X-ray magnetic circular dichroism (XMCD)

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X-ray magnetic circular dichroism (XMCD) is a form of X-ray absorption spectroscopy (XAS) that takes advantage of the unequal population of the 3d shell in magnetic transition metal compounds. By combining magnetic sensitivity with chemical specificity, XMCD allows for unique experiments to be performed on magnetized samples. Most prominently, site occupations, oxidation states, crystalline distortions, orbital ordering and microscopic parameters can be measured. A brief outline of XAS and its main features is presented, followed by a description of XMCD's fundamental ideas. The required experimental setup and selection rules for XMCD are then introduced and explained. Finally, we briefly illustrate the general analysis procedure in terms of ligand field multiplet theory and transition-specific sum rules, without delving into their mathematical intricacies.

I. INTRODUCTION

The proliferation of synchrotron sources has made X-ray absorption (XAS) experiments ubiquitous in physics, chemistry, and materials science. While X-ray diffraction (XRD) remains unmatched when it comes to analyzing the long-range order of a sample, XAS measurements encode information about its short-range structure [1], making them complementary techniques.

Two regions are typically distinguished in a given XAS dataset. Analyzing so-called X-ray absorption near edge structure (XANES) spectra provides information about an atom's oxidation state and crystal field. Meanwhile, extended X-ray absorption fine structure (EXAFS) is concerned with the oscillations that arise away from the "edge" region, which we define in section II. These are associated with self-interference of a photoelectron's wavefunction, and provide information of short-range correlations in the sample. Unlike pair-distribution function (PDF) measurements, which provide similar structural information, XAS measurements provide chemical selectivity. This feature makes them particularly suitable for studying multicomponent systems, where we are often interested in discerning the effect each atom has on the material's electronic structure [2–7].

While XAS is a powerful technique, its capabilities when analyzing magnetic samples can be augmented by using polarized light. The careful selection of the polarization gives rise to two techniques: X-ray magnetic circular dichroism (XMCD) and X-ray magnetic linear dichroism (XMLD). While linear polarization is easier to attain and define, XMLD experiments can only be performed on single crystals, limiting their scope. XMCD, on the other hand, can also be applied to polycrystals and even molecules. Here we focus on XMCD, on account of its greater applicability.

By directly probing the d-shell of transition metals, XMCD attains a high level of magnetic sensitivity. The inherited chemical specificity from XAS then makes XMCD one of the few techniques that can provide a direct measurement of an ion's spin and orbital moments [2]. This work aims to provide a very general view of the field while illustrating the uniqueness of XMCD as a tool for the study of condensed matter. The discussion is centred around the 3d transition metals for simplicity and brevity. However, similar results can be obtained for the rare-earths.

II. X-RAY ABSORPTION SPECTROSCOPY

A basic understanding of the main features of typical XAS spectra is required to understand XMCD, along with the standard terminology. In an XAS experiment, a sample is exposed to X-rays. Some photons are absorbed, while others go on undisturbed. By *edge*, we refer to the sharp rise in absorption that occurs when a photon reaches the energy needed to excite an electron for a given orbital [8], as illustrated for Pt in Fig. 1. These energies are element-specific, granting XAS with its chemical selectivity, and the edges are named according to the transition they describe (the more general case of core-electron spectroscopies is covered in this article's Appendix) The selection of the appropriate edge therefore allows us to measure the states we are interested in. For the 3d transition metals, this will typically mean the $L_{2,3}$ edges, and the analogous $M_{4,5}$ edges for the rare-earths. This consideration does not rule out other states, such as the K edges, as they can relay important structural information. Due to being typically unaffected by many-body effects, they are ideal when analyzing EXAFS data, which is a self-interference phenomenon [8]. Alternatively, the O K edge can complement the analysis of the transition metal L edges in a complex oxide [3].

To begin making sense of these ideas, it is important to consider where the information we get comes from. What all transitions involved in XAS have in common is that they follow Fermi's Golden Rule:

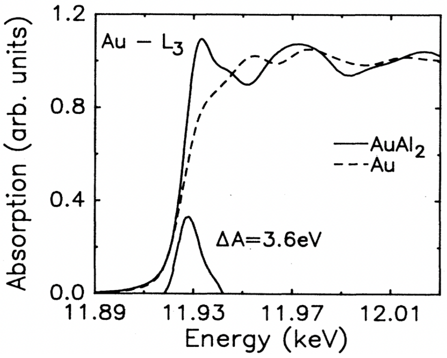

Figure 1. Au L_3 edge absorption spectra for AuAl2 and elemental Au, showing the main features of typical XAS experimental data, including the effect of short-range order. The ΔA region corresponds to further analysis, and can be ignored for our purposes. Taken from [9].

$$W_{fi} \propto \sum_q |\langle f| |\mathbf{e}_q \cdot \mathbf{r} |i\rangle |^2 \delta(E_f - E_i - \hbar\Omega) \tag{1}$$

Where W_{fi} is the transition rate between the two states, $|i\rangle, |f\rangle$ denote the initial and final states, respectively, $\hbar\Omega$ is the energy of the incoming photon, and $\mathbf{e}_q \cdot \mathbf{r}$ is the electric dipole operator. Therefore, XAS (mainly) involves dipole-allowed transitions, following the well established selection rules:

$$\Delta L = \pm 1 \tag{2}$$

$$\Delta m = \pm 1, 0 \tag{3}$$

$$\Delta S = 0 \tag{4}$$

These rules restrict the available final states, simplifying the analysis considerably. However, our discussion does not explain the presence of oscillations in the absorption spectrum, nor how the states themselves relate to the spectral shape. If the one-electron approximation is involved, one can simplify Eq. 1 by replacing $|i\rangle$ by the core electron wavefunction $|c\rangle$, and $|f\rangle$ by a free particle wavefunction $|\epsilon\rangle$, giving:

$$|\langle f| |\mathbf{e}_q \cdot \mathbf{r} |i\rangle |^2 = |\langle \epsilon| |\mathbf{e}_q \cdot \mathbf{r} |c\rangle |^2 = M^2 \tag{5}$$

Where one can safely assume that M^2 only has a small energy dependence [1] Then, the presence of the delta function in Eq. 1 means we are approximately observing the density of empty states, ρ:

$$I_{XAS} \sim M^2 \rho \tag{6}$$

At this level of approximation, the absorption spectrum should resemble the partial density of states of the $\Delta L = \pm 1$ level [1] on the absorbing site [1]. There is also a Lorentzian broadening, which derives from the finite lifetime of the observed core-hole, which amounts to an uncertainty in its energy in agreement with Heisenberg's uncertainty principle [10]. Finally, as the strength of spin-orbit coupling varies significantly depending on the atom being studied, one typically works within the J-coupling scheme. From these features, one can understand the most prominent qualities of XAS, mainly its sensitivity to the oxidation state, spin state and crystal field of the measured ion [1, 11]. Modifying either of them amounts to altering the partial density of states, and thus these changes reflect in the spectral shape. A more thorough look reveals that XAS can also study orbital effects, such as orbital ordering and Jahn-Teller effects [10].

Of course, these approximations rely on being able to treat the transition as a one-electron process, which is not the case when ions contain partially-filled d or f states. However, the one-electron picture provides a rough idea and intuition for the underlying physics in general XAS experiments. When many-body effects are prevalent in absorption spectra (and XMCD, by association), we move to the more sophisticated ligand field multiplet theory (LFMT) [11]. A brief discussion of LFMT applied to XMCD is included in section IV, where the dichroism arises as a natural consequence of the many-body effects. We are now in a position to introduce dichroism effects in X-ray absorption spectroscopy.

III. X-RAY MAGNETIC CIRCULAR DICHROISM

Dichroism implies that the absorption of light in a material is polarization-dependent [10, 11]. For circular dichroism specifically, this can happen by breaking either the inversion or time-reversal symmetries in a system. The former is known as natural circular dichroism and occurs in non-centrosymmetric systems. By XMCD we typically mean the latter effect [10], which is the focus of this work. Historically, XMCD was first predicted in 1985 [12], and observed just one year later [13].

The origin of the XMCD effect in a magnetized sample can most easily be understood in terms of a one-electron picture. In a 3d transition metal, the 2p core states are split in a $j = 3/2$ level (L_3 edge) and a $j = 1/2$ (L_2 edge) level. This corresponds to the spin and orbit

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[1] More accurately, the partial density of states in the presence of a core-hole.

angular momenta being coupled parallel and antiparallel to each other, respective (as $J \in \{|L-S|, ..., |L+S|\}$). XMCD can then be described as a two-step process. Initially, the incoming beam's helicity is parallel (antiparallel) to the 2p orbital moment. This arrangement results in the preferred excitation of electrons in the spin up (down) direction. The second step consists of the electron occupying a state in the 3d band. If there are less spin up than spin down *holes* available, the XMCD spectrum then has a net negative [2] L_3 peak, and a positive L_2 peak [10]. Taking right (μ^+) and left (μ^-) polarizations, and B as the sample magnetization, the XMCD signal can be defined as the difference spectrum between them. The process is presented in Fig. 2.

$$\Delta\mu = \mu^+(-B) - \mu^-(-B) = \mu^-(B) - \mu^+(B) \qquad (7)$$

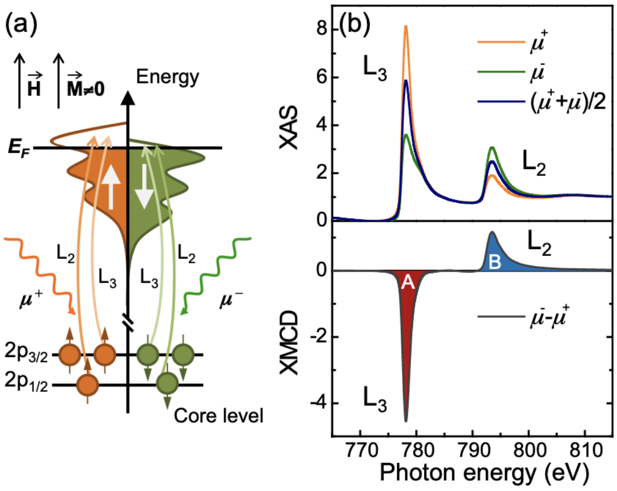

Figure 2. (a) Two-step picture for XMCD of a single-electron system in a magnetic material. Electrons from the $2p_{3/2}$ level are preferentially excited into spin up states in the 3d band, while those from the $2p_{1/2}$ level are preferentially excited into spin down states. (b) XAS and XMCD spectra for the Co $L_{2,3}$ edge, showing the right (μ^+) and left (μ^-) handed polarization, along with their sum (absorption spectrum) and the difference spectrum (XMCD). From [10].

The value of XMCD then becomes evident: it directly probes the 3d magnetic states of transition metals. This capability, in turn, opens up a variety of experimental setups. Describing them all would be well beyond the scope of this work, so we will only discuss a pair of exciting possibilities.

One aspect of XMCD that is perhaps unique amongst magnetic measurement techniques is the ability to perform element-specific magnetometry. Such studies are instrumental in systems where one wants to isolate the magnetic behaviour of each ion [14, 15]. Alternatively, this ability also allows quantification of microscopic parameters such as single-ion anisotropies or next-neighbour exchange for unconventional magnetic systems such as dilute magnetic semiconductors (DMS) [16]. These parameters can, in turn, improve existing model Hamiltonians, or point to discrepancies with them. In single crystals, a thorough description of the magnetic configuration of complex oxides becomes possible [17].

A. Experimental setup

The main hurdle in performing an XMCD experiment is obtaining a monochromatic, circularly polarized beam with sufficient intensity. In practice, this difficulty means that one is restricted to large-scale facilities such as synchrotrons [11]. In the past, another hurdle was the degree of polarization of the photon beam, as one relied in an "inclined angle view" with imperfect polarization [10]. This problem was solved with the advent of third-generation synchrotron sources, where helical or elliptical undulators provide the necessary circularly-polarized X-rays.

The rest of the experimental setup is relatively straightforward, as shown in Fig. 3. An applied magnetic field keeps the states magnetized in a non-random direction. Once impacted by the circularly polarized light, different signals can be collected that provide the desired information. While ideally one would want to measure transmission and directly relate that to absorption, that would require a sample thickness that is difficult to achieve in practice [10]. Various possibilities are available, and their discussion can be arbitrarily intricate. Here we restrict ourselves to the two most common methods. Total electron yield provides a high-quality signal, which consists of secondary electrons ejected from the sample, with the one drawback of being surface-sensitive [10]. Fluorescence yield methods, on the other hand, provide bulk-sensitive, noisier signals by measuring X-rays emitted from the sample [1, 10].

B. Selection rules in XMCD

We now know how XMCD works and what an experimental setup typically looks like. However, to analyze the data from a dichroism experiment, one must consider the spin degree of freedom's interaction with the

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[2] The correct sign of the XMCD is a matter of convention that is hotly debated. For the data analysis, however, being consistent suffices.

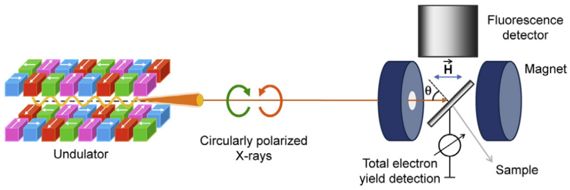

Figure 3. Experimental setup for an XMCD experiment. The circularly polarized X-rays are provided by an undulator, which then irradiates the sample, which is kept magnetized by an applied magnetic field. From [10].

transitions. XMCD therefore comes with its own set of additional selection rules. The derivation is lengthy, so it is not covered here, but extensive discussions exist [1, 10]. Typically, it invokes the Wigner-Eckart theorem and is formulated in terms of the electric multipole operator T_q^Q where Q is the rank of the transition (dipole, quadrupole, et cetera) and the Wigner 3j-symbols. The Hamiltonian now has an additional magnetic term in terms of total angular momentum $\mathbf{J}$, the applied field $\mathbf{B}$, the Bohr magneton μ_B, and g_J is the Landé splitting factor, which arises when describing J-coupled magnetic materials (for a thorough review of magnetism the reader is referred to the standard textbooks by Coey [18] and Blundell [19]):

$$H_{mag} = \mu_B(\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} = \mu_B g_J \mathbf{J} \cdot \mathbf{B} \tag{8}$$

For a transition between a final state $|J', M'\rangle$ and an initial state $|J, M\rangle$, the XMCD selection rules read:

$$\Delta J = J' - J = -Q, -Q+1, ..., Q \tag{9}$$

$$q = M' - M = -Q, -Q+1, ..., Q \tag{10}$$

These rules are the starting point for the in-depth analysis of an XMCD spectrum.

IV. LIGAND FIELD MULTIPLET THEORY

Oftentimes, the objective of XAS and XMCD experiments is to identify the oxidation states present in a given system and their ratio. Another common goal is to identify the coordination of ions in the crystal structure. These analyses are typically achieved through the simulation of spectra from model Hamiltonians. The best description for a given XMCD spectrum then depends on the nature of the sample. Perhaps unsurprisingly, most of the characteristic features of the K edges in (conventional) metallic samples can be reproduced in the one-electron picture [11]. However, we are often concerned with the 3d levels of strongly correlated systems, where many-body effects become significant, and this approximation breaks down. In such cases, we resort to multiplet theory.

When partially-filled 2p and 3d shells are present, such as in the processes involving an $L_{2,3}$ edge, the 2p and 3d wavefunctions overlap significantly. The final states can then be found by considering vector coupling of the 2p and 3d wavefunctions within the appropriate scheme [20]. By multiplet effects, we refer to the large 2p-3d integrals that happen in such systems [1]. Typically, states are coupled in an L-S (J) scheme, so they are now identified by the standard term symbols $^{2S+1}L_J$ [1]. This consideration will then lead to many possible states for a given configuration. They are now taken into account for both the initial and final states. The possibilities then increase drastically, as the degeneracy of a $2p^5 3d^N$ will have a degeneracy that is six times larger than a $3d^N$ configuration. The next step is identifying the term symbols for the degenerate states. Their relative energies are then calculated according to an electron-electron interaction [20], in terms of semi-empirical parameters related to the overlap of the 2p and 3d levels. Calculations for these from atomic Hartree-Fock (HF) theory exist, and a starting point for a model is 80% of their value (HF is known to overestimate such calculations). Importantly, the energies follow Hund's rules, and their difference accounts for the emergence of XMCD in magnetized materials. A thorough description of the parameters involved can be found in DeGroot's excellent review of multiplet effects and LFMT [20].

There is still one piece missing in the puzzle of reproducing the $L_{2,3}$ edges of the 3d transition metals. What we are missing is that we are not dealing with an atom in vacuum. We will fail if we try to simulate most such spectra up to the level of theory described before. Therefore, we resort to crystal field theory, or its more general extension, ligand field theory.

Loosely speaking, one approximates the transition metal as an isolated atom surrounded by the appropriate point charges representing its first neighbours [20]. These neighbours are typically arranged in a symmetry corresponding to some point group. The main goal becomes exploiting the results from group theory to identify the splitting of atomic energy levels. The relation of these splittings with the symmetry, and their effect on the atoms' electronic structure are well developed and understood, allowing for an elegant interpretation of the obtained results [21]. This sensitivity to the symmetry of the local environment provides XAS and XMCD with the ability to account for distortions in the crystal structure and distinguish between crystallographically inequivalent sites. Alternatively, one can also tell apart high, low, and intermediate spin states. These abilities have been exploited in the study of transition metal oxides with unconventional properties, such as the distribution of ions in spinels [6, 22], or unusual spin states in barium cobaltate [3]. An example of one such simulated spectrum is presented in Fig. 4.

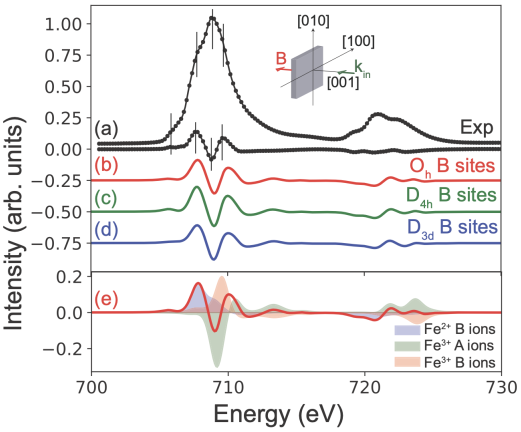

Figure 4. $L_{2,3}$ XAS and XMCD spectra for Fe_3O_4, along with multiplet calculations for different crystal fields. The individual contribution of ions to the XMCD signal is shown. Taken from [6].

V. SUM RULES

No discussion of XMCD is complete without mentioning the various sum rules that can be derived for the expectation value of the orbital and spin angular momentum of an atom. This possibility arises because the incoming radiation only interacts with the *orbital* part of the wavefunction, allowing XMCD to distinguish between the two contributions [1, 2, 10]. Generally speaking, the sum rules relate the integrated intensities of the XMCD to the spin and orbital moments of the ground state [2, 10, 23]. Importantly, they are valid for both localized and itinerant electron systems, and theory independent. Furthermore, when combined with angular-dependent studies, they allow for a thorough exploration of anisotropic magnetic properties with microscopic origins, such as magnetocrystalline anisotropy energies, magnetostriction and coercivity [10].

Sum rules are transition-specific, so different sets of them exist for the $L_{2,3}$ and $M_{4,5}$ edges. The derivations are too lengthy to include in this work, and involve several assumptions that are not necessarily valid for every system [3]. Thorough discussions of different derivations exist in several reviews and textbooks [1, 10, 11]. One such set of sum rules for the 2p3d transition (corresponding to the $L_{2,3}$ edge) can be written in terms of the right and left handed absorption, μ^+ and μ_-, the total absorption μ, and the number of holes in the 3d shell corresponding to the oxidation state of the sample, as well as the spin-quadrupole coupling T_z [2].

$$\langle L_z \rangle = 2\frac{\int \mu_+ + \mu_-}{\int \mu} \langle N_h \rangle \tag{11}$$

$$\left\langle (S_{eff})_z \right\rangle = \frac{3}{2}\frac{\int_{L_3} \mu_+ - \mu_- - 2\int_{L_2} \mu_+ - \mu_-}{\int \mu} \langle N_h \rangle \tag{12}$$

$$\left\langle (S_{eff})_z \right\rangle = \langle S_z \rangle + \frac{7}{2} \langle T_z \rangle \tag{13}$$

One issue that becomes immediately evident comes from the presence of T_z in Eq. 13. In practice, it is either assumed as zero, or previously known [1]. Fortunately, it has been shown to average to zero for powdered samples [11], increasing the applicability of the sum rules. They, therefore, provide a direct, straightforward measurement of the (average) moment of each ion. These results can then be compared with those from other techniques, such as conventional magnetometry or neutron scattering, to thoroughly characterize a material's magnetic structure.

However, one important caveat is that one must be careful when applying the sum rules to a given ion's spectrum. Several of the assumptions involved in their derivation are not always valid. Their fulfillment must then be considered before trusting any results. While some of the conditions relate to the correct experimental setup [10, 11], others pertain to specific properties of the ions under study. First of all, one must have L_3 and L_2 edges with pure $2p_{3/2}$ and $2p_{1/2}$ character, respectively [1]. Multiplet effects can mix them, leading to mixed states. Therefore, the sum rules become more accurate once one goes up the periodic table, as the states are more strongly spin-orbit split. The possibility of unevenly occupied $d_{3/2}$ and $d_{5/2}$ due to spin-orbit coupling must also be accounted for [1].

VI. CONCLUSIONS

X-ray magnetic circular dichroism (XMCD) is a powerful technique for measuring systems where a net magnetization is observed. A specialized form of X-ray absorption spectroscopy (XAS), XMCD can be measured in single crystals, polycrystals, thin films, and even molecules, making it versatile. Its chemical specificity and sensitivity to the local coordination environment of the ions have made it a valuable tool. XMCD allows the quantification of microscopic parameters of magnetic ordering in a material, by enabling experiments

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[3] In fact, this has also led to several sets of sum rules for equivalent transitions.

akin to an "element-specific magnetometer". Such experiments also distinguish between different magnetic states for the same element. XMCD coupled with XAS can also distinguish orbital ordering phenomena. Finally, the XMCD sum rules provide a straightforward way to measure the (average) spin and orbital angular momenta from each ion in the material, complementing other magnetic characterization techniques.

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Appendix: Core-level spectroscopy

One of the central principles in condensed matter physics is that the electronic properties of any material can be understood in terms of its outermost electrons. This insight motivates the division of electrons into so-called "core" and "valence" electrons. The latter, being more exposed to each atom's environment, will be strongly modified by the surrounding crystal field. Core electrons, on the other hand, lie much deeper within the atomic shell, and are thus shielded from these effects. They therefore remain mostly unchanged when we go from isolated atoms into solids. These different responses motivate the use of core electrons as a probe of the valence states of a given solid, through what we appropriately call core electron spectroscopies. XAS and XMCD fall into this category, along with other techniques. A select few are presented in Fig. 5 and loosely described in the following paragraph.

What these spectroscopies have in common is a general mechanism where one excites a core electron and studies one of its possible transitions. By starting from a state that is thoroughly understood and characterized, the effects of the unknown valence states can be singled out. Perhaps more importantly, the chemical selectivity of these techniques emerges because the energies corresponding to these transitions are unique for each element.

Of course, something must change, otherwise these techniques would all be equivalent. The variable that changes is what we *measure.* In an X-ray photoelectron spectroscopy (XPS) experiment the electron is excited to the continuum, and detected as a photoelectron. The main factors that influence the spectral shape are the charge-transfer energy (Δ) and the d-d Coulomb interaction (U_{dd}) for transition metals (the interested reader is referred to the landmark paper by Zaanen, Sawatzky and Allen [24]). In XAS, the core electron is instead excited to the conduction band, and the appropriate level of theory will depend on the measured transition. Ideally, one would want to measure the absorption, which follows a Beer law type of behaviour. Finally, X-ray emission spectroscopies (XES) are a two-particle process where the first electron's excitation induces the decay of a second one in the valence band, emitting a photon which is then measured. It is for this reason that XES provides the most information about the system. We can relate the emitted photon's frequency to the valence band electron's energy (as the core electrons are well-characterized), at the time that we get similar information to XAS. However, its signal is much weaker than XAS, so the latter is more commonly applied.

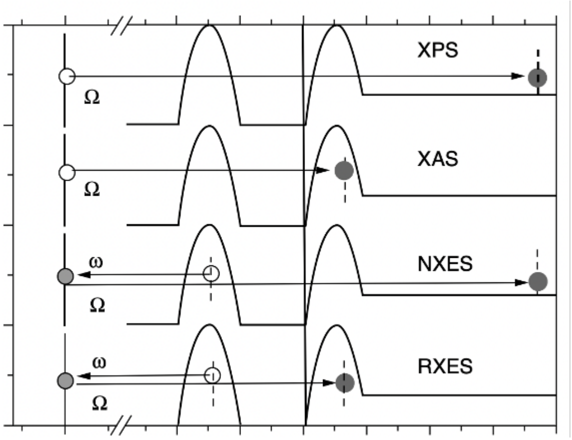

Figure 5. Schematic representation of a select few core electron spectoscopies: X-ray photoelectron spectroscopy (XPS), X-ray absorption (XAS), normal X-ray emission spectroscopy (NXES), and resonant X-ray emission spectroscopy (RXES). Taken from [1]