Journal of Electron Spectroscopy and Related Phenomena 200 (2015) 143–159

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Zen and the art of dichroic photoemission

Gerrit van der Laan

Magnetic Spectroscopy Group, Diamond Light Source, Didcot OX11 0DE, United Kingdom

ARTICLE INFO

Article history:
Available online 14 June 2015

Keywords:
Angular dependent photoemission
Spin resolved
Linear and circular dichroism
Fundamental spectra
Chiral geometry
Sum rules

ABSTRACT

The discovery of magnetic dichroism in photoemission is celebrating its 25th anniversary this year. Here a review of the underlying general theory for the angular and spin dependence of dichroic core-level photoemission is presented using both a single-particle model and a many-body approach. The established methods of angular momentum coupling offer an elegant and powerful way to analyse the magnetic dichroism and spin polarization in photoemission from core and localized valence levels. In the presence of core-valence interactions one can distinguish different fundamental spectra, which via sum rules are related to physical properties described by coupled tensor operators for spin and orbital moments. By separating the angular dependence from the physical information, different geometries can be distinguished to measure the magnetic circular dichroism (MCD), linear dichroism (LD), circular dichroism in the angular dependence (CDAD), and magnetic linear dichroism in the angular dependence (MLDAD). Various ways to probe the core-hole polarization are discussed, such as using the angular dependence, moment analysis of the spectral distribution, and resonant photoemission decay.

1. Introduction

First observed in 1887 by Hertz [1], the photoelectric effect was explained in 1905 by Einstein [2] as caused by the emission of electrons when a material is irradiated with light. Photoemission measurements on solids gained popularly in the 1970s with the appearance of ultra-high vacuum conditions, able to maintain clean surfaces, and high-resolution electron energy analysers, single-electron counting technique and image plates. A further spur came from the advent of synchrotron radiation sources in the 1980s. A wide array of techniques has since become available, such as angle- and spin-resolved photoemission, isochromat spectroscopy and resonant photoemission.

For long it was commonly believed that core level photoemission would not depend on the linear or circular polarization of the incident photons, except near threshold. It came therefore as a large surprise in 1990 when Baumgarten et al. [3] reported the magnetic circular dichroism (MCD) in core-level photoemission from ferromagnets, which was soon confirmed by others [4,5]. It was found that the dichroism did not disappear when the magnetization direction is perpendicular to the light helicity vector [6]. A strong dichroism was observed at the surface of Ni metal due to an enhanced orbital moment [7], and MCD was also reported in resonant photoemission [8].

Reversing the magnetization direction perpendicular to the plane of measurement in a chiral geometry gave rise to a new effect called magnetic linear dichroism in the angular dependence (MLDAD) in photoemission, as first reported in 1993. [9–11] A year later, it was explained as being due to the interference between the two outgoing photoemission channels [12,13].

An invaluable method to the analysis of the photoelectron distribution in a complete experiment, as determined by the photon energy, kinetic energy, emission angle, magnetization direction, crystal orientation and spin direction, is the separation of the transition probability into a dynamic (or physical) part and a geometric (or angular) part. Photoemission is rarely measured angle integrated, instead only a narrow cone of emitted electrons is collected by the analyser. In crystalline and magnetic samples the experiment is then characterized by at least three vectors, i.e., those of the crystal orientation or magnetization direction, **M**, the light polarization, **P**, and the electron emission direction, ε. Additionally, spin resolved photoemission has the spin direction, $\mathbf{P}_S$, of the emitted electron. When these vectors are coplanar the analysis is fairly straightforward, although the emission intensity and spin polarization will strongly depend on the angles. When these vectors are collinear the photoemission is even simpler to analyse and resembles in some aspects the simple case of angle integrated emission, where interesting effects remain hidden. However, when the three vectors are neither coplanar nor mutually perpendicular, the geometry can have a handedness. This means that if one of the odd vectors is reversed, such as the magnetization or the light helicity,

E-mail address: gerrit.vanderlaan@diamond.ac.uk

http://dx.doi.org/10.1016/j.elspec.2015.06.001

the opposite handedness is obtained, which gives a change in the photoemission signal. Such geometries turn out to be of great interest. Whilst a combination of isotropic and linear polarized light can be obtained by adding up the contributions from left and right circularly polarized light, the opposite, creating circularly polarized light from linearly polarized light is excluded by parity conservation. However, by using the handedness (chirality) of the photoemission geometry, it becomes possible to measure with linear polarization the same dichroic spectrum as with circular polarization.

Core-level photoemission has become an important tool for the study of the electronic and magnetic properties of transition metal, rare earth and actinide compounds [14–18]. The presence of core-valence interactions in the final state is evidenced by the occurrence of multiplet structure and charge-transfer satellites in spectra, which allows to extract details about the character of the ground state [19]. The advent of sophisticated insertion devices for polarized synchrotron radiation have enabled the exploration of the polarization dependence in the core excitations.

This paper presents a theoretical overview and treats dichroic photoemission in a wider context, evoking fundamental spectra, moment analysis, core-hole polarization, and resonant decay processes. These topics are captured by the elegant methods of angular momentum coupling, which provide very general solutions, not only for atomic spectroscopy but also for other disciplines such as, e.g., nuclear shell theory [20]. We will present the more general and practical aspects of dichroic photoemission with the emphasis on fundamental spectra, angular dependence and chirality. By recoupling the expression for the transition probability we can separate the geometric and dynamic part. The latter describes the physical properties of the atom, containing information about the properties connected with the electron shell, as well as the relationship between these states and the final state.

We will proceed by following a series of papers by Thole and van der Laan, [21,22,12,23], which give a rather complete account of the theory for spin polarization and circular and linear dichroism in photoemission from core and valence states in localized magnetic systems. After a description of the basic principles in Section 2, [24] first the angle-integrated photoemission is analyzed in Section 3. [21] This provides a solid basis to introduce the fundamental spectra, which in the presence of electrostatic interactions give the correlation between the spin and orbital moments of the core and valence electrons. We discuss the emission from both one-electron states [25] and multi-electronic configurations. Sum rules relate the integrated intensities of the spectra to the expectation values of ground state operators, given by coupled tensor operators [22]. The spectral distribution allows us to extract information about higher order moments [26]. The angular dependence is treated in Section 4. The geometry can be separated from the physical part, which gives the fundamental spectra. The angular distribution exposes the higher multipole moments. Section 5 discusses in more detail the geometrical aspects, where a chiral geometry leads to MLDAD and CDAD. Using group theory it is shown that these spectra form independent linear combinations. Section 6 briefly shows how crystal field symmetry can be implemented into the theory. Section 7 gives a concise comparison with X-ray absorption spectroscopy (XAS) and also discusses the core-hole polarization. Section 8 presents the theory of spin polarization and magnetic dichroism in resonant photoemission decay. Compared to XAS, it can measure different linear combinations of ground state moments. Finally, several illustrations are presented in Section 9. The correlation between spin and orbital moments is extracted from the fundamental spectra in the case of the Gd 4*d* photoemission. The influence of the diffraction effects is shown. The MCD and MLDAD are shown to be equivalent in the case of hard X-ray photoemission. Conclusions are drawn in Section 10.

2. Basic principles

Some insight in the philosophy on which the dichroic photoemission rests can be obtained by considering a core level ℓ which is split into orbital sublevels m. When these sublevels are energy degenerated, the core state has a spherical symmetry. By lifting the degeneracy, the sublevels will split in energy and have distinctly different orbital moments. The core-hole sublevel splitting is caused by the electrostatic interaction with the magnetically polarized valence electrons. Alternatively, in a one-electron model, the splitting can be described as due to an effective spin field in combination with spin–orbit interaction to split the orbital sublevels. For each sublevel m, the dipole transition probability is different for left- ($\Delta m = -1$) and right- ($\Delta m = +1$) circularly polarized radiation. For instance, for emission from a sublevel $m = \ell$ to the continuum state $c = \ell - 1$ with components γ, where $-\ell + 1 \le \gamma \le \ell - 1$, the transition $\Delta m = -1$ is allowed, but the transition $\Delta m = +1$ is not possible. Thus the polarized core state gives rise to a strong circular dichroism in photoemission.

An important ingredient is the conservation of angular momentum in the transition. This is easy to see in angle integrated photoemission, where the emitted electron distribution has zero moment, so that the light transfers its full moment to the atom. We can make new linear combinations of the polarized spectra, the so called fundamental spectra I^{xy}, in which the electric-dipole radiation transfers an orbital moment of $x = 0$, 1, or 2 for the isotropic spectrum, circular, and linear dichroism, respectively, and the photoelectron spin carries away a moment $y = 0$ or 1 in the case without and with spin detection, respectively. Then, the spectra I^{xy} give the probability for removing an electron with moments x and y. In the presence of core-valence interactions, these fundamental spectra will reveal the correlation between spin and orbital moments of the core hole and the valence band. Moreover, the integrated intensities of the fundamental spectra give the expectation values of the spin and orbital moments of the emitting shell. For instance, the magnetic circular dichroism and spin spectrum relate to the ground state orbital and spin magnetic moment, respectively. This is particularly useful in the case of the localized 4*f* shell of the rare earths, which is partly filled.

Since lifting the energy degeneracy leads to an anisotropic charge distribution, the core hole polarization can be measured in angle dependent photoemission. Using momentum conservation we can tackle the angular dependent photoemission, by considering that the emitted photoelectron carries away a moment, which is even due to parity ($b = 0$, 2, or 4). Now, each fundamental spectrum produces a limited set of angular distributions. Higher moments of the atom can be reached compared to angle-integrated photoemission. Interference effects between the two different continuum states gives rise to 'odd' waves, which can be observed in a chiral geometry, spanned by the three vectors of the light polarization, magnetization and emission direction.

We will describe resonant photoemission as a two-step process in which the first step is X-ray absorption that gives a polarized core hole and an additional valence electron. In the second step the core hole decays by Coulomb interaction under emission of an electron whereby a two-hole state is created. In XAS (and XMCD) the sum rules measure only the number of holes (monopole moment) in the core level, and the core hole polarization manifests itself in the spectral line shape. The angular dependence of the resonant photoemission allows us to obtain also the higher moments of the core hole. Compared to XAS, this gives new sum rules which measure different combinations of the ground state moments.

In the following, we use the theory of second quantization to write the transition probability in terms of creation and annihilation operators. This enables us to derive formulae that do not dependent on the precise nature of the initial and final states, and