Theory of resonant inelastic X-ray scattering by collective magnetic excitations

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Resonant Inelastic X-ray Scattering (RIXS) has seen an amazing experimental improvement over the last ten years [1]. Both the resolution as well as the yield have improved by more than one order of magnitude. With this unbelievable progress in mind it is therefore to be expected that this technique will soon evolve into a well-established method to measure all kind of low lying excitations and their dispersions [2–4]. In many respects the technique is comparable to neutron scattering, whereby each technique has its own reason for existence.

The theoretical understanding of the RIXS spectral function is quite complicated. For low energy excitations like magnons, orbitons or inter-band transitions one needs a theory including the full momentum dependence of these excitations. At the same time for the description of the intermediate state it is required to include the full local many body interactions. The local problem can be solved with the use of Multiplet Ligand Field Theory (MLFT) or an Anderson Impurity Model. For dispersing low energy states one needs a model on an infinite lattice and useful solutions in k-space can be obtained. There is no theory that can include full many body interactions on an infinite lattice and a good understanding of RIXS might therefore seem hopeless.

Here I present a solution to this problem [5]. The calculation of the RIXS spectral function can be factorized in two parts that each can be solved by very different but appropriate models: 1) The low energy dispersing Green's function can be calculated with the use of for example linear spin-wave theory. 2) The transition matrix can be factorized into local operators multiplied by fundamental X-ray Absorption Spectra (XAS), like the magnetic linear (XMLD) and circular (XMCD) dichroic spectra. The XAS can either be measured or calculated using models that are very different from the ones used to calculate the dispersing magnon excitation spectra. The current theory

greatly simplifies the interpretation of RIXS as it provides clear selection rules. These selection rules lead to the amazing result that RIXS can excite single magnons with a scattering intensity proportional to the XMCD absorption spectra. The conservation of spin momentum is broken by relativistic spin-orbit coupling (SOC). The cross section to excite single magnons is large at excitonic resonant edges that have a strong core-hole spin-orbit coupling. These are especially the transition metal (TM) L-edge as well as the rare earth (RE) M-edge. The current theoretical work for the first time allows for a full description of the resonant energy dependence, the polarization dependence, as well as the momentum-dependent intensity and energy, of magnetic excitations in transition metal and rare earth compounds.

I will start the derivation with the Kramers-Heisenberg formula for the differential cross section:

$$\frac{\delta^2\sigma}{\delta\Omega\,\delta\omega} = \sum_f \left| \langle f | T_{\varepsilon_o}^\dagger \frac{1}{\omega_i + E_i + \iota\Gamma/2 - H} T_{\varepsilon_i} | i \rangle \right|^2$$
$$\delta(\omega_i - \omega_o + E_i - E_f) \tag{1}$$

with i (f) labeling the set of initial (final) states, E the energy, H the Hamiltonian, Γ the life-time broadening, $\omega_{i(o)}$ the photon energy of the incoming (outgoing) photon, $\varepsilon_{i(o)}$ the polarization of the incoming (outgoing) photon and finally T_ε the optical transition operator given by the perturbation of the photon field on the system $T_\varepsilon = \vec{p} \cdot \vec{A}$. For core level spectroscopy T_ε can be rewritten as a Fourier transform of local transitions:

$$T_\varepsilon = \sum_j e^{\iota\vec{k}\cdot\vec{r}_j} \vec{p}_j \cdot \vec{A}_j = \sum_j e^{\iota\vec{k}\cdot\vec{r}_j} T_{j,\varepsilon} \tag{2}$$

with $\vec{k}$ the photon wavevector, j a sum over all atoms, $\vec{r}_j$ the position of atom j and $\vec{p}_j$ ($\vec{A}_j$) the momentum operator (photon vector field) expanded around atom j.

$T_{j,\varepsilon}$ ($T^{\dagger}_{j',\varepsilon}$) creates (annihilates) a core hole at site j (j'). For core level spectroscopy one can assume that the core hole does not hop from one site to another. The site where the core hole is created, j, is thus the same as the site where the core hole is annihilated, j'. The transition operator connecting the initial and the final state can be rewritten as the Fourier transform of a local transition operator:

$$R^{\varepsilon_i\varepsilon_o} = \sum_j e^{\imath\vec{q}\cdot\vec{r}_j} R_j^{\varepsilon_i\varepsilon_o} \tag{3}$$

with $R_j^{\varepsilon_i\varepsilon_o} = T^{\dagger}_{j,\varepsilon_o}(\omega_i + E_i + \imath\Gamma/2 - H)^{-1} T_{j,\varepsilon_i}$ and $\vec{q} = \vec{k}_i - \vec{k}_o$. Inserting this in the Kramers Heisenberg formula and rewriting the RIXS differential cross section in the spectral representation as $(\delta^2\sigma)/(\delta\Omega\,\delta\omega) = -\Im[\chi_R]$ gives:

$$\chi_R(\vec{q},\omega) = \sum_{j,j'} e^{\imath\vec{q}\cdot(\vec{r}_j - \vec{r}_{j'})} \tag{4}$$
$$\times \langle i|(R_{j'}^{\varepsilon_i\varepsilon_o})^{\dagger} \frac{1}{\omega + E_i + \imath\Gamma/2 - H} (R_j^{\varepsilon_i\varepsilon_o})|i\rangle,$$

with $\omega = \omega_i - \omega_o$.

The final state Green's function

$$(1/(\omega + E_i + \imath\Gamma/2 - H)),$$

which describes the magnons, can be calculated in k-space on an infinite lattice using linearized spin-wave theory or any other more involved method available. The transition matrix $R_j^{\varepsilon_i\varepsilon_o}$ is a local object that describes the probability to make low energy transitions at and around site j. It is given by the X-ray absorption Green's function matrix

$$(T^{\dagger}_{j,\varepsilon_o}(\omega_i + E_i + \imath\Gamma/2 - H)^{-1} T_{j,\varepsilon_i})$$

and can therefore be calculated with the same methods as used successfully for X-ray absorption. The calculation of $R_j^{\varepsilon_i\varepsilon_o}$ can be done by approximating the X-ray absorption spectra of the entire solid by the absorption spectra of a cluster and the use of numerical methods. At strong excitonic resonant edges like the TM $L_{2,3}$ edge or RE $M_{4,5}$ edge, $R_j^{\varepsilon_i\varepsilon_o}$ will only depend on low energy operators acting on site j. For other resonant edges, whereby the intermediate state is less localized, also operators acting on neighboring sites of site j will become important. In general not more then a few sites will contribute as, in the resonant process, the core hole has to be both created and annihilated at the same site j.

Normally one is not interested in all possible low energy excitations. In this work I will focus on magnetic excitations, but a similar formalism is possible for orbital transitions as well. One can down-fold the full Green's-function matrix $R_j^{\varepsilon_i\varepsilon_o}$ to a basis that contains the ground state and the important transitions with respect to the ground state. In the current case these are states with different spin configurations. Using this basis one can rewrite the resulting Green's-function matrix as fundamental X-ray absorption spectra multiplied by spin-operators. In spherical symmetry and including only local spin operators acting on site j one finds:

$$R_j^{\varepsilon_i\varepsilon_o} = \sigma^{(0)}\varepsilon_i \cdot \varepsilon_o^* + \frac{\sigma^{(1)}}{s}\varepsilon_i \times \varepsilon_o^* \cdot S$$
$$+ \frac{\sigma^{(2)}}{s(2s-1)}\left(\varepsilon_i \cdot S\,\varepsilon_o^* \cdot S + \varepsilon_o^* \cdot S\,\varepsilon_i \cdot S - \frac{2}{3}\varepsilon_i \cdot \varepsilon_o^* S^2\right) \tag{5}$$

whereby $\sigma^{(0)}$ is the numerical value of the isotropic complex optical conductivity at the resonant edge, $\sigma^{(1)}$ ($\sigma^{(2)}$) the fundamental XMCD (XMLD) spectra, S is the spin operator and s the expectation value $\langle S^2 \rangle = s(s+1)$. The fundamental spectra are those spectra measured at $0\,\text{K}$ assuming full magnetization. For real crystals the local point-group has to be included. This leads to operators in higher order of S and the fundamental spectra branch according to their irreducible representation [6]. Equation (5) leads to beautiful simple selection rules: One can measure single spin-flip transitions with cross polarized light for spins in the plane of the polarizations. The operator quadratic in S can lead to single ($\Delta S_i = 1$) and double ($\Delta S_i = 2$) spin-flip transitions as well as contributions to the elastic line. For $S = 1$ systems $\sigma^{(2)}$ is zero by symmetry simplifying the RIXS transition operator.

In order to clarify the method I present calculations of RIXS spectra at the $L_{2,3}$ edge of samples containing Cu^{2+} in D_{4h} symmetry and Ni^{2+} in O_h symmetry. Away from spherical symmetry it is often more transparent to write $R_j^{\varepsilon_i\varepsilon_o}$ as a 3×3 tensor whose elements depend on the polarization of the incoming and outgoing light. In such a matrix notation $R_j^{\varepsilon_i\varepsilon_o}$ for Cu^{2+}, a $S = 1/2$ system in tetragonal symmetry, becomes:

$$R_j^{\varepsilon_i \varepsilon_o} = \varepsilon_o^* \cdot \begin{pmatrix} \sigma_{a_{1g}^B}^{(0)} & 2S_z\sigma_{a_{2u}}^{(1)} & -2S_y\sigma_{e_u}^{(1)} \\ -2S_z\sigma_{a_{2u}}^{(1)} & \sigma_{a_{1g}^B}^{(0)} & 2S_x\sigma_{e_u}^{(1)} \\ 2S_y\sigma_{e_u}^{(1)} & -2S_x\sigma_{e_u}^{(1)} & \sigma_{a_{1g}^A}^{(0)} \end{pmatrix} \cdot \varepsilon_i$$

The fundamental spectra of Cu^{2+} determining the RIXS transition at the $L_{2,3}$ edge can be seen in the left panel of Fig. 1. They show a striking feature; the $\sigma_{a_{1g}^A}^{(0)}$ and $\sigma_{e_u}^{(1)}$ spectra are zero. This is a direct consequence of having only one hole with x^2–y^2 symmetry in which one can not excite a p electron with z polarized light. For RIXS this means one can not measure spin-flip excitations for Ising spins oriented perpendicular to the $d_{x^2-y^2}$ orbital. For real systems single magnon excitations will always be measurable as $S = 1/2$ fully aligned Ising spins never exist in a solid.

In the previous paragraph, the form factor of local spin-flips in the cuprates excited with RIXS is discussed. In order to calculate spectra one needs to include the momentum dispersion. This can be done in a convenient way with the use of linearized spin-wave theory. In the bottom panels of Fig. 2 I show the spectral function as one could measure with RIXS in the cuprates. I show calculations for a 1D chain, 2D square and 3D cubic lattice with nearest

neighbor interactions. One finds that the intensity goes to zero at Γ and diverges at the antiferromagnetic Bragg peak. This is a well-known behavior for collective excitations. One should notice that for almost all cuprates one can not reach the entire Brillouin zone at the Cu $L_{2,3}$ edge due to the short wavelength at the resonant energy.
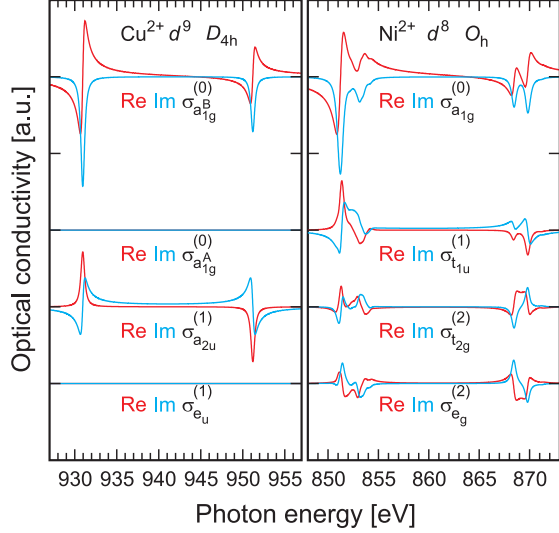
Figure 1: Fundamental X-ray absorption spectra that enter in the RIXS transition operator as energy-dependent complex matrix elements calculated for Ni^{2+} and Cu^{2+}.

For Ni^{2+} in cubic symmetry (a $S = 1$ system) the resonant inelastic scattering transition matrix becomes:

$$R_j^{\varepsilon_i \varepsilon_o} = \varepsilon_o^* \cdot \begin{pmatrix} \sigma_{a_{1g}}^{(0)} + 2(S_x^2 - \frac{1}{3}S^2)\sigma_{e_g}^{(2)} & S_z\sigma_{t_{1u}}^{(1)} + (S_xS_y + S_yS_x)\sigma_{t_{2g}}^{(2)} & -S_y\sigma_{t_{1u}}^{(1)} + (S_zS_x + S_xS_z)\sigma_{t_{2g}}^{(2)} \\ -S_z\sigma_{t_{1u}}^{(1)} + (S_xS_y + S_yS_x)\sigma_{t_{2g}}^{(2)} & \sigma_{a_{1g}}^{(0)} + 2(S_y^2 - \frac{1}{3}S^2)\sigma_{e_g}^{(2)} & S_x\sigma_{t_{1u}}^{(1)} + (S_yS_z + S_zS_y)\sigma_{t_{2g}}^{(2)} \\ S_y\sigma_{t_{1u}}^{(1)} + (S_zS_x + S_xS_z)\sigma_{t_{2g}}^{(2)} & -S_x\sigma_{t_{1u}}^{(1)} + (S_yS_z + S_zS_y)\sigma_{t_{2g}}^{(2)} & \sigma_{a_{1g}}^{(0)} + 2(S_z^2 - \frac{1}{3}S^2)\sigma_{e_g}^{(2)} \end{pmatrix} \cdot \varepsilon_i$$
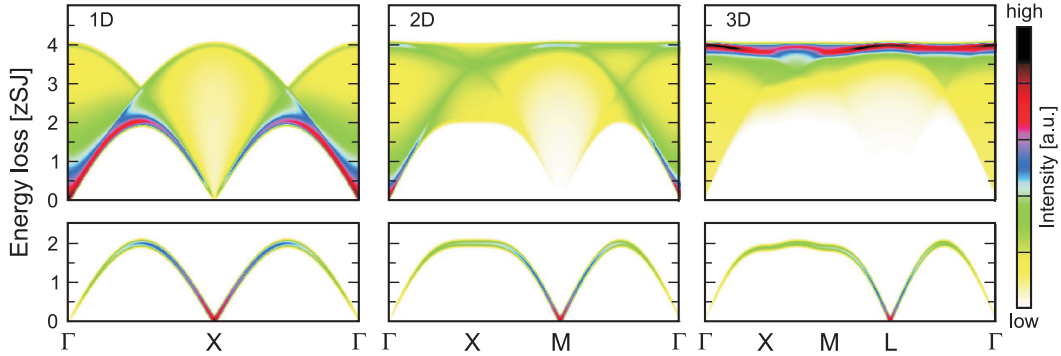

Figure 2: The Cu^{2+} and Ni^{2+} one magnon (bottom) and Ni^{2+} two magnon (top) RIXS spectral function, calculated using linear spin-wave theory for a 1D chain (left), 2D square (middle) and 3D cubic (right) lattice. The energy loss scale is in units of zSJ, number of neighbors times spin times magnetic exchange constant.

The numerical values of the optical conductivity σ at the $L_{2,3}$ edge for Ni^{2+} are plotted in the right panel of Fig. 1. There are four fundamental spectra as the XMLD ($\sigma^{(2)}$) spectra branch to two different representations ($\sigma_{e_g}^{(2)}$ and $\sigma_{t_{2g}}^{(2)}$). In order to separate the different contributions one can use different scattering geometries or different resonant energies. One should realize that also interference terms between the different channels have to be considered. On the positive side the fundamental X-ray absorption spectra (σ) are quite well-known and can be calculated with quite good accuracy, simplifying the disentanglement of the different scattering channels.

In Fig. 2, I show the one (bottom panels) and two (top panels) magnon intensity as one could measure with RIXS in Ni^{2+} samples. For real geometries one would always measure a linear combination of the two spectral functions depending on resonance energy and polarization as discussed above. For the single magnon spectral function only a single peak is seen at every $\vec{q}$ value. For the two magnon spectral function a complete band is measured which fulfills that the sum of the two different $\vec{q}$ values for the two magnons is equal to the transferred momentum.

In conclusion I have presented a tractable theory for the calculation of RIXS spectral functions. It fully incorporates the intermediate state Hamiltonian including the core-hole spin orbit coupling and the multiplet features as well as the momentum dependence of the low energy excited states. The transition operator is written as local operators multiplied by fundamental X-ray absorption spectra. The transition operator has a simple form that allows one to determine simple selection rules depending on the polarization of the incoming and outgoing light. RIXS measurements can provide us with detailed information on both the magnons as well as the incoherent spectral weight, which reveals information on the momentum-dependent interactions of magnons with themselves and other degrees of freedom in the system. The RIXS cross section at the TM $L_{2,3}$ edge is so large that the technique can be used to measure small samples, thin-films or multilayers making it possible to measure magnetic excitations in a whole new class of materials.

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