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Resonant inelastic x-ray scattering studies of elementary excitations

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CHAPTER 2

THEORY OF RESONANT INELASTIC X-RAY SCATTERING

2.1 Introduction

Before embarking on the calculation of RIXS cross sections, we consider the basic theory in this chapter. Starting at a very basic level, we first review how the X-ray photons interact with matter. The relativistic theory of quantum electrodynamics (QED) gives a general description of this interaction, but it deals with positrons which are obviously not needed to describe RIXS experiments on condensed matter systems. Therefore, we start this chapter with an approximation scheme to QED at low energies. This low energy expansion yields a Hamiltonian, which has only two components (electrons with spin up and down) instead of the four degrees of freedom of QED which also include positrons.

The low energy limit of QED requires small electromagnetic fields, and therefore interactions between photons and electrons are weak: the interaction strength is controlled by the dimensionless fine structure constant $\alpha = e^2/4\pi\epsilon_0\hbar c \approx 1/137$. We treat interactions with X-ray photons as a perturbation to the quantum system under study. Resonant X-ray scattering processes can be described by the Fermi Golden Rule to second order. The result is the Kramers-Heisenberg equation, which describes the resonant cross section.

The Kramers-Heisenberg cross section contains many quantities, some pertaining to the material, and some to the experimental setup. It is possible to disentangle them, although this is beyond the scope of this thesis [3, 26]. We

consider only dipole transitions, and isolate the polarization dependence from the collective response of the system.

In Sec. 2.4, we distinguish two RIXS processes: direct and indirect RIXS. Direct RIXS corresponds to two consecutive dipole transitions, with no scattering from the core hole in the intermediate state. Because the RIXS process is a very fast one, this is often a good way of thinking about RIXS: the core hole has decayed before it can scatter an electron. However, some transitions, like the $1s \rightarrow 4p$ edge, cannot produce any excitation unless the core hole and the valence electrons scatter off each other. This process, where the core hole has an impact on the valence electrons in between the two dipole transitions, is called indirect RIXS.

The Kramers-Heisenberg equation is difficult to solve exactly, and we are able to come up with an exact solution only in the case of localized excitations. In Sec. 2.5, we develop an approximation to the Kramers-Heisenberg equation: the Ultra-short Core hole Lifetime (UCL) expansion. It makes use of the fact that RIXS processes are usually very fast, leaving little time for the valence electrons to react to the core hole. The UCL series expansion trades the sum over intermediate states (which is hard to compute) for an expansion in the lifetime of the core hole.

This chapter is organized as follows: we start out with the basic electron-photon coupling theory in Sec. 2.2. Then, we use it to obtain the Kramers-Heisenberg equation in Sec. 2.3. The distinction between direct and indirect RIXS is illustrated in Sec. 2.4. The chapter will be concluded by the introduction of the UCL expansion in Sec. 2.5.

2.2 Electron-photon coupling

To develop the theory of RIXS, one needs to consider the interaction of the X-ray photons with the electrons in the sample under study. This interaction is described by the theory of quantum electrodynamics (QED). A treatment of the RIXS cross section in terms of QED would be very complicated, and one would prefer to use an effective low-energy approximation to QED where the positron degrees of freedom are integrated out. In this section, such a low-energy expansion of QED is developed, which produces a Hamiltonian that describes the interaction of photons with electrons. The expansion applies to cases where the electrons are non-relativistic and the electromagnetic fields are small compared to the electron mass. It is equivalent to the approach of Foldy and Wouthuysen [27].

2.2.1 Low energy expansion of QED

The electromagnetic field, including the incident X-rays, are described by an electric potential $\phi(\mathbf{r})$ and a vector potential $\mathbf{A}(\mathbf{r})$, which are combined in the four-vector $A^\mu = (\phi/c, \mathbf{A})$. The coupling between such a field and electrons is

given by the theory of QED, see Peskin and Schroeder [28] for details. In SI units, the QED action is

$$S_{\text{QED}} = \int d^4x \bar{\psi} (i\hbar\mathcal{D} - mc) \psi + S_{\text{EM}} \quad (2.1)$$

with m the mass of the electron, and where S_{EM} is the action for the electromagnetic field, which contains Maxwell's equations. ψ is a four-component vector describing the fermion field (whose excitation quanta are electrons and positrons), and $\bar{\psi} = \psi^\dagger \gamma^0$. Further, $\mathcal{D} = \gamma^\mu D_\mu = \gamma^\mu (\partial_\mu - ieA_\mu/\hbar)$ with the elementary charge $e \approx +1.6 \cdot 10^{-19}$ C, and γ^μ are the gamma matrices. From this action, one obtains the Euler-Lagrange equation for $\bar{\psi}$:

$$(i\hbar\mathcal{D} - mc) \psi = 0. \quad (2.2)$$

This is the Dirac equation in the presence of an electromagnetic field. The theory has a conserved current $j^\mu = \bar{\psi} \gamma^\mu \psi$, *i.e.*, $\partial_\mu j^\mu = 0$ if ψ obeys the Dirac equation (including A^μ). The formula for the associated conserved charge, $Q = \int d^3x j^0 = \text{const.}$, is a normalization condition, which can be set to 1 by rescaling ψ :

$$\int d^3x \psi^\dagger \psi = 1. \quad (2.3)$$

Eq. (2.2) contains both electrons and positrons, but at the low energy scales of condensed matter physics, the latter are irrelevant. They can be integrated out by taking two limits, and the result will be the Schrödinger equation for electrons in an electromagnetic field. First, we consider the case of the fermions having low speeds v compared to the speed of light, as is typical for condensed matter systems without very heavy nuclei. Second, the electromagnetic field strength is low compared to twice the mass of the electron: $eA^\mu/c \ll 2m$.

In the limiting case $A^\mu = 0$, the solutions to the Dirac equation are plane waves. In the Dirac basis, the fermion field is

$$\psi(x) = e^{-ip \cdot x/\hbar} \begin{pmatrix} \alpha(p) \\ -\frac{\sigma^i p_i}{p_0 + mc} \alpha(p) \end{pmatrix}. \quad (2.4)$$

where the four-vector $p^\mu = (E/c, \mathbf{p})$ must satisfy Einstein's energy-momentum relation $E^2 = (mc^2)^2 + (\mathbf{p}c)^2$. $\alpha(p)$ can be any two-component spinor. The solution for $\mathbf{p} = 0$ in zero field is $\psi(x) = e^{-ip_0 x^0/\hbar} \begin{pmatrix} \alpha \\ 0 \end{pmatrix}$ with $p_0 = mc$ and $x^0 = ct$. For small momenta, the lower spinor is of order $\mathcal{O}(p^i/mc) \sim \mathcal{O}(v/c)$. The plane wave solutions have two degrees of freedom in $\alpha(p)$, corresponding to an electron with spin up and down. In other words, $\psi(x)$ is the mode whose excitation quanta are electrons with momentum \mathbf{p} .

Another solution can be obtained by taking $\psi(x) = e^{ip \cdot x} v(p)$, which again has two degrees of freedom. These are the positron modes, which will not be considered here.

In order to derive the effective low energy electron-photon coupling Hamiltonian from Eq. (2.2), we introduce a small electromagnetic field $eA^\mu/c \ll m$ and allow the electron to have a finite (but small) speed $v \ll c$. In this regime, the equation of motion for the electron is the Schrödinger equation with electron-photon coupling. Departing as said from the extreme limit, the Ansatz $\psi = e^{-imc^2t/\hbar} \begin{pmatrix} \alpha(x) \\ \beta(x) \end{pmatrix}$ is introduced in Eq. (2.2). The idea behind this Ansatz is that for small electromagnetic fields and slow electrons $\alpha(x)$ and $\beta(x)$ will start to oscillate, but at a frequency much lower than mc^2/\hbar . One finds

$$i\hbar D_0 \alpha(x) + i\hbar \sigma^i D_i \beta(x) = 0 \quad (2.5)$$

$$(2mc + i\hbar D_0) \beta(x) + i\hbar \sigma^i D_i \alpha(x) = 0 \quad (2.6)$$

where σ^i are the Pauli spin matrices. Eq. (2.6) can be rewritten as

$$\beta(x) = \tilde{D} \alpha(x) + \tilde{D}_0 \beta(x) = \sum_{n=0}^{\infty} \tilde{D}_0^n \tilde{D} \alpha(x). \quad (2.7)$$

where $\tilde{D} = \frac{-i\hbar}{2mc} \sigma^i D_i$ and $\tilde{D}_0 = \frac{-i\hbar}{2mc} D_0$. (One can think of these quantities as part of the four-vector product $-i\hbar \sigma^\mu D_\mu / 2mc$, with σ^0 the 2×2 unit matrix.) These results are still exact. By substituting Eq. (2.7) in Eq. (2.5), a Schrödinger equation for $\alpha(x)$ can be obtained.

The high- n terms in Eq. (2.7) will be small in the limit of interest: the total wave function has an oscillation frequency set by the energy of the electron, and since the rest energy was explicitly isolated in the Ansatz, the oscillation frequency of $\alpha(x)$ is $(E - mc^2)/\hbar$. For a slow electron in a small electromagnetic field, this is much smaller than $2mc^2/\hbar$. Therefore Eq. (2.7) enables one to expand the Dirac equation in a controlled way, and obtain the Schrödinger equation to any order of precision. A convenient way to keep track of the orders in the expansion is the mass: order n gives a contribution to the Hamiltonian that is proportional to $1/m^{n+1}$.

The expansion is controlled as long as one satisfies the two limits. The first of these was that the electrons should be non-relativistic, i.e., they that travel at speeds small compared to the speed of light. This is a good approximation, even for, for instance, graphene where the Fermi velocity $v_F \approx c/300$, or for copper 1s core electrons, where we estimate $v \sim \hbar Z / ma_0 \approx 0.21c$ with Z the atomic number for copper and a_0 the Bohr radius. At first glance, v/c might appear not small here, but $\gamma = 1/\sqrt{1 - v^2/c^2} \approx 1.02$ and relativistic effects are still small. The second limit was that the potentials related to both the electrons and photons are small compared to twice the mass of the electron: $e\phi/2mc^2$, $e|\mathbf{A}|/2mc \ll 1$ (m is the electron mass). Because the potentials can be gauged, this means that the expansion breaks down if there is a potential *difference* in the problem enough to have an electron gain $2mc^2$ in energy, enough to produce electron-positron pairs. The intrinsic potentials of materials do not strictly satisfy this condition close to

the nuclei. However, the expansion can be consistently applied to cases where the average of the potentials over a region of the size of the reduced Compton wave length satisfies this limit [29]. A crude estimate indicates that the expansion may be applied to all known elements: up to $Z \sim 2 \cdot 10^2$, see also Ref. [30]. However, in future very strongly focussed X-ray Free Electron Lasers, the electric field of the photons is projected to exceed 10^{16} V/m [31], which gives $e|\mathbf{A}| \sim 2mc$ at a photon energy of ~ 8 keV, so the low energy expansion of QED breaks down.

2.2.2 Evaluation of the expansion to third order

First order. The first order of the expansion is obtained by approximating $\beta(x)$ to order $n = 0$. Substitution of $\beta(x)$ in Eq. (2.5) gives the equation of motion for $\alpha(x)$. Using

$$(2mc\tilde{D})^2 = (-i\hbar)^2 (\delta^{ij} + i\epsilon^{ijk}\sigma^k) D_i D_j = (\mathbf{p} + e\mathbf{A})^2 + e\hbar\boldsymbol{\sigma} \cdot \mathbf{B}, \quad (2.8)$$

one obtains the Schrödinger equation

$$i\hbar\partial_t\alpha(x) = \left[\frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 + \frac{e\hbar}{2m}\boldsymbol{\sigma} \cdot \mathbf{B} - e\phi \right] \alpha(x). \quad (2.9)$$

The expression in straight brackets is the electron-photon coupling Hamiltonian to order $n = 0$ (order $1/m$). The first term contains the kinetic energy of the electron $\mathbf{p}^2/2m$, and two different electron-photon coupling terms: $e\mathbf{p} \cdot \mathbf{A}/m$ and $e^2\mathbf{A}^2/2m$. The other terms are the Zeeman and Coulomb energies, respectively.

Second order. Going to second order ($n = 1$) in Eq. (2.7) yields the equation of motion

$$i\hbar D_0\alpha(x) + i\hbar\sigma^i D_i \left(\tilde{D} + \tilde{D}_0\tilde{D} \right) \alpha(x) = 0. \quad (2.10)$$

Using

$$i\hbar [D_0, D_i] = i [\partial_0, -ieA_i] + i [-ieA_0, \partial_i] = e [(\partial_0 A_i) - (\partial_i A_0)] = \frac{e}{c} E^i \quad (2.11)$$

with E^i the electric field components, the $n = 1$ equation of motion is simplified to

$$\begin{aligned} i\hbar\partial_t\alpha(x) &= \left[\frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + \frac{e\hbar}{2m}\boldsymbol{\sigma} \cdot \mathbf{B} - e\phi \right] \alpha(x) \\ &- \left(\frac{-i\hbar}{2mc} \right)^2 \sigma^i \sigma^j (i\hbar c D_i D_j D_0 + e D_i E^j) \alpha(x) = \left[\dots \right] \alpha(x) \\ &- \left(\frac{-i\hbar}{2mc} \right)^2 \sigma^i \sigma^j (D_i D_j i\hbar c D_0 + e(\partial_i E^j) + e E^j D_i) \alpha(x) \end{aligned} \quad (2.12)$$

To obtain a Schrödinger equation from this equation, *i. e.*, an equation linear in ∂_t , one substitutes D_0 on the right hand side by the $n = 0$ Schrödinger equation. The result of this substitution is of higher order than $\mathcal{O}(m^{-2})$, and will be dropped here. The other correction terms become

$$\begin{aligned} & \sigma^i \sigma^j e \left((\partial_i E^j) + E^j D_i \right) \alpha(x) = e \left(\delta^{ij} + i \epsilon^{ijk} \sigma^k \right) \left((\partial_i E^j) + E^j D_i \right) \alpha(x) \\ & = e \left(\frac{\rho}{\epsilon_0} + \frac{i}{\hbar} \mathbf{E} \cdot (\mathbf{p} + e\mathbf{A}) + \boldsymbol{\sigma} \cdot \left[\frac{1}{\hbar} \mathbf{E} \times (\mathbf{p} + e\mathbf{A}) - i \partial_t \mathbf{B} \right] \right) \alpha(x) \end{aligned} \quad (2.13)$$

where Maxwell's equations $\nabla \cdot \mathbf{E} = \rho/\epsilon_0$ and $\nabla \times \mathbf{E} = -\partial_t \mathbf{B}$ are used. The equation of motion for $\alpha(x)$ becomes

$$\begin{aligned} i\hbar \partial_t \alpha(x) = & \left[\frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + \frac{e\hbar}{2m} \boldsymbol{\sigma} \cdot \mathbf{B} - e\phi + \frac{e\hbar}{(2mc)^2} \boldsymbol{\sigma} \cdot \mathbf{E} \times (\mathbf{p} + e\mathbf{A}) \right. \\ & \left. + \frac{e\hbar^2 \rho}{(2mc)^2 \epsilon_0} \right] \alpha(x) + \frac{ie\hbar}{(2mc)^2} [\mathbf{E} \cdot (\mathbf{p} + e\mathbf{A}) - \boldsymbol{\sigma} \cdot (\hbar \partial_t \mathbf{B})] \alpha(x). \end{aligned} \quad (2.14)$$

The appearance of imaginary terms is natural: from the normalization condition Eq. (2.3), one finds

$$\int d^3x \left[\alpha(x)^\dagger \alpha(x) + \beta(x)^\dagger \beta(x) \right] = 1 \quad (2.15)$$

and it is clear that when β acquires a finite value, α cannot constitute the normalized wave function anymore. If one tries to obtain an equation of the form $i\hbar \partial_t \alpha = H_\alpha \alpha$, H_α is expected to have non-Hermitian terms as soon as β acquires a non-zero value. These terms vanish when α is normalized at this stage [32]. We define $\Psi(x) = \Omega \alpha(x)$, and require that Ψ is normalized to 1. Up to order $\mathcal{O}(m^{-2})$, the normalization condition is

$$\int d^3x \left(\alpha(x)^\dagger \alpha(x) + \left(\tilde{D} \alpha(x) \right)^\dagger \tilde{D} \alpha(x) \right) = 1. \quad (2.16)$$

Integrating by parts (assuming that the boundary term vanishes), one obtains

$$\int d^3x \alpha(x)^\dagger \left(1 + \tilde{D}^2 \right) \alpha(x) = 1. \quad (2.17)$$

This gives, to order $\mathcal{O}(m^{-2})$,

$$\Omega = 1 + \frac{1}{2} \tilde{D}^2 = \Omega^\dagger. \quad (2.18)$$

Ψ then obeys the equation

$$i\hbar \partial_t \Psi(x) = \left[\Omega H_\alpha \Omega^{-1} + i\hbar (\partial_t \Omega) \Omega^{-1} \right] \Psi(x) \quad (2.19)$$

with $\Omega^{-1} = 1 - \frac{1}{2}\tilde{D}^2$. The Hamiltonian for Ψ is therefore $H_\Psi = \Omega H_\alpha \Omega^{-1} + i\hbar(\partial_t \Omega)\Omega^{-1}$. The normalization procedure can also be applied at an earlier stage, before expanding the Dirac equation [27]. In that case, it is just a transformation to a different representation of the Dirac theory.

The normalization is non-local and introduces coarse-graining on the scale of the Compton wave length [27, 29]. This can be seen by writing the wave functions in the position representation:

$$\langle \mathbf{x} | \alpha \rangle = \langle \mathbf{x} | e^{-\tilde{D}^2/2} | \Psi \rangle \quad (2.20)$$

In the absence of electromagnetic fields, this becomes

$$\begin{aligned} \langle \mathbf{x} | \alpha \rangle &= \frac{1}{(2\pi\hbar)^3} \iint d\mathbf{p} d\mathbf{x}' e^{i\mathbf{p}\cdot(\mathbf{x}-\mathbf{x}')/\hbar} e^{-\mathbf{p}^2/8(mc)^2} \langle \mathbf{x}' | \Psi \rangle \\ &= \lambda_C^{-3} \sqrt{(2/\pi)^3} \int d\mathbf{x}' e^{-2(\mathbf{x}-\mathbf{x}')^2/\lambda_C^2} \langle \mathbf{x}' | \Psi \rangle \end{aligned} \quad (2.21)$$

where the reduced Compton wave length $\lambda_C = \hbar/mc$. For a specific solution $\Psi(\mathbf{x})$, one obtains $\alpha(\mathbf{x})$ by averaging Ψ over a region around \mathbf{x} of the size of the Compton wave length.

The detailed calculation of H_Ψ is given in Appendix A. The result is

$$\begin{aligned} H_\Psi^{(2)} &= \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + \frac{e\hbar}{2m} \boldsymbol{\sigma} \cdot \mathbf{B} - e\phi + \frac{e^2\hbar}{(2mc)^2} \boldsymbol{\sigma} \cdot \mathbf{E} \times \mathbf{A} + \frac{1}{2} \frac{e\hbar^2 \rho}{(2mc)^2 \epsilon_0} \\ &+ \frac{e\hbar}{2(2mc)^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p} - \mathbf{p} \times \mathbf{E}). \end{aligned} \quad (2.22)$$

This result slightly differs from those of Blume [33] and in the book of Schülke [34]. In the case of electrostatics, it coincides with previous work [32, 35].

The term proportional to ρ is called the Darwin term. In the hydrogen atom, this term shifts the energy of the s orbitals, because they are the only ones to overlap with the charge density of the nucleus. The last term of Eq. (2.22) contains relativistic spin-orbit coupling. This can be seen by inserting the electric field of a nucleus with charge Ze : ignoring commutation relations, one gets $\frac{e^2 Z \hbar}{(2mc)^2 r^3} \boldsymbol{\sigma} \cdot \mathbf{r} \times \mathbf{p} = \frac{e^2 Z}{2(mc)^2 r^3} \mathbf{S} \cdot \mathbf{L}$ [32]. In the absence of electron-electron interactions, the expectation value of $1/r$ is proportional to the charge of the nucleus Ze . The relativistic spin-orbit coupling is then proportional to Z^4 , meaning it is strong in the heavy elements like iridium, the object of study in chapter 6. Further, it can be seen that for fixed Z , the core orbitals with their small $\langle r \rangle$ have a much larger spin-orbit coupling than the valence orbitals, which is important, *e.g.*, for probing the magnon dispersion in cuprates (see chapter 4).

Third order. The derivation of the third order H_Ψ ($n = 2$ or m^{-3}) is given in appendix A. The procedure is analogous to the second order calculation above.

The result is

$$H_{\Psi}^{(3)} = \dots + \frac{1}{(2mc)^3} \left[-c \{(\mathbf{p} + e\mathbf{A})^2 + e\hbar\boldsymbol{\sigma} \cdot \mathbf{B}\}^2 + \frac{e\hbar^2}{2c} \{(\partial_t \mathbf{E}) \cdot (\mathbf{p} + e\mathbf{A}) + (\mathbf{p} + e\mathbf{A}) \cdot (\partial_t \mathbf{E}) + \hbar\boldsymbol{\sigma} \cdot (\partial_t^2 \mathbf{B})\} \right]. \quad (2.23)$$

We interpret the different correction terms. In the absence of electromagnetic fields, only the term proportional to \mathbf{p}^4 is left. It gives a relativistic correction to the classical kinetic energy of the electron. The terms involving time derivatives disappear for static fields, but when one considers plane wave radiation of angular frequency ω , they renormalize lower order terms: $\partial_t \mathbf{E} \rightarrow \omega^2 \mathbf{A}$ and $\partial_t^2 \mathbf{B} \rightarrow -\omega^2 \mathbf{B}$, renormalizing the first order Hamiltonian. The renormalization is of order $(\hbar\omega/mc^2)^2$. In these simple cases of static fields or radiation fields, only the term without time derivatives yields new electron-photon interaction processes, involving three and four photons. Another interesting case is when no electrons are present. Of the three- and four-photon terms, only the \mathbf{A}^4 term remains and gives photon-photon scattering and conversion of three low energy photons to one high energy photon (or vice versa), and is relevant in, for instance, Free Electron Lasers [36].

To conclude this section, we consider the limit of high fields in an X-ray Free Electron Laser (XFEL). The electric field for the LCLS XFEL beam is designed to reach $2.5 \cdot 10^{10}$ V/m for an unfocussed beam at a wave length of $\lambda = 1.5 \text{ \AA}$ (corresponding to a photon energy $\hbar\omega = 8.3 \text{ keV}$) [31]. The electric field strength is related to the vector potential by $|\mathbf{A}| = |\mathbf{E}|/\omega$, where we assumed that the beam is a plane wave in free space. We see that the low field limit is satisfied by the unfocussed beam: $e|\mathbf{A}|/2mc = 5.8 \cdot 10^{-7}$. The electric field can be increased to $\sim 10^{14}$ V/m by focusing the beam to a 100 nm spot, and with future technology, this can perhaps be increased to fields as strong as $\sim 10^{18}$ V/m for a 1 nm spot [37]. At field strengths beyond $|\mathbf{E}| = 4 \cdot 10^{16}$ V/m, $e|\mathbf{A}|/2mc$ is larger than unity and the low energy expansion of QED breaks down.

2.3 Kramers-Heisenberg equation

Now that the Hamiltonian describing the interaction of the X-ray photons with the electrons in the material under study is derived, we proceed to analyze X-ray scattering processes. This section is largely along the lines of Ref. [3].

The initial state of the scattering process is $|g\rangle = |g; \mathbf{k}\epsilon\rangle$, which describes the state g of the material under study, and a photon with wave vector \mathbf{k} , angular frequency $\omega_{\mathbf{k}} = c|\mathbf{k}|$, and polarization ϵ . After the scattering process is completed, the material is left in the state f and the photon is scattered to \mathbf{k}' , $\omega_{\mathbf{k}'}$, ϵ' . The total final state is denoted as $|f\rangle = |f; \mathbf{k}'\epsilon'\rangle$.

We separate the Hamiltonian (2.22) into $H_0 + H'$ where H_0 affects only the electrons or only the photons, while the perturbation H' contains electron-photon

interaction terms. H_0 contains the electron's kinetic and potential energy, the Darwin term, and relativistic spin-orbit coupling. The free photon's energy was omitted after Eq. (2.1), but is also included in H_0 . The states $|g\rangle$ and $|f\rangle$ are eigenstates of H_0 with energies $E_g = E_g + \hbar\omega_{\mathbf{k}}$ and $E_f = E_f + \hbar\omega_{\mathbf{k}'}$, respectively, where E_g and E_f are the initial and final state energy of the material. Photon scattering can induce a transition in the material from the initial state $|g\rangle$ to final state $|f\rangle$, but total energy and momentum are conserved in the scattering process. The photons appear in the electron-photon Hamiltonian through \mathbf{A} , which can be expanded in plane waves as

$$\mathbf{A}(\mathbf{r}) = \sum_{\boldsymbol{\kappa}, \boldsymbol{\varepsilon}} \sqrt{\frac{\hbar}{2\mathcal{V}\epsilon_0\omega_{\boldsymbol{\kappa}}}} (\boldsymbol{\varepsilon} a_{\boldsymbol{\kappa}\boldsymbol{\varepsilon}} e^{i\boldsymbol{\kappa}\cdot\mathbf{r}} + \boldsymbol{\varepsilon}^* a_{\boldsymbol{\kappa}\boldsymbol{\varepsilon}}^\dagger e^{-i\boldsymbol{\kappa}\cdot\mathbf{r}}), \quad (2.24)$$

where \mathcal{V} is the volume of the system. When the electromagnetic field is quantized, $a_{\boldsymbol{\kappa}\boldsymbol{\varepsilon}}^\dagger$ annihilates (creates) a photon in the mode with wave vector $\boldsymbol{\kappa}$ and polarization vector $\boldsymbol{\varepsilon}$. The electric and magnetic fields in the electron-photon coupling Hamiltonian can be expressed in the potentials ϕ and \mathbf{A} .

H' can be treated as a perturbation to H_0 because electron-photon interactions are controlled by the small fine structure constant. We now calculate the X-ray scattering amplitude in this perturbation scheme. Fermi's Golden Rule to second order gives the transition rate w for scattering processes in which the photon loses momentum $\hbar\mathbf{q} = \hbar\mathbf{k} - \hbar\mathbf{k}'$ and energy $\hbar\omega = \hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'}$ to the sample:

$$w = \frac{2\pi}{\hbar} \sum_{\mathbf{f}} \left| \langle \mathbf{f} | H' | \mathbf{g} \rangle + \sum_n \frac{\langle \mathbf{f} | H' | n \rangle \langle n | H' | \mathbf{g} \rangle}{E_g - E_n} \right|^2 \delta(E_{\mathbf{f}} - E_g) \quad (2.25)$$

where the $|n\rangle$ are intermediate states, which are eigenstates of H_0 with energy E_n . The first order amplitude in general dominates the second order, but when the incoming X-rays are in resonance with a specific transition in the material ($E_g \approx E_n$), then the second order amplitude becomes large. The second order amplitude contains resonant scattering, while the first order yields non-resonant scattering only. Third order contributions to w are neglected because they are at least of order $\alpha^{3/2}$.

It is useful to classify the electron-photon coupling terms by powers of \mathbf{A} . Terms of H that are quadratic in \mathbf{A} are the only ones to contribute to the first order scattering amplitude, because they contain terms proportional to $a_{\mathbf{k}'\boldsymbol{\varepsilon}'}^\dagger a_{\mathbf{k}\boldsymbol{\varepsilon}}$ and $a_{\mathbf{k}\boldsymbol{\varepsilon}} a_{\mathbf{k}'\boldsymbol{\varepsilon}'}$. To be specific, the quadratic terms of (2.22) give rise to non-resonant scattering [first term of (2.22)] and magnetic non-resonant scattering [fourth term of (2.22)]. Although both appear in the first order scattering amplitude, they in principle also contribute to the second order, but we neglect these processes because they are of order $\alpha^{3/2}$.

The interaction terms of H that are linear in \mathbf{A} do not contribute to the first order scattering amplitude, but do contribute to the second order. They thus may give rise to resonant processes. In the following, we neglect such contributions

that come from the $\boldsymbol{\sigma} \cdot \nabla \phi \times \mathbf{A}$ term and from the last term of (2.22), because they are of second order in two separate expansions [33]. First, these terms of H are of second order in the low energy expansion of QED, and second, they appear in the second order of the scattering amplitude.

The relevant remaining terms are

$$H' = \sum_{i=1}^N \left[\frac{e}{m} \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i + \frac{e^2}{2m} \mathbf{A}^2(\mathbf{r}_i) + \frac{e\hbar}{2m} \boldsymbol{\sigma}_i \cdot \nabla \times \mathbf{A}(\mathbf{r}_i) - \frac{e^2\hbar}{(2mc)^2} \boldsymbol{\sigma}_i \cdot \frac{\partial \mathbf{A}(\mathbf{r}_i)}{\partial t} \times \mathbf{A}(\mathbf{r}_i) \right], \quad (2.26)$$

where the gauge was fixed by choosing $\nabla \cdot \mathbf{A}(\mathbf{r}) = 0$, and the sum is over all N electrons in the sample.

The two terms of H' that contribute to the first order amplitude are the one proportional to \mathbf{A}^2 and the $\boldsymbol{\sigma} \cdot (\partial \mathbf{A} / \partial t) \times \mathbf{A}$ term. The latter is smaller than the former by a factor $\hbar\omega_{\mathbf{k}(\prime)}/mc^2 \ll 1$, and is therefore neglected [33]. The first order term in Eq. (2.25) then becomes

$$\frac{e^2}{2m} \langle \mathbf{f} | \sum_i \mathbf{A}^2(\mathbf{r}_i) | \mathbf{g} \rangle = \frac{\hbar e^2}{2m\mathcal{V}\epsilon_0} \frac{\boldsymbol{\epsilon}'^* \cdot \boldsymbol{\epsilon}}{\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}}} \langle \mathbf{f} | \sum_i e^{i\mathbf{q} \cdot \mathbf{r}_i} | \mathbf{g} \rangle \quad (2.27)$$

with $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. When the incident energy $\hbar\omega_{\mathbf{k}}$ is much larger than any resonance of the material, the scattering amplitude is dominated by this channel, which is called Thompson scattering (see, for instance, page 51 of Ref. [32]). In scattering from a crystal at zero energy transfer, this term contributes amongst others to the Bragg peaks. It also gives rise to non-resonant inelastic scattering. In practice, RIXS spectra show a strong resonance behavior, demonstrating that, for RIXS, it is the second order scattering amplitude that dominates the first order. Also single atom LDA calculations show that the resonant cross section is larger than the non-resonant cross section by two orders of magnitude [38]. We therefore omit the \mathbf{A}^2 contribution in the following. More details on non-resonant inelastic X-ray scattering can be found in, for instance, Refs. [34, 39].

The second order scattering amplitude in Eq. (2.25) becomes large when $\hbar\omega_{\mathbf{k}}$ matches a resonance energy of the system, and the incoming photon is absorbed first in the intermediate state, creating a core hole. The denominator $E_g + \hbar\omega_{\mathbf{k}} - E_n$ is then small, greatly enhancing the second order scattering amplitude. We neglect the other, off-resonant processes here, though they do give an important contribution to non-resonant scattering, as in the case of Rayleigh scattering [32, 33]. The resonant part of the second order amplitude is

$$\frac{e^2\hbar}{2m^2\mathcal{V}\epsilon_0\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}}} \sum_n \sum_{i,j=1}^N \frac{\langle \mathbf{f} | e^{-i\mathbf{k}' \cdot \mathbf{r}_i} (\boldsymbol{\epsilon}'^* \cdot \mathbf{p}_i - \frac{i\hbar}{2} \boldsymbol{\sigma}_i \cdot \mathbf{k}' \times \boldsymbol{\epsilon}'^*) | n \rangle}{E_g + \hbar\omega_{\mathbf{k}} - E_n + i\Gamma_n} \times \langle n | e^{i\mathbf{k} \cdot \mathbf{r}_j} \left(\boldsymbol{\epsilon} \cdot \mathbf{p}_j + \frac{i\hbar}{2} \boldsymbol{\sigma}_j \cdot \mathbf{k} \times \boldsymbol{\epsilon} \right) | \mathbf{g} \rangle, \quad (2.28)$$

where a lifetime broadening Γ_n is introduced for the intermediate states to account for the usually short lifetime of the core hole (see, for instance, page 341 of Ref. [40]). The decay is dominated by channels other than RIXS, such as Auger decay and fluorescent decay, see page 13 in Ref. [6]. Usually, these processes only involve the core levels, and all Γ_n at a certain edge can then be assumed equal. In the rest of this thesis, we take $\Gamma_n = \Gamma$.

Resonant scattering can thus occur via a non-magnetic and magnetic term. An estimate shows that the former dominates. The size of localized 1s copper core orbitals is roughly $a_0/Z \approx 0.018 \text{ \AA}$ so that for 10 keV photons the exponential $e^{i\mathbf{k}\cdot\mathbf{r}}$ is close to unity and can be expanded. In a typical RIXS experiment, the X-ray energy is tuned to a dipole transition. The magnetic terms can then be neglected because they generate only very small dipole transitions. The non-magnetic term can induce a dipole transition of order $|\mathbf{p}| \sim \hbar Z/a_0 \sim 5.9 \cdot 10^{-23} \text{ kg m/s}$, whereas the magnetic term gives a dipole transition of order $(\mathbf{k} \cdot \mathbf{r})\hbar |\mathbf{k}|/2 \sim 2.5 \cdot 10^{-25} \text{ kg m/s}$. We therefore ignore the magnetic term here, and the relevant transition operator for the RIXS cross section is

$$\mathcal{D} = \frac{1}{im\omega_{\mathbf{k}}} \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_i} \boldsymbol{\epsilon} \cdot \mathbf{p}_i, \quad (2.29)$$

where a prefactor has been introduced for convenience in the following expressions.

The double-differential cross section is obtained by multiplying w by the density of photon states in the solid angle $d\Omega$ ($= \mathcal{V}k'^2 d|\mathbf{k}'|d\Omega/(2\pi)^3$), and dividing by the incident photon flux c/\mathcal{V} [32–34, 41, 42]:

$$\frac{d^2\sigma}{d\hbar\omega d\Omega} = r_e^2 m^2 \omega_{\mathbf{k}'}^3 \omega_{\mathbf{k}} \sum_f |\mathcal{F}_{fg}|^2 \delta(E_g - E_f + \hbar\omega), \quad (2.30)$$

where the classical electron radius $r_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{mc^2}$. The scattering amplitude \mathcal{F}_{fg} at zero temperature is given by

$$\mathcal{F}_{fg}(\mathbf{k}, \mathbf{k}', \boldsymbol{\epsilon}, \boldsymbol{\epsilon}', \omega_{\mathbf{k}}, \omega_{\mathbf{k}'}) = \sum_n \frac{\langle f | \mathcal{D}'^\dagger | n \rangle \langle n | \mathcal{D} | g \rangle}{E_g + \hbar\omega_{\mathbf{k}} - E_n + i\Gamma}, \quad (2.31)$$

where the prime in \mathcal{D}' indicates it refers to transitions related to the outgoing X-rays. Eqs. (2.30) and (2.31) are referred to as the Kramers-Heisenberg equation, which is generally used to calculate the RIXS cross section.

At finite temperature T , this generalizes to

$$\frac{d^2\sigma}{d\hbar\omega d\Omega} = r_e^2 m^2 \omega_{\mathbf{k}'}^3 \omega_{\mathbf{k}} \sum_{i,f} \frac{1}{Z} e^{-E_i/k_B T} |\mathcal{F}_{fi}|^2 \delta(E_i - E_f + \hbar\omega), \quad (2.32)$$

where k_B is Boltzmann's constant and Z is the partition function.

Alternatively, we can rewrite the denominator for the intermediate states in terms of a Green's function, which is also referred to as the core hole propagator:

$$G(z_{\mathbf{k}}) = \frac{1}{z_{\mathbf{k}} - H_0} = \sum_n \frac{|n\rangle \langle n|}{z_{\mathbf{k}} - E_n}, \quad (2.33)$$

where $\{|n\rangle\}$ forms a complete basis set and

$$z_{\mathbf{k}} = E_g + \hbar\omega_{\mathbf{k}} + i\Gamma. \quad (2.34)$$

In the following we will often suppress the explicit label \mathbf{k} of $z_{\mathbf{k}}$ and denote it simply by z , with an implicit incident energy dependence. With the core hole propagator G and transition operators \mathcal{D} in place, the RIXS scattering amplitude \mathcal{F}_{fg} finally reduces to the elegant expression

$$\mathcal{F}_{fg} = \langle f | \mathcal{D}'^\dagger G(z_{\mathbf{k}}) \mathcal{D} | g \rangle. \quad (2.35)$$

2.3.1 Dipole approximation and separation of polarization dependence

Eqs. (2.30) and (2.31) give the Kramers-Heisenberg expression for RIXS. One typically wants to separate the part pertaining to the geometry of the experiment from the fundamental scattering amplitudes that relate to the physical properties of the system. We restrict ourselves here to dipole transitions. Higher multipoles of the transition operator \mathcal{D} can be found in, for instance, Ref. [3].

In the dipole limit, one assumes that $e^{i\mathbf{k}\cdot\mathbf{r}_i}$ is approximately constant at the length scale of the atomic wave functions: $e^{i\mathbf{k}\cdot\mathbf{r}_i} \approx e^{i\mathbf{k}\cdot\mathbf{R}_i}$ where \mathbf{R}_i points to the nucleus of the atom to which the electron i is bound. \mathbf{R}_i is not an operator. This has as a result that the electronic transitions are due to the momentum operator \mathbf{p} and Eq. (2.29) becomes

$$\mathcal{D} = \boldsymbol{\epsilon} \cdot \mathbf{D} \quad \text{with} \quad \mathbf{D} = \frac{1}{im\omega_{\mathbf{k}}} \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{R}_i} \mathbf{p}_i, \quad (2.36)$$

Generally, the matrix elements are expressed in terms of the position operator \mathbf{r} . For example, in the absorption step, one can write

$$\begin{aligned} \langle n | \mathbf{D} | g \rangle &= \sum_{i=1}^N \frac{1}{im\omega_{\mathbf{k}}} e^{i\mathbf{k}\cdot\mathbf{R}_i} \langle n | \mathbf{p}_i | g \rangle = \sum_{i=1}^N \frac{1}{\hbar\omega_{\mathbf{k}}} e^{i\mathbf{k}\cdot\mathbf{R}_i} \langle n | [\frac{\mathbf{p}_i^2}{2m}, \mathbf{r}_i] | g \rangle \\ &\approx \sum_{i=1}^N \frac{1}{\hbar\omega_{\mathbf{k}}} e^{i\mathbf{k}\cdot\mathbf{R}_i} (E_n - E_g) \langle n | \mathbf{r}_i | g \rangle \approx \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{R}_i} \langle n | \mathbf{r}_i | g \rangle \end{aligned} \quad (2.37)$$

where $\hbar\omega_{\mathbf{k}} \approx E_n - E_g$. The operator thus reduces to the well-known dipole operator $\mathbf{D} = \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{R}_i} \mathbf{r}_i$ that causes electronic transitions.

After making the dipole approximation, the next step is to separate the part that pertains to the geometry of the experiment (the polarization vectors $\boldsymbol{\epsilon}'$ and $\boldsymbol{\epsilon}$) from the physical properties of the system. Ultimately, our interest lies in the spectral functions of a material. The experimental geometry is chosen in an optimal way to measure them.

In second quantization, the dipole operator reads

$$\mathbf{D} = \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{R}_i} \sum_{n,\nu,m,\mu} c_{n\nu}^\dagger \langle \phi_{n\nu} | \mathbf{r}_i | \phi_{m\mu} \rangle c_{m\mu} \quad (2.38)$$

where $\phi_{n\nu}$ is the ν^{th} Wannier wave function on site n , and $c_{n\nu}$ is the corresponding annihilation operator. For definiteness, one can use the transition metal K edge ($1s \rightarrow 4p$) as an example. Then, $\phi_{m\mu}$ would be the transition metal $1s$ core states (μ indexes the $1s$ states with spin up and down) and $\phi_{n\nu}$ would be the transition metal $4p$ states (ν could index the orbitals $4p_{x,y,z}$ and spin up and down).

Because the core states are very much localized, only excited states on the same ion are reached¹: $n = m$. The Wannier wave functions are the same at all lattice sites, so

$$\mathbf{D} \approx \sum_{\nu,\mu} \langle \phi_\nu | \mathbf{r} | \phi_\mu \rangle \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} c_{i\nu}^\dagger c_{i\mu} \quad (2.39)$$

where the wave functions ϕ are centered at the origin. For our purposes, the sum over i can be restricted to electrons in the core states. For de-excitation,

$$\mathbf{D}^\dagger \approx \sum_{\nu,\mu} \langle \phi_\mu | \mathbf{r} | \phi_\nu \rangle \sum_i e^{-i\mathbf{k}'\cdot\mathbf{R}_i} c_{i\mu}^\dagger c_{i\nu}. \quad (2.40)$$

Note that the spin is not changed in the radiative transitions, and ν and μ have the same spin.

Since the core orbitals are very small compared to the lattice parameters, it is often assumed that the core hole does not disperse during the RIXS process: it is created and annihilated at the same site. In this case, the scattering amplitude (2.31) is

$$\mathcal{F}_{fg} = \sum_{\mu',\nu',\nu,\mu} T_{\mu'\nu'\nu\mu}(\boldsymbol{\epsilon}', \boldsymbol{\epsilon}) \sum_i e^{i\mathbf{q}\cdot\mathbf{R}_i} \sum_n \frac{\langle f | c_{i\mu'}^\dagger c_{i\nu'} | n \rangle \langle n | c_{i\nu}^\dagger c_{i\mu} | g \rangle}{E_g + \hbar\omega_{\mathbf{k}} - E_n + i\Gamma}, \quad (2.41)$$

¹Considering, for instance, the transition metal K edge, one could object that the $4p$ wave functions are quite large, and there is some overlap between the core states on one ion and the $4p$ wave functions of neighboring ions. However, dipole transitions are still very small since the $4p$ wave functions from the neighboring ions are approximately constant over the core state's volume.

where the polarization factor is

$$T_{\mu'\nu'\nu\mu}(\boldsymbol{\epsilon}', \boldsymbol{\epsilon}) = \langle \phi_{\mu'} | \boldsymbol{\epsilon}'^* \cdot \mathbf{r} | \phi_{\nu'} \rangle \langle \phi_{\nu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{\mu} \rangle. \quad (2.42)$$

μ', ν', ν and μ index the different scattering channels, which have different polarization dependencies $T_{\mu'\nu'\nu\mu}(\boldsymbol{\epsilon}', \boldsymbol{\epsilon})$. In practice, we replace the Wannier wave functions by the atomic wave functions to compute it. The radial parts of the dipole transition amplitudes in Eq. (2.42) are often irrelevant, as they only give an overall scaling factor to the RIXS spectra. In the absence of inter-ionic interactions, $T_{\mu'\nu'\nu\mu}(\boldsymbol{\epsilon}', \boldsymbol{\epsilon})$ gives the full RIXS scattering amplitude. We therefore name it the ‘atomic scattering factor’. It does not carry any information on the material’s correlation functions. The incident energy dependence is the only RIXS-specific part of the cross section that is not included in the atomic scattering factor.

In a typical RIXS experiment, the polarization of the incoming photon is linear. It is mostly chosen to be either parallel ($\boldsymbol{\epsilon}_\pi$) or perpendicular ($\boldsymbol{\epsilon}_\sigma$) to the scattering plane² (the plane spanned by \mathbf{k} and \mathbf{k}'). The outgoing photon’s polarization is not measured, and the cross section should therefore be summed over two orthogonal outgoing polarizations.

2.4 Direct and Indirect RIXS

In Sec. 2.3, the Kramers-Heisenberg expression for the RIXS scattering amplitude \mathcal{F}_{fg} , Eq. (2.31), was derived and re-expressed as a product of a photon absorption operator \mathcal{D} , the intermediate state propagator G and a photon emission operator \mathcal{D}^\dagger , sandwiched between the RIXS final state and ground state, yielding Eq. (2.35). The presence of the intermediate state propagator is what makes the theory of RIXS complicated – and interesting. The propagator G is defined in terms of the inverse of the total Hamiltonian H of the material, $G(z_{\mathbf{k}}) = (z_{\mathbf{k}} - H)^{-1}$, where the operator H naturally divides into the ground-state Hamiltonian H_0 (governing the quantum system without a core hole) and the core hole Hamiltonian H_C perturbing the system after photon absorption: $H = H_0 + H_C$. It should be noted that even if one commonly refers to H_C as the core hole Hamiltonian, it also includes the interaction between the electron excited into the conduction band and the rest of the material. As core hole and excited electron together form an exciton, their separate effects on the system cannot, in principle, be disentangled.

At this point it is useful to separate the full propagator G into an unperturbed one $G_0 = (z_{\mathbf{k}} - H_0)^{-1}$ and a term that contains the core hole Hamiltonian H_C , using the identity $G = G_0 + G_0 H_C G$. This also separates the RIXS amplitude into two parts, which define *direct* and *indirect* RIXS [3, 49]:

$$\mathcal{F}_{fg}^{\text{direct}} = \langle f | \mathcal{D}^\dagger G_0 \mathcal{D} | g \rangle \quad \text{for direct RIXS} \quad (2.43)$$

² π and σ come from the German *parallel* and *senkrecht* – parallel and perpendicular.

Intermediate State Propagator							
Definition	RIXS amplitude $\mathcal{F}_{fg} = \langle f \mathcal{D}^\dagger G \mathcal{D} g \rangle$ Intermediate State Propagator $G(z_{\mathbf{k}}) = \frac{1}{z_{\mathbf{k}} - \bar{H}}$; $H = H_0 + H_C$ H_0 ground state, H_C core hole Hamiltonian						
Exact G	$G = G_0 + G_0 H_C G$ 						
	<table border="1"> <thead> <tr> <th><i>Direct RIXS</i></th> <th><i>Indirect RIXS</i></th> </tr> </thead> <tbody> <tr> <td>$\mathcal{F}_{fg}^{direct} = \langle f \mathcal{D}^\dagger G_0 \mathcal{D} g \rangle$</td> <td>$\mathcal{F}_{fg}^{indirect} = \langle f \mathcal{D}^\dagger G_0 H_C G \mathcal{D} g \rangle$</td> </tr> </tbody> </table>	<i>Direct RIXS</i>	<i>Indirect RIXS</i>	$\mathcal{F}_{fg}^{direct} = \langle f \mathcal{D}^\dagger G_0 \mathcal{D} g \rangle$	$\mathcal{F}_{fg}^{indirect} = \langle f \mathcal{D}^\dagger G_0 H_C G \mathcal{D} g \rangle$		
<i>Direct RIXS</i>	<i>Indirect RIXS</i>						
$\mathcal{F}_{fg}^{direct} = \langle f \mathcal{D}^\dagger G_0 \mathcal{D} g \rangle$	$\mathcal{F}_{fg}^{indirect} = \langle f \mathcal{D}^\dagger G_0 H_C G \mathcal{D} g \rangle$						
Approximate G	<table border="1"> <thead> <tr> <th>Fast Collision [26]</th> <th>Perturbation Expansion [26, 38, 43-47]</th> <th>UCL [48-50]</th> </tr> </thead> <tbody> <tr> <td>$G(z_{\mathbf{k}}) \rightarrow 1/z_{\mathbf{k}}$</td> <td>$G_0 H_C G \rightarrow G_0 H_C G_0$</td> <td>$G_0 H_C G \rightarrow G_0 H_C G_C$</td> </tr> </tbody> </table>	Fast Collision [26]	Perturbation Expansion [26, 38, 43-47]	UCL [48-50]	$G(z_{\mathbf{k}}) \rightarrow 1/z_{\mathbf{k}}$	$G_0 H_C G \rightarrow G_0 H_C G_0$	$G_0 H_C G \rightarrow G_0 H_C G_C$
Fast Collision [26]	Perturbation Expansion [26, 38, 43-47]	UCL [48-50]					
$G(z_{\mathbf{k}}) \rightarrow 1/z_{\mathbf{k}}$	$G_0 H_C G \rightarrow G_0 H_C G_0$	$G_0 H_C G \rightarrow G_0 H_C G_C$					
Valence excitation	<table border="1"> <tbody> <tr> <td>caused by \mathcal{D}'s</td> <td>caused by H_C</td> </tr> </tbody> </table>	caused by \mathcal{D} 's	caused by H_C				
caused by \mathcal{D} 's	caused by H_C						

Table 2.1: Theoretical approach to the intermediate state propagator, classifying direct and indirect RIXS processes and common approximations to the propagator. $G_C = (z - H_C)^{-1}$.

and

$$\mathcal{F}_{fg}^{indirect} = \langle f | \mathcal{D}^\dagger G_0 H_C G \mathcal{D} | g \rangle \quad \text{for indirect RIXS.} \quad (2.44)$$

Note that this definition of direct and indirect RIXS, based on the Kramers-Heisenberg expression, is exact. Adding the two amplitudes, one retrieves the total scattering amplitude \mathcal{F}_{fg} . Table 2.1 summarizes the categorization of the scattering amplitude into direct and indirect RIXS, and also shows the subsequent approximations that are often used.

For the direct RIXS amplitude, the core hole does not play a role – the photon absorption and emission matrix elements determine which electronic transitions are allowed. The physical picture that arises for direct RIXS is that an incoming photon promotes a core electron to an empty valence state and subsequently an electron from a different state in the valence band decays, annihilating the core hole (see Fig. 1.1). Thus for direct RIXS to occur, both photoelectric transitions – the initial one from core to valence state and the succeeding one from valence state to fill the core hole – must be possible. These transitions can, for example, be an initial dipolar transition of $1s \rightarrow 2p$ followed by the decay of another electron in the $2p$ band: $2p \rightarrow 1s$. This happens at the K edge of oxygen, carbon and silicon. At transition metal L edges, dipole transitions causing direct RIXS are possible via $2p \rightarrow 3d$ and $3d \rightarrow 2p$ dipolar transitions. In all these cases, RIXS probes the valence and conduction states directly.

For indirect RIXS, the scattering amplitude depends critically on the perturbing core hole Hamiltonian – without it the indirect scattering amplitude vanishes. In general, the scattering amplitude $\mathcal{F}_{fg}^{indirect}$ arises from the combined impact of H_C and the transition matrix elements \mathcal{D} . Most often, for indirect RIXS $\mathcal{D}/\mathcal{D}^\dagger$ create/annihilate an electron in the same state, far above the Fermi level. For instance at the transition metal K edge, the $1s \leftrightarrow 4p$ process creates/annihilates an electron in $4p$ states several electronvolts above the transition metal $3d$ valence shell. The delocalized $4p$ electron can then be approximated as being a *spectator* because (Coulomb) interactions involving the localized core hole are usually much stronger and dominate the scattering cross section.

It should be noted that if scattering is direct, as for instance at transition metal L edges, indirect processes can also contribute to the total scattering amplitude. However, as indirect scattering arises in this case as a higher order process, it is normally weaker than the leading order direct scattering amplitude. We speak of indirect RIXS when direct processes are absent.

2.5 Ultra-short core hole lifetime expansion

The potential that the core hole exerts on the valence electrons of transition metals is strong: the attraction between a $1s$ core hole and $3d$ electron is typically $\sim 6 - 8$ eV, which is of the same order as the $3d$ - $3d$ intra-ionic Coulomb interaction. Treating such a strong interaction as a weak perturbation renders

a perturbation expansion uncontrolled. To deal with the strong core hole interaction, the Ultrashort Core hole Lifetime (UCL) expansion was developed in Refs. [48–50], which treats the core hole potential as the dominating energy scale (see Table 2.1).

For most RIXS intermediate states, the core hole lifetime broadening is quite large: typically Γ is of the order of 1 eV. This yields a timescale $\tau = 1/2\Gamma = 4$ fs. Only during this ultrashort time, the system is perturbed by the core hole. Many elementary excitations have an intrinsic timescale that is much larger than 4 fs. For example, phonons have a typical energy scale up to 100 meV, and magnons up to 350 meV, thus corresponding to timescales almost an order of magnitude larger. Even low energy electronic valence band excitations can be within this range.

The resulting physical picture of a RIXS process involving low energy excitations is that the dynamics in the intermediate state are limited because of lack of time.

The calculation of the RIXS amplitude within the UCL expansion in Refs. [48–50] is based on a series expansion of the Kramers-Heisenberg equation, Eq. (2.31), which is elaborated on in chapter 3. Here we present an analogous derivation. We first introduce the identity

$$G(z) = \sum_n \frac{|n\rangle \langle n|}{z - E_n} = \frac{1}{i\hbar} \int_0^\infty dt e^{-i(H-z)t/\hbar}. \quad (2.45)$$

The scattering amplitude then becomes

$$\mathcal{F}_{fg} = \frac{1}{i\hbar} \int_0^\infty dt \langle f | \mathcal{D}^\dagger e^{-i(H-z)t/\hbar} \mathcal{D} | g \rangle, \quad (2.46)$$

which gives a natural picture of the RIXS process: it starts with excitation, then the intermediate state evolves over a time t , followed by radiative decay of the core hole. Since z has an imaginary part, RIXS processes with long intermediate state lifetimes are suppressed. Because the decay time t is not measured, all processes with different t 's interfere, hence the integral.

Because Γ is assumed to be the largest energy scale in the problem, we factorize the exponential $e^{-i(H-z)t/\hbar} = e^{-i(H-\Re\{z\})t/\hbar} e^{-\Gamma t/\hbar}$ in Eq. (2.46), and expand the exponential with the smallest exponent:

$$\mathcal{F}_{fg} = \frac{1}{i\hbar} \int_0^\infty dt \langle f | \mathcal{D}^\dagger \sum_{l=0}^{\infty} \frac{1}{l!} \left(\frac{-i\tilde{H}t}{\hbar} \right)^l e^{-\Gamma t/\hbar} \mathcal{D} | g \rangle, \quad (2.47)$$

where $\tilde{H} = H - E_g - \hbar\omega_{\mathbf{k}}$. Integration over time gives

$$\mathcal{F}_{fg} = \frac{1}{i\hbar} \langle f | \mathcal{D}^\dagger \sum_{l=0}^{\infty} \left(\frac{-i\tilde{H}}{\hbar} \right)^l \frac{\hbar^{l+1}}{\Gamma^{l+1}} \mathcal{D} | g \rangle = \frac{1}{i\Gamma} \sum_{l=0}^{\infty} \langle f | \mathcal{D}^\dagger \left(\frac{\tilde{H}}{i\Gamma} \right)^l \mathcal{D} | g \rangle, \quad (2.48)$$

The sum over intermediate states is traded for a series in \tilde{H}/Γ , which converges if the lifetime broadening is the largest energy scale in the problem: $\Gamma > |E_n - E_g - \hbar\omega_{\mathbf{k}}|$ for all n . The idea now is to approximate the series with the first few terms. One just has to calculate the matrix elements of (some power of) H to get the scattering amplitude.

The simplest approximation is to retain only $l = 0$. This is called the fast collision approximation (see table 2.1): the RIXS process is completely determined by the dipole transitions, without any dynamics in the intermediate state. For indirect RIXS, the cross section is therefore zero in this approximation. For direct RIXS however, the fast collision approximation yields a simple description of, *e.g.*, single magnon RIXS in the cuprates (chapter 4) and the L edge cross section of iridates (chapter 6). In certain cases, one can resum a series of terms with different l [48–50].

Convergence is not a priori guaranteed for the expansion: when the incoming photons are far off resonance, $|E_n - E_g - \hbar\omega_{\mathbf{k}}| > \Gamma$. This divergence can easily be removed by modifying the expansion. To better account for the effect of detuning from the resonant edge, we introduce the resonance energy $\hbar\omega_{\text{res}}$, which is chosen to be somewhere in the resonant absorption region (*e.g.*, the peak of the absorption spectrum). Writing $e^{-i(H-z)t/\hbar} = e^{-i(H-E_g-\hbar\omega_{\text{res}})t/\hbar} e^{i(\hbar\omega_{\mathbf{k}}-\omega_{\text{res}}+i\Gamma)t/\hbar}$, we find

$$\mathcal{F}_{fg} = \frac{1}{\Delta} \sum_{l=0}^{\infty} \langle f | \mathcal{D}^\dagger \left(\frac{H - E_g - \hbar\omega_{\text{res}}}{\Delta} \right)^l \mathcal{D} | g \rangle, \quad (2.49)$$

with $\Delta = \hbar(\omega_{\mathbf{k}} - \omega_{\text{res}}) + i\Gamma$. This is the UCL expansion. Now, the series converges if $(E_n - E_g - \hbar\omega_{\text{res}})^2 < (\hbar\omega_{\mathbf{k}} - \hbar\omega_{\text{res}})^2 + \Gamma^2$. Physically, this means that off-resonant scattering is an even faster process than resonant scattering. We conclude that far off resonance, the UCL expansion (2.49) form converges very rapidly.

The UCL series formally diverges in another way: there are always some intermediate states for which $|E_n - E_g - \hbar\omega_{\mathbf{k}}| > \Gamma$, for example, states from another edge. Only when such intermediate states give sufficiently small contributions to the scattering amplitude can one hope to obtain a sensible result from the UCL expansion. Usually, that is the case as these states are far off-resonance. The Hamiltonian can be replaced by an effective Hamiltonian where the far off-resonant states have been integrated out (see, for instance, the treatment of magnetic indirect RIXS in cuprates in chapter 4).

An alternative approach with Green's functions is equally viable [3]. Besides charge excitations [48–50], many other excitations that arise in indirect RIXS were studied with the UCL expansion. The single- and two-magnon response of antiferromagnetic La_2CuO_4 was calculated within the UCL expansion [19, 51, 52], agreeing nicely with experiments [11, 14, 53]. Collective orbital excitations were investigated theoretically for LaMnO_3 [54]. Indirect RIXS investigations within the UCL expansion on charge, magnetic, orbital and lattice excitations will be reviewed in chapters 3, 4, 5, and 7, respectively.