j+\mathrm{i}\hbar(\mathbf{k}\times\mathbf{e}_{\lambda})\cdot\mathbf{s}_j\right]\mathrm{e}^{\mathbf{ik}\cdot\mathbf{r}_j}\,. \qquad (3.42)$$

To calculate the commutator is a tedious operation, but is easily performed remembering the basic commutation rules for components of positions, momenta, spin and arbitrary functions of them, referred to the same electron

$$\begin{aligned}\left[r_\alpha,p_\beta\right] &= i\hbar\delta_{\alpha\beta}\\ \left[p_\alpha,f(\mathbf{r})\right] &= -i\hbar\partial f/\partial r_\alpha\\ \left[s_\alpha,s_\beta\right] &= i\hbar\varepsilon_{\alpha\beta\gamma}s_\gamma\,. \qquad (3.43)\end{aligned}$$

Here the antisymmetric tensor $\varepsilon_{\alpha\beta\gamma}$ was introduced, and it is worthwhile to remember the expression of the cross product of two vectors in terms of it (summation over repeated indices is implied)

$$(\mathbf{v}_1 \times \mathbf{v}_2)_\alpha = \varepsilon_{\alpha\beta\gamma} \mathrm{v}_{1\beta} \mathrm{v}_{2\gamma} \,. \tag{3.44}$$

By a careful use of these rules, of the transversality conditions, $\mathbf{e} \cdot \mathbf{k} = 0$ and of a simple vector identity

$$(\mathbf{A} \times \mathbf{B}) \cdot (\mathbf{C} \times \mathbf{D}) \equiv (\mathbf{A} \cdot \mathbf{C})(\mathbf{B} \cdot \mathbf{D}) - (\mathbf{A} \cdot \mathbf{D})(\mathbf{B} \cdot \mathbf{C}) \tag{3.45}$$

which is applied to the four vectors: $(\mathbf{k} - \mathbf{k}') \equiv \mathbf{q}$, $\mathbf{p}_j$, $\mathbf{e}'^*$, $\mathbf{e}$, the patient reader should obtain

$$\begin{aligned}
\sum_n \frac{\langle f|H_2' + H_3'|n\rangle\langle n|H_2' + H_3'|i\rangle}{E_0 - E_n + \hbar\omega_\mathbf{k}} &= -\mathrm{i}\left(\frac{hc^2}{\Omega\,\omega_\mathbf{k}}\right)\left(\frac{e^2}{mc^2}\right)\frac{\hbar\omega_\mathbf{k}}{mc^2} \\
&\quad \Bigg[\langle 0|\sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\frac{\mathrm{i}\mathbf{q}\times\mathbf{p}_j}{\hbar k^2}|0\rangle(\mathbf{e}'^*\times\mathbf{e}) + \langle 0|\sum_j \frac{\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\mathbf{s}_j}{k^2}|0\rangle \\
&\quad \big[(\mathbf{k}'\times\mathbf{e}'^*)(\mathbf{k}'\cdot\mathbf{e}) - (\mathbf{k}\times\mathbf{e})(\mathbf{k}\cdot\mathbf{e}'^*) - (\mathbf{k}'\times\mathbf{e}'^*)\times(\mathbf{k}\times\mathbf{e})\big]\Bigg] \,.
\end{aligned} \tag{3.46}$$

Now that we have the second order contribution of the $\mathbf{A} \cdot \mathbf{p}$ term in H_2', we can substantiate our claim that the contribution of the $\partial\mathbf{A}/\partial t \times \mathbf{p}$ term of H_4' is negligible. In fact, the magnitude of the latter contribution would be similar to that of the former, which we just evaluated, except for some different prefactors. On the one hand, the time derivative introduces a factor $\omega_\mathbf{k}$, on the other, the constant in front of H_4' introduces, with respect to H_2', another factor of $\hbar/2mc^2$, so that all in all an extra factor $\hbar\omega_\mathbf{k}/2mc^2$ is obtained. This shows that the matrix element of the first part of H_4' is reduced by $(\hbar\omega_\mathbf{k}/2mc^2)^2$ with respect to the Thomson term, and therefore is negligible with respect to the other magnetic scattering terms, which are reduced by $\hbar\omega_\mathbf{k}/2mc^2$.

Finally, by putting Eqs. (3.22), (3.23), (3.34), (3.46), and (3.25) together, we can complete the cross section expression of (3.27) to obtain

$$\frac{\mathrm{d}\sigma}{\mathrm{d}O'} = r_0^2 \left| \sum_j \langle 0|\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}|0\rangle(\mathbf{e}'^* \cdot \mathbf{e}) \right.$$
$$\left. -\mathrm{i}\frac{\hbar\omega_{\mathbf{k}}}{mc^2}\left[\langle 0|\sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\frac{\mathrm{i}\mathbf{q}\times\mathbf{p}_j}{\hbar k^2}|0\rangle\cdot\mathbf{P}_L + \langle 0|\sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\mathbf{s}_j|0\rangle\cdot\mathbf{P}_S\right]\right|^2 , \tag{3.47}$$

where we introduced the polarization factors

$$\mathbf{P}_L = (\mathbf{e}'^* \times \mathbf{e}) \tag{3.48}$$
$$\mathbf{P}_S = (\mathbf{e}'^* \times \mathbf{e}) + [(\hat{\mathbf{k}}' \times \mathbf{e}'^*)(\hat{\mathbf{k}}' \cdot \mathbf{e}) - (\hat{\mathbf{k}} \times \mathbf{e})(\hat{\mathbf{k}} \cdot \mathbf{e}'^*) - (\hat{\mathbf{k}}' \times \mathbf{e}'^*) \times (\hat{\mathbf{k}} \times \mathbf{e})] . \tag{3.49}$$

In this equation, $\hat{\mathbf{k}}$ denotes the unit vector parallel to $\mathbf{k}$, and the indices L and S where adopted for the two factors because the second one is attached to the term related to the spin moment, while the first pertains to a term which, as we shall show, is related to the *orbital* moment. In fact, after noting that $|\mathbf{q}| = 2|\mathbf{k}|\sin\theta$, where 2θ is the scattering angle, the relevant quantity can be transformed as follows

$$\begin{aligned}
\sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\frac{\mathrm{i}\mathbf{q}\times\mathbf{p}_j}{\hbar k^2} &= \frac{\mathrm{i}}{\hbar q}\,(4\sin^2\theta)\sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\hat{\mathbf{q}}\times\mathbf{p}_j \\
&= \frac{\mathrm{i}}{\hbar q}\,(4\sin^2\theta)\hat{\mathbf{q}}\times\int \mathrm{d}\mathbf{r}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\frac{1}{2}\sum_j[\mathbf{p}_j\delta(\mathbf{r}-\mathbf{r}_j)+\delta(\mathbf{r}-\mathbf{r}_j)\mathbf{p}_j] \\
&= \frac{-\mathrm{i}m}{e\hbar q}\,(4\sin^2\theta)\hat{\mathbf{q}}\times\int \mathrm{d}\mathbf{r}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\mathbf{j}(\mathbf{r}) \\
&= \frac{-\mathrm{i}m}{e\hbar q}(4\sin^2\theta)\hat{\mathbf{q}}\times\mathbf{j}(\mathbf{q})
\end{aligned} \tag{3.50}$$

where the electrical current density operator $\mathbf{j}(\mathbf{r}) = (-e/2m)\sum_j[\mathbf{p}_j\delta(\mathbf{r}-\mathbf{r}_j) + \delta(\mathbf{r}-\mathbf{r}_j)\mathbf{p}_j]$ has been expressed in terms of the momentum and the density of electrons multiplied in symmetrized form, because they do not commute.

This current density describes the *microscopic* currents associated to the motion of the electrons, not the *macroscopic* ones, which we can assume to vanish in our system in the absence of external perturbations (remember that all matrix elements in a perturbation calculation refer to the unperturbed system eigenstates). The vanishing of macroscopic currents means that the flux across any surface S internal to the sample vanishes, i.e.

$$\int_S \mathbf{j}(\mathbf{r}) \cdot \mathbf{n}_S \mathrm{d}S = 0\,, \tag{3.51}$$

which implies that the microscopic current is divergence-free, i.e. $\nabla \cdot \mathbf{j}(\mathbf{r}) = 0$, and can therefore be expressed as the curl of a vector field. We write this field so that

$$\mathbf{j}(\mathbf{r}) = c[\nabla \times \mathbf{M}_L(\mathbf{r})]. \tag{3.52}$$

For the purposes of our discussion, we identify $\mathbf{M}_L(\mathbf{r})$ with the density of orbital magnetization. Although a formal identification between operators is analytically involved [20, 21], one can satisfy himself of the plausibility of (3.52) by the classical description of magnetic fields in matter; Maxwell's equations for the fields $\mathbf{H}$ and $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$ (no spin magnetization exists in the classical description, so here $\mathbf{M}$ means $\mathbf{M}_L$) prescribe that the microscopic currents are related to the curl of $\mathbf{M}$ by (3.52) (see for example [22]).

Equation (3.52) implies that $\mathbf{j}(\mathbf{q}) = -\mathrm{i}c\mathbf{q} \times \mathbf{M}_L(\mathbf{q})$. Therefore

$$\sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j} \frac{\mathrm{i}\mathbf{q} \times \mathbf{p}_j}{\hbar k^2} = \frac{mc}{e\hbar q^2} \mathbf{q} \times [\mathbf{M}_L(\mathbf{q}) \times \mathbf{q}]\,. \tag{3.53}$$

We are now ready to collect all the bits and pieces in a formula for the differential cross section

$$\begin{aligned}\frac{\mathrm{d}\sigma}{\mathrm{d}O'} = r_0^2 \Bigg| &\sum_j \langle 0|\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}|0\rangle (\mathbf{e}'^* \cdot \mathbf{e}) \\ &-\mathrm{i}\frac{\hbar\omega_{\mathbf{k}}}{mc^2}\left[\frac{mc}{e\hbar}\langle 0|\hat{\mathbf{q}} \times [\mathbf{M}_L(\mathbf{q}) \times \hat{\mathbf{q}}]|0\rangle \cdot \mathbf{P}_L + \frac{mc}{e\hbar}\langle 0|\mathbf{M}_S(\mathbf{q})|0\rangle \cdot \mathbf{P}_S\right]\Bigg|^2\,.\end{aligned} \tag{3.54}$$

where the polarization factor $\mathbf{P}_L$ was redefined to include the angular factor

$$\mathbf{P}_L = (\mathbf{e}'^* \times \mathbf{e}) 4 \sin^2\theta\,, \tag{3.55}$$

and the Fourier transform of the *spin* magnetization density was introduced

$$\mathbf{M}_S(\mathbf{q}) = \frac{e\hbar}{mc} \sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j} \mathbf{s}_j\,. \tag{3.56}$$

We are now ready to obtain from (3.54) the basic properties of non-resonant magnetic scattering. In a system with an ordered magnetic structure, e.g. an antiferromagnet, the densities of (orbital and spin) magnetization are periodic functions, with Fourier transforms which are non vanishing only for selected $\mathbf{q}$ values corresponding to this periodicity. Some of these vectors may possibly concide with reciprocal lattice vectors of the crystallographic structure, others will correspond to new reflections (*magnetic* reflections) with nonvanishing intensity below the Néel temperature, below which the antiferromagnetic order sets in.

As already noticed, the prefactor $\hbar\omega_{\mathbf{k}}/mc^2$ reduces the intensity of the magnetic terms considerably with respect to the Thompson one. To reinforce this, while all core and valence electrons contribute to Thomson scattering, only electrons in partially filled shells can contribute to magnetic scattering as the orbital and spin moments of filled shells add up to zero. Therefore, apart from the first pioneering experiments [4], the high intensity of synchrotron light sources is necessary for these experiments.

It is important to notice that $\mathbf{P}_L$ contains the factor $4\sin^2\theta$, and since $|\mathbf{q}| = 2|\mathbf{k}|\sin\theta$, for a given reflection, i.e. for a given $\mathbf{q}$, $\sin\theta$ is proportional to $1/\hbar\omega_{\mathbf{k}}$. Thus, the weight of the orbital part decreases at high photon energies, where spin scattering dominates the magnetic cross section; more generally, the $\omega_{\mathbf{k}}$ dependence of the orbital term is not only in the prefactor.

The different polarization factors $\mathbf{P}_L$, $\mathbf{P}_S$ and the well known polarization properties of synchrotron radiation allow to separate the spin and the orbital contributions to the magnetic moments by changing the experimental geometry. This is a much more direct approach to the separation of the two contributions than it is possible with neutron scattering. This method was applied to rare earth systems such as Ho [7], to actinide systems such as UAs [23, 24] and more recently to 3d antiferromagnets such as NiO [25]. Together with the higher momentum resolution allowed by well collimated synchrotron beams, this orbit and spin separation justifies the interest of x-ray scattering for some cases, in spite of the more widespread use of neutron scattering to determine magnetic structures.

A further important point to mention about the magnetic terms in (3.54) is the imaginary prefactor $-i\hbar\omega_{\mathbf{k}}/mc^2$. This means that, upon taking the square modulus, no interference of Thomson and magnetic scattering terms occurs, unless the structure factors

$$\sum_j \langle 0|e^{i\mathbf{q}\cdot\mathbf{r}_j}|0\rangle \tag{3.57}$$

are complex (which means that the crystallographic structure is non-centrosymmetric), or that the polarization vectors are complex (corresponding to non-linear, i.e. elliptic or circular polarization). In such cases one has interference terms, and these can be useful, for example, in detecting magnetic scattering in ferromagnets [26, 27]. Very recently a further application to the multiferroic system $\mathrm{TbMnO_3}$ [19] used charge-magnetic interference scattering to detect small ionic displacements that contribute to the electrical polarization.

3.4 Resonant Scattering

We now abandon the assumption of the non-resonant limit and consider the case in which $E(\Psi_n) - E_0 \simeq \hbar\omega_{\mathbf{k}}$, at least for one excited state Ψ_n (normally, in a solid there will be a continuum of states satisfying this condition). Returning to the expressions of the matrix elements of $H_2' + H_3'$ as written in (3.38), we want first of all to prove that the contribution of H_2' is always much larger than that of H_3'. To establish this, we begin by remarking that the most important excited states which are resonant with x-ray photons are those in which a core electron in one of the atoms is promoted to an empty one-electron state above the highest occupied orbital. Arguing within an approximate scheme in which the states $|0\rangle$, $|n\rangle$ are reasonably well described by an antisymmetric product of one-electron states, then the matrix elements of the operators H_2' or H_3', which are sums of one-electron operators, can be written [28] in terms of an overlap integral over $N-1$ of the coordinates, multiplied by a one-electron matrix element, i.e

$$\begin{aligned}\langle n|H_2'+H_3'|i\rangle &= \left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)^{1/2}\left(\frac{e}{mc}\right)\sum_{j=1}^{N}\langle n|\left[\mathbf{e}\cdot\mathbf{p}_j + \mathrm{i}\hbar(\mathbf{k}\times\mathbf{e})\cdot\mathbf{s}_j\right]\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_j}|0\rangle \\ &= \left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)^{1/2}\left(\frac{e}{mc}\right)\prod_{j=1}^{N-1}\int \mathrm{d}\mathbf{r}_j\,\psi_{vj}^{(n)*}(\mathbf{r}_j)\,\psi_{vj}^{(0)}(\mathbf{r}_j) \\ &\quad\times\int \mathrm{d}\mathbf{r}_N\,\psi_{vN}^{(n)*}(\mathbf{r}_N)\left[\mathbf{e}\cdot\mathbf{p}_N + \mathrm{i}\hbar(\mathbf{k}\times\mathbf{e})\cdot\mathbf{s}_N\right]\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_N}\,\psi_c^{(0)}(\mathbf{r}_N)\,,\end{aligned} \tag{3.58}$$

where ψ_v is a one-electron valence wavefunction, either for the ground or the n-th excited states and ψ_c a core wavefunction which is exponentially decreasing, outside an appropriate core radius r_c. We can then argue that the main contribution to the integral comes from this inner region; and one can see that inside this region $\mathbf{k}\cdot\mathbf{r}_j \ll 1$, for the values of $k = |\mathbf{k}|$ of interest here. This is because at the resonance condition

$$k = \omega/c = E/\hbar c\ , \tag{3.59}$$

where E is the difference of the core and valence energy, i.e. the core ionization energy. This energy is related to the radius of the core orbital by the approximate hydrogen-like relationship

$$E \simeq \hbar^2/2mr_c^2 \tag{3.60}$$

whence one finds $r_c \simeq \hbar/\sqrt{2mE}$ and therefore

$$kr_c \simeq \sqrt{E/2mc^2}\ . \tag{3.61}$$

The right hand side is always small for all core levels, because $2mc^2$ is about 1 MeV, while the deepest core level (1s in Uranium) has a binding energy of about 116 keV. So, in this most extreme case, $kr_c \simeq 0.34$, and is less for all other core levels. It is therefore legitimate, for $r \leq r_c$, to expand

$$\mathrm{e}^{\mathbf{ik}\cdot\mathbf{r}_j} \sim 1 + \mathbf{i}\mathbf{k}\cdot\mathbf{r}_j - (\mathbf{k}\cdot\mathbf{r}_j)^2/2 + \ldots \tag{3.62}$$

and to observe that the terms of the series are rapidly decreasing with increasing order (which is referred to as the multipole order). We can then reach the proof of the statement that H_2' matrix elements dominate over those of H_3', i.e. that the first term in the last integral of (3.58) dominates over the second. The point is that for given $\psi_{vN}^{(n)}, \psi_c^{(0)}$, the lowest nonvanishing order in the series (3.62) for the integral of $\mathbf{p}_N$ is lower by one than the lowest nonvanishing order for the second term (which contains the spin, but no $\mathbf{r}_N$ operator). Remember indeed that the selection rules for atomic transitions are the same for $\mathbf{p}$ or for $\mathbf{r}$ matrix elements (a manifestation of the Wigner-Eckart theorem [29]), and since the H_3'-related operator contains the spin but neither $\mathbf{p}$ nor $\mathbf{r}$'s, it is necessary to have one more $\mathbf{r}$ (with respect to the first term) in order to have a nonvanishing integral, i.e. to go to the next order in $\mathbf{k}\cdot\mathbf{r}_N$.Therefore, near the resonance condition, the resonant terms dominate the cross section, and, among these, only the H_2' matrix elements need to be retained. Equation (3.22) becomes

$$\begin{aligned} w &= \frac{2\pi}{\hbar}\left|\sum_n \frac{\langle f|H_2'|n\rangle\langle n|H_2'|i\rangle}{E_0 - E_n + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2}\right|^2 \delta(\hbar(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'})) \\ &= \frac{2\pi}{\hbar}\left|\left(\frac{hc^2}{\Omega\,\omega_{\mathbf{k}}}\right)\left(\frac{e}{mc}\right)^2 \sum_n \frac{\langle 0|\sum_{j=1}^N \mathbf{e}'^* \cdot \mathbf{p}_j \mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}_j}|n\rangle\langle n|\sum_{j'=1}^N \mathbf{e}\cdot\mathbf{p}_{j'}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_{j'}}|0\rangle}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2}\right|^2 \\ &\quad \times \delta(\hbar(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'})) \,. \end{aligned} \tag{3.63}$$

As a matter of fact, the above equation contains a contribution that was already taken into account in the non-resonant part; remember (3.37), where the first piece on the r.h.s. was included in the previous Section. Therefore, only the second addendum needs to be considered here and that means that in (3.63) we must replace

$$\frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2} \tag{3.64}$$

with:

$$\frac{E(\Psi_n) - E_0 - \mathrm{i}\Gamma_n/2}{\hbar\omega_{\mathbf{k}}}\,\frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2}\,. \tag{3.65}$$

3.4.1 Electric Dipole Approximation

Let us then look in detail into the relevant matrix elements. Consider

$$\langle n|\mathbf{e}\cdot\mathbf{p}_j\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_j}|0\rangle \simeq \langle n|\mathbf{e}\cdot\mathbf{p}_j(1 + \mathrm{i}\mathbf{k}\cdot\mathbf{r}_j + \ldots)|0\rangle \tag{3.66}$$

and, for a given $|n\rangle$, consider only the lowest order term for which the matrix element does not vanish. We established already that all higher order terms are negligible in comparison to it. The largest contributions come from those $|n\rangle$'s for which the first term provides a nonvanishing contribution, so that the exponential is simply replaced by 1. These states are said to be accessible by *electric dipole* transitions. In a full quantum electrodynamical formulation, one can see that electric dipole transitions are induced by photons with a total angular momentum of 1. The name “electric dipole” comes from the fact that in a non-relativistic theory, neglecting the spin-orbit interaction altogether, so that $H_{el} = \sum_j (\mathbf{p}_j^2/2m + V(\mathbf{r}_j))$, one can write

$$\begin{aligned} \langle n|\mathbf{e}\cdot\mathbf{p}_j|0\rangle &= m\langle n|\mathbf{e}\cdot\dot{\mathbf{r}}_j|0\rangle \\ &= \frac{-\mathrm{i}m}{\hbar}\langle n|\mathbf{e}\cdot[\mathbf{r}_j, H_{el}]|0\rangle \\ &= \frac{\mathrm{i}m}{\hbar}[E(\Psi_n) - E(0)]\langle n|\mathbf{e}\cdot\mathbf{r}_j|0\rangle \ . \end{aligned} \tag{3.67}$$

In view of this, and neglecting $\mathrm{i}\Gamma_n/2$ in the numerator of (3.65), the sum over intermediate states in (3.63) becomes

$$\frac{m^2}{\hbar^2}\sum_n \frac{(E(\Psi_n) - E(0))^3}{\hbar\omega_{\mathbf{k}}} \frac{\langle 0|\mathbf{e}'^*\cdot\mathbf{R}|n\rangle\langle n|\mathbf{e}\cdot\mathbf{R}|0\rangle}{E(\Psi_n) - E(0) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2} \ , \tag{3.68}$$

where we defined

$$\mathbf{R} = \sum_j \mathbf{r}_j \ . \tag{3.69}$$

In order to make progress and to make contact with the literature [30], we express all vectors in terms of their *spherical* components, i.e. we define

$$R_0 = \mathrm{i}R_z, R_{\pm 1} = (\mp\mathrm{i}/\sqrt{2})(R_x \pm \mathrm{i}R_y) \ . \tag{3.70}$$

The definitions of the $0, \pm 1$ components apply to any vector, e.g. to the polarization **e** as well, and they are clearly inspired from the definition of the spherical harmonics for $l = 1$,

$$Y_{1,0} = \mathrm{i}\sqrt{\frac{3}{4\pi}}(z/r), Y_{1,\pm 1} = \mp\mathrm{i}\sqrt{\frac{3}{8\pi}}(\frac{x \pm \mathrm{i}y}{r}) \ , \tag{3.71}$$

where we adopted the convention for the phases given in [41]. It is easily verified that the scalar product becomes

$$\mathbf{e}\cdot\mathbf{R} = \sum_{m=-1}^{1} (-1)^{m-1} e_m R_{-m} \ . \tag{3.72}$$

It is then easy to see that

$$\langle 0|\mathbf{e}'^{*}\cdot\mathbf{R}|n\rangle\langle n|\mathbf{e}\cdot\mathbf{R}|0\rangle = \sum_{m,m'}(-1)^{m+m'}e'^{*}_{m}e_{m'}\langle 0|R_{-m}|n\rangle\langle n|R_{-m'}|0\rangle\ . \quad (3.73)$$

To simplify this expresssion further, one must take advantage of the symmetry of the physical system. The simplest case corresponds of course to the highest symmetry, i.e. the spherical symmetry of isolated atoms. Then, the eigenstates $|0\rangle$ and $|n\rangle$ are eigenstates of the angular momentum and of its z-component, and this implies that the sum is restricted to $m=-m'$, because the angular momentum selection rules say that, for the matrix elements

$$\begin{aligned}\langle 0|R_{-m}|n\rangle \neq 0 &\Rightarrow -m_0-m+m_n=0\ ,\\ \langle n|R_{-m'}|0\rangle \neq 0 &\Rightarrow -m_n-m'+m_0=0\ ,\\ &\Rightarrow m=-m'\end{aligned} \quad (3.74)$$

The sum in (3.73) is then simplified and it is worth noticing that

$$\begin{aligned}\langle 0|R_0|n\rangle\langle n|R_0|0\rangle &= -|\langle n|R_0|0\rangle|^2\\ \langle 0|R_{-1}|n\rangle\langle n|R_1|0\rangle &= |\langle n|R_1|0\rangle|^2\\ \langle 0|R_1|n\rangle\langle n|R_{-1}|0\rangle &= |\langle n|R_{-1}|0\rangle|^2\ .\end{aligned} \quad (3.75)$$

The first relationship may look surprising, but remember that, because of the factor i in the definition, coming from the chosen convention on the phases of the spherical harmonics, R_0 is an antihermitian operator. Another consequence of that is the fact that if

$$e_0 = \mathrm{i}e_z \quad (3.76)$$

it is also

$$e_0^{*} = \mathrm{i}e_z^{*}\ , \quad (3.77)$$

i.e. the spherical component 0 of the complex conjugate need not be the complex conjugate of the 0 component. With the help of all of the above we can write

$$\begin{aligned}\langle 0|\mathbf{e}'^{*}\cdot\mathbf{R}|n\rangle\langle n|\mathbf{e}\cdot\mathbf{R}|0\rangle = -e'^{*}_0e_0|\langle n|R_0|0\rangle|^2 + e'^{*}_1e_{-1}|\langle n|R_1|0\rangle|^2\\ +e'^{*}_{-1}e_1|\langle n|R_{-1}|0\rangle|^2\ .\end{aligned} \quad (3.78)$$

Going back to cartesian coordinates for the polarization vectors, it is possible, with a bit of algebra to recast this expression in the following form

$$e_z'^* e_z |\langle n|R_0|0\rangle|^2 + \frac{1}{2}[e_x'^* e_x + e_y'^* e_y](|\langle n|R_1|0\rangle|^2 + |\langle n|R_{-1}|0\rangle|^2)$$
$$- \frac{\mathrm{i}}{2}[e_x'^* e_y - e_x'^* e_y](|\langle n|R_1|0\rangle|^2 - |\langle n|R_{-1}|0\rangle|^2) \; . \qquad (3.79)$$

We define

$$F^e_{1,m} = m_e \sum_n \frac{[E(\Psi_n) - E(0)]^3}{\hbar^3 \omega_{\mathbf{k}}} \frac{|\langle n|R_m|0\rangle|^2}{E(0) - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2} \; , \qquad (3.80)$$

where the label e and 1 on F remind us that this refers to electric (e) dipole (l=1) contributions, and where we introduced the symbol m_e for the electron mass, to avoid any confusion with the index m, which runs over $0, \pm 1$; reinserting the prefactors present in (3.63) and those allowing to relate w to $\mathrm{d}\sigma/\mathrm{d}O'$, see (3.25), we finally obtain

$$\frac{\mathrm{d}\sigma}{\mathrm{d}O'} = |f_{res}|^2 \; , \qquad (3.81)$$

where f_{res} is the resonant scattering *amplitude*, given by

$$f_{res} = -r_0 \; \Bigg[\frac{1}{2}\mathbf{e}'^* \cdot \mathbf{e}(F^e_{1,1} + F^e_{1,-1}) - \frac{\mathrm{i}}{2}(\mathbf{e}'^* \times \mathbf{e}) \cdot \hat{\mathbf{z}}(F^e_{1,1} - F^e_{1,-1})$$
$$+ (\mathbf{e}'^* \cdot \hat{\mathbf{z}})(\mathbf{e}_\lambda \cdot \hat{\mathbf{z}})(F^e_{1,0} - \frac{1}{2}F^e_{1,1} - \frac{1}{2}F^e_{1,-1}) \Bigg] \; , \qquad (3.82)$$

where the unit vector in the z direction (i.e. in the axis of quantization of the angular momenta), $\hat{\mathbf{z}}$, was introduced. Equation (3.82) was derived in [30] using the relativistic formalism of vector spherical harmonics, soon after the discovery of resonant magnetic scattering by Gibbs et al. [7]. Let us pause briefly to analyze some of the consequences of the results derived so far. The three terms in (3.82) describe resonant or anomalous scattering in general, and are rather different in nature. The first is proportional to $(F^e_{1,1} + F^e_{1,-1})$ and is therefore always present. The second is a genuinely magnetic term, because it originates from the difference between the 1 and the -1 components, which arise only in the presence of a magnetic *preference* for one sense of rotation around the quantization axis. Finally, the last term is nonvanishing for any anisotropic system, a system with a preferential axis, identified either by a crystal anisotropy or by a magnetic moment, which translates into a different occupation for one-electron orbitals with different orientation. The difference in occupation translates into a difference in the value of individual $F^e_{1,m}$, which is strongly influenced (see (3.80)) by the availability of states with the appropriate symmetry, at or near the resonance energy, suitable to play the role of intermediate states.As an example, consider first an isotropic or cubic environment for an atom. In this case, $F^e_{1,m}$ is the same for all m 's and can be called simply F^e_1. Then

$$f_{res} = -r_0 \frac{1}{2} (\mathbf{e}'^* \cdot \mathbf{e})(2F^e_1) \,. \tag{3.83}$$

We can represent the polarization dependence by evaluating the above equation for the various cases arising when $\mathbf{e}', \mathbf{e}$ take all possible σ and π orientations and writing the result in terms of a *tensor* scattering amplitude [5, 6]

$$f_{res} = \mathbf{e}'^* \hat{f}_{res} \mathbf{e}. \tag{3.84}$$

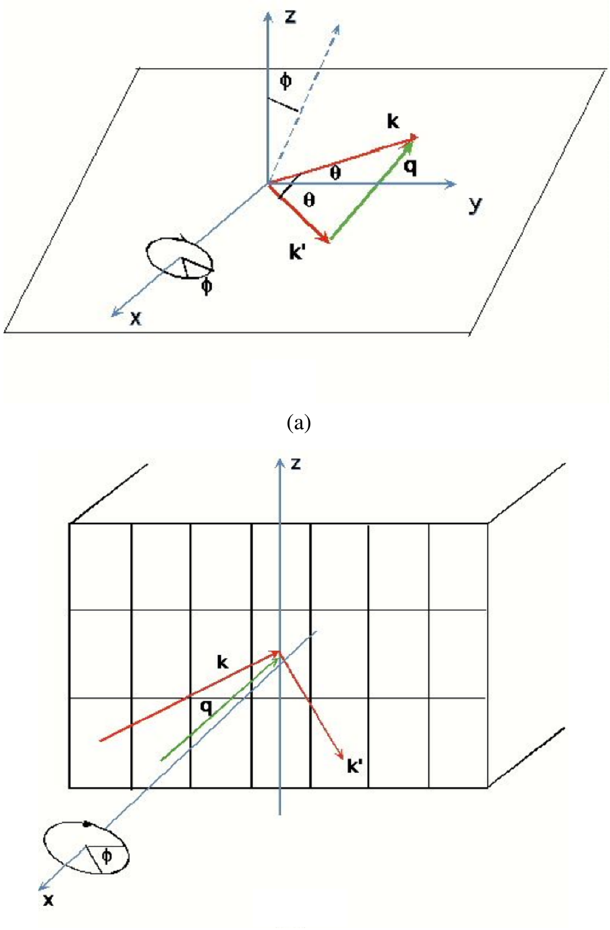
The $\hat{f}_{res}$ tensor is represented in matrix form as

$$\hat{f}_{res} = -r_0 F^e_1 \begin{pmatrix} 1 & 0 \\ 0 & \cos(2\theta) \end{pmatrix} \tag{3.85}$$

where the rows correspond to $\mathbf{e}' = \sigma$ or π' respectively, and the columns to $\mathbf{e} = \sigma$ or π. Consider next the case in which the atom is in a orthorombically distorted environment, in which z is inequivalent to the x, y directions, so that $2F^e_{1,0} - (F^e_{1,1} + F^e_{1,-1}) \equiv F^e_{an} \neq 0$. For a geometry in which the scattering plane is the x, y plane, and the x axis is chosen parallel to the scattering vector $\mathbf{q}$ (see Fig. 3.2a), corresponding to the experimental situation sketched in Fig 3.2b, where the crystal surface and the directions of the incoming and scattered beams are visible, we find that

$$\hat{f}_{res} = -\frac{r_0}{2} \left[(F^e_{1,1} + F^e_{1,-1}) \begin{pmatrix} 1 & 0 \\ 0 & \cos(2\theta) \end{pmatrix} \right. \\ \left. + [2F^e_{1,0} - (F^e_{1,1} + F^e_{1,-1})] \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \right] \,. \tag{3.86}$$

If the crystal in Fig. 3.2b is rotated by an angle ϕ about the x axis, that is around the scattering vector $\mathbf{q}$ (*azimuthal scan*), while leaving the scattering geometry, i.e. the directions of $\mathbf{k}$ and $\mathbf{k}'$ unchanged (it is not easy to rotate a synchrotron !), the molecular preferred axis is rotated by an angle ϕ as shown by the dashed line in Fig. 3.2a. The scattering amplitude becomes



(a)

(b)

Fig. 3.2 **a** Sketch of the scattering plane with the scattering angle 2θ, and the azimuthal angle ϕ, describing rotations about the scattering vector **q**; **b** A sketch of the actual experimental geometry corresponding to **a**.

$$\hat{f}_{res} = -\ \frac{r_0}{2}\left[(F^e_{1,1}+F^e_{1,-1})\begin{pmatrix}1 & 0\\ 0 & \cos(2\theta)\end{pmatrix}\right.$$
$$\left.+\left[2F^e_{1,0}-(F^e_{1,1}+F^e_{1,-1})\right]\begin{pmatrix}\cos^2\phi & -\frac{1}{2}\sin\theta\sin(2\phi)\\ \frac{1}{2}\sin\theta\sin(2\phi) & \sin^2\theta\sin^2\phi\end{pmatrix}\right]. \tag{3.87}$$

This simple example is sufficient to demonstrate how, in the resonant regime, the charge-related scattering may display features such as non-diagonal tensor properties with respect to the polarization of the incoming and scattered beams, and the azimuthal angle dependence, which are absent for the non-resonant Thompson scattering. The tensor nature of the resonant scattering amplitude, which was traditionally written as a single complex number with the notation $f' + \mathrm{i} f''$ has become increasingly important in recent years. As we mentioned in passing, (3.82) also contains magnetic scattering components, as first observed in [7]. The reader may wonder where, in the formulation in terms of electric multipole transitions between the ground and the intermediate states, the sensitivity to magnetic moments may come from. This is a subtle but very important point. In fact, no spin operators appear in the resulting expressions. The sensitivity to magnetic moments comes from the combined action of two ingredients: the Pauli principle and the spin-orbit interaction. The Pauli principle enters because of the already mentioned strong dependence of the scattering amplitude on the availability of states, at or near the resonance energy, suitable to play the role of intermediate states. In a one-electron language, if states with a given spin are predominantly occupied, it is mostly states with the opposite spin which are available to be virtually filled by the promotion of a core electron in the first part of the resonant scattering process. Since the spin is conserved in the optical transition, it is mostly electrons with the same spin as the predominantly available intermediate states which are virtually excited. In the case of all core levels with $l \neq 0$, the spin-orbit interaction is nonvanishing and much larger than in the valence states (for example, the L_2 and L_3 core levels of the rare earths are separated by many hundreds of eV). In a given spin-orbit partner, states with spin up or down have a different orbital character (think for example of $L_{2,3}$ levels, where typically $(p_x + \mathrm{i} p_y)|s_z = -1/2\rangle$ states are, because of the spin-orbit interaction, linearly superposed to $p_z|s_z = +1/2\rangle$ states). Because of the selection rules to the available intermediate states, this orbital polarization translates into a difference between the transition rates for different m's, therefore in an imbalance among the corresponding $F^e_{1,m}$, which is in turn responsible for a nonvanishing magnetic scattering amplitude.The above qualitative description of resonant magnetic scattering must be modified for s core levels, which have a vanishing spin-orbit interaction. In this case, resonant magnetic scattering is also observable [**?**], but it must be ascribed to the much weaker spin-orbit interaction of the valence states, which acts to polarize the final states of given spin and to reproduce the same mechanism. We have so far considered the scattering amplitude for a single atom or ion. In order to consider a lattice of atoms, we must perform a coherent superposition of the scattering amplitudes from all atoms, in which the amplitude from the atom sitting at $\mathbf{R}_{l,m,n}$ acquires a phase factor $e^{i\mathbf{q}\cdot\mathbf{R}_{l,m,n}}$. If the system displays crystallographic or magnetic order, such that the direction of the preferred axis $\mathbf{z}$ changes from atom to atom, this must also be taken into account, as it will affect the value of the scattering amplitude for given polarization, as visible from (3.82). In order to illustrate the consequences of these facts, let us consider the case of a basal-plane antiferromagnet, e.g. the rare earths Ho, Tb, and Dy, sketched in Fig. 3.3. All spins are ferromagnetically aligned in the planes, but their direction rotates by a fixed angle from one plane to the next. It was indeed in Ho, which displays a spiral antiferromagnetic phase in the $20\text{K} \leq T \leq 131\text{K}$ temperature range that the first observations of resonant magnetic scattering took place [7].

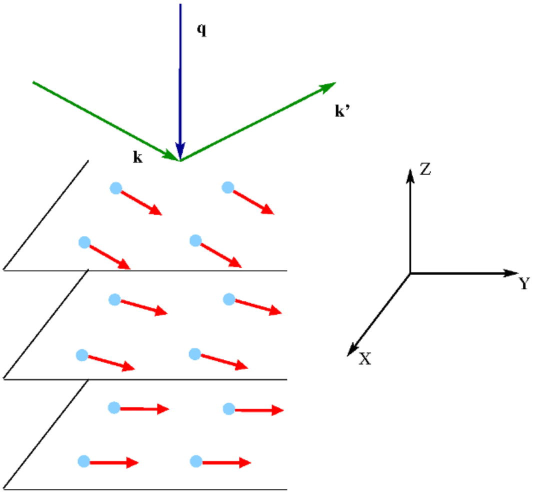


Fig. 3.3 Schematic view of a basal-plane antiferromagnet and of the scattering geometry.

With reference to Fig. 3.3, let us label the atomic positions by a single index $\mathbf{R}_n$, for simplicity, and let us identify the spin direction of the ion n with $\hat{\mathbf{z}}_n$. It is apparent that, with respect to the chosen x, y, z coordinate frame, this vector is given by

$$\hat{\mathbf{z}}_n = (\sin(\tau \cdot \mathbf{R}_n), \cos(\tau \cdot \mathbf{R}_n), 0) \ , \tag{3.88}$$

where τ is the wavevector associated to the spiral pitch, and if we define for short $(F^e_{1,1}+F^e_{1,-1}) \equiv F_0$, $(F^e_{1,1}-F^e_{1,-1}) \equiv F_1$ and $[2F^e_{1,0}-(F^e_{1,1}+F^e_{1,-1})] \equiv F_2$, we are ready to write the scattering amplitude

$$f = \sum_n \mathrm{e}^{\mathbf{iq}\cdot\mathbf{R}_n} f_{res}(\mathbf{R}_n, \hat{\mathbf{z}}_n) \ . \tag{3.89}$$

For the case $\sigma \rightarrow \sigma'$, the F_1 component does not contribute, and we are left with

$$f = -\frac{r_0}{2} \sum_n \mathrm{e}^{\mathbf{iq}\cdot\mathbf{R}_n} [F_0 + F_2 \sin^2(\tau \cdot \mathbf{R}_n)] \ . \tag{3.90}$$

Expressing the $\sin^2$ in terms of exponentials, a bit of algebra gives

$$f = -\frac{r_0}{2} \sum_{h,k,l} [(F_0 + \frac{1}{2}F_2)\delta(\mathbf{q} - \mathbf{G}_{hkl}) - \frac{1}{4}F_2\delta(\mathbf{q} - \mathbf{G}_{hkl} \pm 2\tau)] \ . \tag{3.91}$$

We thus see that the resonant scattering occurs at the crystallographic reciprocal lattice vectors $\mathbf{q} = \mathbf{G}_{hkl}$, with a charge and a magnetic component (F_0 and F_2 respectively) and also at the *second harmonic* magnetic satellite vectors, displaced by $\pm 2\tau$ from each crystallographic reflection. A complete analysis for different polarizations and different satellite is possible using the formula by Hannon and Trammel [7, 30].

The remarkable success of the formalism we just discussed deserves a moment of reflection. In fact, the derivation of the Hannon-Trammel formula rested on the assumption of spherical symmetry of the atoms (see 3.74, where this assumption was explicitly used). Later, we introduced the possibility for the atom to be e.g. in a tetragonal environment, or to have a preferential magnetic orientation, without affecting, however, the basic selection rules deriving from spherical symmetry. In other terms, the rotational character of the wavefunctions was assumed to be intact, external influences being limited to (gently) removing the degeneracies and thus affecting the occupation of the different atomic states. This is a typical situation for *weakly perturbed* atomic states. The reason why the Hannon-Trammel formula is so successful for core resonances of magnetic systems, is that core levels are of course very atomic-like, and that the intermediate states of highest interest in magnetic investigations are those of $d-$ or $f-$ electrons, that are to a larger or lesser extent localized, and preserve a pronounced atomic character.

The example presented so far corresponds to relatively "hard" x-rays, with wavelengths in the range of order ~ 0.1 nm. This wavelength corresponds to the typical order of interatomic distances and is therefore extremely suitable to investigate crystallographic or, possibly, magnetic structures, with periods of the same order. There is however nothing, in our derivations, which would not equally well apply to softer x-rays, and allow the investigation of structures with longer periods. Modern technology for the growth of nanostructures, and in particular of multilayers, has led to the fabrication of structures with characteristic periods in the order of 1 nm or more, which are therefore accessible to investigation by soft x-rays. But also nature provides for systems with order parameters with periods compatible with soft x-ray wavelengths. As pointed out in [32], orbital order in $La_{0.5}Sr_{1.5}MnO_4$ as well as in other manganites, is within reach of the Mn L-edge resonances, with the advantage that L_2 and L_3 resonances access the $3d$ orbitals in the intermediate states, and should therefore be very sensitive to their orbital and magnetic order. This was confirmed by experiments [33, 34, 35, 36, 37] exploring the orbital and magnetic order reflections; comparing their dependence on the incoming photon energy with theoretical calculations within an atomic multiplet scheme in a crystal field [38, 39], it turns out that scattering at the L_2 resonance is very sensitive to orbital order, while the intensity at the L_3 resonance is mostly induced by the Jahn-Teller distortion. This developed in a very intensive field of investigation of strongly correlated systems, and in-vacuum diffractometers for soft x-ray scattering are nowadays quite common around synchrotron sources.

3.4.2 Electric Quadrupole Transitions

Our goal is now to derive expressions for electric quadrupole transitions, i.e. for the case in which the resonant transitions are allowed only when the second term in the expansion of $\mathrm{e}^{\mathbf{ik}\cdot\mathbf{r}} \simeq 1 + \mathbf{ik}\cdot\mathbf{r} + \ldots$ is retained. The important matrix elements in (3.63) reduces to

$$\langle n|\mathbf{e}_\lambda \cdot \mathbf{p}_j \mathrm{e}^{\mathbf{ik}\cdot\mathbf{r}_j}|0\rangle \simeq \langle n|(\mathbf{e}_\lambda \cdot \mathbf{p}_j)(\mathbf{ik}\cdot\mathbf{r}_j) + \ldots|0\rangle \,. \tag{3.92}$$

Using the same approximate trick as in (3.67), the operator $\mathbf{p}_j$ can be expressed in terms of the commutator of $\mathbf{r}_j$ and H, and allowing H to act on $\langle n|$ and on $|0\rangle$ by moving it next to them using the commutation rules one finds

$$\langle n|(\mathbf{e}_\lambda \cdot \mathbf{p}_j)(\mathbf{k}\cdot \mathbf{r}_j)|0\rangle = -\mathrm{i}\frac{m}{\hbar}(E(0)-E(\Psi_n)) \;\; \langle n|(\mathbf{e}_\lambda \cdot \mathbf{r}_j)(\mathbf{k}\cdot \mathbf{r}_j)|0\rangle \\ -\langle n|(\mathbf{e}_\lambda \cdot \mathbf{r}_j)(\mathbf{k}\cdot \mathbf{p}_j)|0\rangle \; . \tag{3.93}$$

Adding to both sides of this equation the same quantity, namely the left hand side, it becomes

$$2\langle n|(\mathbf{e}_\lambda \cdot \mathbf{p}_j)(\mathbf{k}\cdot \mathbf{r}_j)|0\rangle = -\mathrm{i}\frac{m}{\hbar}(E(0)-E(\Psi_n))\langle n|(\mathbf{e}_\lambda \cdot \mathbf{r}_j)(\mathbf{k}\cdot \mathbf{r}_j)|0\rangle \\ + \langle n|(\mathbf{e}_\lambda \cdot \mathbf{p}_j)(\mathbf{k}\cdot \mathbf{r}_j)|0\rangle - \langle n|(\mathbf{e}_\lambda \cdot \mathbf{r}_j)(\mathbf{k}\cdot \mathbf{p}_j)|0\rangle \; . \tag{3.94}$$

Application to the last two terms of this equation of the vector identity (3.45) finally yields

$$\langle n|(\mathbf{e}_\lambda \cdot \mathbf{p}_j)(\mathbf{k}\cdot \mathbf{r}_j)|0\rangle = -\mathrm{i}\frac{m}{2\hbar}(E(0)-E(\Psi_n))\langle n|(\mathbf{e}_\lambda \cdot \mathbf{r}_j)(\mathbf{k}\cdot \mathbf{r}_j)|0\rangle \\ +\frac{1}{2}(\mathbf{k}\times \mathbf{e}_\lambda)\langle n|\mathbf{r}_j \times \mathbf{p}_j|0\rangle \; . \tag{3.95}$$

Now it is easy to recognize in the last term the matrix element between the ground and intermediate states of the orbital angular momentum operator (or, in the language of multipole expansions, the matrix element corresponding to *magnetic dipole* transitions). For the transitions resonant with x-ray photons, which involve promotion of a core electron above the Fermi level, the magnetic dipole matrix elements vanish, because of the orthogonality of the *radial* part of core and valence states, as the angular momentum operators only affect the *angular* part of the wavefunctions. Summarizing, one can conclude that the second term in the expansion of the plane-wave exponential produces terms with the matrix elements of products of two components of the position operator $\mathbf{r}_j$ (*electric quadrupole* terms) plus magnetic dipole terms, which are irrelevant in the x-ray range. In analogy to the discussion following (3.68), define the rank 2 quadrupole moment tensor, with cartesian components $(\alpha,\beta = x,y,z)$

$$Q^{(2)}_{\alpha\beta} = R_\alpha R_\beta - \frac{1}{3}R^2\delta_{\alpha\beta} \; . \tag{3.96}$$

Its spherical components are

$$Q_m^{(2)} = \sqrt{\frac{4\pi}{5}} R^2 Y_m^2(\theta, \phi) \tag{3.97}$$

with $m = -2, -1, ..., 2$. All matrix elements of importance for quadrupole resonant scattering can be written in terms of the quantities

$$F^e_{2,m} = \frac{m_e}{\hbar^3 c^2} \sum_n [E(\Psi_n) - E(0)]^3 \omega_{\mathbf{k}} \frac{|\langle n|Q_m^{(2)}|0\rangle|^2}{E(0) - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + \mathrm{i}\Gamma_n/2} \,. \tag{3.98}$$

The scattering amplitude at the quadrupole level comprises 13 different terms (see e.g. [40]) one of which contains no dependence on $\hat{\mathbf{z}}_n$ and is written as

$$-\frac{r_0}{3}(\mathbf{e}'^*_{\lambda'} \cdot \mathbf{e}_\lambda)(\mathbf{k}' \cdot \mathbf{k})[F^e_{2,2} + F^e_{2,-2}] \,. \tag{3.99}$$

There are then 2 terms in which there is a linear dependence on $\hat{\mathbf{z}}_n$

$$-\frac{r_0}{3}[(\mathbf{k}' \cdot \mathbf{k})(\mathbf{e}'^*_{\lambda'} \times \mathbf{e}_\lambda) \cdot \hat{\mathbf{z}}_n + (\mathbf{e}'^*_{\lambda'} \cdot \mathbf{e}_\lambda)(\mathbf{k}' \times \mathbf{k}) \cdot \hat{\mathbf{z}}_n][F^e_{2,2} - F^e_{2,-2}] \,. \tag{3.100}$$

The other terms have 2, or 3 or 4 factors of $\hat{\mathbf{z}}$ and they give rise to reflections up to the fourth harmonic magnetic satellites, in agreement with the observations of [7] in Ho.

3.5 Absorption Spectroscopies

It is actually possible to discuss the absorption spectroscopies very efficiently, by using the variety of results obtained so far, if we remember the general connection between the photon scattering amplitude and the optical absorption spectrum of the system by the *Optical Theorem* [41] of general scattering theory. This theorem states that

$$\frac{k}{4\pi}\sigma_t = \mathrm{Im} f(0) \,, \tag{3.101}$$

where σ_t is the total cross section, comprising all elastic and inelastic processes, and f(0) is the *forward* scattering amplitude, i.e. the amplitude of scattering for $\mathbf{k}' = \mathbf{k}$ and $\mathbf{e}' = \mathbf{e}$, which can be easily obtained as a special case of the general expressions derived in the preceding Sections. In the case of photons in the energy range of interest here, the total cross section σ_t for the interaction with electronic matter is dominated by photoelectric absorption processes, all other processes having cross sections that are smaller by a few orders of magnitude (see [42] for typical examples). Therefore, the left-hand side of (3.101) reproduces, with good approximation, the absorption spectrum.

In the traditional crystallographic notation in which the atomic scattering amplitude is a simple scalar quantity, written as the sum of the non-resonant amplitude f_0 and the real and imaginary resonant parts $f' + \mathrm{i} f''$, the optical theorem identifies f'' as proportional to the optical absorption spectrum, because, in the case of forward scattering, $\mathbf{k} - \mathbf{k}' = 0$, f_0 is purely real. In our formulation, we can write $f = f_{0c} + f_{0m} + f_{res}$ and, for the pure real character of the charge (or Thomson) part f_{0c}, see (3.23); and the magnetic part, f_{0m}, (3.47) , it vanishes altogether as the orbital term is zero for $\mathbf{q} = 0$ and $\mathbf{P}_S$ is also zero under forward conditions (this requires a bit of vector algebra). So, in conclusion, the only contribution comes from the resonant amplitude. This result has general validity. However, in the spirit of concentrating on the conditions that are met in the investigation of magnetic systems, we shall make use of the expressions derived in the previous section under the assumptions underlying the results of Hannon and Trammel, that, as discussed there, are well suited for this case.

Considering the application of the theorem to the expression derived at the dipole level, (3.82), which provides the most intense resonances, gives the following expression [43] for the absorption cross section

$$\begin{aligned}\sigma_t = -\lambda r_0 [\mathrm{Im}(F^e_{1,1} + F^e_{1,-1}) - \mathrm{i}(\mathbf{e}^* \times \mathbf{e}) \cdot \hat{\mathbf{z}}\, \mathrm{Im}(F^e_{1,1} - F^e_{1,-1}) \\ + |\mathbf{e} \cdot \hat{\mathbf{z}}|^2\, \mathrm{Im}(2F^e_{1,0} - F^e_{1,1} - F^e_{1,-1})]\end{aligned} \qquad (3.102)$$

where $\lambda = 2\pi/k$ is the photon wavelength.Notice that the expression $(\mathbf{e}^* \times \mathbf{e})$ vanishes for a real polarization vector (i.e. for linear polarization) and is purely imaginary in other cases.Therefore the imaginary part of the expressions (3.80) is determined by

$$\begin{aligned}\mathrm{Im} F^e_{1,m} &= m_e \sum_n \frac{[E(\Psi_n) - E(0)]^3}{\hbar^3 \omega_{\mathbf{k}}} \frac{-\Gamma_n/2}{(E(0) - E(\Psi_n) + \hbar\omega_{\mathbf{k}})^2 + (\Gamma_n/2)^2} \\ \mathrm{Im} F^e_{1,m} &\equiv -w^e_{1,m}\end{aligned} \qquad (3.103)$$

so that the absorption spectrum is described as a sum of Lorentzians, $w^e_{1,m}$, each with the broadening parameter determined by the inverse lifetime of the corresponding excited state.

In terms of this quantity the absorption cross section is written

$$\sigma_t = \lambda r_0 [(w^e_{1,1} + w^e_{1,-1}) - \mathrm{i}(\mathbf{e}^* \times \mathbf{e}) \cdot \hat{\mathbf{z}}(w^e_{1,1} - w^e_{1,-1}) \\ + |\mathbf{e} \cdot \hat{\mathbf{z}}|^2 (2w^e_{1,0} - w^e_{1,1} - w^e_{1,-1})] \,. \quad (3.104)$$

and this expression is very convenient because it explicitly shows the dependence on photon polarization and is therefore immediately applicable to describing various forms of dichroism. As a first example, consider linear polarization; in the case $\mathbf{e} \parallel \hat{\mathbf{z}}$ or $\mathbf{e} \perp \hat{\mathbf{z}}$ one finds respectively

$$\sigma_{\parallel} = 2\lambda r_0 w^e_{1,0} \quad (3.105)$$

$$\sigma_{\perp} = \lambda r_0 \left(w^e_{1,1} - w^e_{1,-1}\right) \quad (3.106)$$

so that linear dichroism is expressed as

$$\sigma_{\parallel} - \sigma_{\perp} = \lambda r_0 \left(2w^e_{1,0} - w^e_{1,1} - w^e_{1,-1}\right) \,. \quad (3.107)$$

In the same way we can derive general expressions for the circular dichroism, a technique of very wide use in the study of magnetic systems since the discovery of sum rules [44, 45]. Consider first the Faraday geometry, in which $\mathbf{k} = \hat{\mathbf{z}}$. The two circular polarization states are: $\mathbf{e}_+ = -\mathrm{i}\frac{x+iy}{\sqrt{2}}$, $\mathbf{e}_- = \mathrm{i}\frac{x-iy}{\sqrt{2}}$, and with the help of the expressions

$$\mathbf{e}^*_+ \times \mathbf{e}_+ = -\mathbf{e}^*_- \times \mathbf{e}_- = \mathrm{i}\hat{\mathbf{z}} \quad (3.108)$$

we easily derive the circular dichroism formula

$$\sigma_+ - \sigma_- = 2\lambda r_0 \left(w^e_{1,1} - w^e_{1,-1}\right) \,. \quad (3.109)$$

In the more general case of a propagation direction forming an angle θ with the direction of magnetization $\hat{\mathbf{z}}$, that coincides with a symmetry axis of a cubic or hexagonal ferromagnet, some trigonometry delivers the following results for the absorption of photons circularly polarized in the plane normal to the propagation direction

$$\sigma_+ = \lambda r_0 \Big[\left(w^e_{1,1} + w^e_{1,-1}\right) + \cos\theta \left(w^e_{1,1} - w^e_{1,-1}\right) \\ + \frac{1}{2}\sin\theta^2 \left(2w^e_{1,0} - w^e_{1,1} - w^e_{1,-1}\right)\Big] \quad (3.110)$$

$$\sigma_- = \lambda r_0 \left[\left(w^e_{1,1} + w^e_{1,-1} \right) - \cos\theta \left(w^e_{1,1} - w^e_{1,-1} \right) + \frac{1}{2} \sin\theta^2 \left(2w^e_{1,0} - w^e_{1,1} - w^e_{1,-1} \right) \right] \quad (3.111)$$

so that the circular dichroism is, in this more general case

$$\sigma_+ - \sigma_- = 2\lambda r_0 \cos\theta \left(w^e_{1,1} - w^e_{1,-1} \right) . \quad (3.112)$$

3.6 Resonant Inelastic X-ray Scattering

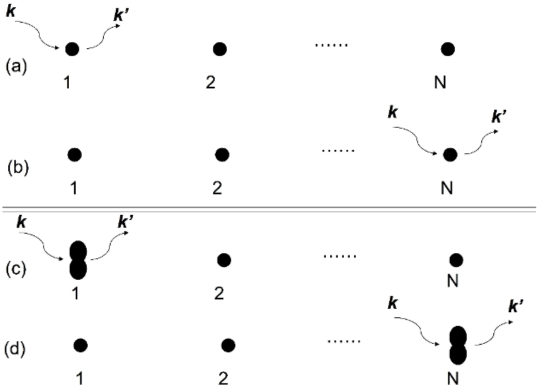


Fig. 3.4 Photon scattering from an atom chain. Upper panel: elastic scattering, the final state is the same, irrespective of which of the atoms is scattering the photon (the first one in **a**, the N-th in **b**). The amplitudes for the N different ways to reach the same final state must be first summed and than squared. Bottom panel: inelastic scattering: the final state is different, depending on which atom scatters the photon and is promoted to an excited state (the first in **c** or the N-th in **d**), therefore the amplitudes are first squared and then added.

In this Section inelastic processes are considered, in which the state of the material system after the scattering event (the final state) has a different energy than the initial state (for simplicity assumed to be the ground state). In recent years, inelastic scattering with synchrotron radiation has acquired a growing importance.

Inelastic processes can take place in the non-resonant as well as in the resonant regime. The two regimes provide different information on the properties of the system, and both of them are in general extremely valuable. Here we shall mostly discuss the resonant regime, defined as usual by the condition that the incoming photon energy is close to one of the absorption edges of the system: this is because resonant inelastic scattering is much more relevant for the investigation of magnetic properties.

One thing that is important to underline at the outset is that inelastic scattering is a *photon-starved* technique. There is indeed a very large intensity difference between elastic and inelastic scattering: a simple argument to see that [46], at least in the limit of wavelength larger than the inter-atomic distance, is that the intensity of elastic scattering is proportional to N^2, the square of the number of scattering atoms; the intensity of inelastic scattering to N. A schematic illustration of the reason is offered in Fig. 3.4, for a chain of identical non-interacting atoms. The difference is that in elastic scattering, scattering processes through different atoms represent different paths through which the same final state is reached: the laws of quantum mechanics say that one must add the amplitudes for different paths, and then square; on the other hand, in the inelastic case, the atom contributing to an inelastic scattering process is left with some energy, i.e. in an excited state: scattering on different atoms lead therefore to different final states and now intensities must be added, after squaring the amplitudes. The argument can be carried over to the more realistic cases in which atoms are interacting, electrons are tunneling from one to the other and the energy eigenstates are Bloch states, and even electron-hole interactions can be included.

In the non-resonant case, we can proceed by generalizing the treatment of Section 3 (equation (3.27)) to include scattering from the initial electronic state $|i_e\rangle$, with energy E_i, to a different electronic state $|f_e\rangle$ with energy E_f (see (3.21)). One can show that the Thomson scattering analog becomes

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}O'\mathrm{d}\omega_{\mathbf{k}'}}\right) = r_0^2\,\frac{\omega_{\mathbf{k}'}}{\omega_{\mathbf{k}}}\,\left(\mathbf{e}'^*\cdot\mathbf{e}\right)^2 S(\mathbf{q},\omega) \tag{3.113}$$

where the *dynamic structure factor* $S(\mathbf{q},\omega)$, with $\omega = \omega_{\mathbf{k}} - \omega_{\mathbf{k}'}$, is defined as

$$(\mathbf{q},\omega)=\sum_f\left|\langle f|\sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}|i\rangle\right|^2\delta\left(\frac{E_f-E_i}{\hbar}-\omega_{\mathbf{k}}+\omega_{\mathbf{k}'}\right)\,. \tag{3.114}$$

In a famous paper, Van Hove [47] showed how $S(\mathbf{q},\omega)$ is related to a density-density correlation function, in space and in time, of the system

$$S(\mathbf{q},\omega)=\int \mathrm{d}\mathbf{r}\mathrm{d}t\mathrm{e}^{\mathrm{i}(\mathbf{q}\cdot\mathbf{r}-i\omega t)}\int \mathrm{d}\mathbf{r}'\langle i|\rho(\mathbf{r}',0)\rho(\mathbf{r}+\mathbf{r}',t)|i\rangle\,. \tag{3.115}$$

This shows, not surprisingly, that the inelastic analog of the non-resonant charge scattering (Thomson scattering) allows to explore the spectrum of charge density fluctuations; this allows to investigate phonons, electronic excitations, plasmons [48]. One can expect that magnetic information is delivered by the inelastic analog of the non-resonant magnetic scattering terms: this is in principle the case, but if you remember that magnetic scattering amplitudes are reduced by the factor $\hbar\omega/mc^2$ with respect to charge scattering amplitudes, and that already magnetic elastic scattering is an experiment suffering from low-count rate, you can anticipate that non-resonant inelastic magnetic scattering shall be extremely difficult to measure; in fact, except for early magnetic scattering experiments in the Compton limit (when the transferred energy is much larger than the ionization energy) [48], there are hardly any further attempts in the literature.

We shall therefore turn to the resonant inelastic x-ray scattering (RIXS) case, defined as usual by the condition that the incoming photon energy is close to one of the absorption edges of the system. In this case one can consider the dominant resonant terms only, and obtain, in full analogy to (3.63)

$$w=\frac{2\pi}{\hbar}\sum_f\left|\sum_n\frac{\langle f|H_2'|n\rangle\langle n|H_2'|i\rangle}{E_0-E_n+\hbar\omega_{\mathbf{k}}+\mathrm{i}\Gamma_n/2}\right|^2\delta(\hbar(\omega_{\mathbf{k}}-\omega_{\mathbf{k}'})-(E_f-E_i))\,. \tag{3.116}$$

Figure 3.5 shows schematically how an inelastic scattering process can leave the system in a final state with an electron-hole pair in the valence levels or with a pair where the hole is in a core shell. In the latter case the term "resonant x-ray Raman scattering" is used. There an obvious similarity between resonant inelastic x-ray scattering (RIXS) and other techniques such as x-ray fluorescence spectroscopy and absorption spectroscopy in the fluorescence detection mode. The presence of an electron-hole pair in the final state also suggests an analogy with absorption spectroscopy, either in the visible-

UV region, for valence holes, or in the soft x-rays for the Raman case. There are however significant differences, because the inelastic scattering process has different selection rules, and the sampling depth of a technique using hard x-rays is always larger than that of soft x-ray spectroscopies. A good illustration of the relationship between inelastic scattering and absorption spectroscopy is provided by the results by Hämäläinen et al. [49] on the Dy L_3 edge in dysprosium nitrate. After quadrupolar excitation from the $2p_{3/2}$ to the $4f$ manifold by the incoming photon, a high resolution analyzer accepts only a narrow band of the outgoing photons corresponding to $3d_{5/2}$ electrons filling the $2p_{3/2}$ holes.

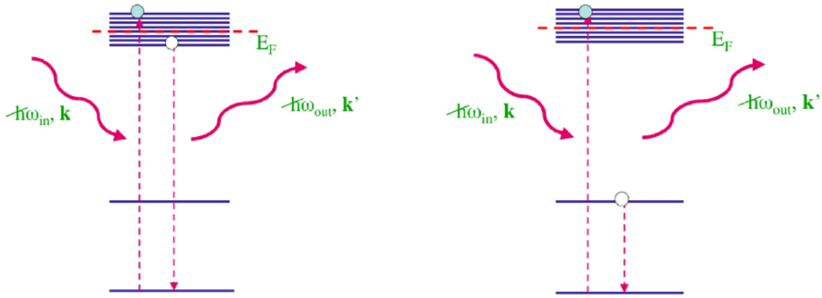


Fig. 3.5 Schematic description of resonant inelastic scattering processes

The outgoing photons can be analyzed both in energy and in momentum: this gives the possibility to map the momentum dispersion of elementary excitations. In order to be really interesting for the study of many-body systems, however, this must be done with an appropriate resolution; and although the enhancement due to the resonance is brought to bear, a RIXS experiment is always a compromise between resolution and count rate. They are therefore performed at modern high brilliance synchrotron sources; in addition, in recent years, a tremendous progress in the design of spectrometers has taken place and nowadays the best instruments are able to deliver spectra with resolving power $\Delta E/E$ exceeding 10,000. A figure of 33,000 around 1 keV is quoted for the instrument ADRESS at the Swiss Light Source, and the transmission of the beamline is delivering some $\simeq 10^{11} - 10^{12}$ photons per second on the sample [50].

To exemplify the remarkable progress of RIXS spectroscopy (for reviews, see [51, 52]), we shall briefly mention recent investigations of high-temperature cuprate superconductors and related compounds with strongly correlated electrons. Here the $L_{2,3}$ edges of Cu, in an energy region around 940 eV are conveniently investigated, as they are dipole-coupled to the Cu d-electrons, that are universally considered to play a key role in the superconductivity. In addition, the complex perovskite crystal structures of the cuprates have rather large unit cells, therefore rather small Brillouin zones; so that the momentum transfer region accessible to the soft x-ray photons near these edges covers about 80% of the way from the zone centre to the edge [53]. The study of momentum dispersion for a variety of excitations becomes therefore possible and can be of high value. Interestingly, besides charge and inter-orbital ($d-d$ electron) excitations, also magnetic excitations (spin waves) and their dispersion are accessible to this technique [54]. In the case of elastic scattering, we already explained the sensitivity to magnetic order of a resonant elastic scattering process based on electric dipole transitions (see the discussion in subsection 3.4.1) in terms of the strong spin-orbit interaction for electrons in the $L_{2,3}$ core levels. A similar argument [55] explains the possibility to explore magnetic excitations (i.e. spin-flip excitations) by RIXS. With reference to Fig. 3.6 , and to our previous discussion, we can understand how the mixed spin-up / spin-down character of the core wavefunctions allows to populate a spin-down level near the Fermi edge with the incoming photon, and to fill the hole by removing a spin-up electron near the Fermi level with the outgoing one, leaving a spin-flip excitation in the system. Remarkably, the dispersion of spin-waves measured by RIXS [54] agrees with that obtained by neutron scattering, and offers the possibility of a complementary technique in those cases (e.g. samples too small, low momentum region) where neutron techniques are difficult.

The complexity and variety of information contained in RIXS spectra makes theoretical calculations a major challenge. The approaches which have so far been applied most frequently are based either on atomic multiplet models, or on their extension to include the neighbouring ligands via Anderson impurity models or small cluster calculations [51, 52]. On the other hand, from the experimental point of view, this technique, in spite of all the difficulties connected to the low cross-section and the limitations in resolution, can provide rather unique information of importance for many-body physics. In conclusion, one can say that RIXS is a technique with great promise, as advances in instrumentation should lead to continued improvement in energy resolution.

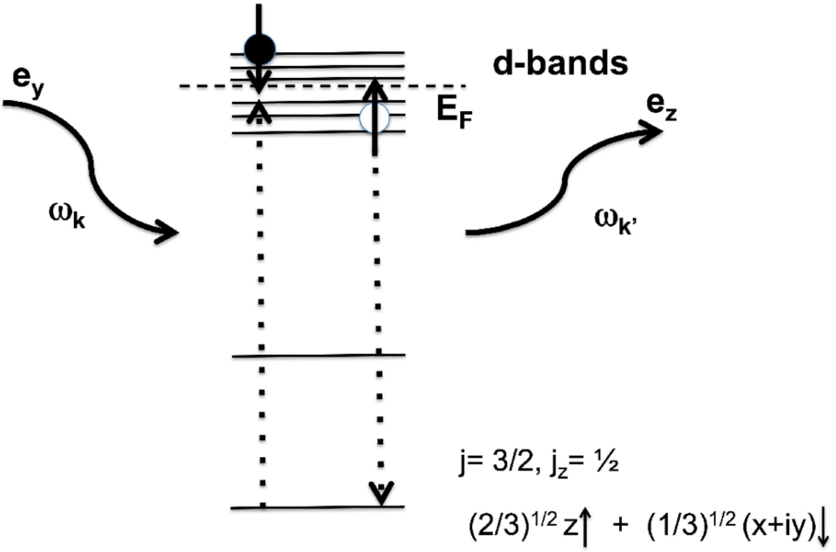


Fig. 3.6 Schematic description of spin-flip resonant inelastic scattering processes at the L_3 edge

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