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Resonant inelastic x-ray scattering studies of elementary excitations

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CHAPTER 1

INTRODUCTION

The subject of this thesis is Resonant Inelastic X-ray Scattering (RIXS), which is a technique to study, amongst others, the properties of materials. This is done by making a sort of X-ray photo (called a spectrum) in a synchrotron – a huge, circular particle accelerator (with a circumference of a few hundred meters) that produces very high intensity X-rays. These X-ray spectra are compared to calculations based on various models of the material under study. This way, it is possible to falsify the models.

An important category of materials that are often investigated with RIXS are the strongly correlated electron materials. To this class belong, for instance, the high critical temperature superconductors that can conduct an electrical current without resistance when they are cooled below the so-called critical temperature. In this thesis, we calculate and discuss the RIXS spectra for various models of a range of strongly correlated electron materials, each with its own special properties.

1.1 Resonant Inelastic X-ray Scattering (RIXS)

1.1.1 What is RIXS?

RIXS is an X-ray ‘photon in – photon out’ technique, meaning that one irradiates a sample with X-rays, and observes the scattered X-ray photons. In RIXS, one is only interested in processes in which the photons lose energy (and momentum) to the sample, leaving it in an excited state. Hence the ‘inelastic’. RIXS is a resonant technique, meaning that the energy of the incident photons corresponds

to a certain resonance in the system: an electron from a deep-lying atomic core state is promoted to an empty state around the Fermi level. An example is the atomic $1s \rightarrow 4p$ transition in Cu^{2+} ions. After a very short time, the hole in the core levels (the so-called core hole) is filled by the same or another electron, producing the outgoing X-ray photon.

The quantities one measures in RIXS are the momentum and energy of the outgoing photons. Because the energy and momentum of the incident photons can be chosen by the experimentalist, one can deduce what energy and momentum were left behind in the sample, using conservation laws. Thus RIXS enables one to measure the dispersion of excitations. In principle, it is also possible to measure the outgoing photon's polarization, although this has rarely been done in practice yet [1]. It would provide additional information on the type of excitations that are created in the RIXS process. Basically all excitations of solids can be probed by RIXS, ranging from charge, spin, orbital and lattice excitations to exotic mixed spin-orbital ones. In principle, the only constraint is that the excitations should be overall charge-neutral, as no electrons are added to or removed from the system.

One might wonder what the advantage is of tuning to a resonance, because the theoretical treatment of resonant scattering processes is much more complicated than non-resonant ones. A big advantage is that at resonance, the cross section is enhanced by many orders of magnitude. Choosing a resonance also gives control over where in the unit cell excitations are made. Further, the more complicated scattering process enables one to probe more types of excitations, like magnetic ones.

Comprehensive overviews of RIXS can be found in Refs. [2] and [3]. Much of this chapter is published in the latter work.

1.1.2 Direct and indirect RIXS

Excitations can be made in two distinct ways, which are called *direct* RIXS and *indirect* RIXS. Direct RIXS is the simplest of the two: a core electron is excited into the valence band, and then an electron from another valence state fills the core hole, emitting an outgoing X-ray photon. The process is illustrated in Fig. 1.1. The RIXS process creates a valence excitation with momentum $\hbar\mathbf{k} - \hbar\mathbf{k}'$ and energy $\hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'}$, where the primed quantities refer to the outgoing photon and the unprimed ones to the incoming photon.

Indirect RIXS has one extra step compared to direct RIXS: in the intermediate state, the valence electrons scatter off the core hole. This leads to excitations of the valence electrons. When the core hole decays, the system is left in an excited state. This process is shown in Fig. 1.2. The interaction is mediated either by the Coulomb force of (mainly) the localized core hole, or by the Pauli exclusion principle. The latter interaction occurs when the photo-excited electron blocks the movements of the valence electrons. Typically, the photo-excited electron ends up far above the Fermi level and acts as a spectator, *i.e.*, it does not interact

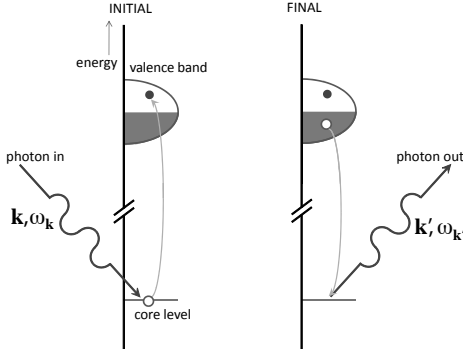


Figure 1.1: In the direct RIXS process the incoming X-ray photon excites an electron from a deep-lying core level into an empty valence level. The empty core state is then filled by an electron from the occupied valence states under the emission of an X-ray. Figure reproduced with permission from Ref. [3].

strongly with the valence electrons [4, 5].

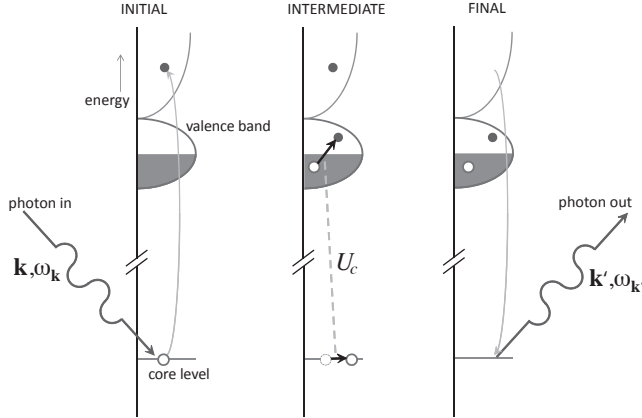


Figure 1.2: In an indirect RIXS process, an electron is excited from a deep-lying core level into the conduction band. Excitations are created through the Coulomb interaction U_c between the core hole (and in some cases the photo-excited electron) and the valence electrons. In chapter 4, we show that the interaction can also be the consequence of the Pauli exclusion principle. Finally, the core hole is filled by the photo-excited electron. Figure reproduced with permission from Ref. [3].

1.1.3 Features and limitations of RIXS

RIXS has a number of features that set it apart from other spectroscopic techniques like Angle-Resolved Photo-Emission Spectroscopy (ARPES) and inelastic neutron scattering:

1. RIXS measures the *energy and momentum dependence* of excitations in a

large part, or even all, of the Brillouin zone. This comes about because X-ray photons have a very high energy and momentum, in contrast to optical photons (see Sec. 1.1.4). Therefore, the available phase space for RIXS experiments is huge compared to many other probes.

2. *Polarization sensitivity.* In principle, it is possible to measure the outgoing photon's polarization. This has rarely been done in practice yet [1], though the incident photon's polarization is frequently varied. One can make use of various polarization-related selection rules to characterize the symmetry and nature of the excitations. It is important to note that a polarization change of the photon is related to an angular momentum change. Conservation of angular momentum ensures that any angular momentum lost by the scattered photons has been transferred to the excitations in the solid.
3. *Chemical specificity.* Varying the energy of the incident photons, it can be tuned to different resonances, and one can choose which core electron to excite to which valence orbital. The different resonances are called 'edges'¹. This makes RIXS not only element-specific, but also orbital-specific. Further, it is possible to tune the incident photons to chemically inequivalent ions, like in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, where one can probe either occupied or unoccupied copper ions, see Sec. 4.6. This is possible only if the two chemically inequivalent sites are resolvable in the X-ray absorption spectrum.
4. *Bulk sensitivity.* The penetration depth of X-rays depends strongly on their energy. This depth can be of the order of a few μm in the hard x-ray regime (*i.e.*, around 10 keV) and of the order of 0.1 μm in the soft x-ray regime (around 1 keV). This makes RIXS bulk-sensitive: in general, the scattering takes place far away from the surface of the sample.
5. *Small sample volume.* Compared to neutron scattering, X-ray scattering experiments need only very tiny samples. This is because neutron sources produce much less particles per second per m^2 than X-ray synchrotrons. Further, the interaction of neutrons with the sample is much weaker than that of X-rays. That RIXS needs only very small samples enables one to study nano objects or materials that can only be grown in thin films.

There are also a number of limitations to RIXS:

1. The experiments require *many incident photons* to collect enough scattered photons in a reasonable time. Higher energy and momentum resolutions require more time.

¹The edges are labelled according to the core electron that is excited: promoting an electron with principal quantum number $n = 1$ is called the K edge, $n = 2$ is called the L edge, $n = 3$ M edge, etc. [6]

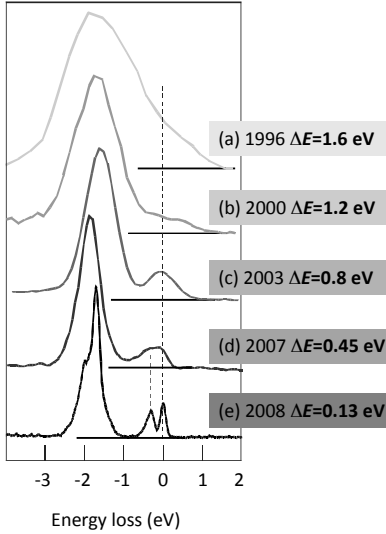
RIXS spectra of La_2CuO_4 at Cu L_3 edge

Figure 1.3: Progress in RIXS resolution at the Cu L edge (931 eV). (a) Ichikawa *et al.* [7], BLBB @ Photon Factory (b) Duda *et al.* [8], I511-3 @ MAX II, (c) Ghiringhelli *et al.* [9], AXES @ ID08, ESRF (d) Braicovich *et al.* [10], AXES @ ID08, ESRF (e) Braicovich *et al.* [11], SAXES @ SLS. Figure by G. Ghiringhelli and L. Braicovich, reproduced with permission.

2. *Energy resolution.* Because there is a huge difference between the energy scale of the X-ray photons and the energy scale of the elementary excitations we are interested in, a tremendous resolving power is needed for RIXS experiments. For example, at the $\text{Cu}^{2+} 1s \rightarrow 4p$ transition (corresponding to roughly 9 keV) the resolving power needs to be 10^5 in order to get an energy resolution of 90 meV. For a long time, RIXS has been limited to energy resolutions of the order of 1 eV. However, recent progress in RIXS instrumentation has been dramatic and this situation is now changing, see Fig. 1.3.

Note that these two limitations are not independent of each other: a low photon flux can be one of the factors that limit the energy resolution. (Other factors that play a role are, *e.g.*, the instrument's spectrometer or the distribution of the energy of the incident photons.)

1.1.4 Comparison to other spectroscopies

When one wants to probe the properties of solid state systems, there are many spectroscopies available, each with its own advantages and disadvantages. In this section we briefly outline the contrasts of RIXS with some of the more established experimental techniques of condensed matter physics. We restrict ourselves to spectroscopies that do not change the total charge of the system.

- IXS. The term inelastic X-ray scattering (IXS) is reserved for non-resonant processes where the photon scatters inelastically by interacting with the

charge density of the system. IXS does not involve core holes to excite the system. It measures the dynamics charge structure factor $S(\mathbf{q}, \omega)$.

- XAS. X-ray absorption spectroscopy (XAS) is the first step of the RIXS process: an electron is excited from a core orbital to an empty state, above the Fermi level. A common way to measure X-ray absorption is to study the decay products of the core hole that the absorbed X-ray has created, either by measuring the electron yield from a variety of Auger and higher-order processes (known as electron yield) or by measuring the radiative decay (fluorescence yield). The total fluorescence yield corresponds approximately to the integration of all possible RIXS processes.
- Raman scattering. Raman scattering with optical or UV photons is confined to zero momentum transfer because of the low energy of these photons². It is still possible to probe elementary excitations with non-zero momentum $\hbar\mathbf{k}$ in an indirect way by exciting two of them: one with momentum $+\hbar\mathbf{k}$ and one with $-\hbar\mathbf{k}$. This is done in, for instance, bimagnon Raman scattering in the high- T_c cuprates. An advantage of Raman scattering over RIXS is its energy resolution, which not only makes it possible to probe excitations at very low energies, but also resolve their line shapes. Optical Raman scattering can be employed at resonance as well, although it is restricted to resonances up to a few eV due to the low energy of the optical photons.
- Inelastic neutron scattering. The dispersion of neutrons in free space is $E = (\hbar\mathbf{k})^2/2m$ where $m = 1.67 \cdot 10^{-27}$ kg. To reach the Brillouin zone boundary at momentum $\hbar k \approx 1 \text{ } \hbar\text{\AA}^{-1}$, the neutrons need to have an energy of at least $E \approx 2.1$ meV. This is a problem for probing excitations at the energy scale of 1 eV, some two orders of magnitude larger than the energy carried by neutrons with momenta corresponding to the inverse lattice parameter. High energy neutrons pass through the crystal very fast, reducing the already small neutron cross section. Further, spin-1/2 neutrons can transfer 0 or 1 unit of angular momentum to the system, while spin-1 photons can also probe $\Delta J_z = 2$ final states.
- EELS. The Electron energy loss spectroscopy (EELS) cross section is determined by the charge structure factor $S(\mathbf{q}, \omega)$ of the system under study [12, 13] and is, therefore, closely related to IXS and RIXS (see chapter 3). It is an electron-in electron-out process. The EELS intensity is limited due to space charge effects in the beam. It has the advantage that

²Visible light has a wave length of $\lambda \approx 500$ nm, and therefore carries momentum $\hbar k = 2\pi\hbar/\lambda \approx 1.3 \cdot 10^{-3} \text{ } \hbar\text{\AA}^{-1}$. At the edge of the Brillouin zone, the momentum is typically $\pi\hbar/a \sim 10^{10} \text{ } \hbar\text{m}^{-1} \approx 1 \text{ } \hbar\text{\AA}^{-1}$ (assuming a lattice constant $a \approx 3 \text{ } \text{\AA}$). Therefore, Raman scattering experiments can only probe the center of the Brillouin zone. For comparison, the photon energy necessary to probe this Brillouin zone boundary is approximately $\hbar ck \approx 2.0$ keV.

it is very sensitive for low momentum transfers, but its intensity rapidly decreases for large momentum transfers. Further, at large momentum transfer, multiple scattering effects become increasingly important, making it hard to interpret the spectra above $\sim 0.5 - 1.0 \text{ \AA}^{-1}$. Since momentum resolved EELS is measured in transmission, it requires thin samples. Measurements in the presence of electromagnetic fields are not possible due to their detrimental effect on the electron beam. There are no such restrictions for X-ray scattering.

1.1.5 General features of RIXS spectra

Most RIXS spectra have a number of features in common: almost all have an elastic peak, *i.e.*, scattered photons with zero energy loss. Next to the elastic peak, there is the inelastic spectral weight, in which one is ultimately interested because it gives information about the energy and momentum of the excitations of the material. Then, there is the question of normalization of the data, which comes up in every RIXS study. In the next chapters of this thesis, the inelastic features are extensively discussed. Here, we will briefly touch upon the elastic line and the normalization.

Elastic line. Elastic scattering obscures the low energy excitations in many RIXS experiments. For instance, at the transition metal K and M edge, the elastic line is huge compared to the low energy inelastic features [14, 15].

The amplitude for elastically scattering a photon from wave vector $\mathbf{k}$ to $\mathbf{k}'$, starting from a source at position $\mathbf{r}_a$ and scattering from an ion at position $\mathbf{r}$ to the detector at position $\mathbf{r}_b$, is composed of three parts. First, the amplitude to go from the source to the scattering ion is³ $e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_a)}$. Second, the amplitude of the scattering event itself, including both resonant and non-resonant scattering, is denoted by the complex number ζ . Third, the amplitude to go from the ion to the detector is $e^{i\mathbf{k}'\cdot(\mathbf{r}_b-\mathbf{r})}$. Multiplying all amplitudes, we get a total scattering amplitude of $\zeta e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}_a + i\mathbf{k}'\cdot\mathbf{r}_b}$. The second exponential does not depend on the position of the scattering ion, and it may be absorbed in ζ .

RIXS is a coherent process, which means that an incident photon can be absorbed at any of the N equivalent sites i of the solid, and all these processes interfere. The total elastic scattering amplitude is therefore

$$\mathcal{F}_{\text{el}} = \frac{1}{N} \sum_i \zeta_i e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i}. \quad (1.1)$$

In the case of a perfect crystal, all ζ_i are equal, resulting in Bragg peaks: $\mathcal{F}_{\text{el}} = \zeta \sum_{\mathbf{G}} \delta_{\mathbf{q},\mathbf{G}}$ where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and $\mathbf{G}$ is a reciprocal lattice vector. For transferred momenta away from Bragg conditions, there is no elastic line. Note that this is a general statement, independent of the details of the scattering process. The

³We discard the modulus of this amplitude because it is irrelevant to the calculation.

question therefore is not why transition metal L edges have a small elastic line, but why it is big at the K and M edges (see, *e.g.*, Refs. [11, 14, 15]).

One reason could be that the huge observed elastic peaks are not truly elastic peaks, but rather consist of low energy excitations, like phonons, that cannot be resolved from the true elastic signal [3]. There is evidence for this from high resolution measurements at the Cu K edge of CuO₂ by Yavaş *et al.* [16].

Elastic scattering can also be seen away from Bragg conditions for crystals with imperfections. There are many ways for crystals to be imperfect:

- N does not go to infinity, for example, because the X-ray beam illuminates only a finite volume, or some ions are missing. When the sample is a very smooth slab of finite thickness (say n ions), crystal truncation rods appear: the Bragg peaks broaden in the direction perpendicular to the slab as $2/nq_{\perp}^2$ where n is the thickness (in number of layers) and $q_{\perp}$ is the transferred momentum perpendicular to the surface, measured from the Bragg peak [17]. Taking into account the penetration depth gives a similar effect.
- Thermal motion, defects or inhomogeneities, strain, etc. cause the ions to go out of their equilibrium position: $\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i$, where $\mathbf{u}_i$ is the displacement from the equilibrium position $\mathbf{R}_i$. For small, uncorrelated displacements in an otherwise perfect crystal, one finds to order $\mathcal{O}(\langle \mathbf{u}^2 \rangle)$:

$$\langle I_{\text{el}}(\mathbf{q}) \rangle = \sum_{\mathbf{G}} \delta_{\mathbf{q}, \mathbf{G}} \left(1 - \frac{1}{3} \langle \mathbf{u}^2 \rangle \mathbf{G}^2 \right) + \frac{1}{3N} \langle \mathbf{u}^2 \rangle \mathbf{q}^2 \quad (1.2)$$

where $\langle \dots \rangle$ denotes an average over many experiments, assuming that the lattice moves a lot over the course of the experiment. Spectral weight is transferred from the Bragg peaks to other parts of the Brillouin zone. The elastic scattering away from Bragg conditions increases with $\mathbf{q}^2$, and is therefore expected to be strongest at the high energy edges [18].

- $\zeta_i \neq \zeta_j$. When one ion's electronic structure is different, the amplitude for scattering a photon changes. When the change is periodic, as in typical resonant (elastic) X-ray scattering experiments, this generates additional elastic peaks away from the Bragg peaks.

Normalization. The theoretical calculations of RIXS cross sections presented in this thesis are often given in arbitrary units. For current experiments, this suffices because one cannot measure the cross section on an absolute scale. Even comparing spectra at different transferred momenta is difficult because the scale might not be the same. There are two main factors that set the intensity scale in experiments:

- Self-absorption. A scattered photon might be absorbed a second time by the sample. Since the vast majority of core hole decay processes are through

Auger or fluorescence channels, self-absorption attenuates the RIXS intensity. The longer the path of the scattered photons through the sample is, the stronger is the attenuation. Self-absorption is $\mathbf{q}$ dependent because different $\mathbf{q}$ generally have different scattering geometries, meaning exit paths of different lengths. Self-absorption can be corrected for, see for example Ref. [4].

- Irradiated volume. The cross section scales with the irradiated part of the sample volume: if a photon meets more ions, that increases the probability of scattering. The irradiated volume is not easily determined because of the penetration depth (which depends on, amongst others, polarization), beam profile, surface effects, etc. In practice, correcting for the effects that determine the irradiated volume is very difficult.

Further, variations in the beam's intensity can also play a role. Obtaining experimental RIXS spectra on an absolute intensity scale is thus near-impossible, making comparison of spectra at different $\mathbf{q}$ a complicated affair. If one wants to compare the intensities at different $\mathbf{q}$, one has to normalize the data in one way or another. There are several options:

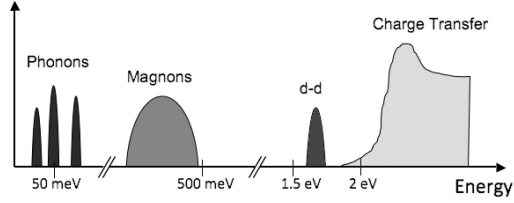
- Normalization to acquisition time. This is the simplest approach, which basically ignores the normalization problems. In experiments on thin films, however, this might be a viable approach since the penetration depth and beam size can be larger than the sample, reducing the uncertainty in the irradiated volume. Note that self-absorption and variations in the beam intensity should be corrected for in this approach.
- Normalization to well-known features. If one of the features in the experimental RIXS spectra is very well understood, it can be used as a reference for normalization. In experiments at the Cu L edge of cuprates, for example, the line shapes of the dd excitations are reproduced very well by theory [19, 20], and one can normalize the data to the spectral weight of the dd excitations [21].

1.2 Excitations of strongly correlated systems

In this thesis, we investigate how numerous types of excitations show up in RIXS spectra. The types of excitations that one encounters in this thesis are briefly reviewed here. The focus is on strongly correlated systems. Fig. 1.4 schematically indicates the energy scales of the excitations.

Charge transfer excitations. In a Mott insulator, the electrons are distributed over the ions of the material in such a way to minimize Coulomb repulsion between them. The electrons are very much localized: because of their

Figure 1.4: Approximate energy scales of different excitations in condensed matter systems. Reproduced with permission from Ref. [3].



large Coulomb repulsion, they block each other's way. On top of this ordering, one can create charge transfer excitations: an electron is transferred from one type of ion to another. The energy scale of such an excitation is set by the intra-ionic Coulomb repulsion, which can be several eV in typical Mott insulators, and the on-site energies of the different ions [22]. Charge excitations across the Mott gap between ions of the same type are very similar; only the energy scale is different. In chapter 3, we study the RIXS spectra of, amongst others, a single-band Hubbard model, and find that the cross section is proportional to the dynamical charge response function $S(\mathbf{q}, \omega)$ for spinless fermions, a model applicable to many doped cuprates. Charge transfer excitations are interesting by themselves, and in addition they can provide us with the parameters of the high energy theories of solids (*e.g.*, the Hubbard model's t and U), who in turn determine the parameters of the effective low energy theories.

Orbital excitations. Many strongly correlated systems exhibit an orbital degree of freedom, that is, the valence electrons can occupy different sets of orbitals. Orbital active ions are also magnetic: they have a partially filled outer shell. The orbital degree of freedom determines many physical properties of the solid, both directly, and because the orbitals couple to other degrees of freedom. For instance, the orbital's charge distribution couples to the lattice, and according to the Goodenough-Kanamori rules for superexchange the orbital order also determines the spin-spin interactions. The orbitally active ions can couple to each other via the lattice or via superexchange interactions. Both can drive the system into an orbitally ordered state.

Orbital excitations appear in many different forms. They all have in common that they involve a transition of an electron from one orbital to another, on the same ion. In some materials, the crystal field is very large, and the orbitals are split by ~ 1 eV. The transitions between the crystal field levels are called dd excitations (in transition metal compounds, the 3d levels are the orbitally active levels, hence the name). In highly symmetric materials, the crystal field splitting is small and the orbital dynamics are dominated by superexchange interactions between neighboring ions. In this case, collective orbital excitations arise. These excitations, called orbitons, are the main subject of chapter 5. The energy scale of orbitons is thus set by superexchange interactions, which can be as large as 250 meV.

Magnetic excitations. Many transition metal compounds contain magnetic ions, whose outer shell is only partly filled. The magnetic moments of these ions often interact with each other, and this can result in magnetic order: the global spin rotation symmetry in the material is broken. As a result, characteristic collective magnetic excitations emerge. These quasiparticles (*e.g.*, magnons and spinons), and the interactions between them determine all low temperature magnetic properties. Magnon energies can extend up to ~ 0.4 eV (*e.g.*, in cuprates) and their momenta up to $\sim 1 \hbar \text{\AA}^{-1}$, covering the entire Brillouin zone. Melting of the long-range ordering, for instance through the introduction of mobile charge carriers in a localized spin system or by the frustration of magnetic interactions between the spins, can result in the formation of spin-liquid groundstates. Spin liquids potentially have elusive properties such as high-temperature superconductivity or topological ordering.

In most transition metal compounds, the magnetic interaction is governed by superexchange, which yields an isotropic, Heisenberg form of the interaction between neighboring spins. Alternatively, spin ice compounds [23] with their huge magnetic moments also have magnetic dipole-dipole interactions, leading to an Ising interaction. Often, the strength of a magnetic bond is determined by the involved orbitals, as described above.

Combined spin-orbital excitations. When the crystal field forces the orbitals to order, the magnetic degrees of freedom are usually still active: the magnetic and orbital degrees of freedom are separated. Alternatively, when the crystal field is weak, the spin and orbital degrees of freedom can become intertwined. This can happen, for example, via Kugel-Khomskii superexchange interactions [24] or via intra-ionic, relativistic spin-orbit coupling [25]. The energy scale of the excitations of these models is set, respectively, by the superexchange interaction ($\sim 50 - 500$ meV) and by the relativistic spin-orbit coupling (~ 400 meV in the late transition metals).

Phonons. Excitations of the lattice are found at low energies (10 – 100 meV), comparable to the present state-of-the-art energy resolution of RIXS experiments. The spatial arrangement of the lattice is adapted to minimize the total Coulomb energy of the system. Lattice displacements can be induced by changes in the distribution of the electrons of the solid, as the ions are charged as well. The quanta of lattice displacement modes are called phonons. Phonons are crucial for many properties of condensed matter, ranging from sound propagation to superconductivity.

1.3 This thesis

Now that we have given a general introduction to RIXS, how it works, and what it can measure, we will proceed with the theory of RIXS in chapter 2. The

basic formula for the RIXS cross section (the Kramers-Heisenberg formula) is (re-)derived and discuss in detail the approximation scheme used often in this thesis: the Ultra-short Core hole Lifetime (UCL) expansion. In the following chapters, we set out to investigate how RIXS probes the various excitations discussed above. Chapters 3, 4, 5, 6, and 7 deal with charge, magnetic, orbital, combined spin-orbital and lattice response, respectively. Finally, we conclude this work with an outlook in chapter 8.