

Extracting the Electronic Structure of Warm Dense Matter via Resonant Inelastic X-ray Scattering



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Thesis Submitted for the Degree of
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Dedicata a Giulio e Adriano, che sono nati insieme al mio dottorato

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Abstract

Understanding how material properties evolve under extreme thermodynamic conditions is essential for advancing our knowledge of matter in such environments, with applications ranging from planetary science to nuclear fusion research. However, the challenges associated with recreating these thermodynamic conditions in laboratory settings, combined with their transient nature, have limited the number of experimental techniques suitable for their study. At the same time, the complexity of High-Energy Density (HED) systems necessitates experimental investigation to benchmark and refine theoretical models. This thesis introduces a novel approach based on Resonant Inelastic X-ray Scattering (RIXS) spectroscopy to measure the electronic density of states (DOS) of materials—a fundamental quantity from which many other material properties can be derived. Unlike traditional techniques such as absorption spectroscopy, RIXS encapsulates information about the global electronic structure of a material in a single spectrum, albeit in a complex form. This feature is particularly advantageous in HED science, where achieving stable and reproducible conditions is inherently difficult. However, this advantage is accompanied by the drawback of a relatively low signal-to-noise ratio (SNR), making the extraction of DOS from RIXS spectra a complex task. To this purpose, I developed a method that combines neural networks with physical modelling to perform this extraction. This approach also deconvolves the source spectrum by correlating it with the RIXS measurements, allowing for the reconstruction of DOS with a resolution that surpasses the limitation given by the source spectrum’s bandwidth. The method is first introduced in a general framework as a way to solve complex inverse problems and is subsequently tailored to the RIXS problem. This approach is tested on synthetic RIXS data and its performance is compared with those of more conventional numerical techniques. Additionally, I show that this RIXS-based methodology can also measure the temperature of the probed material. I then apply this method to analyse RIXS spectra from two experiments conducted at the EuXFEL and LCLS facilities. The first experiment investigated warm-dense Fe, FeO, Fe₂O₃, and gadolinium, extracting their thermodynamic conditions and electronic structures with sufficient resolution to detect the microscopic environment in which ions are embedded and resolve fine details such as bandgaps. The extracted DOS showed good agreement with density functional theory (DFT) calculations. While the investigation of gadolinium primarily showcased the method’s flexibility in analysing various materials through different electronic excitations, the study of iron oxides attracted particular interest due to their distinctive behaviour under high-pressure conditions and their relevance in geophysics. In the other experiment, the DOS of compressed and ambient FeO is extracted, revealing a systematic bandgap closure consistent with theoretical predictions of a insulator-to-metal transition under high compression. The electronic structure evolution was studied in parallel with changes in the crystalline structure, highlighting RIXS’s potential for time-resolved studies of dynamic processes. While these results retrieved the expected trends, higher-quality raw data are required to achieve more precise and conclusive findings. Overall,

these results hold promise for this RIXS-based methodology to monitor the evolution of electronic structures in materials undergoing fast dynamic processes, paving the way for innovative diagnostic approaches in this field.

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List of Acronyms

ADU	Analog-to-Digital Units
BE	Binding Energy
DAS	Density of Accessible States
DFT	Density Functional Theory
DOS	Density of States
EOS	Equation of State
EXAFS	Extended X-ray Absorption Fine Structure
FC	Flat Crystal
FT-DFT	Finite Temperature Density Functional Theory
HAPG	Highly Annealed Pyrolytic Graphite
HED	High Energy Density
ICF	Inertial Confinement Fusion
IF	Instrument function
MD	Molecular Dynamics
ML	Machine Learning
NN	Neural Network
PSF	Point Spread Function
RC	Rocking Curve
RIXS	Resonant Inelastic X-ray Scattering
RL	Richardson-Lucy
SASE	Self Amplified Spontaneous Emission
SNR	Signal-to-Noise Ratio
STEP	Surrogate Training Embedded in Physics
VH	von Hámos
VISAR	Velocity Interferometer System for Any Reflector
XAS	X-Ray Absorption Spectroscopy
XANES	X-Ray Absorption Near Edge Spectroscopy
XES	X-Ray Emission Spectroscopy
XFEL	X-Ray Free Electron Laser
XRD	X-Ray Diffraction
XRS	X-Ray Raman Scattering
XRTS	X-Ray Thomson Scattering

List of Symbols

Quantity	Symbol	Value	Units
Boltzmann constant	k_B	8.617×10^{-5}	eV/K
Bragg angle	θ_B		rad
Camera noise	σ_N	/	ADU
Charge spreading radius	R_s	/	cm
Charge spreading kernel	H	/	/
Chemical potential	μ	/	eV
Coupling parameter	Γ	/	/
Cross-section	σ	/	cm ²
De Broglie wavelength	Λ	/	cm
Degeneracy parameter	θ	/	/
Density of states	$\rho(\epsilon)$	/	states/(eV · cm ³)
Effective density of states	$\rho_{\text{eff}}(\epsilon)$	/	states/(eV · cm ³)
Electron charge	e	1.6×10^{-19}	C
Electron density	n_e	/	particle/cm ³
Electron energies	ϵ	/	eV
Electron mass	m_e	9.11×10^{-28}	g
Electron wavefunctions	ψ	/	cm ^{-3/2}
Energy spectrum	I	/	arb. units
Fermi-Dirac distribution	f_{FD}	/	/
Fill fraction	λ	/	/
Free electron density	n_f	/	particle/cm ³
Ion density	n_i	/	particle/cm ³
Matrix transition elements	M	/	/
Normalized energy spectrum	S	/	arb. units
Particle velocity	U_p	/	Km/s ³
Photons frequency	ω	/	s ⁻¹
Pressure	p	/	Pa
Reduced Planck constant	$\hbar$	4.136×10^{-15}	eV · s
RIXS operator	P_{RIXS}	/	/
Single-photon ADU value	ADU_{sp}	/	ADU
Shock velocity	U_s	/	Km/s ³
Solid angle	Ω	/	sr
Source spectrum	Φ	/	arb. units
Speed of light	c	2.998×10^{10}	cm/s
Temperature	T	/	eV

Chapter 1: Introduction

1.1 Quantum Plasmas

The physical systems studied in this thesis are high-energy density (HED) plasmas, which are ensembles of particles (e.g. atoms, electrons, ions) characterised by high temperatures, ranging from approximately 1 eV to several hundreds eV ($1 \text{ eV} \approx 11600 \text{ K}$), and high densities, going from typical solid state values ($\approx 1 \text{ g/cm}^3$) up to densities of thousands of g/cm^3 . In these temperature conditions, atoms are ionised with respect to their ambient condition state, ultimately forming a plasma — an ensemble of electrically charged particles interacting via electromagnetic forces¹. On the other hand, the high densities strengthen the interactions among particles and amplify quantum effects, making their behaviour resemble that of solid-state systems. Hence, these systems are often referred to as “quantum plasmas”. Considering the thermodynamic relationships between pressure, energy, density, and temperature, HED systems are fundamentally characterised by extreme pressures (exceeding 1 Mbar) or, equivalently, energy densities surpassing 10^{11} J/m^3 . In this context, compressed solids are included within the category of quantum plasmas. This consideration is also justified by the fact that, at such pressures and energy densities—comparable to the binding energies of valence electrons—ions in the solid undergo ionisation. Though these states of matter may seem extreme, they are common throughout the universe², appearing in the interiors of the stars and giant gaseous planets [1–3]. Thanks to the development of technology, nowadays, it is possible to recreate these states of matter in laboratory, including inertial confinement fusion (ICF) [4–7], dynamic and static compression [8, 9], and isochoric heating [10]. As a result, there is substantial interest in studying and modelling

¹There is no sharp phase transition to a plasma state, as the degree of ionisation in a system increases gradually with temperature, and in certain regimes, also with density.

²Actually, the plasma state, whether high-density or not, is the most present in the universe, as stars are made of it.

HED systems, driven both by fundamental scientific inquiry and practical applications, especially considering the recent advances towards ignition in ICF [11–13].

The theoretical modelling of quantum plasmas, however, presents significant challenges. Due to their high densities, these systems inherit the complexities of solid-state materials, where electrons exhibit quantum behaviour and ions display strong correlations. In addition to this, the elevated temperatures modify the interactions and the local environment experienced by the particles - affecting properties like the mean ionisation state and introducing a range of phenomena, such as collisional excitation and electron recombination [14, 15]. To address these challenges, the modelling of dense plasmas employs a multiscale approach [16], which is explored more in detail in Section 1.3. With this approach, different models are used to study the system at different length scales: atomistic (or more generally, microscopic) models calculate plasma properties, which are then incorporated as input parameters into continuum (or macroscopic) models to predict the system’s behaviour for most practical applications [17]. Therefore, accurately estimating plasma properties, such as the equation of state and transport coefficients, is crucial for practical models to produce reliable predictions. Given the complexity of these systems, experimental investigations are indispensable for validating and complementing theoretical estimates, which may vary significantly between different models [18]. Thus, experimentally-measured quantities are used as input parameters in simulations, or more frequently, theoretical models are employed to interpret experimental data, producing measurable outputs with plasma properties acting as fitting parameters. In this context, the goal of this thesis is to introduce experimental methods, which, alongside theoretical models, provide a measure of the electronic density of states (DOS) of materials under extreme thermodynamic conditions. The DOS is a fundamental material property that affects its equation of state [19], as well as its transport and spectral properties [20], underscoring the need for accurate DOS estimation to predict a system’s dynamics and behaviour. These connections are explored in more detail in Section 1.3.2.

Plasmas can be classed by a few dimensionless parameters, which will now be reviewed. Typically, a plasma consists of free electrons with number density n_f and temperature T_e , as well as ions with number density n_i and temperature T_i ³. The ion population consists

³In solid-density plasmas, this assumption can break down, as they may contain electrons that are

of N_s ion species with charge state z_j and number density n_j , with $j = 1, 2, \dots, N_s$. Since free electrons remain in the system, plasmas are globally neutral, meaning that $n_f = \langle z \rangle n_i$, where $\langle z \rangle = \frac{1}{n_i} \sum_{j=1}^{N_s} \langle z_j \rangle n_j$, with $\langle z_j \rangle$ representing the mean charge state of the j -th ion species. For classical plasmas, correlations between particles are mainly quantified by the *Coulomb coupling parameter* $\Gamma_{\alpha\beta}$, which is the ratio of the average electrostatic potential energy between particles of species α and the average thermal energy of particles of species β . For example, the ion-ion coupling parameter is given by:

$$\Gamma_{ii} = \frac{\langle z \rangle^2 e^2}{4\pi\epsilon_0 k_B T_i a_i}, \quad (1.1)$$

where k_B is the Boltzmann constant, e is the elementary charge, ϵ_0 is the vacuum permittivity, and $a_i = (4\pi n_i/3)^{-1/3}$ is the *ion-sphere radius*, which measures the typical distance between ions. Similar expressions can be defined for the electron-electron and the average electron-ion coupling parameters [22]:

$$\Gamma_{ee} = \langle z \rangle^{-5/3} \frac{T_i}{T_e} \Gamma_{ii} \quad , \quad \Gamma_{ei} \sim \langle z \rangle \Gamma_{ee} \quad . \quad (1.2)$$

Given the significant mass difference between electrons and ions—and consequently their differing heat capacities—thermal equilibration between the two occurs at asymmetric rates. If the ions are initially hotter than the electrons, the electrons rapidly equilibrate to the ion temperature, whereas, in the opposite case, the ions heat up at a slower rate. As a result, in typical scenarios, $T_e \geq T_i^4$ (and often $T_e \approx T_i$), leading to $\Gamma_{ii} \geq \Gamma_{ee}$. A plasma is considered weakly coupled if $\Gamma_{ii} \ll 1$, meaning Coulomb interactions are weak and the plasma can be treated similarly to a gas, where almost no structure is present. In this regime, collective effects dominate, effectively screening microscopic electric fields, which decay exponentially over a characteristic length scale known as the *Debye length*, $\lambda_{D,i} \sim a_i/\sqrt{\Gamma_{ii}}$ [23]. Within a sphere of radius $\lambda_{D,i}$, the plasma contains a sufficiently large number of particles (ideal plasma), allowing it to be described as a continuum with correlations occurring only on length scales larger than $\lambda_{D,i}$.

In contrast, a strongly coupled plasma ($\Gamma_{ii} > 1$) exhibits stronger Coulomb interactions,

neither fully bound nor entirely free. For such systems, even defining ionisation becomes challenging [21].

⁴Exceptions include systems undergoing nuclear reactions, which continuously supply energy to the ions, maintaining their temperature higher than that of the electrons.

reducing the shielding and correlation lengths to the scale of the interparticle spacing a_i [24], so that, under sufficiently strong coupling, ordered structures can form [25]. In these strongly coupled systems, characterised by high density and low temperatures, quantum effects often plays a significant role. These effects enter in two primary ways: through the uncertainty principle, which causes the position of particles to be probability distributions over space, and via symmetry effects arising from the indistinguishability of particles, which alter the statistical population of energy levels.

To quantify the first effect, one can start by recalling the thermal De Broglie wavelength of particles α ,

$$\Lambda_\alpha = \left(\frac{2\pi\hbar^2}{2\pi m_\alpha k_B T_\alpha} \right)^{1/2}, \quad (1.3)$$

where m_α is the rest mass of the particle species and $\hbar$ is the reduced Planck constant. This wavelength, which estimates the spatial extension of α particle's wavefunctions, is then compared with the average interparticle spacing $a_\alpha \equiv (4\pi n_\alpha/3)^{-1/3}$ by defining the degeneracy parameter $\chi_\alpha = \Lambda_\alpha/a_\alpha$ [26]. If $\chi_\alpha \gtrsim 1$, particles cannot be treated as pointlike objects and quantum mechanics must be employed to describe their dynamics, especially for short-range interactions, where classical collisions become a quantum scattering problem between two particles [27]. Given the significantly larger mass of ions compared to electrons, ions in quantum plasmas are typically treated as pointlike particles obeying the classical laws of motions, an assumption that is also adopted in this thesis.

Symmetry constraints - a fundamental requirement of quantum mechanics - further influence particle dynamics, for instance by preventing two identical particles from occupying the same region of space.⁵ However, their primary impact lies in determining the statistical population of electronic energy levels, which follows the Fermi-Dirac distribution⁶:

$$f_{FD}(\epsilon; T, \mu) = \frac{1}{1 + e^{(\epsilon - \mu)/k_B T}}, \quad (1.4)$$

with ϵ representing the energy of the electronic states and μ denoting the chemical poten-

⁵These constraints can be incorporated into semiclassical frameworks by introducing *exchange* or *Pauli potentials* into the particles' equations of motion [28].

⁶While this distribution is strictly valid for an ideal fermion gas, its deviations due to interactions are typically small [29], and thus neglected in this thesis.

tial. To quantify the symmetry effects, one can introduce another parameter θ_e , defined as follows:

$$\theta_e = \frac{T_e}{T_{F,e}}, \quad \text{with } T_{F,e} = \frac{\hbar^2}{2k_B m_e} (3\pi^2 n_e)^{2/3}, \quad (1.5)$$

where $T_{F,e}$ is the Fermi temperature of the electron population. Considering Eq. (1.4) and the relation between n , T and μ for an ideal fermion gas [30] (as a first approximation), one can calculate that, if $\theta_e \lesssim 1$, μ is positive, indicating that the system is degenerate and the electrons follow Fermi-Dirac statistics. Conversely, when $\theta_e \gg 1$, $\mu/k_B T$ becomes very negative, so that the expression in Eq. (1.4) reduces to the classical Maxwell-Boltzmann distribution. Considering that $\chi \approx 1.84 \theta^{-1/2}$, the condition $\chi_e \gtrsim 1$ is equivalent to $\theta_e \lesssim 1$, showing that the statistical and dynamical behaviour of the system transition to the quantum regime simultaneously. By incorporating the Fermi-Dirac distribution in the calculation of the average kinetic energy, a modified definition of the coupling constants for electrons is obtained [31], such that Γ_{ee} scales with $n_e^{-1/3}$ and is independent of temperature in the quantum regime. This modification ensures that free electrons in solid systems are weakly correlated, as expected.

Figure 1.1 presents a temperature-density phase diagram of matter, highlighting the regions belonging to the most common plasmas found in nature and in laboratories. For reference, the diagram includes also isolines of the ion-ion coupling parameter Γ_{ii} and the electron degeneracy parameter θ_e . Near these lines, there exists an intermediate regime where classical equations describe the general behaviour, but quantum corrections are required. This thesis deals with the regions of the diagram occupied by isochorically-heated matter (in blue) and compressed solid generated by laser-driven planar shocks (in orange), both of which are strongly-coupled and partially-degenerate plasmas.

1.2 Experimental Realisation of HED Systems

Over the years, various methods have been developed to recreate extreme thermodynamic states in laboratory settings, beginning with explosive-driven compressions conducted both at Los Alamos National Laboratory and independently in Russia in the 1930s and 1940s, which were used to study the physics of shock wave propagation [32, 33]. In the 1950s, the

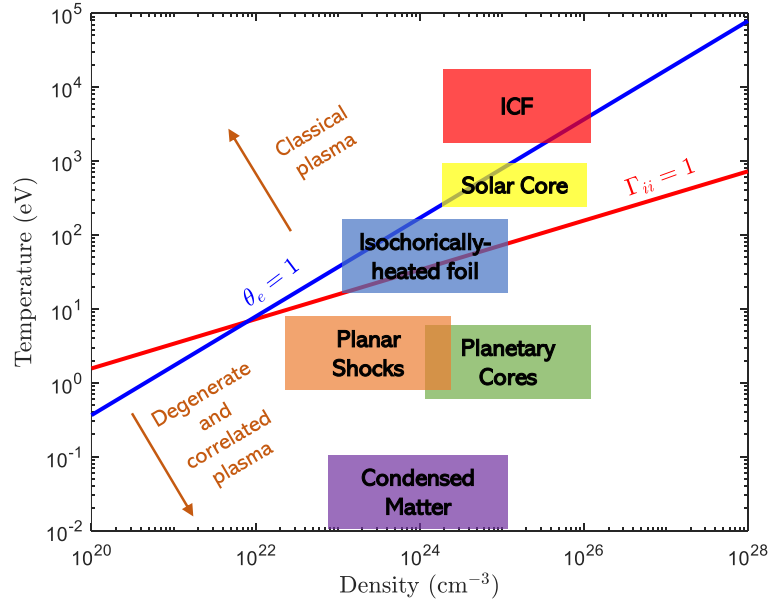


Figure 1.1: A temperature-density phase diagram for matter, with regions associated to typical systems indicated by the coloured areas. The plasma is assumed to be in thermal equilibrium, with the temperature here being $T_e = T_i$. Isolines of the ion-ion coupling parameter ($\Gamma_{i,i} = 1$, for $\langle z \rangle = 1$) and the degeneracy parameter ($\theta_e = 1$) are included. The region below these lines is occupied by quantum plasmas, whereas the part above is associated with classical plasmas.

invention of diamond anvil cells, inspired by Bridgman’s pioneering work, enabled the static compression of materials to unprecedented pressures, up to hundreds of GPa [9, 34]. In the following years, significant advancements were made in dynamic compression techniques, including the development of z-pinch machines [35], gas guns [36], and intense optical lasers. The latter played a pivotal role in the then-nascent field of ICF research [37] and flourished in the following years, driven by rapid advancements in laser technology, allowing pressures of a few TPa to be reached [38]. Only more recently, a new type of HED systems has emerged through isochoric heating, achieved by irradiating targets with modern x-ray free electron lasers (XFELs) [10, 39], which can drive electronic pressures into the terapascal regime. This section gives an overview of the mechanisms behind the creation of HED matter with optical and x-ray free-electron lasers, which constitute the systems investigated in this thesis. Plasmas generated by powerful lasers are typically very short-lived, lasting only tens of nanoseconds, as extreme thermodynamic conditions quickly dissipate due to processes like heat conduction and hydrodynamic expansion. Consequently, *in situ*

techniques, commonly based on diffraction and spectroscopy, are necessary for experimental investigations of these systems.

1.2.1 Laser-Compressed Systems

To reach the extreme pressures found in the interiors of large planets and stars, laser-driven compression is required. This technique can be classified into two categories: planar compressions [33], commonly used for pure physical investigations, and spherical compressions [4], mostly employed in nuclear fusion applications. For the purposes of this thesis, only planar shocks are examined below.

In a typical planar shock experiment, the target consists of a series of material slabs glued together. Starting from the side exposed to the laser, the first layer is called the *ablator*, usually made of plastic for their high energy absorption, ease of manufacture, and low cost. Behind it lies the material to be compressed and studied, potentially followed by additional layers for diagnostic purposes and tamper windows designed to sustain the high-pressure conditions within the sample for longer times (see below and Chapter 5 for details). In many cases, a thin layer of suitable material (e.g. aluminium) is placed between the ablator and the sample to shield against laser and ablator radiation, preventing target preheating. Nanosecond optical lasers, such as standard Nd:glass lasers [40], or modern diode-pumped lasers [41], are typically used to compress matter. When the laser strikes the target, it heats the outer layers of the ablator, causing them to vaporise and ionise. These outer layers enter a plasma state, allowing the laser radiation to pass through the solid layers until they reach the so-called *critical density*. For the typical wavelengths, durations and intensities of these lasers, where *inverse bremsstrahlung* is the primary absorption mechanism (see also below), this density is given by [4]:

$$n_C = \frac{\pi m_e c^2}{e^2 \lambda_L^2}, \quad (1.6)$$

where c is the speed of light and λ_L is the laser wavelength. The laser radiation, along with the emission from the outer plasma layers, can penetrate deeper into the target, ionizing and transforming additional layers into plasma. Heat conduction also contributes to raising the temperature of the inner layers. Using hydrodynamic equations, one can see that the

outer plasma layers expand outward and are ablated. Due to momentum conservation, this outward expansion causes the inner, still-solid layers to accelerate in the direction of the beam, driven by the resulting *ablation pressure*. In this absorption regime dominated by inverse bremsstrahlung, this pressure can be estimated with the following expression [42]:

$$p_{\text{abl}} = p_0 \left(\frac{A}{2Z} \right)^{1/3} \left(\frac{1}{\lambda_L [\mu\text{m}]} \right)^{2/3} \left(\frac{I_L [\text{Wcm}^{-2}]}{10^{14}} \right)^{2/3} \text{ Mbar} , \quad (1.7)$$

where I_L is the laser intensity, A and Z are the average atomic mass and atomic number of the target material, respectively, and p_0 is a dimensionless prefactor, typically around 10. For typical laser wavelengths and intensities (100s of μm and $\sim 10^{12} \text{ W cm}^{-2}$), ablation pressures on the order of $\sim 100 \text{ GPa}$ can be achieved.

As the compressibility of a solid generally decreases with density, the local sound velocity rises under compression. This effect causes compression waves to steepen as they propagate, eventually transforming into shock waves if they have sufficient distance to travel⁷. Consequently, the ablation pressure generated by the laser often induces a series of shock waves into the solid layers, with their structure determined by the shape of the laser pulse. These shocks contribute to the overall compression of the material, distorting its lattice and heating its constituents, which eventually leads to melting in some cases. Since the presence of shocks tends to reduce the levels of compression achieved for a given amount of supplied energy, their formation is typically suppressed by carefully shaping the laser pulse [4, 23]. However, they may be intentionally generated for specific applications or research purposes. A more detailed description of the equations and the mechanics of shock compressions can be found in the next section.

The nanosecond optical lasers used to compress matter interact primarily with free electrons through collective excitations [43]. The radiation generates electron plasma waves, which are dampened by electron-ion collisions and, to a lesser extent, by kinetic effects [44]. Laser energy is therefore absorbed primarily through inverse bremsstrahlung (and under certain conditions, through other mechanisms like resonant absorption), and then dissipated in the plasma via electron-ion collisions.

⁷Shocks are defined and theoretically modelled as discontinuities in thermodynamic fields. However, in practice, they always possess a finite width set by the viscosity or stresses of the medium.

Mechanisms and Equations of Shock Compressions in Solids

In shock compression, the material conditions before and after the shock front must satisfy conservation equations, as established in the 19th century by Rankine and Hugoniot. These equations express the conservation of mass, momentum, and energy across the shock, and link the initial density, pressure⁸, and energy of a material to its post-shock state. For a solid, they can be written as (using the subscript 0 for the pre-shock quantities):

$$\rho_0 U_S = \rho(U_S - U_P) \quad (1.8)$$

$$p - p_0 = \rho_0 U_S U_P \quad (1.9)$$

$$\varepsilon - \varepsilon_0 = \frac{1}{2} (p + p_0) \frac{(\rho - \rho_0)}{\rho \rho_0} \quad (1.10)$$

where U_P and U_S are the particle velocity (in the post-shock state) and the shock velocity, respectively, p is the pressure, ρ is the density ($\rho \approx m_i n_i$), and ε is the energy per unit mass. Given that the initial density, pressure, and energy are known, these three equations contain five unknowns (ρ , ε , p , U_S , and U_P). To resolve this system, two parameters need to be measured. Typically, the particle and shock velocity are selected, as these can be determined by monitoring the shock transit time and the surface or interface velocity at shock breakout, i.e. when the shock reaches the rear of the target. Today, both quantities are commonly measured using the VISAR (Velocity Interferometer System for Any Reflector) technique [45], which is described in more detail in Chapter 5. In many instances, the equation of state (EOS) of the compressed material is already known and tabulated from previous studies [46], reducing the number of unknowns that has to be measured to one⁹. If the primary goal is to determine the shock pressure without focusing on energy densities, it is possible to solve only the first two Hugoniot equations with the aid of a so-called “shock EOS”, which is an empirical linear relation between U_S and U_P :

⁸For simplicity, I consider isotropic stresses in the solid to illustrate the main concepts, while keeping in mind that stresses in solids are often anisotropic.

⁹When stresses in the material are anisotropic, an additional equation is needed to relate the longitudinal stress along the compression axis to the hydrostatic pressure. This relationship is typically described by a strength model, which is often complex and highly material-specific, making it an active area of ongoing research [47].

$$U_S = C_0 + sU_P, \quad (1.11)$$

where C_0 is the ambient bulk sound speed, and s is a material-dependent parameter of order unity. Substituting this relationship into the first two Hugoniot equations and eliminating U_P yields the following commonly used expression for p :

$$p - p_0 = \rho_0 C_0^2 \kappa / (1 - s\kappa)^2, \quad (1.12)$$

where $\kappa = (\rho - \rho_0)/\rho$ is the compressibility. While this expression simplifies the calculation of the shocked thermodynamic parameters, it should be applied cautiously, as this linear relationship is not a universal rule.

The locus of states achieved through shock compression is known as the *Hugoniot*. Considering the constraints imposed by the Hugoniot equations and the material's EOS, only one free parameter remains, making the Hugoniot a curve in the thermodynamic plane (e.g. $p = p(\rho; \rho_0, p_0)$ if ρ is chosen as the independent variable). Due to shock heating, for a given compression, the Hugoniot results in temperatures that lie above the isentrope. As an example, in Fig. 1.2 the Hugoniot and isentrope curves for iron are illustrated in the p - T plane, alongside its melting curve.

As shown in the figure, due to the sharp increase in entropy during a shock, the Hugoniot intersects the melting curve at low compression levels. To reach higher compression while keeping the material solid, the shock can be fractioned into a series of smaller shocks by properly modulating the laser pulse profile. This multishock process - displayed schematically in Fig. 1.2 - can achieve greater compression with smaller temperature rises, allowing the investigation of solid states at higher pressures. The limit case of multishock compression is the *ramp compression*, where the laser pulse is precisely shaped to achieve compression without generating shocks [8], resulting essentially in an isentropic process.

A common practice in compression experiments is to add a tamper layer, made of a suitable material, behind the sample to help maintain compression conditions for a longer period. When the shock wave reaches the interface between the sample and the tamper, the inability of the tamper atoms to fully withstand the stresses exerted by the sample allows the outermost layers of the sample to expand more freely. This interaction causes the

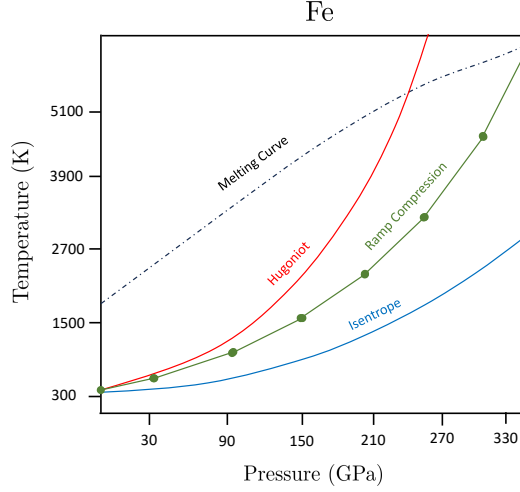


Figure 1.2: Key curves in high-pressure physics for iron are shown on a pressure-temperature diagram, including the melting curve, the Hugoniot, and the isentrope (data from [48, 49]). A schematic representation of a multishock process, approximating ramp compression, is also included. Smaller individual shocks result in reduced heating of the target, allowing the compression path to remain closer to the isentrope. The Hugoniot in the p - T plane is computed considering the additional EOS relating T to ρ and p .

shock to propagate into the tamper window, while a release wave is reflected back into the sample, further altering its thermodynamic state. Over time, the release wave broadens due to the reduction in sound speed in the decompressed material, without generating additional shocks. In contrast, when no tamper is used, the smaller resistance, compared to the tamper case, offered by air (or vacuum) to the motion of the target's outer layers results in significantly lower pressures in the released state. Additionally, if the Hugoniot curve of the tamper material is known, along with the Hugoniot and the EOS of the sample¹⁰, the thermodynamic parameters of the compressed and released sample's states can be found using the impedance matching method [50, 51]. This approach is illustrated in Fig. 1.3, which schematically depicts the thermodynamic history of a shocked sample with a tamper window in both the x - t and ρ - p planes.

Understanding the microscopic mechanisms that occur upon solid compression is complex, and many studies, experimentally based on x-ray diffraction, have been performed in this regard [54–56]. Here, a brief description of the main findings is given. If the shock is not too intense, only elastic deformations occur (elastic wave), temporarily distorting

¹⁰There exist experimental setups including a tamper layer that can perform the impedance matching method without knowing the sample's EOS. This is achieved by measuring also shock velocities, in addition to particles velocities.

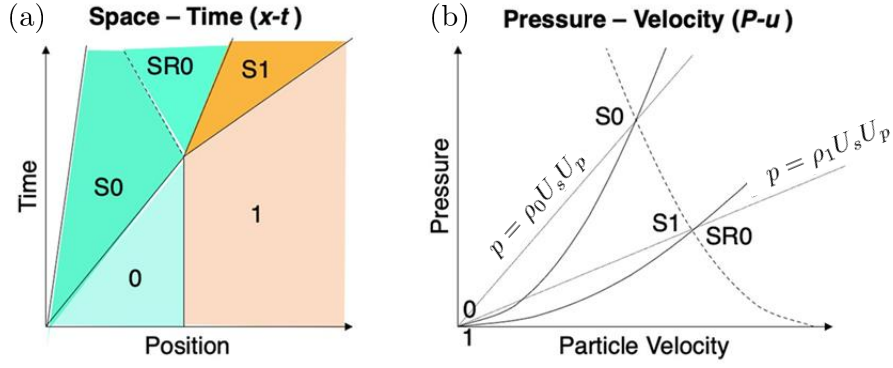


Figure 1.3: Space-time (a) and pressure-velocity (b) diagrams of a shock propagating through a layered target consisting of a sample and a window. These diagrams (adapted from [52]) are helpful for understanding the impedance matching method. The shock transitions the sample from its initial state (0) to a shocked state (S0). Upon reaching the interface with the window, the shock propagates through the window, transitioning it from state (1) to shocked state (S1), while a release wave reflects back into the sample, relaxing it to state (SR0). These states are represented in the p - U_P , where p and U_P are the pressure and particle velocity of both the shocked window (S1) and the released sample (SR0) for the conservation of physical quantities at the interface. By measuring U_P and knowing the two Hugoniot curves along with the sample's relaxation curve (an isentrope as a first approximation [53]), all states can be determined. In practise, the release curve is often approximated as the sample's reflected Hugoniot that, properly translated, goes through the state (SR0). The pressure equations shown in the diagram correspond to the second Hugoniot equation, with initial pressure assumed negligible.

the interatomic bonds and increasing the material's potential energy. This stored energy is then released, generating a relatively ordered macroscopic motion, with minimal heat production in the process.

If the shock strength exceeds the *Hugoniot elastic limit* (HEL), the shear strains induced by elastic deformations reach a critical value (yield point) along specific planes, determined by the type of compression and the crystal structure¹¹. Beyond this point, these critical planes begin to slip relative to one another, resulting in plastic deformation of the solid, with the atoms settling into new stable positions through mechanisms such as rotation and twinning [58, 59]. These plastic deformations alleviate stresses¹², which are proportional (in the linearised strain theory) solely to elastic deformations. When plastic flow begins, in fact, the elastic deformations decrease in magnitude ensuring that the total deformation—comprising both elastic and plastic components—satisfies the geometric

¹¹Models such as the simple *Schmidt's law* [57] are often used to predict which planes will activate.

¹²This stress relief actually means that shear stresses remain constant during plastic flow, provided *work hardening* is not considered [58].

constraints imposed by the macroscopic setup. For instance, in shock compression, the total deformation is modelled to be purely longitudinal along the compression axis, as the bulk of shocked material is *laterally confined* by the surrounding uncompressed solid.

Since, for energy reasons, it is not possible to break too many interatomic bonds, these plastically deformed regions are localised and are referred to as *dislocations*. The theory of dislocations, first proposed independently in 1934 by E. Orowan, M. Polanyi, and G.I. Taylor [60, 61], connects the nature and density of dislocations to the rate and type of plastic deformations.

A simple model [58] demonstrates that when compression exceeds the HEL, the resulting shock wave separates into two distinct components: a faster elastic wave and a slower plastic wave, with the latter relieving the stresses introduced by the former. This same model predicts that, above a certain shock strength, this two-wave structure disappears, with the plastic and elastic waves propagating together. If the plastic deformations induced by the shock are extensive, they can lead to shock-induced phase transitions in the crystalline structure.

Sample heating occurs during plastic relaxation, as ions overcome potential barriers to fall into a more stable configuration upon compression. In fact, the energy required to cross these barriers is released as random oscillations around the new equilibrium positions, which manifests macroscopically as a temperature increase. This also explains, on a microscopic level, why stronger shocks lead to greater heating—since more plastic/relaxation work occurs. Additionally, in release waves, defect annihilation contributes to heating as the energy stored in distorted atomic bonds within defects is released as thermal agitation.

Data from shock compression experiments, mostly based on x-ray diffraction, are typically interpreted using elastoplasticity theory [57, 62], or, in a more *ab initio* approach, molecular dynamics (MD) simulations. While computationally intensive, MD simulations can be employed to benchmark or refine analytical elastoplastic models [59].

1.2.2 Isochorically-Heated Systems

Another way for creating HED matter is by means of x-ray free electron lasers. Below, a brief overview of their key features and operating principles is provided, with a schematic representation shown in Fig. 1.4. For a more detailed discussion, readers are encouraged

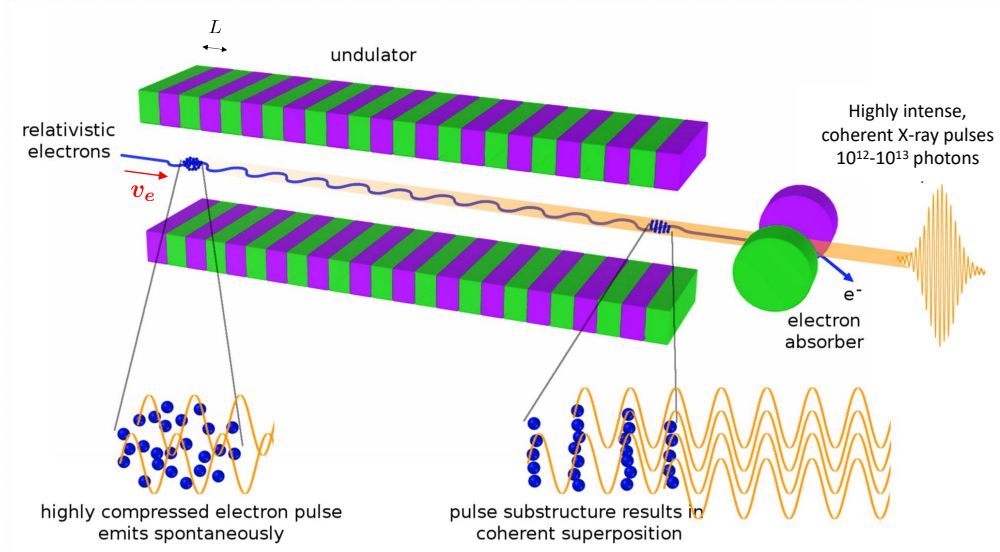


Figure 1.4: Scheme of an XFEL laser, adapted from [63].

to consult the extensive literature on the subject [64–66]. Unlike conventional lasers, which rely on specific atomic or molecular transitions in a gain medium, FELs generate radiation through the interaction of a beam of high-energy electrons with a magnetic field. The process begins with an electron gun or a linear accelerator (linac) that produces a beam of relativistic electrons. After acceleration, the electron beam passes through an *undulator*, a magnetic structure with alternating poles that forces the electrons to oscillate transversely, and therefore emit synchrotron radiation. This radiation interacts with the electron beam itself, leading to a process called *microbunching*, where the electrons form bunches that are spaced at the wavelength of the emitted radiation [64] (see Fig. 1.4). This microbunching allows the electrons to radiate coherently, thereby amplifying the intensity of the emitted light. In turn, this intensified radiation further increases the bunching effect, creating a positive feedback loop as in standard lasers. This process, which exponentially amplifies the intensity of the x-ray beam, is known as self-amplified spontaneous emission (SASE). Eventually, enough energy is extracted from the electrons that they begin to lag behind, drawing energy out of the radiation field. Beyond this point, the x-ray beam intensity saturates, and the electrons are subsequently removed by an absorber located at the end of the undulator.

To a first approximation, the central wavelength λ_L of the laser radiation is related to the undulator period L and the Lorentz factor of the electron beam, $\gamma_e = (1 - v_e^2/c^2)^{-1/2}$,

by the expression $\lambda_L = L/2\gamma_e^2$ [64]. This relationship can be understood as arising from two relativistic effects: first, from the electron's frame of reference, the undulator appears Lorentz contracted by a factor γ_e , resulting in emitted radiation with a wavelength of L/γ_e . When transforming back into the undulator's frame, the radiation emitted in the forward direction is further Doppler shifted by a factor of $2\gamma_e$. Therefore, by accurately gauging the characteristics of the electron bunch (e.g. its initial velocity) and the geometry of the magnetic field, a very short, intense and coherent x-ray pulse is produced, with a tunable central energy and a narrow bandwidth. To give some numbers, the Linac Coherent Light Source (LCLS), the first hard XFEL to become operational, delivers approximately 1 mJ of x-rays with a 0.3% bandwidth in pulse durations on the order of 10s of femtoseconds [67]. This results in a spectral brightness over a billion times higher than that of traditional synchrotron sources [68]. Considering also the impressive x-ray-beam divergence of only 2 μrad , focal spot size of ~ 100 nm are now achievable by means of specific refractive lenses and/or mirrors [69], allowing spatially localised investigations with radiation intensity of 10^{20} Wcm^{-2} on the target. Additionally, thanks to the relative large penetration depths of x-rays, XFELs can volumetrically heat the sample, creating quite uniform thermodynamic conditions. Recent works have demonstrated the capability to generate ultrashort XFEL pulse with durations on the order of attoseconds by properly shaping and manipulating the electron bunch [70], as well as ultrafocused beams with intensities surpassing 10^{22} W/cm^{-2} , thanks to spot sizes as small as 10 nm [71]. These breakthroughs advance the frontiers of x-ray science, unlocking new opportunities such as the study of electron dynamics and non-linear optical phenomena [72].

At the onset of the radiation-generation process, the electron emission is spontaneous, resulting in a noisy pattern in the frequency domain, which is preserved during the amplification, yielding a final spiky SASE spectrum with a relative wide bandwidth of approximately 0.3%. To overcome this limitation, in 2012, *Amann et al.* [73] introduced a technique known as *self-seeding*, designed to enhance the coherence and spectral purity of x-ray pulses generated by XFELs. In self-seeding, the undulator is divided into two sections. At the end of the first section, the produced SASE radiation (not yet saturated) is diffracted through a crystal to be monochromatised. Meanwhile, the electron bunch is sent through a magnetic chicane, specifically designed to delay the electron bunch by the

same amount of time required for the monochromatised radiation (seed pulse) to emerge from the crystal. This ensures that the electrons and the seed pulse can be spatially and temporally re-aligned at the start of the second undulator section. Interacting with the electrons, the seed pulse imprints an energy modulation onto the electron bunch, which, as with spontaneous emission in the standard SASE mode, creates a periodic structure that matches the wavelength of the seed. The process then proceeds as in the standard SASE, with coherent emission being exponentially amplified. However, due to the imposed initial modulation of the electron bunch, the resulting x-ray pulse exhibits significantly improved temporal coherence and a much narrower bandwidth - down to 0.01% - compared to typical SASE output. This comes at the expense of reduced pulse energy. This “self-seeded” mode is utilised to collect part of the data analysed in Chapter 4.

Contrary to optical lasers, the interaction of the XFEL with matter is more single-particle based. In fact, at x-ray energies, photons interact primarily with bound electrons, causing photoionisation if the photon energy exceeds the electron’s binding energy, or excitation to another bound state if the energy matches a specific transition energy. Since probability of photoionisation decreases with increasing kinetic energy of the ejected electron, deep core electrons are more likely to be excited. When photoionisation occurs, the ejected electron thermalises with the surrounding free electrons through collisions in a few fs, raising the overall electron temperature and leaving the ion in an excited state. Ultimately, an electron - whether thermalised or not, bound or free - recombines with the ion via various processes (e.g. radiative emission) filling the core hole. For the materials relevant to this work, the principal process is Auger decay [14], which ejects another non-thermal electron, which further contributes to the population of free electrons and to the rise of T_e . In general, energy is transferred from the laser to the electron population on timescales typical of Auger decay and electron collisions (all within a few fs). This energy transfer continues throughout the FEL irradiation, with modulations due to the pulse shape, the evolution of free electrons temperature and density, and the ion charge distribution. Well after the x-ray pulse - on the timescale of ps - the electrons thermalise with the ion population through electron-phonon interaction, eventually causing the solid to melt and consequently expand. However, if the system is probed on shorter timescales, one can analyse a solid material, with an ordered crystalline structure, but with a hot

electron population - representing an example of quantum plasma. This task is achieved by using the XFEL itself, which heats and probe the target simultaneously [10] (*self-scattering* experiment). Data from such experiments is presented and analysed in Chapter 4. Alternatively, XFELs can serve as probes when coupled with optical lasers to perform time-resolved diffraction or spectroscopy on dynamically compressed systems [74]. This time-resolved spectroscopy constitutes the ultimate focus of this thesis and is explored in Chapter 5.

1.3 Theoretical Methods: An Overview

Dense plasmas are complex many-body quantum systems, making them challenging to model. As previously mentioned, a multiscale approach is often used for these systems. Although not rigorously exact, this approach is effective due to the clear separation of timescales and lengthscales between the different processes and components in the plasma.

At the largest length scales, continuum mechanics models are employed. For compressed materials that are still solid, elastoplasticity models [57, 75] or, even more commonly, fluid models [17] — occasionally incorporating corrections to account for material strength - are applied. In these approaches, macroscopic material properties, such as elastic/plastic constants, EOS and heat capacities, are calculated using smaller-scale models or comparing against experimental data. These microscopic models are typically based on molecular dynamics simulations of atoms in the solid [76], where the interatomic potentials, often parametrised with the embedded atom method [77], can be determined using the same methods applied to dense non-solid plasmas, which is discussed below.

The most widely used methods for describing hot-dense plasmas at macroscopic scales are radiative-magnetohydrodynamic models [17, 78], particularly in scenarios where a laser compresses a solid, causing it to melt. These models account for interactions with laser radiation, treated semiclassically and often using ray optics approximation [79]. The radiation's behaviour is governed by transport equations, with opacity and emissivity coefficients derived from atomic physics [14], while the dynamics of the plasma is described by the magnetohydrodynamic equations [80]. In cases where ion motion and non-uniformities can be neglected, such as in isochoric heating experiments, zero-dimensional radiative codes are

used, which evolve ion populations through collision-radiative atomic kinetics equations and the free-electron distribution via a Fokker-Planck equation [81].

To obtain transport coefficients and EOS for the fluid equations, smaller-scale models are necessary. These models generally fall into two categories: kinetic theory approaches¹³, such as particle-in-cell codes [83], and, at even smaller length scales, molecular approaches, which can also treat interparticle correlations and includes methods such as Monte Carlo simulations [84] (for statistical properties) and molecular dynamics calculations [85]¹⁴. The latter is particularly popular for the plasmas studied in this thesis. For these MD simulations, the interatomic potential between ions - evolved using classical equations of motion - is calculated by going to even smaller length scales, and evaluating the electronic wavefunctions, for a frozen ion configurations, with density functional theory (DFT). This approach, known as DFT-MD [87], relies on the adiabatic separation of ion and electron motion and is highly effective for modelling quantum plasmas. An alternative method for handling electronic length scales is the path integral Monte Carlo (PIMC) [88]. While PIMC is more accurate than DFT at higher temperatures, it is less effective at lower temperatures and cannot directly describe dynamic processes [89]. Despite the different timescales of ion and electron dynamics, non-adiabatic effects can still subtly influence certain quantities [90, 91], particularly in out-of-equilibrium conditions. Hence, approaches that treat simultaneously ion and electron motion have been proposed [27, 92, 93], relying on effective interaction potentials that account for the quantum nature of particles, such as the finite extent of their wavefunctions. Since DFT, with some of its variants, is the primary theoretical framework employed in this thesis to support the experimental findings, its main concepts are now briefly outlined.

1.3.1 Density Functional Theory

Density functional theory is a computational quantum mechanical method used to explore the electronic structure of many-body systems, including atoms, molecules, and solids [94]. DFT simplifies the complex 3N-dimensional problem of solving the N-electron

¹³Standard kinetic theory, like the Vlasov-Fokker-Planck equation, must be modified when quantum effects are relevant (see for example the Wigner model [82]). Kinetic theory approaches can actually describe the macroscopic length scales as well, replacing the fluid models.

¹⁴When particle interactions are weak, analytical methods like the *hypernetted chain* approach [86] can also be used to estimate particle correlations.

time-independent Schrödinger equation by mapping it to a functional minimisation problem based solely on the electron density, $n(\mathbf{r})$, of the system (the subscript “e” is omitted for simplicity). This approach is founded on the two Hohenberg-Kohn (HK) theorems [95], which establish that the ground-state properties of a many-electron system are uniquely determined by the ground state electron density, which is the unique 3D function that minimises the total energy functional. While the Hohenberg-Kohn theorems only apply to systems at zero temperature without spin or external magnetic fields, various extensions have been developed to handle more complex conditions [96–99].

In light of the scopes of this thesis, the next section discusses the finite temperature (FT) DFT [100], for which Mermin extended the (HK) theorems. For a fixed electron temperature $T_e = (k_B\beta)^{-1} > 0$ and chemical potential μ , the relevant functional is the Mermin grand potential functional $\Omega[n(\mathbf{r})]$, rather than the total energy functional. Mermin’s theorems state that minimizing $\Omega[n(\mathbf{r})]$ over the 3D functions space yields the equilibrium density $n_0(\mathbf{r})$, from which many system properties can be determined. At this density, the Mermin functional becomes the grand potential of the grand canonical ensemble, $\Omega_0 = \Omega[n_0(\mathbf{r})]$. $\Omega[n(\mathbf{r})]$ is composed of a universal functional $G[n(\mathbf{r})]$ and the external potential functional $V_{ext}[n(\mathbf{r})]$:

$$\begin{aligned}\Omega[n(\mathbf{r})] &= G[n(\mathbf{r})] + V_{ext}[n(\mathbf{r})] = G[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\ \text{with } G[n(\mathbf{r})] &= T_e[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] + \mu N[n(\mathbf{r})] - \beta^{-1}S[n(\mathbf{r})],\end{aligned}\tag{1.13}$$

where v_{ext} is the external potential and $T_e[n]$, $V_{ee}[n]$, $N[n]$ and $S[n]$ are, respectively, the kinetic energy, the electron-electron potential energy, the particle number and the entropy functional. While the Mermin theorems simplify the many-body problem and establish that these functionals exist, they do not provide practical forms for some of them. This obstacle has led to various approximation methods, such as orbital-free DFT [101] and the widely used Kohn-Sham (KS) scheme [102], which is the one used in this thesis for comparison with experimental data.

This scheme is based on the following ansatz: *The equilibrium density of the fully-interacting system is equal to the equilibrium density of a non-interacting system with*

a proper effective potential v_{eff} , accounting for the interactions. Although unproven in general, this assumption has been proven in certain systems and is considered valid in the HED community. Under this assumption, the all-electron wavefunction is factorisable in the product of single particle wavefunctions obeying the following Schrödinger equations:

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + \overbrace{v_{ext}(\mathbf{r}) + \frac{e^2}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'}^{v_{eff}(\mathbf{r})} + v_{xc}(\mathbf{r}) \right) \psi_\alpha(\mathbf{r}) = \epsilon_\alpha \psi_\alpha(\mathbf{r}) \quad (1.14)$$

where α is the collection of quantum numbers that uniquely identify the eigenstate, and v_{XC} is the exchange-correlation potential, defined as the functional derivative of the famous exchange-correlation functional V_{XC} :

$$v_{xc}(\mathbf{r}) = \frac{\delta V_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} . \quad (1.15)$$

This functional contains all the quantum effects – namely exchange and correlation – that are lost during the passage to the non-interacting system and not accounted for by the integral term in v_{eff} (Hartree term). Since the exact form of V_{XC} is unknown, various approximations have been developed over the years, which are discussed below.

To close the system of equations, the density $n(\mathbf{r})$ must be expressed in terms of the single-particle orbitals. This can be done through the Fermi-Dirac occupation number distribution $f_{FD}(\epsilon_\alpha; T_e, \mu)$:

$$n(\mathbf{r}) = \sum_{\alpha=1}^{\infty} f_{FD}(\epsilon_\alpha; T_e, \mu) |\psi_\alpha(\mathbf{r})|^2 . \quad (1.16)$$

Assuming V_{XC} is known, Eqs. (1.14)–(1.16) form a closed system that constitutes the KHDFT problem, which is solved in a self-consistent manner. First, an initial guess of the equilibrium density is made (often chosen randomly), providing a starting approximation for the total potential. Then, using Eq. (1.14), the wavefunctions ψ_α are computed based on the initial density guess. From these wavefunctions, a new density is derived, and the process is repeated iteratively until certain criteria—such as convergence of the density, potential, wavefunctions, or total energy—are met. The solution of Eq. (1.14) is the most computationally expensive step in this cycle, and many techniques have been devised to make it efficient. Some of these methods reduce the number of electrons for which

wavefunctions must be explicitly computed. Among these, frozen core approximation [103], which assumes that deep core electrons retain their atomistic wavefunctions, creating a pseudopotential that influences the remaining electrons and must be included in Eq. (1.14). Another method for this purpose is the so-called hybrid KS orbital-free DFT [104], which assumes electrons in the high-energy states to be plane waves. This scheme is useful in systems with high temperatures, and is therefore used in this thesis. Other techniques, like the Projector Augmented-Wave method [105], serve instead to narrow the basis set (e.g. plane waves) necessary for decomposing the ψ_α function in order to solve the Schrödinger equation¹⁵.

All the remaining difficulties of the many-body problem have been confined to V_{XC} , whose general form is still unknown. A significant area of research in DFT focuses on developing approximations for this term, as the choice of XC functional greatly impacts the accuracy of DFT results. Numerous XC functionals have been developed, ranging from generalised ones to those tailored for specific materials.

The most widely used XC functionals are based on the free electron gas model [106]. The local density approximation (LDA) is the simplest form, suitable for systems where the electron density varies slowly, and given by:

$$V_{xc}^{LDA}[n] = \int n(\mathbf{r}) \epsilon_{XC}^{LDA}(n(\mathbf{r})) d\mathbf{r} \propto \int n(\mathbf{r})^{4/3} d\mathbf{r}. \quad (1.17)$$

For systems with larger spatial gradients in electron density, the generalised gradient approximation (GGA) is used, for which the exchange-correlation energy per unit density ϵ_{XC} depends on the density gradient as well, $\epsilon_{XC}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r}))$. Many other types of exchange-correlation functionals exist, like higher-order expansions of the density function (e.g. metaGGA), or the so-called "hybrid" functionals. Traditionally, XC functionals ignored explicit temperature dependence, but recent research incorporating quantum Monte Carlo simulations has shown that temperature can have a significant effect [107]. This has led to the development of finite-temperature versions of LDA, GGA, hybrid functionals, and ongoing efforts for meta-GGA [108, 109]. In this thesis, a finite-temperature

¹⁵The *energy cut-off* technique [16] is also a basis set reduction method in which basis functions that contribute minimally to the expansion are excluded, transforming an infinite discrete basis set into a finite one. The omitted basis functions are typically those associated with the highest kinetic energy [16], giving the technique its name.

adaptation of the popular GGA-PBE functional is utilised [108, 110].

Finally, it is worth pointing out that the KS orbitals ψ_α and their energies ϵ_α do not have a rigorous physical meaning [111], but are just introduced as a construction for solving the KS equations. However, depending on the quality of exchange-correlation functional approximation and the strength of the correlations in the system, KS orbitals and energies can resemble the real eigenstates and eigenvalues. In fact, it is common practice (also adopted in this thesis) to derive physical quantities, such as the electronic DOS, from KS eigenstates and eigenvalues, and they generally yield good comparisons with experimental investigations. That said, there is no guarantee that this is true, and therefore caution is needed. A well-known example is the “band-gap problem”, a phenomenon where the KS-DFT underestimates the true bandgap [112], particularly in systems with strong electron correlations [113]. More generally, binding energies are also typically underestimated by the KS method. To address these issues, various *ad hoc* modifications have been introduced to the DFT framework. These issues are discussed in more detail in the following section, as they are directly relevant to materials investigated in this thesis.

1.3.2 Electronic Structure of Materials and Related Quantities

This work focuses on determining the electronic structure of warm-dense materials, specifically examining the electron energy levels ϵ_α , summarised by the density of states, and, to a more qualitative extent, the wavefunctions associated with these levels ψ_α . The electronic structure is a cornerstone from which various material properties can be derived, including the electronic contribution to the equation of state [19] and the electronic heat capacity [114]. Furthermore, the real component of the frequency-dependent optical conductivity, $\sigma_R(\omega)$, can be calculated from $(\psi_\alpha, \epsilon_\alpha)$ using the Kubo-Greenwood formula [115, 116]

$$\sigma_R(\omega) = \frac{\pi \hbar^3 e^2}{3 m_e \omega V} \sum_{\alpha, \alpha'} [f_{FD}(\epsilon_\alpha) - f_{FD}(\epsilon_{\alpha'})] |\langle \psi_{\alpha'} | \nabla | \psi_\alpha \rangle|^2 \delta(\epsilon_{\alpha'} - \epsilon_\alpha - \hbar\omega) , \quad (1.18)$$

where ω is the frequency of the incident radiation and V is the volume of the system. Knowledge of $\sigma_R(\omega)$ enables the calculation of optical properties, such as the refraction index $n(\omega)$ and absorption coefficient $\alpha(\omega)$ [117], which, in turn, allow for the determina-

tion of the Rossland mean opacity [118, 119], κ_R , widely used in radiative-hydrodynamic codes [78]:

$$\frac{1}{\kappa_R} = \frac{\int_0^\infty d\omega n^2(\omega) [\frac{\partial B(\omega, T)}{\partial T}] / \alpha(\omega)}{\int_0^\infty d\omega n^2(\omega) B(\omega, T)}, \quad (1.19)$$

where B is the normalised Planck function. Additionally, $\sigma_R(\omega)$ also gives access to the electrical conductivity in the limit $\omega \rightarrow 0$, which can be related to the electronic thermal conductivity through Kubo's relations [115, 120, 121].

The electronic structure of materials changes with density and temperature variations [21, 122], as these parameters modify the microscopic environment experienced by ions and electrons. Notably, electron binding energies are altered through mechanisms such as Ionisation Potential Depression (IPD) [123, 124]. In DFT, the electronic density of states $\rho(\epsilon)$ are computed from the eigenvalues ϵ_α , where α represent the quantum numbers of spin-1/2 fermions in a periodic system with large unit cells (supercells) [16]. These quantum numbers include the spin $s = \pm 1/2$, the crystal momentum $\mathbf{k}$ varying in the Brillouin Zone (BZ), and the band index b . In this case, $\rho(\epsilon)$ has the following expression:

$$\rho(\epsilon) = \frac{1}{\sqrt{2\pi W_s^2}} \sum_{\mathbf{k} \in \text{BZ}} \sum_s \sum_{b=1}^{\infty} e^{-\frac{(\epsilon - \epsilon_{b, \mathbf{k}, s})^2}{2W_s^2}}, \quad (1.20)$$

where W_s is the so-called smearing width. Typically, only a subset of $\mathbf{k}$ -points within the Brillouin zone is chosen to evaluate this sum, with each selected $\mathbf{k}$ -point assigned a weight $w_{\mathbf{k}}$ to account for its contribution [125]. The summation over the bands is naturally truncated when the band energies become significantly distant from ϵ . Sufficient computational resources must be available to accurately compute the states up to these bands.

Another quantity relevant to this thesis, which can also be computed from ϵ_α and ψ_α , is the absorption cross-section for photons of energy $\hbar\omega$, exciting electrons from a fully occupied core orbital, ψ_c . This quantity is expressed as:

$$\sigma_{abs}(\omega) = \frac{1}{\sqrt{2\pi W_s^2}} \sum_{\mathbf{k} \in \text{BZ}} \sum_s \sum_{b=1}^{\infty} e^{-\frac{(\hbar\omega - \epsilon_{b, \mathbf{k}, s})^2}{2W_s^2}} [1 - f_{FD}(\epsilon_{b, \mathbf{k}, s})] |\langle \psi_{b, \mathbf{k}, s} | \nabla | \psi_c \rangle|^2, \quad (1.21)$$

which is effectively a weighted average of the transition probabilities $|\langle\psi|\nabla|\psi_c\rangle|^2$. As expected, this quantity is strictly connected to, and shares a similar mathematical form with, the optical conductivity, given by Eq. (1.18).

The energy levels in DFT, and consequently $\rho(\epsilon)$, are not guaranteed to match the true eigenvalues of the system. Discrepancies from reality arise especially in strongly correlated systems, as DFT is essentially a mean field theory, since V_{XC} is approximated and could be very different from the physical one. In such cases, when Coulomb interactions between valence electrons on the same or neighbouring site¹⁶ are strong enough, electron hopping between sites is drastically hindered, causing electrons to localise around atoms. This localisation leads to a drop in conductivity and the emergence of a bandgap, characteristic of what is known as a "Mott insulator" [126]. A well-known example of such materials are iron oxides, which constitute the principal systems examined in this thesis.

To account for these strong electron-electron interactions, the simplest theoretical approach is the Hubbard Model (HM), which has been studied in various forms and solved using different methods [127]. Several approaches can be used to address strong correlation effects within DFT, such as the GW approximation [128] and Dynamical Mean-Field Theory (DMFT) [129, 130]. In this work, the DFT+U method [131] is used for comparison with experimental data, while also referencing results from studies involving DFT coupled with DMFT.

In the DFT+U approach, an additional term is incorporated into the exchange-correlation potential to account for the electron interactions on the same site, along the line of the HM. The strength of this term is parameterised by the Hubbard parameter U , which is typically calibrated through comparisons with values of physical quantities reported in the literature due to the complexity of determining it from theory. In contrast, DMFT maps the many-body lattice problem to a local many-body impurity model, where interactions between electrons on different sites are replaced by a single electron interacting with an electronic "bath."

¹⁶This thesis examines compressed and isochorically heated solids, where relatively ordered ion structures are maintained. Consequently, the concept of "site" remains well-defined.

1.4 Iron Oxides under Compressed Conditions

Iron oxides are important for understanding Earth’s core and mantle dynamics. The core, primarily composed of iron and nickel, contains up to 5.3% oxygen, with smaller percentages for the inner core [132]. Furthermore, iron oxides like Fe_2O_3 may be present near the core-mantle boundary (CMB) due to subduction of ancient iron formations [133]. These oxides can remain stable under extreme pressures and temperatures. Furthermore, several studies suggest that, between 40 and 160 GPa and at temperatures around 0.1 eV, iron oxides undergo a Mott transition, becoming conductive, and that this could affect Earth’s global dynamics [133–138]. Therefore, the analysis of the electronic structures of iron oxides in extreme conditions is of great interest both to geophysics, and to the field of strongly correlated systems.

During compression, iron oxides experience metal-insulator, spin and structural transitions, which are essentially due to the deformation of the lattice produced by pressure-induced strains. The distortion of atomic bonds and the cell-volume reduction may change the most favourable lattice structure and modify the localisation of states and the charge transfer, affecting the conduction properties of the material. The change in the atomic bonds may also induce changes in the average electron spin state (spin crossover), as electrostatics interaction between orbitals of neighbouring ions starts to dominate over exchange energy [139]. There have been many studies on the correlations between these metal-insulator, structural and spin transitions, but the argument remains still debated [140–142].

Although the techniques developed in this thesis are applicable to any material, this work focuses specifically on two iron oxides: Fe_2O_3 (Hematite) and FeO (Wüstite). Theoretical studies using DFT+DMFT have shown that Fe_2O_3 undergoes a structural transition around 50 GPa from a corundum-type structure to a double-perovskite (DPv) phase [135]. This transition is accompanied by a site-selective spin and Mott transition, where only one of the two iron ions in the basic unit experiences these changes [135, 141]. The 3d orbitals of this ion delocalise, causing the band gap to close, and simultaneously, the energy splitting between the valence orbitals¹⁷ increases, leading to a collapse of the local spins.

¹⁷These valence orbitals, for these crystalline structures, are divided into two symmetry groups - e_g and

These findings are supported by Mossbauer spectroscopy and x-ray diffraction data [135].

For FeO, analogous studies have revealed a complex phase diagram with several structural transitions, including shifts from the B1 (NaCl) phase to the B8 (NiAs) and B2 (CsCl) phases at various pressures and temperatures [136, 138, 143]. At approximately 70 GPa and temperatures below 1500 K, the B1 phase of FeO becomes metallic, linked to the delocalisation of the iron 3d orbitals and the consequent collapse of the Mott insulating gap. Interestingly, the high-spin (HS) to low-spin (LS) transition in FeO appears to occur independently of metallisation, with the HS metallic phase persisting up to pressures of 150 GPa, depending on the temperature [136]. Beyond this point, FeO transitions to the B8 phase, with the collapse of the iron ions' local magnetic moments. These structural changes have a significant impact on FeO's properties, including its bulk modulus and volume [136].

1.5 Overview of the Diagnostic Techniques and Instruments

As mentioned earlier, due to the short life of experimentally-created HED systems, photon-based techniques are predominantly used to investigate their properties. Over the past few decades, various forms of spectroscopy have been employed to study both the electronic and ionic structures of these systems, while simultaneously diagnosing their thermodynamic conditions. X-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS), in particular, have played a pivotal role in seminal studies by measuring changes in binding energies under extreme thermodynamic conditions [123, 144, 145]. Within XAS, it is possible to distinguish two regimes—x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS)—which allow for the investigation of the electronic structure around the chemical potential, as well as the oxidation state, coordination state, and interatomic distances of ions [146–149]. These techniques, particularly relevant to the topics covered in this thesis, are discussed in more detail in Chapter 3. To examine the local environment around ions and crystallographic structures more generally, XRD remains the most widely used method [150, 151]. Investigating how material properties evolve with changes in temperature and density also requires precise thermody-

t_{2g} - which have different energies

namic diagnostics. Traditionally, this has been achieved using x-ray Thomson scattering (XRTS) [152–155], though as discussed in Chapter 3, XAS and XES can also directly measure thermodynamic parameters. In all these methods, thermodynamic properties are found by fitting theoretical models to experimental data.

Only in the last years, resonant inelastic x-ray scattering (RIXS) - another typical spectroscopic technique of solid state physics - begun to be applied in the field of warm dense matter [156, 157]. RIXS is a spectroscopic technique used to probe the electronic, magnetic, and vibrational properties of materials with high sensitivity. In the RIXS process, an incident x-ray photon excites, via an energy non-conserving absorption, a core electron into an unoccupied state, creating a core hole. This hole is subsequently filled by an electron from another shell, resulting in the emission of a photon. The energy of the emitted photon is such that the overall scattering process conserves energy. It is intuitive that this process reveals information about the system’s structure of vacant states. Unlike other forms of x-ray scattering, RIXS is resonant, meaning the incident photon energy is tuned close to specific absorption edges of the material, enhancing the sensitivity to particular electronic states. One of RIXS’s key advantages over traditional absorption or emission techniques is its ability to capture the electronic structure of a material across a broad electron energy range in a single spectrum, thereby providing a global picture of this structure. This makes this technique particularly useful for time-resolved studies of dynamic processes. As RIXS is the technique employed in this thesis for the extraction of electronic structures, a detailed description of the theory behind this process is given in Chapter 3.

Now a brief overview of the typical experimental instruments used in XFEL facilities for HED physics investigations is provided. For further details, refer to the specific documentation [74, 158, 159]. Before reaching the experimental chamber, the FEL beam travels through several optical components and diagnostic tools, such as x-ray gas monitor (XGM), spectrometers and various imagers that measure the beam characteristics (e.g. energy, spatial and spectral profile) [74]. Additionally, the beamline includes attenuators, a system of mirrors, refractive lenses, and slits to guide and focus the laser pulse, along with a monochromator [160], and a rotating slit to select specific laser pulses, known as pulse picker unit (PPU) [74].

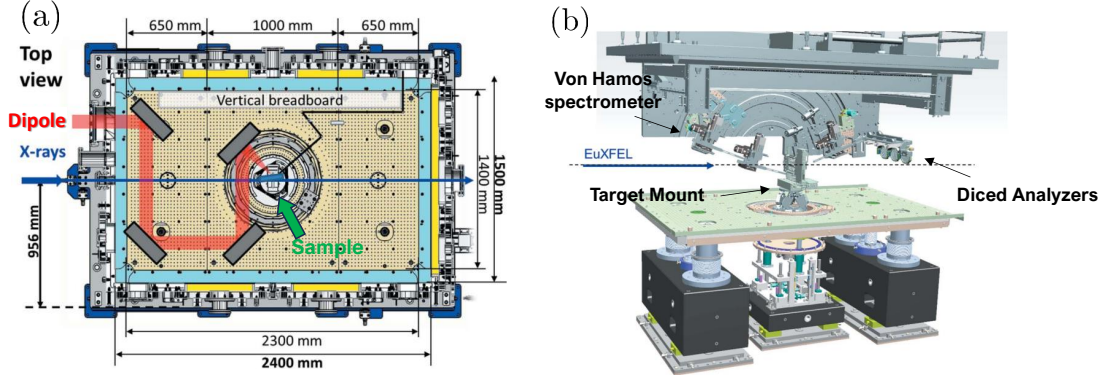


Figure 1.5: (a) Top view of a CAD model of the EuXFEL HED Chamber 1, illustrating the primary laser beam paths and sample position. (b) Perspective view of the same chamber, highlighting the configuration of the facility’s main spectrometers, including a von Hámós spectrometer and diced analysers. The VISAR system, not shown in the images, is located in the separate HED Chamber 2, downstream of Chamber 1. Both images were taken from Ref. [74].

Upon entering the experimental hutch, the laser passes through more focusing lenses and diagnostic tools, including a photon arrival monitor (PAM) to synchronise the FEL beam with the optical lasers, and devices for their spatial alignment. The optical lasers are typically diode-pumped lasers, with an optional chirped pulse amplification scheme, capable of delivering up to dozens Js at a repetition rate of 10 Hz, in a pulse duration as short as few ns, and with wavelengths ranging from 500 nm to 1000 nm. The optical laser system, integrated into the HED instrument, includes deformable mirrors for wave-front corrections and off-axis parabolas for focusing. Fig. 1.5 illustrates an example of the laser paths, alongside a CAD model of the experimental chamber at the EuXFEL facility. The main components of the experimental chamber, which operates under vacuum conditions, include a motorised and highly mobile target mount [158], a VISAR system, and various pixel detectors and dispersing crystals used for different types of spectroscopy and diffraction experiments [74]. A detailed description of the typical pixel detectors and spectrometers used in HED experiments is provided in the next chapter.

1.6 Structure of Thesis and Author Contributions

This thesis is organised into six chapters.

Chapter 1 serves as a comprehensive introduction, focusing on complementary topics pertinent to the thesis but not covered in its main body, which is dedicated to the development of the theory and techniques central to this work. Serving as a general introduction, this chapter draws its content from the existing literature. The author would like to thank Mr. Pontus Svensson for the useful discussions on the theoretical models for HED systems and for reviewing this chapter.

Chapter 2 provides a step-by-step guide on how to construct a spectrum from the initial camera images, focusing on the spectrometers and detectors commonly used in experiments, and describing their primary challenges. In doing this, the chapter presents methods for enhancing the signal-to-noise ratio and the resolution of a camera image, designed to handle simultaneously regions with high and low photon densities. These methods are tested on synthetic images and experimental data from HED science. While this discussion is motivated by the potential application to the spectroscopic techniques used in HED experiments, the methods presented are generalisable to other scientific fields and hold intrinsic interest. Notably, the content of this chapter has been compiled into a paper published in the *Journal of Applied Physics*.

This paper draws inspiration from the previous work of Dr. Oliver Humphries [161], to whom the author is highly indebted. Portions of the code for photon-counting algorithms and spectrometers' calibration were developed collaboratively with Dr. Thomas Gawne, Mr. Thomas Campbell, and Mr. Yuanfeng Shi, while the remainder of the code was independently written by the author, who also conducted all simulations. The author further acknowledges Prof. Sam M. Vinko, Dr. Oliver Humphries, and Dr. Thomas Gawne for their valuable discussions and their thoughtful revisions of the paper.

Chapter 3 opens with a comprehensive review of the theory behind the RIXS process, tailored to the specific cases relevant to this work and essential for developing the model used to interpret the experimental RIXS data. The chapter then provides a brief overview of alternative spectroscopic techniques within the context of HED physics, highlighting their advantages and, especially, their limitations compared to the RIXS technique. Following this, the method for extracting electronic structures from RIXS measurements—based on neural networks and differentiable physical models—is introduced. This approach is first presented in the broader context of machine learning techniques for solving inverse prob-

lems in physics and is then specialised to the RIXS case. The method, labelled as STEP, is validated using synthetic RIXS data, with its performances analysed across various aspects, including comparisons with standard numerical techniques and the extraction of scalar quantities such as temperature.

This method originated from discussions between the author and Prof. Sam M. Vinko and was subsequently developed and implemented by the author. The author wishes to acknowledge Mr. Karim K. Alaa El-Din for polishing the code and the generalisation of the method’s framework to other physical problems. The generation and analysis of the synthetic RIXS data were conducted by the author in collaboration with Mr. Karim K. Alaa El-Din, leading to the publication of a paper in *Royal Society Open Science*, mainly written by Mr. Karim K. Alaa El-Din. The comparison of the method with numerical techniques was carried out solely by the author, while the study on temperature extraction presented here was predominantly conducted by Mr. Karim K. Alaa El-Din.

Chapter 4 focuses on the analysis of experimental RIXS spectra collected at the Eu-XFEL facility for warm-dense iron, iron oxides, and gadolinium (Gd). After introducing the experimental setup and primary diagnostics, the extracted electronic structures of Fe and Fe₂O₃ are presented, allowing also the determination of sample temperature and electron binding energies. I further show that this method can extract DOSs with a resolution exceeding the x-ray source bandwidth, enabling clear differentiation between the two materials. The reliability of the reconstructed structures is validated by repeating the extraction process on datasets recorded with different instruments and XFEL operational modes. To further enhance resolution, the spectrometer’s instrument function is deconvolved from the FeO RIXS spectra, achieving DOS for this material with resolutions on the order of a few eV. Finally, the RIXS technique is applied to gadolinium, showcasing its flexibility for analysing various materials through different electronic excitations. All extracted electronic structures were compared with finite-temperature DFT calculations, showing excellent agreement.

The analysis of these experimental data was performed entirely by the author. The results for Fe and Fe₂O₃, along with some synthetic data analysis (see Chapter 3), were published in *Communications Physics*, serving as a proof of principle for the method’s effectiveness. This experiment was made possible through the collaborative efforts of many

contributors, and the author extends special thanks to Prof. Sam M. Vinko for proposing the experiment and to Dr. Céline Crépinsson, Dr. Oliver Humphries, Dr. Thomas Preston and Dr. Thomas Gawne for their significant help. The results for FeO and gadolinium have been drafted for a separate publication, with the choice of journal still under consideration. The DFT calculations presented were performed by Dr. Thomas Gawne.

Chapter 5 presents the analysis of experimental RIXS spectra collected at the LCLS facility for dynamically compressed FeO. This study represents the ultimate goal of the thesis, showcasing the application of this RIXS diagnostic technique to dynamical physical processes within the context of HED physics. Similarly to the previous chapter, the discussion begins with an overview of the experimental setup and primary diagnostics, with a focus on the functioning of the VISAR system, which was used to measure pressure conditions. The chapter then delves into the XRD analysis of the compressed targets, which was employed to observe the evolution of the ionic structure under compression, concurrently with changes in the electronic structure, measured using this RIXS-based approach. Applying this method to RIXS spectra collected on both ambient and compressed FeO revealed a systematic bandgap closure upon compression, consistent with the insulator-to-metal transition predicted by theory and earlier studies.

The author expresses deep gratitude to all participants in this experiment, particularly Prof. Sam M. Vinko and Dr. Danae N. Polsin for proposing the study and involving the author. The analysis of VISAR and XRD data, as well as target fabrication, was conducted by Dr. Marion Harmand, Dr. Céline Crépinsson, Dr. David McGonegle, Dr. Alexis Amouretti, Dr. David A. Chin, and Dr. Danae N. Polsin. The spectrometer design was a collaborative effort between the author, Dr. Thomas Gawne, and Mr. Thomas Campbell. The DFT calculations presented were performed by Dr. Sam Azadi. All other work presented in this chapter was carried out by the author.

Chapter 6 concludes the thesis with a summary of key findings and a discussion of potential next steps to enhance and refine this diagnostic technique and the associated extraction method. It also offers an outlook on the possible generalisations of the STEP method to other physical investigations. On this last point, the author extends his gratitude to Dr. Patrick Heighway for the valuable discussions.

In general, like all theses, much of the work presented here reflects years of development

and is collaborative in nature. My foremost acknowledgment goes to my supervisor, Prof. Sam M. Vinko, whose extensive guidance and support have been fundamental to shaping my research. I have also had the opportunity of regularly presenting my work to the members of the Vinko-Wark research group, who provided me with valuable feedback throughout this journey. I am very grateful to every member of this group and especially to Prof. Justin S. Wark, Dr. Thomas Gawne, Mr. Pontus Svensson, Mr. Thomas Campbell, Dr. Sam Azadi, Dr. Céline Crépissou, and Mr. Karim K. Alaa El-Din for their insights and support. A particular acknowledgment goes to Dr. Thomas Gawne and Dr. Sam Azadi for performing the DFT calculations included in this thesis.

1.7 Relevant Publications

- **A. Forte**, T. Gawne, K. K. Alaa El-Din, O. S. Humphries, T. R. Preston, C. Crépissou, T. Campbell, P. Svensson, S. Azadi, P. Heighway, Y. Shi, D. A. Chin, E. Smith, C. Baetz, V. Bouffetier, H. Hoppner, A. Amouretti, D. McGonegle, M. Harmand, G. W. Collins, J. S. Wark, D. N. Polsin, and S. M. Vinko, "Resonant inelastic x-ray scattering in warm-dense Fe compounds beyond the SASE FEL resolution limit", *Communications Physics*, **7**, 266, (2024).
- **A. Forte**, T. Gawne, O. S. Humphries, T. Campbell, Y. Shi, S. M. Vinko, "Methods for energy dispersive x-ray spectroscopy with photon-counting and deconvolution techniques", *Journal of Applied Physics*, **7**, 134501, (2025).
- K. K. Alaa El-Din, **A. Forte**, M. F. Kasim, F. Miniati, S. M. Vinko, "STEP: extraction of underlying physics with robust machine learning", *Royal Society Open Science*, **11**, 231374, (2024).

Contribution and Relevance: The paper is based on the methodology developed by the author of this thesis and detailed in Chapter 3. Nearly all of the results were produced collaboratively by the first two authors of the paper, with a portion of them presented in Chapter 3.

- A. Amouretti, C. Crépissou, S. Azadi, D. Cabaret, T. Campbell, D. A. Chin, B. Colin, G.R. Collins, L. Crandall, G. Fiquet, **A. Forte**, T. Gawne, F. Guyot, P.

Heighway, H. J. Lee, D. McGonegle, B. Nagler, J. Pintor, D. N. Polsin, G. Rousse, Y. Shi, E. Smith, J. S. Wark, S. M. Vinko, M. Harmand, "Phase transitions of Fe_2O_3 under laser shock compression", arXiv:2402.18432, (2024)

Contribution and Relevance: The data presented in this paper were obtained during the LCLS experiment detailed in Chapter 5, in which the author contributed. These results provided deeper insights into the evolution of ionic structure under compression, along with further details on the techniques employed in the investigations. This paper was recently accepted for publication in *Physical Review Letters*.

- C. Cr  pisson, A. Amouretti, M. Harmand, C. Sanloup, P. Heighway, S. Azadi, D. McGonegle, T. Campbell, D. A. Chin, E. Smith, L. Hansen, **A. Forte**, T. Gawne, H. J. Lee, B. Nagler, Y. Shi, G. Fiquet, F. Guyot, M. Makita, A. Benuzzi-Mounaix, T. Vinci, K. Miyanishi, N. Ozaki, T. Pikuz, H. Nakamura, K. Sueda, T. Yabuuchi, M. Yabashi, J. S. Wark, D. N. Polsin, S. M. Vinko, "Shock-driven amorphization and melt in Fe_2O_3 ", *Physical Review B*, **111**, 024209, (2025).

Contribution and Relevance: Part of the data presented in this paper were obtained during the LCLS experiment detailed in Chapter 5, in which the author contributed. These results provided deeper insights into the evolution of ionic structure under compression, along with further details on the techniques employed in the investigations.

- T. Gawne, T. Campbell, **A. Forte**, P. Hollebon, G. Perez-Callejo, O. Humphries, O. Karnbach, M. F. Kasim, T. R. Preston, H. Ja Lee, A. Miscampbell, Q. Y. Berg, B. Nagler, S. Ren, R. B. Royle, J. S. Wark, S. M. Vinko, "Investigating Mechanisms of State Localization in Highly-Ionized Dense Plasmas", *Physical Review E*, **108**, 035210, (2023).

Contribution: The author collaborated to the analysis of the experimental data used to benchmark the theoretical model, where some of the techniques described in Chapter 2 were employed.

Chapter 2: X-Ray Dispersive Spectroscopy Methods in HED Science

The birth of spectroscopy as a scientific discipline can be traced back to Joseph von Fraunhofer's work, where he used diffraction gratings to systematically divide the spectral component of the electromagnetic radiation, dispersing them into distinct regions of space [79]. Following this, the invention of the photographic plate in the mid-19th century enabled the first permanent recording of spectral lines, representing the earliest example of a light detector. The following discovery of the photoelectric effect, along with the development of quantum mechanics to support the underlying theory, led to the development of modern detectors, such as photomultiplier tubes (PMTs) [162] and later, semiconductor-based detectors like charge-coupled devices (CCDs) and finally hybrid detectors [163], which are the most commonly used nowadays and are the detectors considered in this thesis. These detectors consist of individual units, called pixels, arranged in ordered arrays. Each pixel is composed of two distinct components (hence the term "hybrid"): a semiconductor layer that captures photon energy and a readout electronics layer that amplify and quantify the signal produced by the photon capture.

As mentioned in the previous chapter, x-ray spectroscopy is an essential tool to investigate numerous properties (e.g. chemical composition, electronic structure) of HED systems, as extreme thermodynamic conditions can only be maintained experimentally for very short times, necessitating the use of *in situ* photon-based diagnostics. Furthermore, the deep penetration of x-rays allows for the exploration of bulk material properties, while their short wavelengths enable the excitation of inner-shell electrons and detailed probing of material structure, expanding the range of spectroscopic techniques available. Lastly, the typical short pulse durations of x-ray sources (see Introduction) allow for time-resolved

studies of dynamic processes, usually driven by other coupled instruments.

X-ray spectroscopy is predominantly performed using dispersive elements such as crystals or gratings, coupled with a detector in various geometries. These elements disperse (or selectively transmit in scanning mode [164]) the spectral components of the radiation emitted by the target, which are then collected by the detector. In the following sections, I will analyse separately two of the most common crystal-based configurations in HED science: the flat crystal and the von Hámos geometries. Additionally, the focus will be on how to treat camera images characterised by low photon counts, except for small regions around transition lines – a common occurrence in HED physics. These low photon numbers typically result from the low cross-sections of some spectroscopic processes used in HED physics (e.g., RIXS, which, as discussed in Chapter 3, is a second-order scattering process), short exposure times due to the brief lifespan of HED systems, and limited solid angle coverage driven by the pursuit of high resolution and geometrical constraints within the experimental chambers. If the photon density is low everywhere on the camera and resolution requirements are not stringent, single-photon counting spectroscopy (SPCS) [165] - a method suited to pixel detectors - becomes preferable to dispersive spectroscopy. In SPCS, photon energies are determined based on the signal generated by each photon hit, rather than their position on the detector. Although SPCS is widely used with modern detectors, it has not been employed in this thesis and therefore will not be discussed further.

The objective of this chapter is first to provide a step-by-step guide on how to construct a spectrum from the initial detector images, a resource which, to the best of our knowledge, is not found in existing literature as a single comprehensive document, but rather scattered across various sources. In doing this, I also present methods, which are validated on synthetic and HED experimental data, for enhancing the signal-to-noise ratio (SNR) and the resolution of a camera image, and capable of treating simultaneously regions with high and low density of photons. Although these cases are motivated by the typical features occurring in HED experiments, the techniques discussed are applicable to other science fields with analogous image characteristics and geometrical setups.

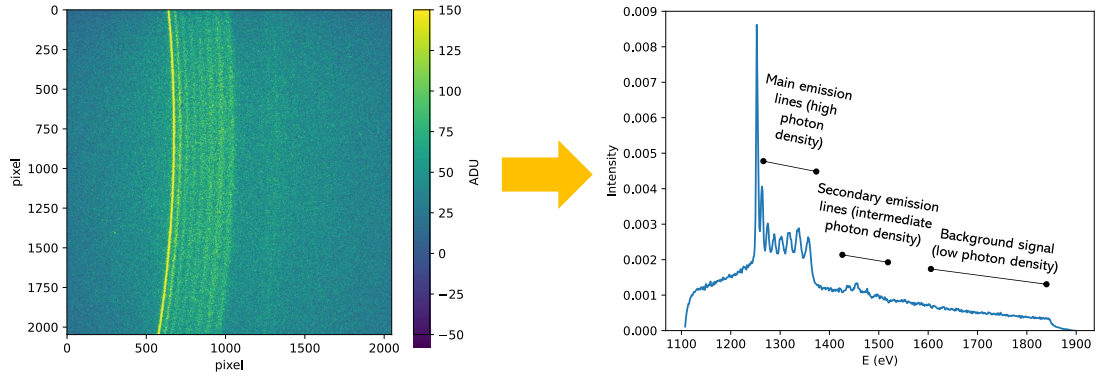


Figure 2.1: Example of the construction of a spectrum (right) from the relative camera image A_{ij} (left), which is a 2048x2048 pixel array. The image presents area with different photon density, labelled in the associated spectrum. In this example, the signal is the emission spectrum of warm-dense MgF_2 from Ref. [166]. The bright arcs in the image correspond to the $K\alpha$ (main) and $K\beta$ (secondary) emission lines, coming from different ionisation states of the Mg ions. The different strength of the lines comes from the different ion populations.

2.1 Constructing a Spectrum

In this section, the techniques used to construct the spectrum from the initial camera image are outlined. For completeness, the section begins with a brief overview of how a semiconductor pixel detector works, which will be beneficial for subsequent discussions. Next, the process of finding the energy map for two of the most common types of spectrometers is detailed. Finally, the process of converting the Analog-to-Digital Units (ADU) map to the distribution of photon hits by means of single photon counting algorithms and image deconvolution techniques is explained. In the following, the underlying physical processes generating the photons detected by the spectrometer is disregarded, focusing only on the problem of constructing a spectrum from the initial matrix A_{ij} , whose elements represent the total signal on pixel (ij) . Here, the pixels form a two-dimensional array labelled by $i = 1, \dots, N_y$ and $j = 1, \dots, N_x$, with N_y and N_x representing the number of pixels in the vertical and horizontal directions, respectively. As an example, Fig. 2.1 illustrates the construction, from the corresponding camera image, of the emission spectrum of warm-dense MgF_2 . This data, taken from Ref. [166], was obtained by irradiating MgF_2 with intense x-rays approximately 300 eV above the atomic K-edge of Mg (~ 1303 eV). As described in [10], this radiation generates a population of Mg and F ions in various ionisation states,

with their relative abundances determined by the rates of atomic processes. The energy of photons emitted during electron photodecays depends on the ionisation state of the ion involved, yielding a series of spectral lines. The resulting spectrum is divided into different regions based on the signal intensity, which corresponds to the local photon density on the camera. This data is analysed in Section 2.6.2 using the image processing methods introduced in the following sections.

The construction of the spectrum can be roughly divided into 3 independent and sequential steps:

1. **Computing the energy map of the camera.** This process involves determining the energy associated with each pixel, E_{ij} . These energies represent averaged values for each pixel, accounting for effects such as source broadening and finite pixel size. These effects mix the energies of photons hitting a single pixel, ultimately reducing the maximum achievable spectral resolution. Section 2.2 details the techniques for computing this energy map;
2. **Estimating the photon hits on the detector.** For a given camera image, A_{ij} , this step calculates the most likely distribution of photon hits on the detector, N_{ij}^γ , providing a good estimate for the number of photons hitting each pixel (i, j) . The methods for performing this operation are discussed in Section 2.4;
3. **Constructing the spectrum.** This final step involves placing N_{ij}^γ into the appropriate energy bin according to the energy map E_{ij} , with corrections applied for the varying solid angles associated with each energy level.

The specifics of how the image is converted to a spectrum depends on the specific geometry of the spectrometer. While all the spectrometers relevant to this work are based on Bragg's law and this is ultimately used to construct the spectrum, in practice specific geometries (such as von Hámos geometry which is given some attention later) may allow for simpler dispersion equations.

2.1.1 Pixel Detectors

Pixel detectors are integral components in the detection and measurement of light in various scientific applications, including spectroscopy, astronomy, and medical imaging. These

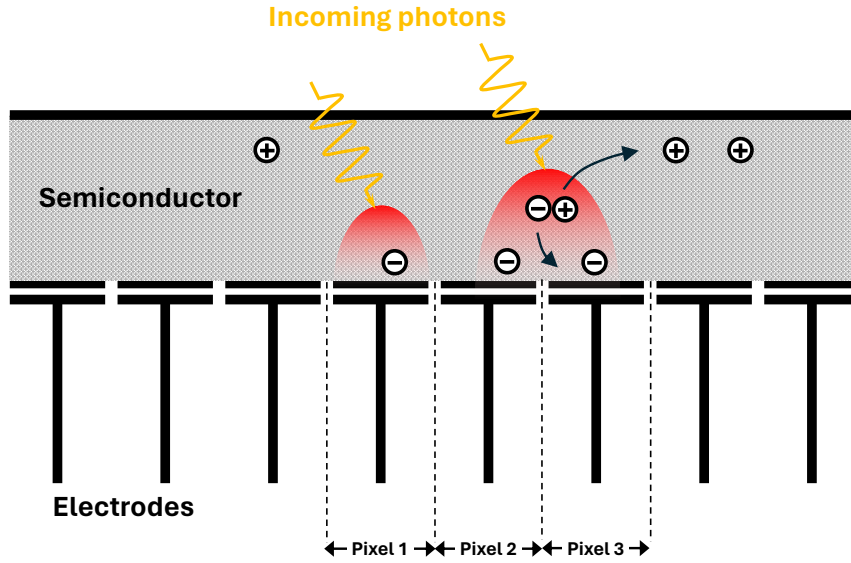


Figure 2.2: Simplified scheme of a pixel detector section with illustration of charge spreading.

detectors work by converting incoming photons into electronic signals that can be quantified and analysed. A simplified diagram of a pixel detector is shown in Fig. 2.2. The general functioning of a pixel detector involves several stages: photon absorption, charge generation and collection, charge transfer, and signal readout.

1. **Photon absorption.** The process begins when photons enter the detector and strike the photosensitive surface, usually made of a doped or compound semiconductor (e.g. doped silicon, GaAs). At x-ray energies, photons interact with the semiconductor atoms via photoionisation, generating electron-hole pairs. The number of these pairs is approximately proportional to the energy of the photon hitting the surface, with random fluctuations quantified by the Fano factor [167]. The efficiency in converting the photon energy into electrons energy is instead measured by the quantum efficiency (QE) [168], which is essentially the probability that a photon is photoabsorbed, creating a photocurrent.
2. **Charge Generation and Collection.** The generated electrons are collected in potential wells created by an array of electrodes on the detector surface. Each pixel in the detector corresponds to one potential well. The number of electrons collected in each well is roughly proportional to the energy contained in the light hitting that

pixel, making the detector highly effective for capturing detailed images. However, thermal noise, which is intrinsic to the detector and depends on its temperature, can also generate electron-hole pairs, known as “dark current”, which disturbs the measurement [169]. Additionally, the electron cloud generated by a photon absorption can diffuse over multiple pixels, causing image blurring. This diffusion is quantified by the Point Spread Function (PSF) [170], which is a two-dimensional decaying function (typically a Gaussian, but sometimes distorted) with a characteristic width referred to as charge spreading radius (R_s) [171, 172]. The spreading radius can be estimated both theoretically and experimentally [172, 173], and depends on various parameters, including detector thickness and incoming photon energy. While reducing the sensor thickness can mitigate this spreading effect, it also decreases the probability of photon absorption, thereby impacting the quantum efficiency. Furthermore, even though R_s is rigorously dependent on the photon energy — affecting the depth at which the photon is absorbed (see Fig. 2.2) — it is assumed to be constant in this thesis, as our analysis can be restricted to a portion of the detector illuminated by a sufficiently narrow photon energy range, thanks to Bragg spectroscopy.

3. **Charge Transfer.** Once the exposure is complete, the collected charge needs to be transferred to the readout electronics. For modern hybrid detectors, this is done *in situ* with the readout electronics connected to each individual pixel. In the case of CCDs, this is achieved through a process known as charge transfer, where the charges are moved sequentially through the CCD’s structure to the output register. This transfer is carefully controlled to preserve the spatial information of the image. The loss of electrons occurring in this operation, which is not present in modern detectors, is measured by the so-called Charge Transfer Efficiency (CTE) [174, 175]. For these reasons, hybrid detectors offer faster and more accurate readout than traditional CCDs.
4. **Signal Readout.** In the final stage, the collected charges are read out by converting them into a voltage signal. This is done using a charge amplifier that translates the charge into a corresponding voltage. The voltage signal is then sent to an Analog-to-Digital Converter (ADC), which converts it into digital counts known as Analog-

to-Digital units (ADU) [176]. These ADUs represent the total energy of the photons incident on each pixel, combined with noise, and form the basis of the digital image.

For the following analysis, the relevant detector characteristics include R_s , the level of noise of each pixel, and the ADU counts associated to a photon of energy E , $ADU_{sp}(E)$, which in general depends upon the pixel. The noise on each pixel is measured simply by running the detector multiple times while the source is blocked (known as “dark runs” [177]), and then looking at the statistics of the empty frames for each pixel across the different shots. The dark runs are taken regularly during an experiment to measure the pixel noise as the detector conditions naturally change over time, and their mean - usually computed excluding tail values to account for anomalies (e.g. stray photons) - is then subtracted from the raw image to remove any bias on the ADU values due to thermal noise. Typically, this subtraction is executed by the facility’s software, as part of automatic post-processing. Additionally, it is now common for facilities to provide the detector images, with the background subtracted, in energy units. The ADU to energy unit conversion of detectors, i.e. $ADU_{sp}(E)$, is already regularly measured as part of performance testing, and usually, this is automatically applied to the raw ADU image in a post-processing step. However, in this discussion, I always assume to work with background-subtracted images, but in ADU units, and I show how to compute $ADU_{sp}(E)$ directly from the experimental images. R_s instead, is typically given in the camera documentation, but accounting for the charge spread between pixels remains a task for the user as it is computationally quite intensive, and not always necessary depending on the detector geometry or experiment. Lastly, image post-processing often includes masking or correcting faulty pixels, with special attention to edge pixels, where leakage currents reduce charge collection efficiency [178].

In the regions with low photon densities, which cover most of the detector in our cases, it is possible to identify a photon hit by searching clusters of neighbouring pixels with ADU counts consistently above the noise. This technique, known as single photon counting, allows one to count the photons on the detector, thereby reducing the uncertainties in estimating N_{ij}^γ by exploiting the spatial correlation between ADU values of neighbouring pixels. The small regions with medium to high photon densities require instead more elaborated techniques to improve signal quality, which is discussed in the following. Although

it is possible to estimate the energy of the photon directly from the ADU count, as done in SPCS [165, 179], working in dispersive (or Bragg) spectroscopy enables one to determine the energy of the photons by their positions, facilitating the use of the photon counting techniques.

2.2 Energy Calibration

For both spectrometers of interest, the energy map depends on the geometrical parameters of our setups (e.g. source-detector distance):

$$E_{ij} = E(x'_{ij}, y'_{ij}; \mathbf{\Lambda}), \quad (2.1)$$

where x'_{ij} and y'_{ij} are the coordinates of the centre of pixel (ij) on the planar detector and $\mathbf{\Lambda}$ collects all the geometrical parameters. These parameters are used as fitting variables to find the energy map, ensuring that it is consistent with known experimental lines. The two types of geometries are now examined separately.

2.2.1 Flat Crystal Spectrometer

Starting from the assumption that the rocking curve of the reflecting crystal [151] is a Dirac delta centred at the Bragg angle, θ_B , and that the sample acts as a point source, thereby neglecting source broadening. Under these assumptions, using Bragg's law [151] and referring to Fig. 2.3, one can derive the following relation between E_{ij} , the coordinates of the pixel and the geometrical parameters [161]:

$$\begin{aligned} E_{ij} &= E(\theta_B(x'_{ij}, y'_{ij}; \mathbf{\Lambda})) \\ &= \frac{hc}{2d \sin(\theta_B(x'_{ij}, y'_{ij}; \mathbf{\Lambda}))} \\ &= \frac{hc}{2d} \frac{\|\mathbf{r}_0 + \mathbf{R}\mathbf{r}'_{ij}\|}{\hat{\mathbf{z}} \cdot (\mathbf{r}_0 + \mathbf{R}\mathbf{r}'_{ij})} \quad , \end{aligned} \quad (2.2)$$

where θ_B is the Bragg angle associated with pixel (i, j) , h is the Planck constant, c is the

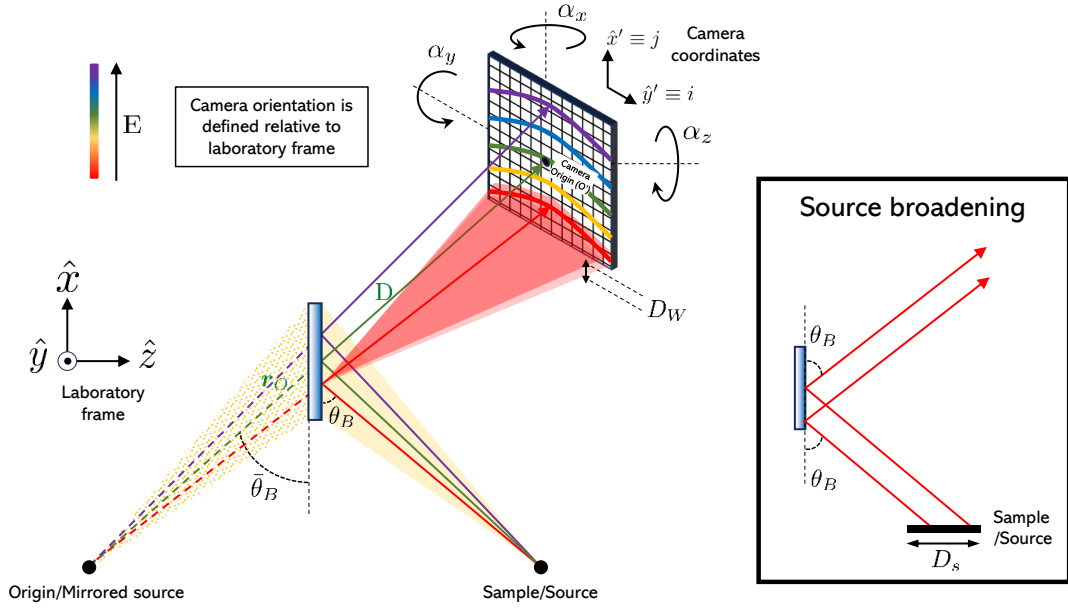


Figure 2.3: Scheme of flat crystal (FC) spectrometer geometry with the illustration of source broadening (inset). The laboratory frame is defined by $\hat{z}$ being the normal of the crystal, $\hat{x}$ such that $\mathbf{r}_0$ is contained in the $\hat{x} - \hat{z}$ plane, and $\hat{y}$ chosen for the frame to be an orthonormal right-handed triad. The camera frame is defined with $\hat{x}$ and $\hat{y}$ aligned with the pixel array, $\hat{z}$ orthogonal to the camera plane, and the origin O' at the centre of the detector.

speed of light and d is the spacing between the reflecting planes of the crystal. In this thesis, the first-order reflection ($n = 1$) is considered, but the generalisation of equations to any arbitrary order n is straightforward. The geometrical quantities $\mathbf{r}_0$, $\mathbf{r}'_{ij}$, $\mathbf{R}$, are given by the following expressions (see Fig. 2.3):

$$\mathbf{r}_0 = D (\cos \bar{\theta}_B, 0, \sin \bar{\theta}_B), \quad (2.3)$$

$$\mathbf{r}'_{ij} = (x'_{ij}, y'_{ij}, 0) \quad (2.4)$$

$$\mathbf{R} = \mathbf{R}_x(\alpha_x) \mathbf{R}_y(\alpha_y) \mathbf{R}_z(\alpha_z). \quad (2.5)$$

Here, $\mathbf{R}$ is the rotation matrix that specifies the orientation of the camera relative to the laboratory frame, parametrised with the Euler's angles $(\alpha_x, \alpha_y, \alpha_z)$ [180]. Such angles, along with the distance D from the source to the camera origin O' and the Bragg angle $\bar{\theta}_B$ associated to O' , constitute the geometrical parameters $\mathbf{A}$ for fitting and determining the energy map. In order to do this, one first identifies, in terms of pixels coordinates, a

bright curve S_{exp} on the experimental image A_{ij} associated with an emission line of known energy $\bar{E}$:

$$S_{exp} = \left\{ (i, f(i)) , i = 1, \dots, N_y \right\} \quad (2.6)$$

with $f(i) = \max_{N_1 \leq j \leq N_2} A_{ij} ,$

where N_1 and N_2 are properly chosen to isolate the emission line of energy $\bar{E}$. A more sophisticated and accurate method is to fit, for each row, the emission line to an analytic function and to take the peak of the fit as the line position. This approach is less susceptible to noise and allows for sub-pixel resolution, by constructing the energy map on a finer sub-pixel grid. However, for the purposes of this thesis, the method described by Eq. (2.6) is adopted. As a second step, the relative theoretical contour $\{(ij) | E_{ij} = \bar{E}\}$ is computed using Eq. (2.2) with a guess for $\mathbf{\Lambda}$:

$$S_{th}(\mathbf{\Lambda}) = \left\{ (i, g(i; \mathbf{\Lambda})) , i = 1, \dots, N_y \right\} \quad (2.7)$$

with $g(i; \mathbf{\Lambda}) = \min_j |E_{ij}(\mathbf{\Lambda}) - \bar{E}| .$

S_{exp} and S_{th} are parametrised with i as independent variable because of the expected shape for these curves. Finally, one calculates a loss function $\mathcal{L}$, dependent on the geometrical parameters $\mathbf{\Lambda}$, measuring a distance between the experimental line S_{exp} and the theoretically-computed contour S_{th} :

$$\mathcal{L}(\mathbf{\Lambda}) = \frac{1}{N_y} \sum_{i=1}^{N_y} (f(i) - g(i; \mathbf{\Lambda}))^2 \quad (2.8)$$

At this point, $\mathcal{L}$ is minimised over the space of the geometrical parameters with standard optimisation routines [181]. The loss function can include multiple emission lines by summing the loss functions of each individual line, as previously defined. Each line in the summation can also be weighted proportionally to its intensity. Figure 2.4 illustrates an example of this calibration for the Mg spectrum discussed earlier. Here, the geometrical parameters of the setup are determined by fitting the $K\alpha$ lines of the Mg ion in its

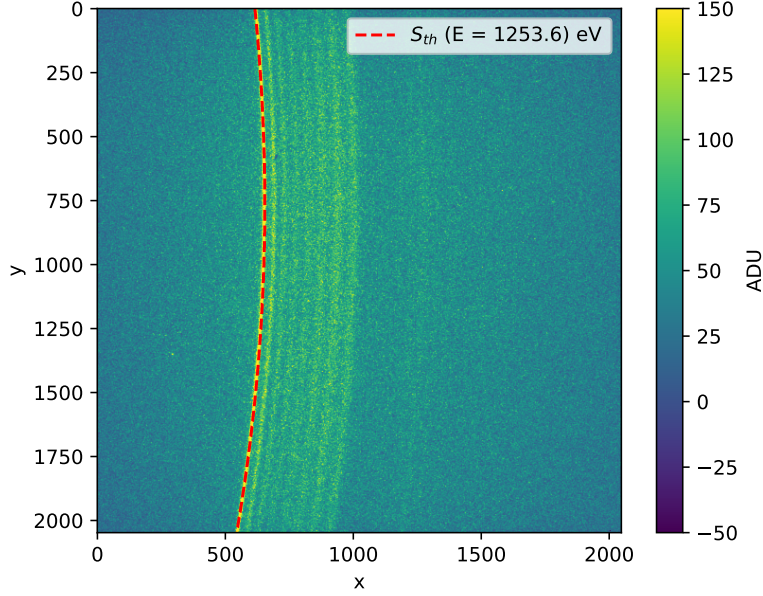


Figure 2.4: Detector image of MgF_2 emission spectrum with the theoretically-computed energy contour (red) fitted to a $\text{Mg } K\alpha$ line.

fundamental charge state, and they are as follows:

$$\begin{aligned}
 (\alpha_x, \alpha_y, \alpha_z) &= (-1.9^\circ, 55.8^\circ, 0^\circ) \\
 D &= 79.5 \text{ mm} \\
 \bar{\theta}_B &= 34.7^\circ .
 \end{aligned} \tag{2.9}$$

As it is observed from these values, it is common practise to work with the camera orthogonal to $\mathbf{r}_0$ in order to maximise the solid angle detected by the detector, as well as to minimise any grazing incidence broadening in the sensor layer (see Section 2.2.3). In this work, the uncertainties in the $\mathbf{\Lambda}$ parameters arising from the fitting process are disregarded, as their impact on the final energy map is minimal. This is justified by the fact that these errors are typically small, especially when multiple emission lines are used for fitting. Consequently, their contribution to the energy map uncertainties is negligible compared to the broadening effects discussed in Section 2.2.3.

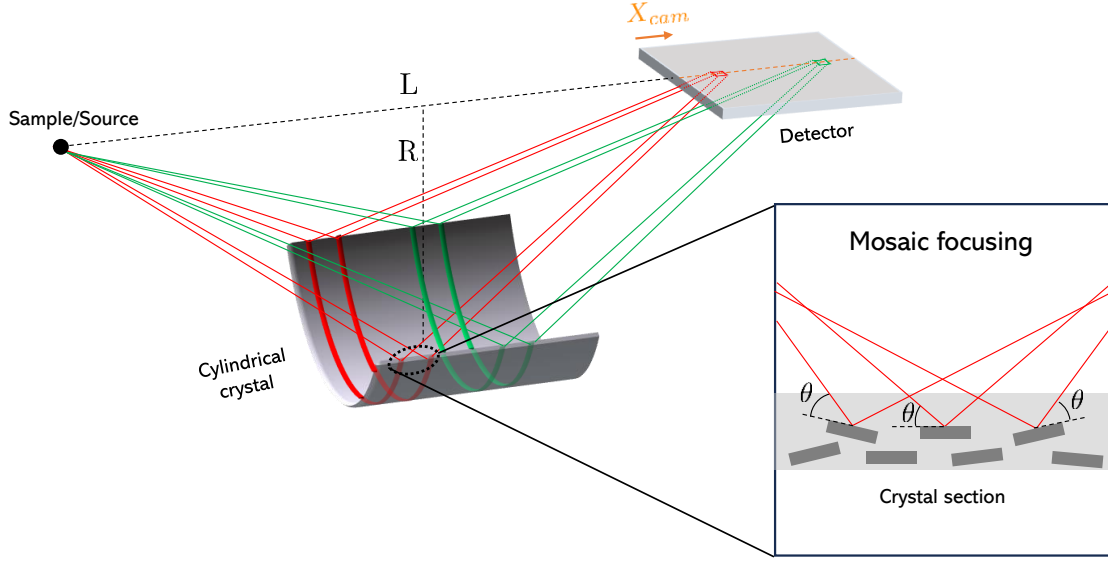


Figure 2.5: Scheme of the von Hámós spectrometer with an illustration of mosaic focusing (inset). The mosaicity of the crystal increases the area that reflects a certain photon energy. For the correct functioning of the spectrometer, the crystal must be placed halfway between the source and the centre of the detector. As in the flat crystal case, $\bar{\theta}_B$ is defined as the Bragg angle associated with the centre of the detector.

2.2.2 Von Hámós Spectrometer

In Von Hámós (VH) geometry [182], an axis (the dispersion axis) is drawn between the source and the detector, and the detector surface lies along this line (see Fig. 2.5). A cylindrically-bent crystal is then placed parallel to this axis, with the crystal positioned at its radius of curvature below this axis. The crystal therefore acts to focus the reflected rays back on to the dispersion axis at a distance twice as far away in the dispersive direction. This results in a simple dispersion relationship between the photon energy E , the position from the source to the front of the camera along the dispersion axis L , and the position on camera along the dispersion axis X_{cam} :

$$E = \frac{hc}{2d} \sqrt{1 + \frac{(L + X_{\text{cam}})^2}{4R^2}}, \quad (2.10)$$

where R is the radius of curvature of the crystal, and the remaining symbols have the same meaning as before. The calibration is also quite simple and involves the optimisation of R and L using analogous techniques to those described for the flat crystal geometry. Bright

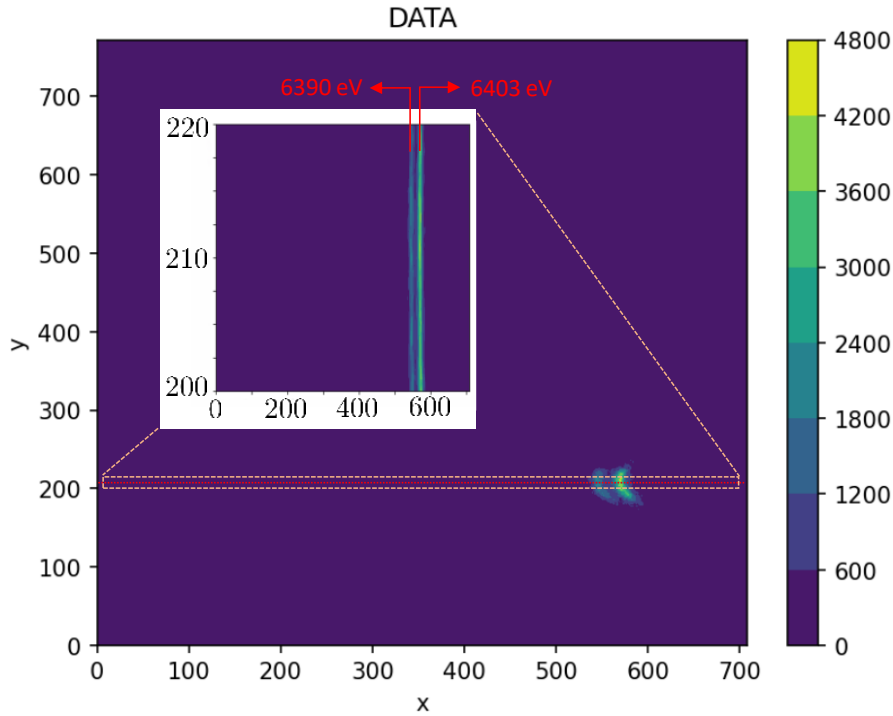


Figure 2.6: Detector image of Fe emission using a von Hámós spectrometer from the experiment reported in Ref. [183] with a zoom (inset) around the central dispersion axis, indicated by the red dotted line. The two vertical bright lines in the inset correspond to the isoenergy contours of the Fe K-alpha lines used for the calibrations. In reality, the greater the energy separation between these reference lines, the more accurate the calibration becomes. Generally, the central dispersion axis may be slightly tilted relative to the detector's edge. This tilt is accounted for by adjusting the region of interest while moving along the dispersive direction. However, Eq. (2.10) remains valid, as corrections due to the tilt are typically negligible.

emission lines with known energies are well-suited to this task. Two sets of lines that cover the detector range are ideal for the calibration and results in a very well-constrained dispersion relationship. An example of an experimental calibration is shown in Fig. 2.6.

The primary benefit of a von Hámós spectrometer is its collection efficiency. By focusing all the rays onto a single axis instead of arcs as with the flat crystal spectrometer, it is easier to detect events above the noise. As the bending process deforms the lattice of a perfect crystal, its rocking curve becomes extended, which degrades the intrinsic resolution of the crystal [184, 185]. It is therefore common to use mosaic crystals as the dispersive crystal to further increase the collection efficiency of the spectrometer. Common examples of such crystals are highly annealed pyrolytic graphite (HAPG), highly oriented pyrolytic graphite (HOPG) and Lithium Fluoride (LiF). A mosaic crystal is one that consists of

small perfect crystallites with their normal vectors randomly distributed around the crystal surface normal. As a result, in contrast to perfect crystals where reflections only take place around the Bragg angle within the rocking curve, the Bragg condition can be satisfied anywhere on a mosaic crystal by finding a crystallite appropriately angled to the normal (see Fig. 2.5). This effect increases the area of the crystal reflecting a certain photon energy on a specific spot of the detector (mosaic focusing). The end result is that von Hámos spectrometers have very high collection efficiencies, and so are often employed in situations where photon numbers are very low, such as in x-ray Thomson scattering and resonant inelastic x-ray scattering experiments [156, 183, 186].

As the x-rays are focused onto the dispersion axis, the spectrum is produced by integrating over a few pixels along the non-dispersive direction. The number of pixels used is chosen to maximise the signal-to-resolution ratio (see [187]). Outside this region of interest (RoI), unfocused x-rays are disregarded, as different photon energies overlap on the same pixels.

The drawback to mosaic crystal VH spectrometers is that their resolution tends to be worse than for flat crystal spectrometers. The bulk of this is due to the mosaicity of the crystal, which both enhances depth broadening and itself contributes directly to the broadening. As a result, photons of a specific energy are sent to different locations on the detector rather than to a precise, nominal point, producing a quite broad, X-shaped instrument function, as demonstrated in ray-tracing simulations [186]. This broadening leads to the aforementioned energy mixing outside the central RoI. In the experimental image presented here, however, these characteristic shapes are not visible, as broadening is dominated by defocusing, which deforms the energy contours towards those of a FC spectrometer, creating small and thick bright arcs (see Fig. 2.6). Focal aberrations are in fact an additional factor that degrades the resolution [188], but this effect can be reduced by using a relatively narrow crystal [187, 188]. Typical resolutions of von Hámos spectrometers range from 1 to 10s eV [187, 189, 190].

2.2.3 Broadening Effects

So far it has been assumed that there is a one-to-one relationship between the photon energy and the position it lands on the detector. However, in practice there are numerous

effects that result in photons of the same energy being detected at different points on the detector away from their nominal position. As the spectrometer is calibrated so that spatial points on the detector correspond to specific energies, there is no way to distinguish between a photon arriving at its nominal position, and a photon with a different energy landing at the same point due to the broadening effects. This point spread function, also known as the instrument function (IF), means that the features of the measured spectrum appear broader than they actually are.

While high resolution spectra are generally desirable, there is a trade-off between resolution and signal intensity as the very effects that result in broadening also tend to result in higher spectrometer efficiencies. For example, a broader rocking curve reduces resolution but increases crystal reflectivity, while a larger pixel size leads to greater quantisation errors yet allows more photons to be detected by a single pixel, yielding a better SNR.

Broadening effects are generally complex to account for, as the instrument function (IF) can be strongly geometry-dependent and varies between experiments and setups. Furthermore, the IF rigorously depends also on the photon energies incident on the crystal [186]. In other words, the broadening of the spectrum due to the IF cannot be expressed as a simple convolution, but must be formulated as a Fredholm integral equation (FIE):

$$I(E) = \int K(E, E_0) I_{orig}(E_0) dE_0, \quad (2.11)$$

where I and I_{orig} represent the measured and original spectra, respectively, and the kernel $K(E, E_0)$ is the energy-dependent instrument function. Methods for determining K are outlined in Ref. [186] and rely on a combination of quasi-elastic signal measurements and theoretical modelling of the IF. Once K is known, I_{orig} can be retrieved using standard techniques for solving FIEs. Even in cases where the dependence of the IF on the incident energy could be neglected – making the calculation of I_{orig} a simpler deconvolution problem – finite spectral windows and experimental noise introduce instability in the deconvolution process. As a result, a small amount of noise in I can cause significant distortions in I_{orig} .

Here, the main effects that deteriorate the resolution of the measured spectra are summarised.

- **Finite pixel size and quantisation error:** Pixels are rectangles with sides of

finite length L_p , causing each pixel to collect photons within an energy range of order $O(\frac{2hc}{d} \frac{\cos \bar{\theta}_B}{\sin^2 \theta_B} \frac{L_p}{D})$. In other words, the energy calibration of a pixel E_{ij} actually represents an average energy. For the cameras used in the experiments, typical L_p values are in the range $\sim 10\text{-}100 \mu\text{m}$ [191], which is typically small enough to measure a smooth spectrum with energy bins $\lesssim 2 \text{ eV}$. The energy bin width ΔE must in fact be chosen as small as possible to reduce the quantisation error ($\sim \Delta E/\sqrt{12}$), but large enough to contain several E_{ij} in order to obtain smooth spectra. As an aside, there is a trade-off to be considered in pixel size – while smaller pixels have less pixel broadening, they also suffer from increased charge spreading between pixels. If the charge of a photon is spread between too many pixels, it may become difficult to detect above the noise. As a result, there is a balance between the possible energy bin size and the ability to reliably detect photons above the noise. These two broadening effects, unlike the ones discussed next, degrade resolution without affecting the correspondence between photon energy and its position on the detector.

- **Source broadening (SB):** As the incident beam has a finite size, photons leave the target from a region on the sample surface with an effective size D_s , typically ranging from several nm to dozens of μm (this region is often approximated as a circle, although imprints of the beam show that the FEL beam spatial profile is decidedly non-trivial [192]). Additionally, as samples have finite thickness, photons also emerge from different points from within the sample. Consequently, photons of the same energy emitted from different points in the sample reach the detector at different points, representative of the shape of the source, which results in photons of different energies landing on the same point, and therefore, in the measured spectrum being broadened (see Fig. 2.3). The energy uncertainty on each pixel, due to this effect, is of order $O(\frac{2hc}{d} \frac{D_s \cos \bar{\theta}_B}{D})$.
- **Depth Broadening (DB):** A photon can travel a finite depth into a crystal before being reflected back out. As a result, it reflects at a point displaced from the nominal position it would reflect on the surface, and therefore hits the detector at a different point. The DB resembles an exponential function as it represents the probability a photon reflects from a certain depth in the crystal. For perfect crystal, this is

typically an extremely narrow function and does not contribute significantly to the broadening. However, for mosaic crystals the broadening is quite substantial (several eV) due to the distribution of the crystallites [186], and is made even broader by non-negligible multi-reflection paths within the crystal [193]. When the path travelled inside the crystal is much smaller than its attenuation length - a necessary condition to maintain the crystal's reflectivity - the SB is proportional to $t/\sin(\theta_B)$, with t representing the crystal thickness. Since t cannot be reduced excessively without compromising reflectivity, it is important to avoid working at overly shallow incidence angles. The same consideration applies to the detector, where small incidence angles influence the depth and, depending on L_p , the pixel position of the photoabsorption, thereby impacting pixel detection and increasing charge spreading [194].

- **Finite width of the rocking curve:** Another source of energy broadening is the finite width of the crystal rocking curve (RC), D_W ¹. The RC allows for a photon that does not satisfy the Bragg condition to nevertheless be reflected from the crystal, albeit with a lower reflectivity [151]. For perfect crystals, their intrinsic RC is calculated using dynamic diffraction theory, and it is an extremely narrow function [151]. Typical values for D_W are dozens of μrad . For mosaic crystals, the mosaic distribution of the crystallites also contributes to the RC, and is about an order of magnitude larger than the intrinsic RC of the crystallites [195]. The energy uncertainty per pixel from this effect is then simply of order $O(\frac{2hc}{d}D_W)$. D_W is generally weakly dependent on the photon energy [195], and is often assumed to be constant for typical spectrometer energy windows.

For the geometrical setup of the Mg experiment, summarised by the parameters provided in (2.9), with typical values for L_p , D_s and D_W , the energy resolution losses produced by these effects are all around 0.5 – 1 eV. Normally in HED science, these resolution losses are of secondary importance, as other factors such as source bandwidth dominate [196]. Nevertheless, they must be considered if one wants to reach high resolutions (sub eV). These resolutions can be achieved by means of specific experimental setups, characterised by large source-detector distances and high resolution crystals with very narrow RC [197, 198].

¹This notation stems from its common name in dynamical diffraction theory, the *Darwin width*.

However, these features also tend to decrease the SNR of the single-shot images. It is therefore useful to contrive alternative methods that mitigate these resolution losses, without compromising the signal intensity. One potential solution to overcome the resolution limitations imposed by the finite pixel size is to analyse the charge distribution between neighbouring pixels. Techniques used to manage charge spreading, based primarily on centroid calculations, have been successfully employed in the past to handle such correlations and achieve sub-pixel resolutions [171, 172]. Nevertheless, it is important to note that these methods are applicable only when the pixel dimensions are sufficiently small compared to R_s and in low photon-density regimes. Section 2.4 introduces an alternative approach to treat these correlations, based on deconvolution algorithms and capable of handling also cases with large photon densities on the detector.

The other three effects can instead be mitigated by studying the instrument function of the experimental setup and then solving the integral equation mentioned earlier. Assuming the pixel size effect is negligible or that it has already been accounted for, the broadening due to the spectrometer instrument function can be determined by irradiating the target with a monochromated source and comparing the elastic scattering measured on the spectrometer to a high-resolution beam spectrometer. For this method to work, a material with very weak inelastic scattering in the vicinity of the elastic scattering must be chosen – good choice include plastics such as polymethyl methacrylate and polypropylene, or metallic glasses [186, 199]. Another common way to determine the resolution of a setup is from emission lines with known lineshapes; e.g. Hölzer *et al.*'s 3d metal transition lines [200]. In any case, the FWHM of the instrument function used provides an estimate of the spectrometer resolution.

2.3 Experimental Estimation of Camera Parameters

A fundamental quantity for converting the ADU map to the photon distribution hits is the RMS of the camera read noise, σ_N , which measures the level of thermal noise in the detector. This can be measured pixel-wise by simply running the camera without the source and calculating the variance of the pixel values during these dark runs. However, for simplicity, this quantity is assumed to be constant across the camera, which is a reasonable

approximation for the typical detectors employed [191, 201]. In these cases, σ_N is directly inferable from the histogram of the camera images with signal present, whose shape is now discussed.

This work deals with detector images that have undergone dark image subtraction, so that the expected value of the ADU count for a pixel not hit by any photon is zero. Additionally, for our cases, the analysis of the histogram is simplified because, in Bragg spectroscopy, photons energies are determined by their position on the detector. Consequently, the camera can be subdivided into regions (e.g. rectangles that tile the entire camera) sufficiently small to approximate $ADU_{sp}(E)$, the ADU counts produced by a photon of energy E , as constant (ADU_{sp}) in each region. The shape of the histogram for a single region is in general a series of peaks centred approximately in the following sequence of values:

$$P_n = \zeta n ADU_{sp}, \quad n = 0, 1, 2, \dots \quad (2.12)$$

where ζ is a constant smaller than 1 (typically around 0.8-0.9), whose origin is discussed below. The n -th peak contains the pixels which have been likely been hit by n photons. In reality, only the initial peaks of this sequence appear in the histogram, depending on the density of photon hits, which is measured by the so-called fill fraction λ . This important parameter is defined as:

$$\lambda = \frac{\# \text{ photons on the camera}}{\# \text{ pixels in the camera}} \quad (2.13)$$

Each peak is then broadened by the intrinsic noise of the detector and the charge spreading, quantified by σ_N and R_s , respectively. The magnitude of these broadening effects determines whether the peaks are merged together or remain distinct. Additionally, charge spreading systematically shifts the peaks, initially centred at $nADU_{sp}$, towards lower ADU values, as some of the photon energy is deposited across multiple pixels. The constant ζ in Eq. (2.12) accounts for this shift, decreasing as R_s increases. To illustrate these effects, Figs. 2.7 (a-d) present histograms generated from synthetic camera images with various levels of noise and fill fractions. More details on the fabrication of these synthetic images

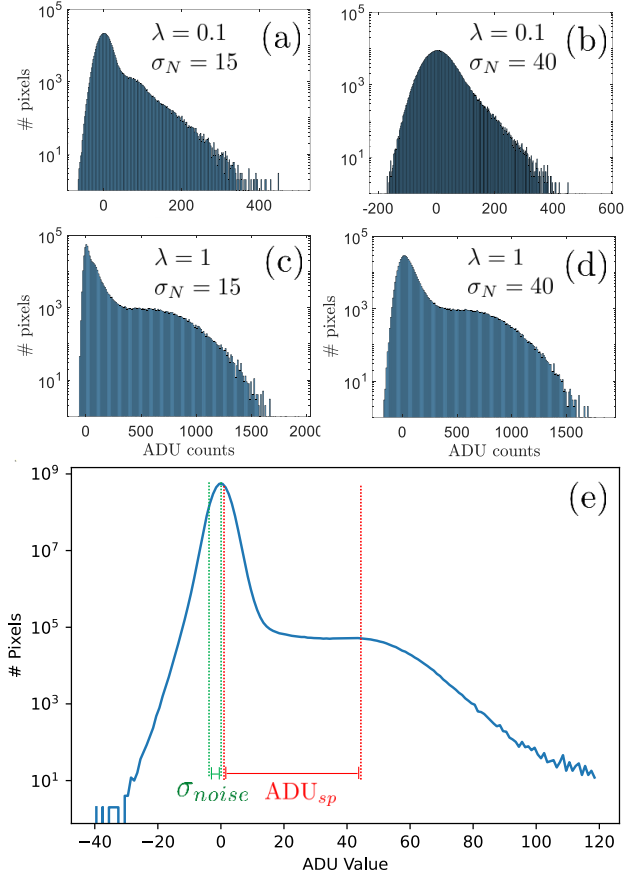


Figure 2.7: (a-d) Synthetic histograms of 700x700 images for various levels of noise and fill fractions. ADU_{sp} is taken equal to 120. (e) Histogram of the experimental image reported in Fig. 2.1, acquired using a PIXIS-XF camera. This camera employs 16-bit analog-to-digital converters, enabling quantisation into 65,536 discrete signal levels.

are provided in Section 2.6.1. Alongside these synthetic data, an experimental histogram for MgF₂ is included in Fig. 2.7e for data from Ref. [166].

If $ADU_{sp}(E)$ is not provided by the facility, it can be directly inferred from the position of the first peak in the series given by Eq. (2.12), which corresponds to single photons hitting pixels on the camera. Similarly, from the width of the peak centred around 0, one can estimate σ_N . Intuitively, the more the peaks merge together, the more challenging it becomes to accurately determine these quantities. In such cases, one approach to extract these two parameters is to fit the experimental histograms to a simulated one. The latter can be constructed (see Section 2.6.1) given certain values for ADU_{sp} , σ_N , and λ , which can be estimated from the expected number of photons, and R_s , usually provided in the camera documentation.

2.4 Estimate of the Photon Hits Distribution

The objective of this section is to describe how to compute the distribution of photon hits, N_{ij}^γ , from the camera image A_{ij} , thereby eliminating the distortions due to thermal noise and charge spreading. Depending on the spectrum of photons hitting the camera, the image has regions with different local fill fractions (see Fig. 2.11), which must be treated with distinct methods. Therefore, to process the image, the following two techniques are applied:

1. **Photon counting algorithms:** To address regions with small fill fractions ($\lambda \lesssim 0.1$), where single photon clusters are present, photon counting algorithms are used. These algorithms can identify the single photon clusters, exploiting the correlation between neighbouring pixels to reduce the uncertainty on the photon detection.
2. **Image deconvolution techniques:** To treat the regions with large fill fractions ($\lambda \gtrsim 1$), where agglomerated clusters are present (see next section), the image is processed with the Richardson-Lucy deconvolution method [202].

As discussed below, these two operations can be carried out sequentially, improving the signal quality across the entire range of λ , including also intermediate fill fractions. Following the discussion in Section 2.3, the camera parameters ADU_{sp} , σ_N and R_s are considered known quantities in the following analysis.

2.4.1 Clustering Algorithms

If one supposes, as it is often the case, that the charge produced by a photon does not spread further than a pixel side length, then the shapes of single-photon clusters (i.e. the pixels in which the charge produced by the photon has leaked) are few, and given in Fig. 2.. As there are only 13 possible shapes, a simple clustering algorithm can be employed to identify these clusters and re-accumulate the intensity back on to the central pixel. The benefit of doing so is that this makes the pixel brighter relative to the background, allowing for more of these events to be included once the final thresholding is performed.

The first step to identify the photon hits from the ADU map is thresholding the camera image. Although different choices are possible for the thresholding value, here, $1.5 \sigma_N$ is

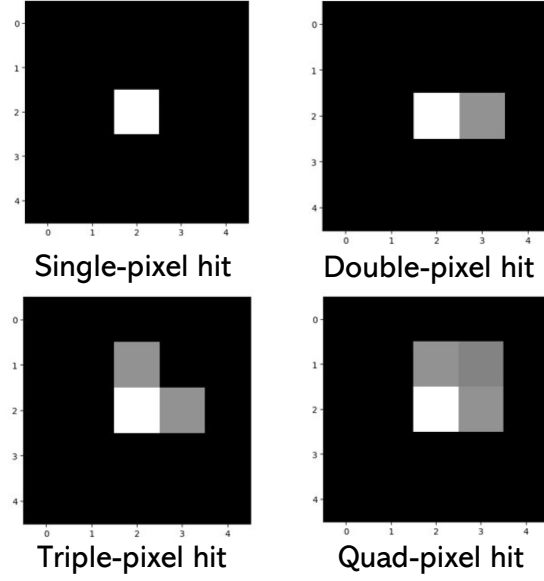


Figure 2.8: The 4 layouts for a single photon cluster. The brighter pixel represents the pixel hit by the photon. Each of the last 3 can rotate by 90° , 180° and 270° to produce 13 layouts in total.

chosen, as a good compromise to cut the noise and retain the signal:

$$A_{ij}^{th} = \begin{cases} A_{ij} & A_{ij} \geq 1.5 \sigma_N \\ 0 & A_{ij} < 1.5 \sigma_N \end{cases} \quad (2.14)$$

The thresholding value can be chosen in a systematic way by analysing their performances over multiple synthetic images for a given set of parameters (ADU_{sp} , σ_N and R_s). This method, adopted for this thesis, is briefly described in the following section. After the thresholding, the pixels with an ADU value different from zero are the ones that most likely received a contribution to their ADU by a photon hit. One may also set pixels exceeding some upper threshold to zero to mask out possible faulty pixels or high intensity events that do not correspond to real signal.

Next, all the clusters are located and it is determined whether they have fall into one of two cases:

1. **Single-photon clusters.** If the shape of the cluster C matches that in Fig. 2.8, then the charge spread is considered to originate from the brightest pixel, and all the

ADU values of the cluster are accumulated onto its brightest pixel $(\bar{i}, \bar{j})$:

$$ADU'_{\bar{i}, \bar{j}} = \sum_{ij \in C} A_{ij}^{th} \quad (2.15)$$

$$A'_{ij} = 0 \quad \text{for } (i, j) \in C \text{ and } (i, j) \neq (\bar{i}, \bar{j}) .$$

2. **Agglomerated clusters.** In this case the ADU values are not modified:

$$A'_{ij} = A_{ij}^{th} \quad (2.16)$$

After the clustering algorithm is applied, the image is thresholded once more with a higher threshold, assuming that any events that fall below the threshold did not originate from a single photon event. Using the method described in the following section, $(ADU_{sp} - \sigma_N)$ is chosen as the second threshold, which results in discarding roughly 20% of the single photons (A'_{ij} has a larger variance than A_{ij}), but eliminates almost entirely noise fluctuations. This second threshold can also be systematically determined using the method outlined in the next section. Charge accumulation over the brightest pixel can also be carried out by considering the centroid of the single-photon cluster, enabling subpixel resolution [171]. However, this more advanced process is beyond the scope of this thesis.

Fig. 2.9 presents an example of this operation using a synthetic camera image (see Section 2.6.1 for more details). As it is observed, agglomerated clusters remain unchanged by this algorithm and are addressed in the following section.

Exploiting the correlation of ADU values across neighbouring pixels enables one to boost the signal. As an example, consider three adjacent pixels arranged in an L-shape, with ADU values between the first and second thresholds. If the correlation is ignored, and consequently, the ADU values are not accumulated on the brightest pixel, all three pixels are zeroed after the second thresholding, resulting in a loss of signal that likely corresponds to a photon. In fact, a simple analysis shows that the probability of three L-shaped pixels with values above $1.5 \sigma_N$ being caused by a photon is significantly higher than by noise.

In addition to this, thresholding mitigates the noise-related fluctuations in the reconstructed spectrum. The noise reduction is approximately proportional to $\mathcal{P}(N_{ij}^\gamma \geq 1) < 1$, where $\mathcal{P}(N_{ij}^\gamma \geq 1)$ is the probability that at least one photon lands on pixel (i, j) . This

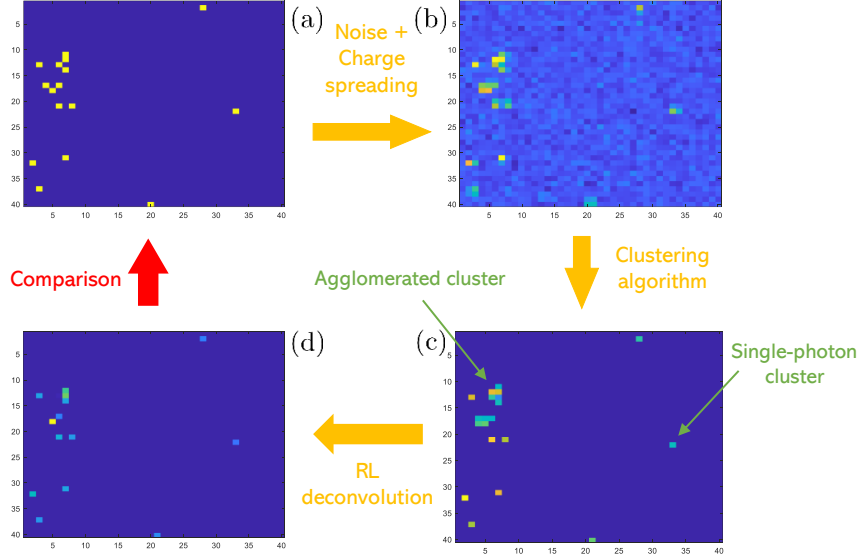


Figure 2.9: Illustration of the various steps in the camera image processing. (a) Map of photon hits on the camera for a small λ , to which thermal noise and charge spreading have been applied to obtain the camera image (b). The same image, processed with the clustering counting algorithm (c), and then with the deconvolution algorithm (d). In the figure, an example of a single-photon cluster and of an agglomerated cluster are indicated. All camera images, except the first initial photon map, are in ADU units.

result is derived by considering the variance of the random variables $A_{ij} \approx N_{ij}^\gamma \text{ADU}_{sp} + \eta_{ij}$ (see Section 2.4.2) and A_{ij}^{th} (as defined earlier), where η_{ij} represents the random noise on pixel (i, j) , which is assumed to be Gaussian-distributed with mean 0 and variance σ_N : $\eta_{ij} \sim \mathcal{N}(0, \sigma_N)$. Firstly, fixing the number of photons N_{ij}^γ , one finds:

$$\begin{aligned} \mathbb{V}(A_{ij}|N_{ij}^\gamma) &= \mathbb{V}(\eta_{ij}) = \sigma_N^2 \quad \forall N_{ij}^\gamma, \\ \mathbb{V}(A_{ij}^{th}|N_{ij}^\gamma) &= \begin{cases} \sigma_N^2 & A_{ij} \geq \kappa\sigma_N \\ 0 & A_{ij} < \kappa\sigma_N \end{cases}, \end{aligned} \quad (2.17)$$

where $\mathbb{V}(\cdot)$ represents the variance and $\kappa\sigma_N$ is a generic threshold proportional to σ_N . Now, taking the mean values $\mathbb{E}$ over the random variable N_{ij}^γ , one obtains:

$$\begin{aligned}\mathbb{E}(\mathbb{V}(A_{ij})) &= \sigma_N^2 \mathcal{P}(N_{ij}^\gamma = 0) + \sigma_N^2 \mathcal{P}(N_{ij}^\gamma = 1) + \dots = \sigma_N^2 , \\ \mathbb{E}(\mathbb{V}(A_{ij}^{th})) &= 0 \cdot \mathcal{P}(N_{ij}^\gamma = 0) + \sigma_N^2 \mathcal{P}(N_{ij}^\gamma \geq 1) < \sigma_N^2 ,\end{aligned}\tag{2.18}$$

having taken as an approximation that $\mathcal{P}(A_{ij} < \kappa\sigma_N | N_{ij}^\gamma > 1) = 0$ and $\mathcal{P}(A_{ij} > \kappa\sigma_N | N_{ij}^\gamma = 0) = 0$. Summing the ADU values over the energy contours preserves the ratio between the variance of the raw and thresholded values.

Determination of Thresholding Values

The two thresholding values can be determined using the following procedure. First, one generates N_s synthetic images (see also Section 2.6.1) for specified parameters (ADU_{sp} , σ_N , R_s), and for a small fill fraction (e.g. $\lambda = 0.1$), so that single-photon clusters are predominant. It is important to note that generating these synthetic images requires knowledge of the underlying spectrum. For experimental applications, a reasonably accurate approximation of the underlying spectrum can be obtained from the experimental images prior to optimizing the thresholding values. Each of these synthetic images is then processed with the photon clustering algorithm, applying a trial pair of thresholding values, and divided by ADU_{sp} to reconstruct the photon hits map $\{N^{rec}\}$. The reconstructed photon maps are then compared to the original photon map $\{N^{orig}\}$, and a global loss function is computed:

$$\mathcal{L}_{oss} = \frac{1}{N_s} \sum_{l=1}^{N_s} ||\{N^{rec}\}_l - \{N^{orig}\}||_F , \tag{2.19}$$

where $\{N^{rec}\}_l$ and $\{N^{orig}\}$ are two matrices and $||\cdot||_F$ is the Frobenius norm. The optimal threshold pair is obtained as the one that minimises this loss function.

2.4.2 Images Deconvolution

To address the charge spreading and the noise contributions in regions with large λ , the Richardson-Lucy (RL) deconvolution algorithm [202] is applied to the matrix A'_{ij} . This method is an iterative procedure, based on Bayesian inference, that computes the most likely expected values V_{ij} of the Poissonian and independent variables X_{ij} , given a realisation R_{ij} , which has been blurred out by a known kernel function H and corrupted by

random noise. In formulas:

$$\begin{aligned}
R_{ij} &= (X * H)_{ij} + \eta_{ij}, \\
X_{ij} &\sim \text{Poisson}(V_{ij}), \quad \eta_{ij} \sim \mathcal{N}(0, \sigma_N^2) \\
R_{ij} &\xrightarrow{\text{RL algorithm}} V_{ij}
\end{aligned} \tag{2.20}$$

where ‘ $*$ ’ denotes the convolution symbol, and X_{ij} and η_{ij} are uncorrelated random variables for each i and j . It is intuitive to see that this problem is analogous to our case, where X_{ij} is the number of photons landing on pixel (i, j) , V_{ij} is the intensity of the spectrum at that pixel energy $I(E_{ij})$, H is an effective charge spreading function (defined in the next section), η_{ij} is the thermal noise on pixel (i, j) and R_{ij} is the ADU map. Therefore, defining A_{ij}^{proc} as:

$$A'_{ij} \xrightarrow{\text{RL algorithm}} A_{ij}^{proc}, \tag{2.21}$$

it constitutes an estimate for $I(E_{ij})$, the quantity of interest. A more rigorous justification for the application of this method is presented in the next section.

Fig. 2.9d illustrates the result of applying the RL algorithm to the camera image already treated with the photon counting algorithms. As observed, the algorithm decomposes the agglomerated clusters into the most likely distribution of photon hits (still in ADU units), leaving the single-photon clusters unchanged. The comparison between the reconstructed map A_{ij}^{proc} and the original photon hits is excellent, with only very few mismatches.

Finally, the camera units are converted to photon numbers, which provides the intensity in the measured spectrum:

$$N_{ij}^\gamma = \frac{A_{ij}^{proc}}{ADU_{sp}}, \tag{2.22}$$

Probability Distribution of the ADU Counts

Let us focus on regions with high local λ , where the photon counting algorithm leaves pixel values unchanged. While this discussion can be extended to include thresholding and charge accumulation operations, doing so adds complexity without altering the fundamental concepts. First, consider the signal on a sufficiently fine subgrid $k, l = 1, 2, \dots$ (see also

Section 2.6.1):

$$A_{kl} = \sum_{k'l'} ADU_{sp}(N_{k'l'}^\gamma + \beta_{k'l'})H_{k-k' \ l-l'} \quad , \quad (2.23)$$

where H is the charge spreading function, and $N_{k'l'}^\gamma \sim \text{Poisson}(I_{k'l'})$, with $I_{k'l'}$ denoting the spectral intensity at subpixel $(k'l')$. The term $\beta_{k'l'} \sim \mathcal{N}(0, fN_{k'l'}^\gamma)$ is a compound probability distribution accounting for random fluctuations in e-h pairs production, quantified by the Fano factor f . This factor is usually small (e.g. $f = 0.12$ in Silicon [161]), and therefore this noise source is often neglected. The value A_{ij} is obtained by summing A_{kl} over the subpixels within each pixel, and then adding the thermal noise specific to the pixel:

$$A_{ij} = \sum_{k,l \in (i,j)} A_{kl} + \eta_{ij} \quad , \quad (2.24)$$

where $k, l \in (i, j)$ indicates that subpixel (k, l) lies in pixel (i, j) . Using the properties of the Poisson distribution and neglecting the e-h pairs production noise, one now writes:

$$\begin{aligned} A_{ij} &= \sum_{k,l \in (i,j)} \sum_{k'l'} ADU_{sp} \text{Poisson}(I_{k'l'}) H_{k-k' \ l-l'} + \eta_{ij} \\ &= ADU_{sp} \text{Poisson} \left(\sum_{k,l \in (i,j)} \sum_{k'l'} I_{k'l'} H_{k-k' \ l-l'} \right) + \eta_{ij} \\ &= ADU_{sp} \text{Poisson} \left(\sum_{i'j'} \sum_{k'l' \in (i',j')} I_{k'l'} \sum_{k,l \in (i,j)} H_{k-k' \ l-l'} \right) + \eta_{ij} \\ &\approx ADU_{sp} \text{Poisson} \left(\sum_{i'j'} \bar{I}_{i'j'} \sum_{k'l' \in (i',j')} \sum_{k,l \in (i,j)} H_{k-k' \ l-l'} \right) + \eta_{ij} \\ &= ADU_{sp} \text{Poisson} \left(\sum_{i'j'} I_{i'j'} \tilde{H}_{i-i' \ j-j'} \right) + \eta_{ij} \\ &= ADU_{sp} \sum_{i'j'} \text{Poisson}(I_{i'j'}) \tilde{H}_{i-i' \ j-j'} + \eta_{ij} \quad , \end{aligned} \quad (2.25)$$

where $I_{k'l'}$ was reasonably assumed to be constant within each pixel and equal to $\bar{I}_{i'j'}$. Here, I defined $I_{i'j'} = \sum_{k'l' \in (i',j')} I_{k'l'} \approx N_p \bar{I}_{i'j'}$, with N_p representing the number of subpixels per pixel, and an effective charge spreading function as:

$$\tilde{H}_{i-i' \ j-j'} = \frac{1}{N_p} \sum_{i'k' \in (i'j')} \sum_{ik \in (ij)} H_{k-k' \ l-l'} . \quad (2.26)$$

The translation invariance of $\tilde{H}$ follows directly from the inherent translation invariance of H . Equation (2.25) proves that the operation defined by Eq. (2.21), combined with the division in Eq. (2.22), yields an estimate for I_{ij} .

To account for the e-h pairs production noise as well, one can perform Bayesian inference on the camera image before applying the Richardson-Lucy algorithm. Defining $\chi_{ij} = ADU_{sp} \sum_{i'j'} \text{Poisson}(I_{i'j'}) \tilde{H}_{i-i' \ j-j'}$, from Eq. (2.23) one has:

$$\begin{aligned} A_{ij} &= \chi_{ij} + \eta_{ij} + ADU_{sp} \sum_{kl \in (ij)} \sum_{k'l'} \beta_{k'l'} H_{k-k' \ l-l'} \\ &= \chi_{ij} + \mathcal{N}(0, \sigma_N^2) + \mathcal{N}(0, f ADU_{sp}^2 \sum_{kl \in (ij)} \sum_{k'l'} N_{k'l'}^\gamma H_{k-k' \ l-l'}^2) \\ &= \chi_{ij} + \mathcal{N}(0, \sigma_N^2 + f ADU_{sp}^2 \sum_{kl \in (ij)} \sum_{k'l'} N_{k'l'}^\gamma H_{k-k' \ l-l'}^2) \\ &\approx \chi_{ij} + \mathcal{N}(0, \sigma_N^2 + f \chi_{ij} ADU_{sp}) , \end{aligned} \quad (2.27)$$

where the Gaussian distribution properties are used, and the charge spreading is ignored as a zero-order approximation ($H_{0,0} = 1$ and 0 elsewhere). This approximation can be refined by expressing N_{kl}^γ in terms of $\chi_{ij}, \chi_{i+1,j}, \chi_{i,j+1}, \dots$, using the relations $\chi_{ij} = ADU_{sp} \sum_{kl \in (i,j)} \sum_{k'l'} N_{k'l'}^\gamma H_{k-k' \ l-l'}$ (H is known). While Eq. (2.27) could incorporate thresholding and charge accumulation, doing so would significantly complicate the expressions without bringing large benefits. From Eq. (2.27), one obtains:

$$\mathcal{P}(A_{ij} | \chi_{ij}) = \frac{\exp\left(-\frac{1}{2} \frac{(A_{ij} - \chi_{ij})^2}{\sigma_N^2 + f \chi_{ij} ADU_{sp}}\right)}{\sqrt{(2\pi(\sigma_N^2 + f \chi_{ij} ADU_{sp}))}} . \quad (2.28)$$

Next, by Bayesian inference and assuming a flat prior for χ_{ij} , one estimates χ_{ij} from a given ADU map as:

$$\langle \chi_{ij} \rangle = \int_{\mathbf{R}} d\chi_{ij} \chi_{ij} \mathcal{P}(\chi_{ij} | A_{ij}) \quad \text{with} \quad \mathcal{P}(\chi_{ij} | A_{ij}) = \frac{\mathcal{P}(A_{ij} | \chi_{ij}) \mathcal{P}(\chi_{ij})}{\int_{\mathbf{R}} d\chi_{ij} \mathcal{P}(A_{ij} | \chi_{ij})} , \quad (2.29)$$

where the integrals are convergent and can be evaluated numerically. This approach allows one also to estimate the uncertainty on χ_{ij} as the standard deviation of $\mathcal{P}(\chi_{ij}|A_{ij})$. The RL method can then be applied to $\langle\chi_{ij}\rangle$, providing an estimate for I_{ij} , along with an error that comes from the uncertainty on $\langle\chi_{ij}\rangle$ propagated through the RL algorithm.

2.5 Construction of the Spectrum and Solid Angle Corrections

The final step is to construct an estimate of the photon emission spectrum, $S(E)$, in the direction of the detector, based on the photon hit distribution N_{ij}^γ obtained in the previous section. In the following, the emission spectrum is assumed to be independent of the unit direction $\hat{\mathbf{k}}$ in the solid angle detected by the camera Ω_{det} . If this assumption does not hold, the following discussion remains largely unaffected, except that the calculated spectrum would represent values averaged over all detected directions for a given energy. $S(E)$ describes the probability that, given a source spectrum, a photon of energy E is scattered in the direction observed by the camera. Its units are $\text{sr}^{-1}\text{eV}^{-1}$. The measured spectrum $I(E_l)$, which represents the probability of detecting a photon within a given energy interval, can then be expressed as follows:

$$I(E_l) = \int_{\Omega_{det}} d\Omega(\hat{\mathbf{k}}) \int_{E_l - \Delta E/2}^{E_l + \Delta E/2} dE S'(E, \hat{\mathbf{k}}) \quad (2.30)$$

$$l = 1, \dots, N_b ,$$

where E and $\hat{\mathbf{k}}$ are the energy and unit wave vector of the photons, ΔE is the energy resolution, and N_b is the number of energy bins. Here, $S'(E, \hat{\mathbf{k}})$ is the emission spectrum $S(E)$ modified by the action of the Bragg crystal, summarised in the shape function $F(E, \hat{\mathbf{k}})$:

$$S'(E, \hat{\mathbf{k}}) = S(E)F(E, \hat{\mathbf{k}}) . \quad (2.31)$$

Integrating Eq. (2.30) over the energies, one obtains:

$$I(E_l) = \int_{\Omega_{det}} d\Omega(\hat{\mathbf{k}}) \bar{S}'(\hat{\mathbf{k}}; E_l) . \quad (2.32)$$

Given the energy-dispersive effect of the crystal on the radiation, and assuming that crystal broadening (including depth and mosaicity effects) is sufficiently small, $\bar{S}'(\hat{\mathbf{k}}; E_l)$ ($l=1, \dots, N_b$) can be approximated in the following way:

$$\begin{aligned} \bar{S}'(\hat{\mathbf{k}}; E_l) &= \bar{S}(E_l) = \int_{E_l - \Delta E/2}^{E_l + \Delta E/2} dE S(E) \\ \forall k \mid E_l &= \arg \min_{E_{ij}} |E(\hat{\mathbf{k}}) - E_{ij}| , \end{aligned} \quad (2.33)$$

and equal to zero for all the other values of $\hat{\mathbf{k}}$. Here, $E(\hat{\mathbf{k}})$ is given by Eq. (2.2), with:

$$\hat{\mathbf{k}} = \frac{\mathbf{r}_0 + \mathbf{R}\mathbf{r}'}{\|\mathbf{r}_0 + \mathbf{R}\mathbf{r}'\|} , \quad \mathbf{r}' = (x', y', 0) . \quad (2.34)$$

Now, the integration over the solid angle in Eq. (2.32) becomes:

$$I(E_l) = S(E_l) \cdot \sum_{ij \mid E_{ij} \in \Delta(E_l)} \Omega_{ij} . \quad (2.35)$$

Having denoted the interval $(E_l - \Delta E/2, E_l + \Delta E/2)$ as $\Delta(E_l)$, and Ω_{ij} the solid angle associated with pixel ij . This solid angle for the flat crystal spectrometer is then computed through the following formulas:

$$(\hat{z}')_{\text{lab}} = \mathbf{R}(\hat{z}')_{\text{cam}} \quad \text{with} \quad (\hat{z}')_{\text{cam}} = (0, 0, 1) \quad (2.36)$$

$$\mathbf{x}_0 = \hat{z}'(\hat{z}' \cdot \mathbf{r}_0) \quad \text{with} \quad (\mathbf{r}_0)_{\text{lab}} = D(\cos \bar{\theta}_B, 0, \sin \bar{\theta}_B) \quad (2.37)$$

$$|\mathbf{x}_0| = |\hat{z}' \cdot \mathbf{r}_0| = D' \quad \longrightarrow \quad (\mathbf{x}_0)_{\text{cam}} = (0, 0, D') \quad (2.38)$$

$$\mathbf{x}'' = \mathbf{r}_0 - \mathbf{x}_0 + \mathbf{x}' \quad \longrightarrow \quad (\mathbf{x}'')_{\text{cam}} = (x'', y'', 0) \quad (2.39)$$

$$\text{with} \quad (\mathbf{r}_0)_{\text{cam}} = \mathbf{R}^{-1}(\mathbf{r}_0)_{\text{lab}} \quad \text{and} \quad (\mathbf{x}')_{\text{cam}} = (x', y', 0) \quad (2.40)$$

$$\mathbf{x} = \mathbf{x}_0 + \mathbf{x}'' \quad \longrightarrow \quad (\mathbf{x})_{\text{cam}} = (x'', y'', D') \quad (2.41)$$

$$\Omega(x, y) = \frac{dxdy \cos(\beta)}{|\mathbf{x}|^2} = \frac{dxdy |\mathbf{x}_0|}{|\mathbf{x}|^3} = \frac{D'}{(x''^2 + y''^2 + D'^2)^{3/2}} \quad (2.42)$$

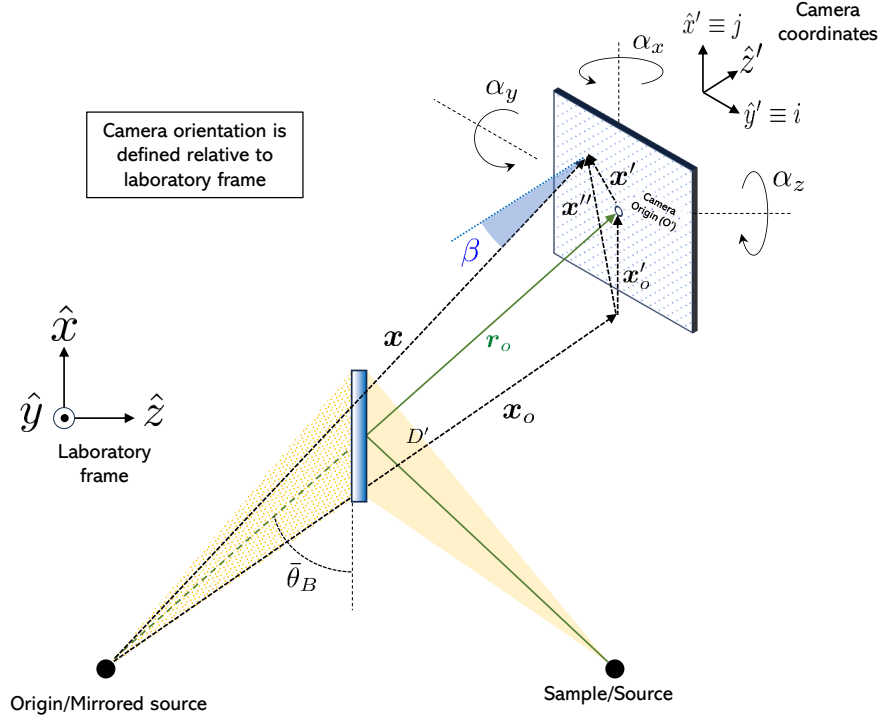


Figure 2.10: Scheme for the solid angles calculations in the flat crystal spectrometer case.

where the relative quantities are defined in Fig. 2.10. Similar reasoning can be carried out for computing the solid angles in the von Hámos geometry.

On the other hand, $I(E_l)$ can be estimated (see also Section 2.6.2) from the distribution of photon hits N_{ij}^γ as:

$$\tilde{I}(E_l) = \sum_{ij|E_{ij} \in \Delta E_l} N_{ij}^\gamma . \quad (2.43)$$

Putting Eq. (2.35) and (2.43) together, one finally obtains an estimate $\tilde{S}(E_l)$ for the emission spectrum:

$$\tilde{S}(E_l) = \frac{\sum_{ij|E_{ij} \in \Delta E_l} N_{ij}^\gamma}{\sum_{ij|E_{ij} \in \Delta(E_l)} \Omega_{ij}} . \quad (2.44)$$

When summing the number of photons over the energy contours associated to these bins, the fluctuations due to the thermal noise and Poissonian statistics are reduced, thanks to the large numbers of pixels.

2.6 Application to Synthetic and Experimental Data

In this section, the discussed methods are applied to both synthetic and experimental data. The synthetic data are first utilised to evaluate the algorithms' performance in enhancing resolution and SNR for different conditions. The experimental data then demonstrate how these methods can amplify specific spectral features that would otherwise be weak, showcasing the efficacy of these techniques in real situations.

2.6.1 Synthetic Data

In order to test these techniques, some artificial camera images were generated through the following steps (illustrated in Fig. 2.11):

1. A 40x40 array is created to represent the camera pixels and a finer 4000x4000 subgrid to depict its surface. For simplicity, the energy contours on the camera are vertical, corresponding to the columns of the pixel matrix.
2. A number of photons, specified by the selected λ , are then sent onto the subgrid. Their energy, which determines the pixel column they land on, is sampled from the spectrum $S(E_l)$ shown in Fig. 2.11a and then converted to an ADU value, taking $\text{ADU}_{sp} = 120$.
3. Charge spreading is applied by convolving the subgrid image with a gaussian kernel of width R_s . The ADU values of the subgrid belonging to the same pixel are then summed together to obtain the actual camera image (see Fig 2.11c)
4. Finally, gaussian random noise with standard deviation σ_N is added to the image (Fig. 2.11d).

The performances of these techniques were evaluated for different values of λ , R_s and σ_N by computing the $\mathcal{L}_2$ distance between $S(E_l)$ and the reconstructed spectrum $\tilde{S}(E_l)$. The latter is obtained by integrating the processed camera images along its columns and then normalising it for comparison with $S(E_l)$. Fig. 2.12 compares, for $\lambda = 0.1$ and $\lambda = 1$, the original spectrum with the spectra reconstructed using different methods to treat the camera image: only simple thresholding, only the photon counting algorithm,

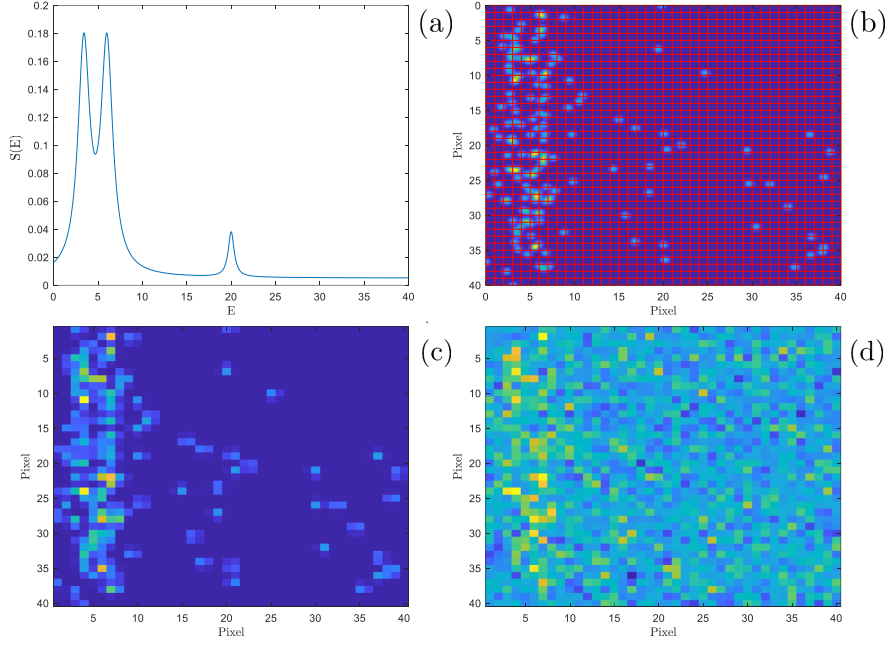


Figure 2.11: (a) The normalised spectrum used for producing the synthetic camera images. (b) The charge deposited on the camera surface, with the pixel grid depicted. (c) The ADU map on the pixel grid. (d) The final camera image with the noise applied.

only the deconvolution algorithm, and the sequential application of photon counting and deconvolution techniques (‘Hybrid’ mode), as discussed in the previous sections. Panel (a) shows that, for small λ values, the photon counting algorithm alone outperforms the deconvolution algorithm alone and the simple thresholding. This is because, in regions with very few photons—where ADU counts are mostly produced by noise—the photon counting algorithm achieves higher accuracy, outweighing the contributions from regions with a stronger signal. In contrast, for large λ values (panel (b)), the photon counting algorithm and the simple thresholding offer little improvement over the raw image, whereas the deconvolution algorithm is able to treat better regions with high λ , enhancing and better resolving the closely spaced spectral features (as seen in the two spectral lines at the lower end of the energy range). The sequential application of these two techniques (‘Hybrid’ mode) combines their benefits, yielding the best performances for both values of λ . It is noted that the applied method can have a substantial effect on the extracted spectral features, such as spectral linewidths or line ratios, which are often used as key diagnostics in experiments. For the implementation of the RL deconvolution, the Python’s Scikit-image library was used [203]. The number of iterations used in the RL algorithm was

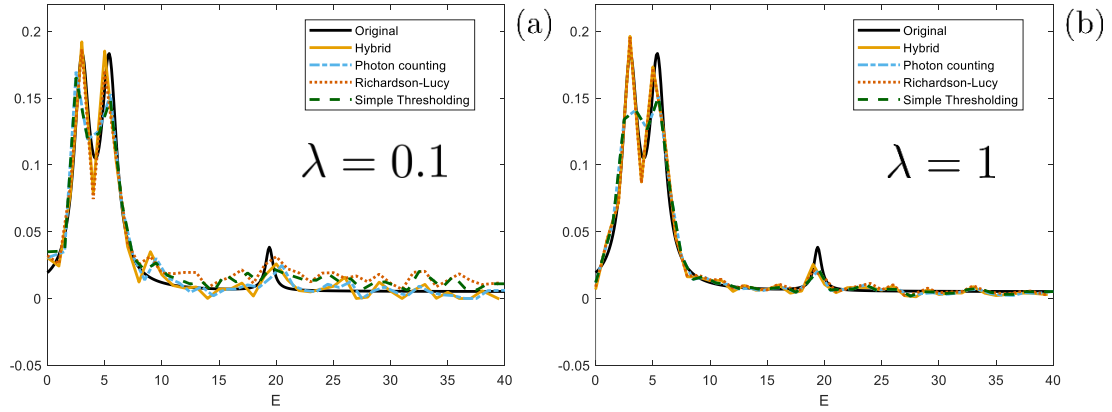


Figure 2.12: The original spectrum compared, for $\lambda = 0.1$ (a) and $\lambda = 1$ (b), to the spectra reconstructed with different methods: only the photon counting algorithm (‘Photon counting’), only the deconvolution algorithm (‘Richardson-Lucy’), both the techniques combined (‘Hybrid’), none of them (‘Simple Thresholding’). The camera parameters are $R_s = 0.4$, $\sigma_N = 30$.

selected from a range of values by determining which provided the best match between the processed and original spectrum. The optimal value, found to be 100, was also applied to the analysis of experimental data, considering comparable levels of noise and charge spreading to the synthetic images.

To evaluate performance, the quality of the spectrum reconstructed from the ‘Hybrid’-processed image was studied by comparing it to that obtained through ‘Simple thresholding’ of the raw image, as a function of the filling fraction. The effect of changing the noise level is included in this study, as the ratio λ/σ_N is the dominant parameter determining the quality of the reconstruction. This analysis was conducted for two values of the charge spreading, $R_s = 0.3$ and $R_s = 0.6$ in pixel units, and its results are reported in Fig. 2.13.

As anticipated, the ‘Hybrid’-processed image consistently yields a higher quality spectrum than the thresholded image across all λ values and for each R_s . The smallest difference occurs at intermediate λ values, where neither the photon counting algorithm nor the deconvolution algorithm are particularly effective. Additionally, the quality of the reconstruction improves for smaller R_s and larger λ , reaching an asymptote as $\lambda \rightarrow \infty$. This behaviour is expected, as a larger number of photons on the camera reduces the Poissonian error and the relative strength of noise, while a smaller R_s facilitates the deconvolution process and the identification of the thresholding value, better separating the 0th and 1st peak in the histogram of photon counts.

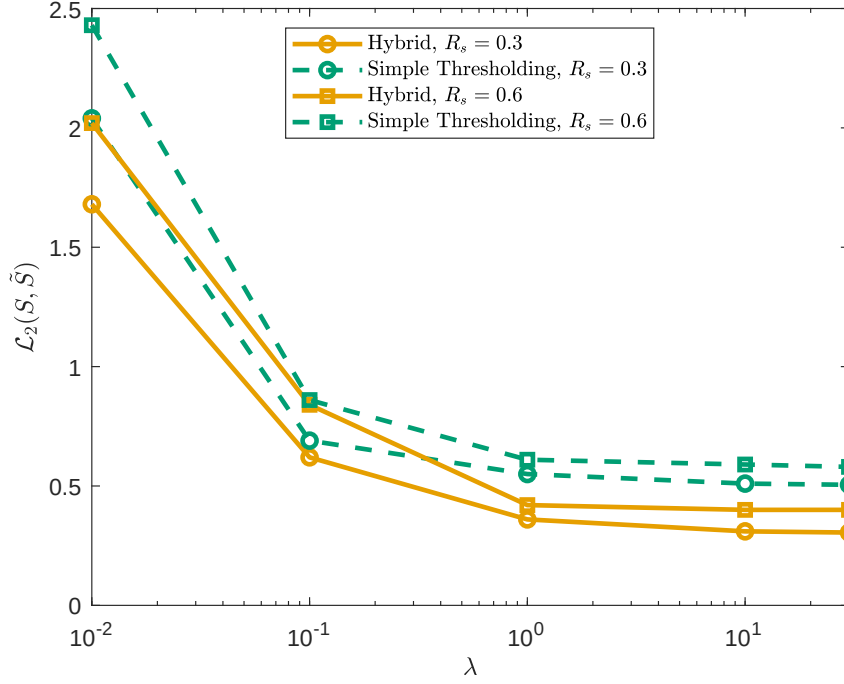


Figure 2.13: $\mathcal{L}_2$ distance between the original spectrum and the one reconstructed from the processed and thresholded image as a function of the filling fraction, for two values of R_s . Note that the asymptote value is not zero, as discrepancies from charge spreading and finite pixel size persist in the limit $\lambda \rightarrow \infty$.

2.6.2 Experimental Data

This section shows the application of this analysis approach to a real camera image and the resulting improvements in the spectrum obtained. Figure 2.14 reports the MgF_2 emission spectrum computed either with simple thresholding or with the image processing described in Section 2.4. The parameters used in these operations (ADU_{sp} , σ_N , λ) were determined by fitting a synthetic histogram to the experimental one (see Fig. 2.7e). To generate the synthetic histogram, I used an estimated spectrum computed by integrating the camera signal over the energy contours defined by the energy map, and the parameters of the PIXIS-XF camera (the detector employed for this experiment), which were provided in the relevant documentation [204]. Using this documentation, the fitting process obtained $R_s = 1.7$ in pixel unit, $ADU_{sp} = 43$ ADU and $\sigma_N = 4$ ADU, which were applied in the processing of the experimental images. For the thresholding, the values specified in Section 2.4.1 were used. The error bars for the two spectra were computed using Poissonian inference, and neglecting noise-related errors, drastically reduced by thresholding and integration over

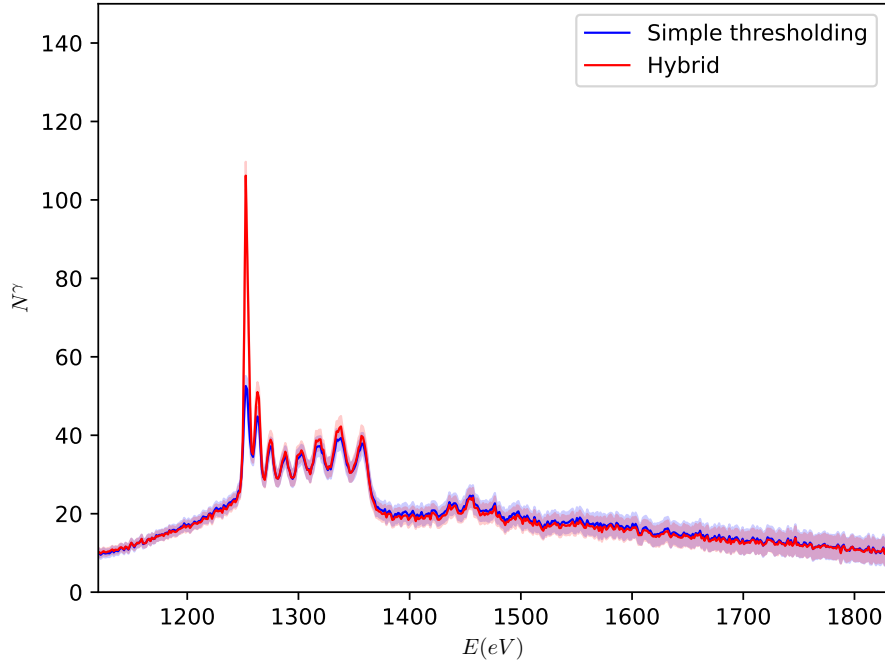


Figure 2.14: Emission spectrum of MgF_2 obtained with simple thresholding (red), and processing the images with the photon counting and deconvolution methods (blue). Error bounds are indicated by shaded regions. The peaks in the spectrum correspond to the $K\alpha$ (from 1250 to 1370 eV) and $K\beta$ (from 1430 to 1500 eV) emission lines of the different ionisation states of the Mg ions.

the energy contours. Details of these error calculations are provided in the next section.

The enhancement of features is particularly noticeable for the narrowest and most intense ones, such as the low-energy peaks around 1260 eV. I believe that such improvements are mainly due to the reduction of the background noise, and they could therefore be essential when the physical information of the probed system is contained in weaker features (e.g. Raman scattering peaks). Moreover, the enhanced resolution achieved through the deconvolution algorithm for the narrowest and most intense peaks has significant implications for HED science, where line ratios and widths play a critical role. In this example, line ratios are essential for determining relative ion populations and, consequently, plasma temperature [205]. Temperature is also commonly inferred using x-ray Thomson scattering via detailed balance, where precise line ratio measurements are equally crucial [206]. On the other hand, accurate estimation of line widths can be important for determining internal electromagnetic field intensities and collision dynamic through Zeeman, Stark and collisional broadening [207–210]. For the photon counting algorithm to be effective, it must

be applied to single-shot images rather than averaged ones, where single photon clusters are reduced by summation. This requirement, combined with the typical size of a camera image (here 2048x2048 pixels), makes the process time-consuming for real-time analysis. However, this procedure can be performed during post-analysis, where time constraints are less demanding. The current implementation takes approximately 8 minutes to process a single 2048×2048 image, which remains quite slow even for post-analysis. Improving the efficiency of these algorithms would greatly enhance their practical usability. Additionally, the computation can be parallelised by distributing different regions of the image across multiple processors, significantly reducing processing time.

Error calculations

To compute the uncertainties on the experimental spectra, one begins by calculating the best estimate of the parameter I (also the mean) of a Poisson distribution, given an observation n :

$$N \sim \text{Poisson}(I) \Rightarrow \mathcal{P}(N = n|I) = \frac{I^n e^{-I}}{n!}. \quad (2.45)$$

Assuming a flat prior distribution for I over a large interval $[0, M]$ (since I cannot be infinitely large), and noting that $\mathcal{P}(n) = \int_0^M \mathcal{P}(n|I) \mathcal{P}(I) = \int_0^M dI \frac{I^n e^{-I}}{n!} \frac{1}{M} \approx \frac{1}{M}$ if M is sufficiently large, from Bayes' theorem one finds:

$$\mathcal{P}(I|n) = \frac{\mathcal{P}(n|I) \mathcal{P}(I)}{\mathcal{P}(n)} = \mathcal{P}(n|I) . \quad (2.46)$$

From this equation, one can calculate the best estimate for I as:

$$\langle I \rangle(n) = \int_0^M dI I \mathcal{P}(I|n) = \int_0^M dI I \frac{I^n e^{-I}}{n!} \approx n + 1 . \quad (2.47)$$

Similarly, the error on this estimate is determined as the standard deviation of $\mathcal{P}(I|n)$:

$$\sqrt{\langle I^2 \rangle(n) - \langle I \rangle(n)^2} \approx \sqrt{n + 1} . \quad (2.48)$$

To analyse our case, $\tilde{I}(E_l) = \sum_{ij|E_{ij} \in \Delta E_l} N_{ij}^\gamma$ is considered as a realisation of the random variable $I(E_l) \sim \text{Poisson}(\Omega(E_l)S(E_l))$. Here, the contribution to $I(E_l)$ from noise, which

is generally small due to the thresholding operations and the summation over many pixels, is disregarded. Additionally, the error propagation through processing steps is not considered, taking instead directly N_{ij}^γ as the estimate of the photon hits map. Under these assumptions, the spectrum and its error, for each energy bin, are given by:

$$\langle S(E_l) \rangle = \frac{\tilde{I}(E_l) + 1}{\Omega(E_l)} \quad \sigma(S(E_l)) = \frac{\sqrt{\tilde{I}(E_l) + 1}}{\Omega(E_l)} . \quad (2.49)$$

As a final consideration, it is observed that the error normalised to the signal, $\frac{\sigma(S(E_l))}{\langle S(E_l) \rangle} = \frac{1}{\sqrt{\tilde{I}(E_l) + 1}}$, correctly decreases as the number of photons per bin increases.

2.7 Summary

This chapter provided a detailed guide for constructing spectra from the relative camera images, for two of the most common geometries employed in HED science spectroscopy. Specifically, I examined the computation of the energy map and the solid angle correction for the pixel array, the estimation of important camera parameters such as the thermal noise intensity, and presented techniques to estimate the distribution of photon hits from the raw camera data, with the aim of increasing the SNR. These image processing techniques are based on the sequential combination of clustering algorithms and deconvolution methods for simultaneously treating regions with different local fill fractions. Application of these methods to both synthetic and experimental data demonstrated notable improvements in SNR and feature clarity, proving their potential in contexts where the measured physical features are weak and the precise determination of line widths and intensities is crucial. Future work could explore introducing in this framework the capacity of multiple photons-cluster identification, or expanding the variety of allowed cluster shapes. Additionally, it would be useful to integrate this work with studies on the instrument function to combine the improvement of SNR with resolution enhancement. The experimental data presented in this thesis were collected using detectors and setups where pixel broadening is negligible compared to IF broadening. As a result, deconvolution techniques were not applied to process the experimental images. Photon counting algorithms were instead applied to the camera images from the flat crystal spectrometer. However, for the von Hámos data,

photon counting was not necessary due to the high fill fraction in the region of interest. The analysis of the von Hámos data, which constitutes the primary focus of this work, relies solely on simple thresholding.

Chapter 3: Extraction of Electronic Structures from RIXS Measurements

Understanding the electronic structure of a material is essential for predicting its physical and chemical properties, such as conductivity and reactivity, and in particular its interactions with electromagnetic radiation. In this context, as shown in this chapter, the electronic structure of a material is embedded in the cross-section of x-ray photons resonantly scattered by that material. Resonant inelastic x-ray scattering (RIXS) spectra, therefore, encode a wealth of information about the material’s density of states, albeit in a complex way. Extracting the electronic structures from RIXS measurements, which is connected to the inversion of a function operator, is feasible but at the same time challenging and, more importantly, unstable due to factors like experimental noise. This chapter presents a method that combines neural networks (NNs) and physics modelling, devised to perform this extraction. Additionally, this approach is capable of deconvolving the source spectra (and potentially the spectrometer’s instrument function), thereby removing the major broadening effects and providing high-resolution measurements of the DOS. The method described here is generalisable to other physical processes, provided they satisfy certain conditions, which are discussed in detail. Since the RIXS cross-section also depends on thermodynamic parameters - particularly the sample temperature T - it is possible to also extract T from RIXS spectra, provided the sample’s DOS is already known (e.g. through DFT calculations). The accuracy of the temperature estimate relies on various experimental parameters and material characteristics, including its electronic structure.

This chapter begins by describing the general theory of RIXS, focusing on the approximations relevant to our scientific cases and deriving the theoretical expressions used throughout this thesis to model our experiments. For completeness and to enable instruc-

tive comparisons, I then review alternative techniques for measuring electronic structures, including XAS (divided into EXAFS and XANES), XES, and x-ray Raman scattering (XRS), highlighting their respective advantages and disadvantages in relation to RIXS. The second part of this chapter provides an overview of the most common machine learning (ML) methods applied within physics, followed by a description of my approach for the extraction of physical quantities embedded in experimental measurements, with an emphasis on its capabilities and limitations. This method is then tailored to the RIXS case and validated on synthetic data. Application of the method to experimental data will be discussed in the final two chapters.

3.1 RIXS Theory

Resonant inelastic x-ray scattering is an experimental technique in which one scatters x-ray photons inelastically off matter (*photon-in/photon-out* type of spectroscopy). During this process, the photons exchange energy, momentum, and polarisation with the probed physical system. By measuring how these quantities change upon scattering, one can extract information from the analysed matter (e.g. electronic energy levels). RIXS is a resonant technique in which the energy of the incident photons is chosen such that it coincides with, and hence resonates with, one of the atomic transitions of the sample. The resonance greatly enhance the inelastic scattering cross-section and therefore simplify the spectroscopic analysis of the system. Here, I start from a general treatment of RIXS and then specify the results to the specific cases of interest.

The RIXS cross-section can be derived from standard quantum mechanics perturbation theory. The Hamiltonian of the full system (matter + radiation) is given by [211]:

$$H = H_0 + H_{int} \tag{3.1}$$

$$H_{int} = \frac{e}{mc} \sum_j \mathbf{p}_j \cdot \mathbf{A}(\mathbf{r}_j) + \frac{e^2}{2mc^2} \sum_j |\mathbf{A}(\mathbf{r}_j)|^2 = O(A) + O(A^2) , \tag{3.2}$$

where the index j refers to the electrons of the sample, H_0 is the Hamiltonian of the full system neglecting the matter-radiation interactions, and $\mathbf{A}$ is the quantised electromagnetic

vector potential [211]. In order to compute the differential cross-section of the scattered photons, one needs to calculate the following matrix element [212]:

$$\langle i, \lambda_1 | H_{int} | f, \lambda_2 \rangle, \quad (3.3)$$

where i and f are the initial and final state of the probed system, and λ_1 and λ_2 are the initial and final state of the photon. The state λ includes the photon wavevector $\mathbf{k}$ (with associated energy $\hbar\omega = c|\mathbf{k}|$) and the polarisation vector ϵ . This matrix element is associated with the scattering process ($i + \lambda_1 \rightarrow f + \lambda_2$) and can be computed with perturbation theory. The perturbation expansion is carried out in terms of A and must be brought up to order $O(A^2)$ to retrieve the RIXS process¹. To do that, one must use quantum perturbation theory (or alternatively the Dyson series) to the first order for the $O(A^2)$ term in H_{int} and up to second order for the $O(A)$ term. The first order of the $O(A)$ term describes the absorption/emission of a photon and therefore gives no contribution to the scattering process.

After performing the expansion, the total double differential cross-section of the scattering process is found to be (see [213] for a step-by-step derivation):

$$\begin{aligned} \frac{d^2\sigma}{d\Omega_{\mathbf{k}_2} d\omega_2} = & \hbar \frac{\omega_2}{\omega_1} \left(\frac{e^2}{mc^2} \right) \sum_f \delta(E_f - E_i + \hbar\omega_2 - \hbar\omega_1) \times \\ & \left| \langle f | \rho_{\mathbf{k}_1 - \mathbf{k}_2} | i \rangle (\epsilon_1 \cdot \epsilon_2) + \right. \\ & \frac{1}{m} \sum_n \left(\frac{\langle f | \mathbf{p}(\mathbf{k}_2) \cdot \epsilon_2 | n \rangle \langle n | \mathbf{p}(-\mathbf{k}_1) \cdot \epsilon_1 | i \rangle}{E_n - E_i - \hbar\omega_1} + \right. \\ & \left. \left. \frac{\langle f | \mathbf{p}(\mathbf{k}_1) \cdot \epsilon_1 | n \rangle \langle n | \mathbf{p}(-\mathbf{k}_2) \cdot \epsilon_2 | i \rangle}{E_n - E_i + \hbar\omega_2} \right) \right|^2, \end{aligned} \quad (3.4)$$

where $|i\rangle$, $|n\rangle$, and $|f\rangle$ indicate the initial, intermediate, and final electronic states of the probed system, with respective energies E_i , E_n and E_f . The indexes ‘1’ and ‘2’ refer respectively to the incoming and outgoing photon (e.g. $d\Omega_{\mathbf{k}_2}$ is the differential solid angle around the direction of the scattered photon). Here, the following notation was used:

¹Actually, the expansion is done in an adimensional parameter of the form (κA) , with $[\kappa] = [A]^{-1}$ [213]. This parameter is small for the typical photon energies and electrons momenta occurring in our systems.

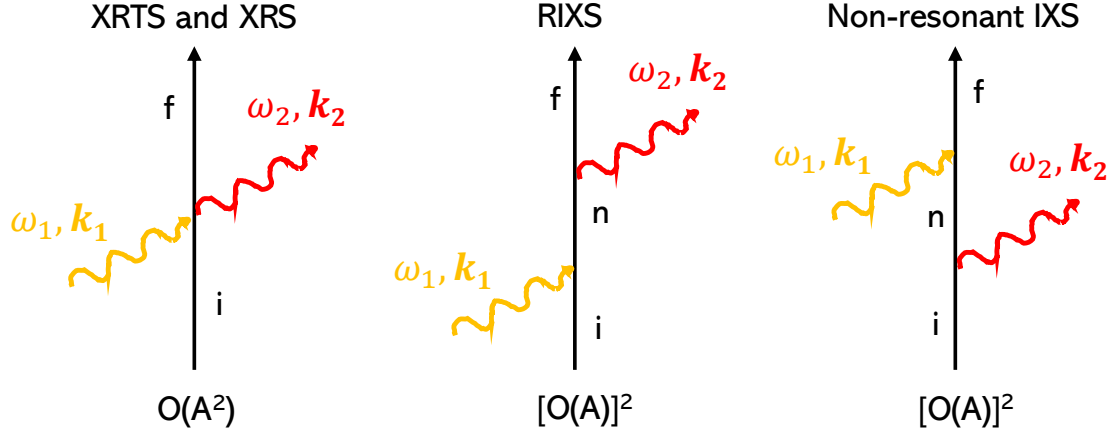


Figure 3.1: Feynman diagrams of (XRTS+XRS), RIXS, and non-resonant IXS processes. In RIXS the initial state i pass through the intermediate state n by absorbing a photon and then end up in the final state f by emitting a photon. The subprocesses of emission and absorption are not individually energy-conserving, making the intermediate state a virtual state.

$$\rho_{\mathbf{k}} = \sum_j \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \quad \mathbf{p}(\mathbf{k}) = \sum_j \mathbf{p}_j \exp(-i\mathbf{k} \cdot \mathbf{r}_j) . \quad (3.5)$$

These two operators are often used in their multipole approximations [117], expanding the exponentials in power series. This approximation is valid as long as the photon wavelength is much larger than the spatial extension of the electron wavefunctions (of order a_B/Z for bound electrons, with a_B the Bohr radius), which is usually the case. Eq. (3.4) is also known as the Kramers-Heisenberg dispersion formula, named after the two physicists who first derived it. The summation $\sum_n(\dots)$ is the second order contribution of the $O(A)$ term in H_{int} , and it describes the absorption of a photon followed by the emission of another photon (first addend), and the reverse process (second addend). These two terms represent, respectively, RIXS and a non-resonant inelastic x-ray scattering (IXS) processes, once the incoming photon energy is properly tuned. The other term inside the modulus is instead the first order contribution of the $O(A^2)$ piece of H_{int} and it describes both x-ray Thomson scattering [214] and XRS, depending on the specific excitations probed (e.g. bound-bound transitions). In terms of Feynman diagrams, these three types of scattering are illustrated in Fig. 3.1.

In RIXS analysis, the incident photon energy is taken close to an electron excitation threshold, so that the first term in the sum over n becomes dominant as the denominator vanishes. If the lifetime of the intermediate state is considered, the energy of the state is modified $E_n \rightarrow E_n + i\Gamma_{nf}$, with Γ_{nf} inversely proportional to the lifetime, and the divergence is removed. The RIXS double differential cross-section is then given by:

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}_2}d\omega_2} = \hbar \frac{\omega_2}{\omega_1} \left(\frac{e}{mc} \right)^4 \sum_f \delta(E_f - E_i + \hbar\omega_2 - \hbar\omega_1) \times \left| \sum_n \frac{\langle f | \mathbf{p}(\mathbf{k}_2) \cdot \boldsymbol{\epsilon}_2 | n \rangle \langle n | \mathbf{p}(-\mathbf{k}_1) \cdot \boldsymbol{\epsilon}_1 | i \rangle}{E_n + i\Gamma_{nf} - E_i - \hbar\omega_1} \right|^2. \quad (3.6)$$

While the δ function ensures the energy conservation of the whole scattering process, the sum over n describes the absorption of a photon $(\mathbf{k}_1, \boldsymbol{\epsilon}_1)$, causing the system to transition from $|i\rangle$ to a generic intermediate state $|n\rangle$, followed by the emission of a photon $(\mathbf{k}_2, \boldsymbol{\epsilon}_2)$, relaxing the system to the state $|f\rangle$. The transition matrix elements inside the sum give the probability for these two subprocesses, which are then summed over all the possible intermediate states. Note also that, even though these subprocesses are not required to conserve energy, the denominator penalises the non-energy conservation.

In this thesis, RIXS technique is applied to the study of pure Fe, iron oxides (FeO and Fe₂O₃) and gadolinium (Gd) under extreme thermodynamic conditions. The discussion now focuses on iron and iron oxides, with modifications for the gadolinium case discussed directly in Chapter 4. For RIXS to occur, as mentioned earlier, the incident photon energy must be set close to an absorption edge. For the experiments with iron compounds, this energy was tuned just below the Fe K-edge ($|\epsilon_K| = 7112$ eV). Working below the edge allows one also to suppress direct absorption and the consequent radiative recombinations (e.g. K_α decay), leaving RIXS as the predominant process². Under these circumstances, there are two dominant RIXS channels for these systems, which are schematically depicted in Fig. 3.2.

In the left-hand diagram, the initial state, which is assumed to be thermalised (i.e. the

²If the incident photon energy is larger than $|\epsilon_K|$, that is the energy necessary to ionise a K-shell electron, the K-shell ($1s$ states) would be filled with holes, which would then be eliminated mainly by electrons decaying from $2p$ states via radiative recombination. Since these two processes combined have a larger cross-section than RIXS, one could risk weakening the RIXS signal.

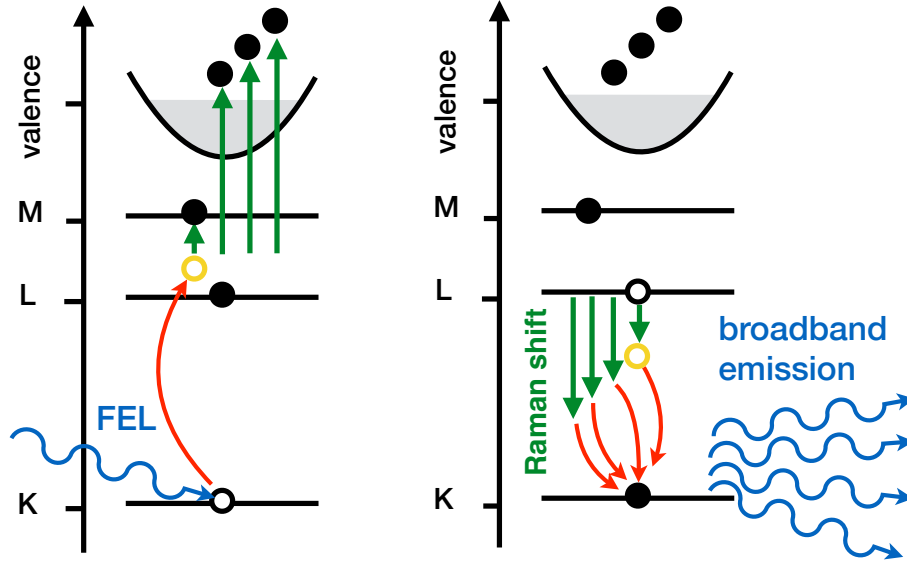


Figure 3.2: Scheme of the RIXS process in iron compounds. This is composed of an energy non-conserving absorption, which excites a K-shell electron (left), followed by an energy non-conserving emission produced by the decay of a L-shell electron into the K-shell core hole (right). The overall process conserves energy. The accessible states are the vacant states in the valence bands (first channel) or, for finite temperature systems, the thermally ionised states in the M-shell (second channel).

electrons' population follows a Fermi-Dirac distribution), absorbs a photon that excites, without conserving the energy, an electron from the K-shell ($1s$ states) into either a valence state (first channel) or an M-shell one (second channel). Then the hole in the K-shell is filled by an electron of the L-shell ($2p_{1/2}$, $2p_{3/2}$ states), as it is shown in the right-hand diagram. In order to conserve the energy over the whole process, the emitted photon has a lower energy than the K-L resonances (6392 and 6405 eV for iron compounds). Thus, in our case, the intermediate state n is the initial state with a hole in the K-shell and an electron in an unoccupied valence or M-shell state, whereas the two possible final states f are the initial state with an electron in the continuum or in the M-shell and a hole in one of the two L-states. Since one does not discern the final state of the system during the measurement, the total RIXS differential cross-section for these materials is given by Eq. (3.6), with a sum over all the possible final states $f = 1, 2$. To activate the M-shell channel, the temperature of the system must be sufficiently high to have vacancies in the bound M-shell ($3p_{1/2}$, $3p_{3/2}$ states). This latter characteristic, as demonstrated shortly, can be exploited to estimate the temperature of the system.

A simpler form of Eq. (3.6), specific to our cases of interest, will now be considered.

The aim is to show that the electronic structure of a material can be efficiently extracted from its RIXS spectra. However, one is ultimately limited on the resolution of the extracted DOS by the instrument function of the setup, which is a few eV wide in our cases. One can therefore neglect the interactions between the core-hole potential and the electrons in the continuum (the intermediate state has a hole in the K-shell), as they introduce an uncertainty in the energy of the intermediate state given by the inverse of the core-hole lifetime [106], equivalent to a few eV in Fe [215]. These interactions are therefore responsible for modulations in the RIXS cross-section on an energy scale constrained by this lifetime³. Starting from these considerations, Eq. (3.6) is simplified through the following approximations and substitutions [156]:

- Neglecting the core-hole potential, the transition matrix element of the K_α decay becomes independent of the intermediate state n , which has an additional electron in a continuum state, and therefore

$$|\langle f | \mathbf{p}(\mathbf{k}_2) \cdot \boldsymbol{\epsilon}_2 | n \rangle|^2 = A_f, \quad (3.7)$$

where A_f is the K_α line intensity. Note that in this approximation the emission is assumed to be isotropic;

- For analogous reasons, the lifetime of the intermediate state can be approximated to be dependent only on the final state f and given by the core hole lifetime, Γ_f

$$\Gamma_{nf} \rightarrow \Gamma_f ; \quad (3.8)$$

- One can substitute the summation over the intermediate states $|n\rangle$ with an integration over the accessible (via Pauli's principle) density of states $\rho(E_n)$

$$\sum_n \rightarrow \int_{\mathbb{R}} dE_n \rho(E_n) [1 - f_{FD}(E_n; T)] ; \quad (3.9)$$

³Potential future studies with higher resolution would require DFT calculations that incorporate a K-shell hole in the pseudopotential of the intermediate state.

- Assuming the absorption to be isotropic as well, and considering that the initial state of the electron is fixed (1s state), the absorption matrix element can be rewritten as

$$\langle n | \mathbf{p}(-\mathbf{k}_1) \cdot \boldsymbol{\epsilon}_1 | i \rangle := M(E_n) ; \quad (3.10)$$

- The energy difference between the initial and final states corresponds to the disparity between the energy of the ionised electron, $\epsilon_{\mathbf{k}}$, and the binding energy of the L-shell electron $\epsilon_{L,f}$, that undergoes decay to occupy the core hole

$$E_f - E_i = \epsilon_{\mathbf{k}} - \epsilon_{L,f} ; \quad (3.11)$$

- Likewise, for the intermediate state, the energy difference corresponds to the disparity between the energy of the ionised electron and the binding energy of the core hole state, ϵ_K

$$E_n - E_i = \epsilon_{\mathbf{k}} - \epsilon_K . \quad (3.12)$$

Applying these substitutions to Eq. (3.6) and identifying E_n with $\epsilon_{\mathbf{k}}$ (one-to-one correspondence), one obtains⁴:

$$\begin{aligned} \frac{d^2\sigma}{d\Omega_{\mathbf{k}_2} d\omega_2} = & \hbar \frac{\omega_2}{\omega_1} \left(\frac{e}{mc} \right)^4 \sum_f \int_0^\infty d\epsilon_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_{L,f} + \hbar\omega_2 - \hbar\omega_1) \\ & \times [1 - f_{FD}(\epsilon_{\mathbf{k}}; T)] \rho(\epsilon_{\mathbf{k}}) \left| \frac{\sqrt{A_f} M(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}} - \epsilon_K - \hbar\omega_1 + i\Gamma_f} \right|^2 . \end{aligned} \quad (3.13)$$

Finally, evaluating the integral and squaring the denominator, one finds:

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}_2} d\omega_2} = \hbar \frac{\omega_2}{\omega_1} \left(\frac{e}{mc} \right)^4 \sum_f \frac{[1 - f_{FD}(\epsilon; T)] \rho(\epsilon) A_f |M(\epsilon)|^2}{[\hbar\omega_2 - (\epsilon_{L,f} - \epsilon_K)]^2 + \Gamma_f^2} , \quad (3.14)$$

where $\epsilon = \hbar\omega_1 - \hbar\omega_2 + \epsilon_{L,f}$. Under these approximations, the RIXS cross-section as a function of ω_2 (RIXS spectrum) is approximately described as an absorption cross-section $[\propto \rho(\epsilon(\omega_2)) |M(\epsilon(\omega_2))|^2]$ modulated by a Lorentzian centred in the K-L resonance $(\epsilon_{L,f} - \epsilon_K)$ with a width given by Γ_f . The quantity $\rho |M|^2$ represents the density of states accessible

⁴One can bring the squared modulus inside the integral thanks to the δ function properties.

from a 1s core state, and it is the part of the electronic structure, with the addition of a thermal modulation given by $(1 - f_{FD})$, that RIXS is capable to investigate. This experimentally accessible quantity is denoted as the effective density of states, ρ_{eff} , given by:

$$\rho_{\text{eff}}(\epsilon) = [1 - f_{FD}(\epsilon; T)]\rho(\epsilon)|M(\epsilon)|^2 . \quad (3.15)$$

Note that if either T or $\rho|M|^2$ is known from other measurements or calculations, the other quantity can be estimated. For instance, when T is already known, along with the matrix transition elements M , the actual density of states of the system can be determined. Since atomistic transition rules are still partially obeyed in solid systems [216], certain states of the DOS (e.g. 4s in this case) are suppressed in the density of accessible states (DAS).

Equation (3.14) demonstrates that, with just one single shot, the RIXS analysis provides an entire spectrum, which contains information on the electron temperature via the shape of the Fermi distribution and on the DAS via the scattering intensity⁵. As discussed in the next section, this property of RIXS is a huge advantage with respect to the absorption/emission spectroscopy, where instead several shots with different XFEL photon energies across the edge are needed to reconstruct a spectrum. The wealth of information provided by RIXS in just a single shot, together with the short duration of XFEL pulse, makes this technique particularly well suited for time-resolved studies.

Integrating Eq. (3.14) over the solid angle detected for each outgoing energy $\Omega(\omega_2)$ and over energy bins of width ΔE given by the pixel size (see also Chapter 2), the intensity of scattered radiation measured by the detector at discrete energies $\hbar\omega_{2,i} = E_i$ is obtained:

$$I(E_i) = \int_{E_i - \Delta E/2}^{E_i + \Delta E/2} \Omega(\omega_2) \overbrace{\frac{d\sigma}{d\omega_2}}^{S_{\text{RIXS}}} d(\hbar\omega_2) . \quad (3.16)$$

Here $\Omega(\omega_2)$ is a known function, calculable from the geometry of the experimental setup (see Chapter 2). Until this point, a monochromatic radiation incoming on the target has been considered. In a real experiment, the incident XFEL radiation possesses a finite spectral width. In this case, Eq. (3.16) is modified as:

⁵In principle, relative binding energies between core shells—and thus the IPD—can also be investigated by examining global shifts in the RIXS spectrum.

$$I(E_i) = \int_{E_i - \Delta E/2}^{E_i + \Delta E/2} d(\hbar\omega_2) \int_{\mathbb{R}} d(\hbar\omega_1) \Omega(\omega_2) \Phi(\omega_1) S_{RIS}(\omega_1, \omega_2), \quad (3.17)$$

where $\Phi(\omega_1)$ is the XFEL spectrum. Recalling Eq. (3.14), one observes that this integral has the characteristic form of a convolution of the scattering cross-section with the incident FEL pulse. It is intuitive that this convolution lowers the resolution with which one is able to extract $\rho(\epsilon)$ from $I(E)$ since different ϵ contribute to the same $I(E_i)$. Performing this deconvolution is a challenging task due to the complexity of Eq. (3.14), combined with the typical stochastic and spiky profile of XFEL pulses [217]. The approach to the solution of this problem is described in Section 3.3.2. To rigorously compare $I(E_i)$ with the experimental measurements, it ought to be convolved with the instrument function of the experimental setup.

It is finally worth noticing that in all the previous equations, the absorption in the target was not considered. This assumption is justified as long as the absorption does not change significantly with ω_1 belonging to the probe bandwidth⁶. In this case, there is just a multiplicative constant in front of the integral 3.17, which does not affect the results, as will be discussed later on.

3.2 Alternative spectroscopic techniques

In absorption spectroscopy, the transmitted radiation intensity I through a material is measured and compared to the incident intensity I_0 . These two intensities are related by the Beer-Lambert law:

$$I(\omega_1) = I_0(\omega_1) \exp\{-nz\sigma(\omega_1)\}, \quad (3.18)$$

where n is the number density of particles that absorb and scatter light, z is the sample thickness, ω_1 is the frequency of the photon source (assumed to be monochromatic here) and σ is the total cross-section encompassing all scattering and absorption processes. Measuring the transmission function $\ln(I/I_0)(\omega_1)$ thus provides a measurement of $\sigma(\omega_1)$. By scanning the incoming photon energy $\hbar\omega_1$ across an absorption edge—a necessary condition

⁶This assumption holds true in our cases, where $\Phi(\omega_1)$ lies entirely below the absorption edge.

to probe the electronic structure near the chemical potential—the photons cross-section becomes dominated by absorption ($\sigma(\omega_1) \approx \sigma_{\text{abs}}(\omega_1)$). The x-ray absorption cross-section can also be calculated theoretically using methods similar to those for RIXS, as given in [218]:

$$\sigma_{\text{abs}}(\omega_1) = \frac{C}{\omega_1} \int_{\mathbb{R}} dE_f \delta(E_f - E_i - \hbar\omega_1) [1 - f_{FD}(E_f)] \rho(E_f) |\langle f | \mathbf{p}(-\mathbf{k}_1) \cdot \boldsymbol{\epsilon}_1 | i \rangle|^2, \quad (3.19)$$

where C is a physical constant. This cross-section, for an incident spectrum $\phi(\omega_1)$ with a finite bandwidth, becomes:

$$\begin{aligned} \sigma_{\text{abs}} &= \frac{C}{\bar{\omega}_1} \int_{\mathbb{R}} \int_{\mathbb{R}} d(\hbar\omega_1) dE_f \delta(E_f - E_i - \hbar\omega_1) [1 - f_{FD}(E_f)] \rho(E_f) |\langle f | \mathbf{p}(-\mathbf{k}_1) \cdot \boldsymbol{\epsilon}_1 | i \rangle|^2 \Phi(\omega_1) \\ &= \frac{C}{\bar{\omega}_1} \int_{\mathbb{R}} d(\hbar\omega_1) [1 - f_{FD}(E_i + \hbar\omega_1)] \rho(E_i + \hbar\omega_1) |M(E_i + \hbar\omega_1)|^2 \Phi(\omega_1) \\ &= \frac{C}{\bar{\omega}_1} \int_{\mathbb{R}} d(\hbar\omega_1) \rho_{\text{eff}}(E_i + \hbar\omega_1) \Phi(\omega_1) \approx \frac{C}{\bar{\omega}_1} \int_{\bar{\omega}_1 - \Delta B/2}^{\bar{\omega}_1 + \Delta B/2} d(\hbar\omega_1) \rho_{\text{eff}}(E_i + \hbar\omega_1) \Phi(\omega_1), \end{aligned} \quad (3.20)$$

where $\bar{\omega}_1$ is the central incoming photon frequency, pulled out from the integral by assuming a sufficiently narrow source bandwidth ΔB (as is typical in the analysed cases). Here, the notation introduced in the previous section was used. This equation shows that to obtain a spectrum with a form resembling that of Eq. (3.17), which allows for the extraction of ρ_{eff} through deconvolution as with RIXS, multiple measurements are needed. Specifically, one has to shift the source spectrum Φ and compute σ_{abs} for varying central energies $\hbar\bar{\omega}_1$.

This requirement poses significant challenges in warm dense matter experiments, where thermodynamic conditions achieved through laser heating are difficult to stabilise and may vary widely between shots. Consequently, there is a risk of assembling a spectrum from data obtained under varying conditions, compromising its reliability. Additionally, absorption spectroscopy requires crossing an edge. This not only introduces variability in thermodynamic conditions—as crossing the edge notably increases sample heating—but also causes fluctuations in signal intensity across shots, potentially leading to technical issues like detector saturation. In contrast, RIXS avoids these challenges by capturing

an entire spectrum in a single shot while working below the absorption edge. However, because the cross-section for RIXS is smaller than for absorption, more shots are required to achieve the same SNR, which can reintroduce the issue of shot-to-shot variability, as seen for XAS. Nonetheless, rapid advancements in laser facility performance—especially in intensity and pulse control—are expected to mitigate these downsides of RIXS.

The expression for σ_{abs} in the previous equation applies specifically to absorption in the states closest to the chemical potential, which are probed by what is known as x-ray absorption near edge structure (XANES). The structure of these states is highly sensitive to the local environment surrounding the atoms, allowing small variations in properties like coordination number and interatomic distance to be detected using XANES [219]. As the incoming photon energy increases, the kinetic energy of photoejected electrons rises, reducing their de Broglie wavelengths k_w until they approach the scale of interatomic distances. At this point, the final state of the ejected electron $|f\rangle$ is altered by the interference of its wavefunction with the neighbouring atoms. This effect becomes relevant at about 40 eV above the edge. Above these energies, this interference modifies the absorption cross-section, introducing a modulation factor [219]:

$$\chi(k_w) = \sum_j \frac{N_j e^{-2k_w^2 \zeta_j^2} e^{-2R_j/\lambda(k_w)} f_j(k_w)}{R_j^2 k_w} \sin(2k_w R_j + \delta_j(k_w)) , \quad (3.21)$$

where j represents the individual coordination shell of N_j identical atoms at approximately the same distance R_j from the central atom, with scattering properties summarised by $f_j(k_w)$ and $\delta_j(k_w)$ [219]). Here, ζ_j^2 is the mean-square-displacement in the bond distance R_j due to disorder sources like thermal agitation, and $\lambda(k_w)$ is the mean-free-path of the ejected electron. This modulation factor, as mentioned earlier, is not valid for small k_w values, but it is necessary for σ_{abs} to describe absorption when sufficiently far above the edge. This type of spectroscopy is known as extended x-ray absorption fine structure (EXAFS). Because of the $\lambda(k_w)$ term and $1/R_j^2$ factor, the sum is limited only to the closest shells, making EXAFS a local probe of the material structure. In fact, since $f_j(k_w)$, $\delta_j(k_w)$ and $\lambda(k_w)$ are known, one can fit this theoretical model of EXAFS (essentially given by $\sigma_{EXAFS} = \sigma_{abs}\chi$) to the experimentally-measured absorption cross-section to determine values for N_j , R_j and ζ_j [219]. An example of an x-ray absorption spectrum for FeO is

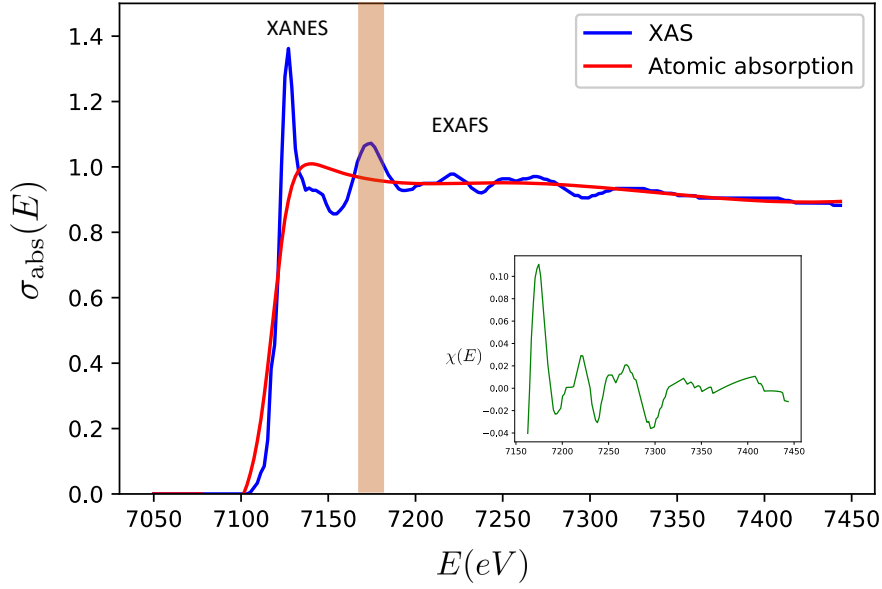


Figure 3.3: X-ray absorption spectrum for FeO around the K-edge (blue curve), shown after baseline subtraction and edge jump normalisation. By subtracting the atomic absorption spectrum (red line), the resulting modulation function $\chi(k_w(E))$ (shown in the inset) can be fitted to the theoretical model or Fourier transformed to extract the structural parameters of the material. The XAS spectrum is divided into two distinct regions (XANES and EXAFS), approximately separated 50 eV above the edge. Only the portion of the spectrum corresponding to the EXAFS regime is used to compute χ . Data is sourced from Ref. [219].

shown in Figure 3.3. In developing the RIXS expressions, these distortions of the excited electron's final state $|f\rangle$ have been neglected. As for the simpler absorption process, this assumption holds as long as the interpretation of the extracted ρ_{eff} is limited to energies within approximately 50 eV above the chemical potential.

In x-ray emission spectroscopy, core electrons of the probed system are excited by the incident photons, and then the photoemission, occurring during relaxation, is measured, revealing information about the system's energy levels [220]. However, the large line broadening in the emission from continuum states—primarily due to collisional broadening—has limited the use of XES for investigating these states with detailed resolutions. Instead, XES has been primarily applied to analyse bound-bound transitions, enabling measurements of phenomena such as ionisation potential depression and pressure ionisation [21, 123, 221]. One advantage of XES is that it probes the filled states rather than vacant ones, therefore providing complementary information to those extracted with RIXS and XAS.

Lastly, I highlight x-ray Raman scattering (XRS) as an additional method for probing

electronic structures [199]. This process is described by the first term in Eq. (3.4):

$$\sigma_{\text{XRS}}(\omega, \mathbf{k}) \propto \sum_f |\langle f | \rho_{\mathbf{k}} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) , \quad (3.22)$$

where $\mathbf{k} = \mathbf{k}_2 - \mathbf{k}_1$ and $\omega = \omega_2 - \omega_1$ were defined. This expression encompasses various inelastic scattering processes, which are distinguished differently by the type of transitions and the energy transfers involved. For instance, XRTS is described by the same formula but pertains to smaller energy transfers than XRS and involves also collective excitations [155].

The XRS process is always present and has the advantage of versatility, enabling the exploration of a wide range of energy and momentum transfers, and thus a variety of initial and final states. However, the XRS signal is extremely weak and, can often be obscured by other competing processes. By contrast, RIXS benefits from a larger cross-section due to resonance, making it more effective when the set of states under investigations can perform this type of resonant scattering.

3.3 Method for RIXS Analysis

Modern physics experiments increasingly depend on indirect or proxy measurements because direct access to quantities of interest is often limited. Instead, these experiments utilise known physical processes—dependent on the relevant quantities—to generate measurements that, in principle, allow for their extraction. However, these processes are frequently complex, making extraction a challenging inverse problem. The determination of ρ_{eff} from the RIXS spectrum, specifically through Eq. (3.17), is an example of such a problem. To address these challenges, a method based on neural networks designed to solve problems of this nature is now introduced. While addressing inverse problems with neural networks is not new, a variety of methods have evolved around it. Many of these methods involve fully inverting the forward process with end-to-end estimators [222], which, in experimental analysis, essentially means re-learning known physics. This approach can improve speed compared to traditional numerical models, albeit often at the expense of accuracy.

A recent alternative, focused on accuracy, is emerging in differentiable modelling. Extending parameter fitting via gradient descent and backpropagation [223], the use of neural

networks embedded within differentiable physical models—hereafter referred to as surrogate training embedded in physics (STEP)—has gained momentum in fields such as robotics and quantum chemistry. Similar approaches based on differentiable modelling are also seen in fluid dynamics, where neural networks have been used to refine or accelerate solvers of partial differential equations (PDEs) [224]. Additionally, physics-informed neural networks (PINNs) [225] achieve similar results through differentiable programming, although PINNs rely on physics modelling (PDEs in their case) as additional constraints to those posed by experimental observations [226], rather than directly backpropagating the experimental constraints through the physical model. Therefore, in PINNs physics modelling is used alongside experimental data in a parallel way, instead of a sequential way, as is the case with STEP. Likewise, most STEP applications in quantum chemistry use either extensive high-quality datasets [227], specialised estimators [227, 228], or both. A notable exception is the work by Kasim and Vinko [229], which demonstrates that the exchange-correlation functional can be accurately learned with comparatively small datasets, a finding also supported by Li *et al.* [228]. Kasim and Vinko further show that a simple feed-forward neural network (FFNN) with three hidden layers of 32 nodes each is sufficient for this purpose. The simplicity of this neural network architecture and its ability to work with limited data are both significant for physics research, where data scarcity and the need for tailored ML architectures often pose challenges for end-to-end models to reach high accuracy.

Here, I first present a formal description of the STEP paradigm for inverse problems, demonstrating that STEP generalises well, offers interpretability, and resists overfitting—as long as the forward model is accurately defined. Then this method is applied to extract ρ_{eff} from RIXS spectra solving the deconvolution described by Eq. (3.17).

3.3.1 The STEP Paradigm

Consider a known physical process P , which takes as input a set of N functions B_i with $i = 1, \dots, N$, and returns another function A , i.e. P is a functional which may be written as

$$A(x) = P[B_1, \dots, B_N](x). \quad (3.23)$$

Now consider the case where one wants to determine one specific function B_i given that one knows A , P , and B_j for any $j \neq i$. Mathematically, this entails finding an inverse functional P^{-1} w.r.t. B_i such that

$$B_i(y) = P^{-1}[A, B_1, \dots, B_{i-1}, B_{i+1}, \dots, B_N](y). \quad (3.24)$$

To construct this inverse map, one can employ an estimator $\tilde{P}^{-1}$ to approximate P^{-1} , which gives us an estimate for B_i as

$$\tilde{B}_i(y) = \tilde{P}^{-1}[A, B_1, \dots, B_{i-1}, B_{i+1}, \dots, B_N](y). \quad (3.25)$$

While this is a highly successful approach [230], particularly in image analysis [222], it also relies on the approximate inversion of the potentially highly complex process P . Therefore, non-trivial design choices are usually made regarding the estimator, as it has to invert a potentially highly complex process. Furthermore, this method does not necessarily generalise beyond the domain of the data it was trained on, making predictions outside the range of training values for A and B_i non-trustworthy. Finally, many distinct data pairs A and B_i are also required for an estimator to learn the general inverse P^{-1} , data which may not be readily available.

To address these issues, the STEP method offers an alternative approach that emphasises accuracy, though at the expenses of longer computational times. Instead of approximating the complex object P^{-1} , STEP directly estimates the much simpler function B_i as $\tilde{B}_i^{(STEP)}$, represented with a neural network. One then has

$$\tilde{A}(x) = P[B_1, \dots, \tilde{B}_i^{(STEP)}, \dots, B_N](x), \quad (3.26)$$

and may compute a loss $\mathcal{L}(A, \tilde{A})$ to measure the estimate's performance on the data. Provided that the process P is known, mathematically differentiable, and implemented using automatic differentiation, backpropagation and gradient descent can be applied to iteratively refine $\tilde{B}_i^{(STEP)}$ toward an accurate approximation of the true B_i . In the physical applications, P and B_i can be defined as known and unknown processes, respectively, isolating B_i as the physical quantity one aims to uncover. This distinction helps us focus

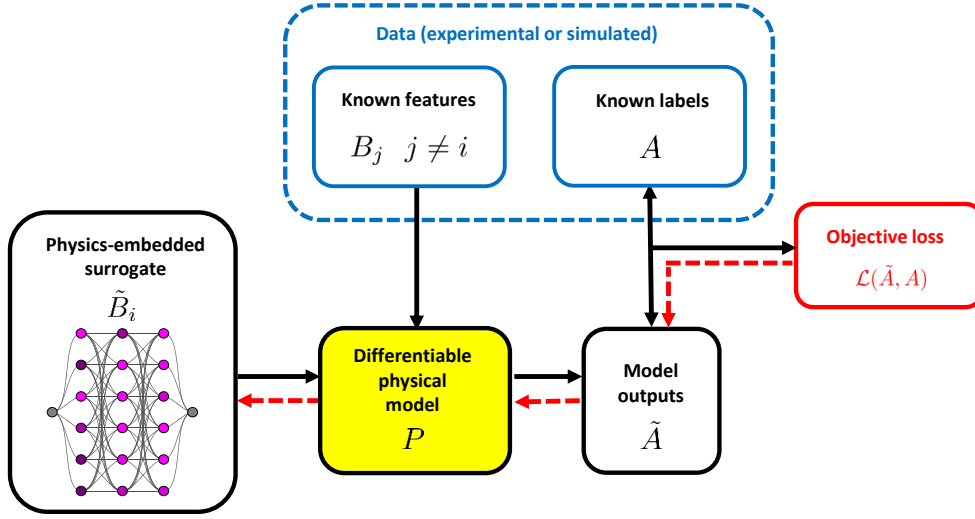


Figure 3.4: An illustration of a supervised learning scheme under the STEP paradigm. Note the existence of the differentiable physical model, which allows us to represent the unknown learnable physical object B_i as an estimator with much smaller architecture than the ones typically used for representing an inverse operator. Black arrows indicate forward passes, and red ones backpropagation.

on inferring unknown physical quantities rather than inverting well-understood processes P . Finally, STEP allows generalizing to arbitrary B_i with confidence, and ensures that $\tilde{B}_i^{(STEP)}$ always has an intuitive and meaningful interpretation as the exact estimate of B_i , two important features in physical ML.

Limitations

When using STEP, there are some important limitations to consider. The foremost requirement is the ability of the operator P to accurately model the underlying physical process, and to be implemented in an automatically differentiable way. However, for measurement processes in physics, the former is in fact the underlying assumption in measurement routines. For automatic differentiation of P , one may leverage the plethora of tools for differentiable physical programming [227, 231, 232] developed in the context of supervised learning. These tools, embedded in growing frameworks like PyTorch [233] and JAX [234], enable full differentiability in physical models by reducing intractable computational graphs and non-differentiable effects into feasibly differentiable forms using automatic differentiation (e.g. autograd [233]). In practice, such frameworks allow gradient descent and backpropagation to be performed within physical processes, making it possible to apply STEP.

However, care must be taken to manage issues like vanishing gradients in backpropagation (see below), which can affect optimisation.

Secondly, the use of STEP incurs a significant increase in computational time, as it relies on repeated fittings for every B_i , rather than the single evaluation of the approximate inverse map. This issue has become less significant with the continuing rise in available computing power, and importantly, it is most critical for real-time applications. Most physics experiments, however, record all data and rely primarily on post-experimental analysis, where accuracy supplants fitting time as the key performance metric. Additionally, the B_i of interest are often constant for a given set of experiments (as in RIXS), or even for all physics (as in the case of the exchange correlation functional [229]), and consequently, different datasets can be treated together to extract a single B_i .

3.3.2 STEP for the RIXS Process

The expression for the RIXS spectra given in Eqs. (3.14) and (3.17) takes the form of a sum of convolutions with a dynamic kernel $\Phi(\omega_1)$. The kernel is dynamic because it represents the XFEL pulse, which is commonly formed of a series of narrow spikes in photon energy that change stochastically from shot to shot. If a typical dataset is assumed to contain N RIXS single shots indexed by k , with associated RIXS spectra $I_k(\omega_2)$, then each is given by Eq. (3.17) using the corresponding XFEL spectra $\Phi_k(\omega_1)$. The following primarily focuses on XFELs operating in SASE mode to demonstrate how this method enables the extraction of electronic structures with resolutions surpassing the probe's bandwidth. However, this approach is general and can be applied to XFEL spectra of any shape, such as those obtained in seeded mode [73].

The relation that links the k measured spectra I_k to the effective density of states ρ_{eff} and the spectral FEL kernel Φ_k , given by Eqs. (3.14 and (3.17), can be formally written with the notation introduced in the previous section, defining an operator P_{RIXS} as:

$$I_k(\omega_2) = P_{\text{RIXS}}[\Phi_k, \rho_{\text{eff}}](\omega_2), \quad (3.27)$$

which is an example of the general problem 3.23. As already discussed, one possible solution

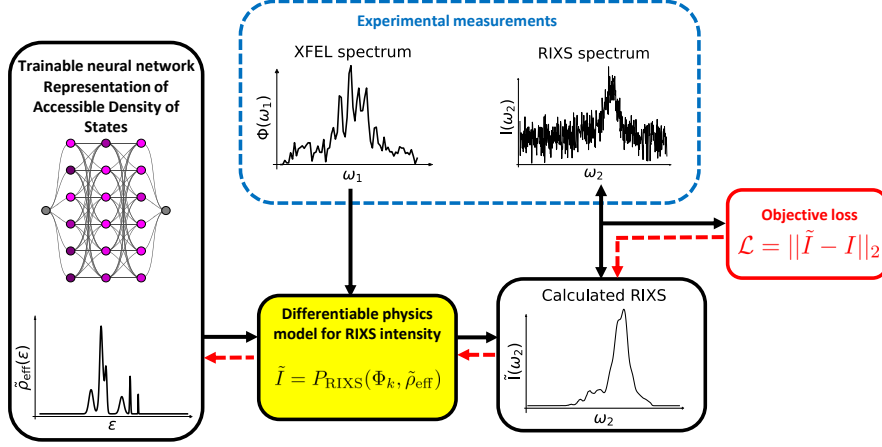


Figure 3.5: Representation of the scheme used to extract physical information on the electronic structure of a material from a SASE-based RIXS measurement. The estimate of ρ_{eff} , represented by a feedforward neural network, is fed to the RIXS differentiable model alongside the measured XFEL spectrum. The model outputs the calculated RIXS spectrum, which is then compared with the experimental spectrum. This comparison generates a loss function used to adjust the neural network parameters, thereby refining the ρ_{eff} estimate. The resolution of the resulting density of states depends on the resolutions of the spectrometers used to measure the RIXS signal and the profile of the XFEL pulse, but is independent of the XFEL pulse structure or bandwidth.

to find the effective DOS is by inverting the RIXS operator P_{RIXS} with respect to ρ_{eff} :

$$\rho_{\text{eff}}(\epsilon) = P_{\text{RIXS}}^{-1}[I_k, \Phi_k](\epsilon), \quad (3.28)$$

which is valid for each k .

However, since the RIXS cross-section is relatively small, so that single-shot measurements typically have low SNR, the use of standard inversion techniques via deconvolution, such as the Richardson-Lucy method, is unsuitable for single-shot analysis. Integrating over many shots ($I_k \rightarrow \bar{I}$ and $\Phi_k \rightarrow \bar{\Phi}$) can mitigate such limitations in SNR, but, as discussed shortly, it also limits the resolution with which one can extract ρ_{eff} . The lack of a robust approach to process low SNR data actually represents a considerable bottleneck for x-ray spectroscopy in high energy density physics applications [217]. Alternatively, one could use the ML method introduced in the previous section and represent P_{RIXS}^{-1} with a neural network. Nevertheless, given the stochastic nature of the FEL pulse profile and the complexity of the RIXS operator, the construction of a NN estimator to approximate P_{RIXS}^{-1} from a large labelled dataset of known pairings $(\rho_{\text{eff}}, I_k, \Phi_k)$, is not effective. This,

in fact, would require a highly complex estimator and the collection and validation of a sufficiently large dataset, which is not a straightforward task.

Therefore, rather than searching for a general estimator to approximate the highly complex object P_{RIXS}^{-1} , one can instead look for a suitable approximation $\tilde{\rho}_{\text{eff}}$ to the much simpler function ρ_{eff} , using the STEP method. A comparison of the performances, for the RIXS problem, between the STEP method and an end-to-end inversion estimator is presented in Ref. [235]. For the RIXS case, the scheme of the STEP method is illustrated in Fig. 3.5. The known forward model P_{RIXS} is used to calculate the predicted spectral intensity given a known Φ_k and the estimate $\tilde{\rho}_{\text{eff}}$:

$$\tilde{I}_k(\omega_2) = P_{\text{RIXS}}[\Phi_k, \tilde{\rho}_{\text{eff}}](\omega_2). \quad (3.29)$$

Considering that, for this cases with low photon rates, the uncertainties of the single shots are approximately constant over ω_2 , the spectral intensity $\tilde{I}_k$ is then used to compute an L_2 loss function

$$\mathcal{L}_k = \|\tilde{I}_k(\omega_2) - I_k(\omega_2)\|_2, \quad (3.30)$$

which provides a measure of the quality of the approximate $\tilde{\rho}_{\text{eff}}$ given the observed $I_k(\omega_2)$ and $\Phi_k(\omega_1)$. More generally, for uncertainties varying significantly across the spectrum, a weighted L_2 norm should be employed, where the weights for each point $\omega_{2,i}$ are taken inversely proportional to the uncertainty on $I(\omega_{2,i})$, which can be determined with the methods outlined in Chapter 2. Using the STEP methodology, $\tilde{\rho}_{\text{eff}}$ is represented using a trainable feed-forward neural network acting as a universal approximator, and P_{RIXS} is implemented in an automatically differentiable form [227]. Improving the approximation for $\tilde{\rho}_{\text{eff}}$ can now be viewed as a standard machine learning optimisation problem. Thanks to the differentiability of the forward model, the gradients of this loss function can be propagated back to the NN parameters, which are therefore adjusted through a gradient-descent optimisation, in order for the forward model predictions to match the experimental measurements. In this framework, the learning process is essentially just a fitting of the experimental RIXS spectra through the reconstruction of ρ_{eff} .

Since convolution is an injective operation, there is a one-to-one correspondence between ρ_{eff} and the corresponding RIXS spectrum. This property ensures that, in absence

of noise, the NN reconstructs the correct ρ_{eff} as long as the forward model describes accurately the physical process. In reality, due mainly to the signal suppression away from the K_α lines, caused by the Lorentzian factor in Eq. (3.14), P_{RIXS} is an operator that maps very different ρ_{eff} into very similar RIXS spectra (contraction map). This fact, along with the noise in I_k , makes the solution to the inverse problem and the relative estimate of ρ_{eff} very challenging.

The energy resolution with which $\tilde{\rho}_{\text{eff}}$ can be extracted is given by the SNR of the single RIXS spectra and the energy resolutions with which I_k and Φ_k are measured. While the method can, in principle, be used to optimise single shot data, it is more effective to perform batching of the data to improve the SNR across multiple shots (see next section for more information). In contrast to standard averaging approaches, the resolution is not degraded by such a merging of multiple shots, since each pairing (I_k, Φ_k) is still considered individually in the optimisation process.

Details of the STEP Method Implementation

The feed-forward NN used to reconstruct ρ_{eff} has a single input (ϵ), a single output ($\rho_{\text{eff}}(\epsilon)$), 4 hidden layers with 40 nodes each, and the *softplus* activation function [236]. These architectural choices were selected based on extensive testing and are used throughout this thesis. However, alternative architectures may be more suitable for specific problems. For example, achieving a higher resolution for ρ_{eff} might require increasing the number of hidden layers or nodes. The neural network is trained by means of the ADAM [237] optimiser with the initial learning rate set to 10^{-3} . This optimisation, together with the automatic differentiation of the forward model, is carried out using the library PyTorch [238]. To ensure a good performance of this scheme, it is necessary to address the vanishing gradient problem [239] by omitting exponentially small factors in the gradient backpropagation. The training is generally performed splitting the set of experimental spectra $(I_k, \Phi_k$ for $k = 0, 1, \dots, N)$ into batches, whose size is increased dynamically during the training to shift from exploratory to exploitative training. The optimisation routine considers the loss function, and the respective gradients, on an entire batch to update model parameters at each step. Furthermore, the training is carried out over many epochs, i.e. rolling over all the N shots multiple times. Finally, during the training, the output of the neural network

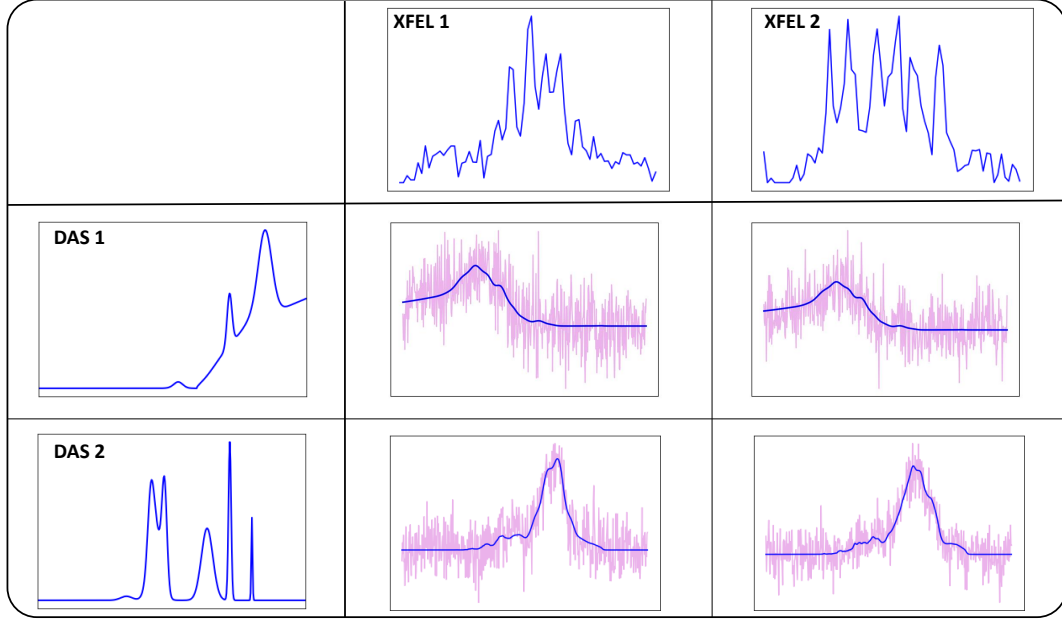


Figure 3.6: An illustration of the RIXS synthetic spectra. The real XFEL pulses 1 and 2 (spectra shown in top row) are used as incoming radiation into a simulated RIXS processes in materials with DAS A and B (left column). The 4 panels in the bottom right show the simulated scattering spectra before (blue) and after (magenta) noise is applied.

$\tilde{\rho}_{\text{eff}}(\varepsilon)$ is constrained to be positive, a fundamental physical requirement.

3.3.3 Validation on Synthetic Data

To show the efficacy of the method, it was tested on synthetic data, generated using the following procedure:

1. Create an artificial DAS ($\rho|M|^2$) designed to resemble a real one (Gaussian energy bands and an optional square-root continuum);
2. Compute the relative ρ_{eff} choosing a temperature T and an electron number density n_e . The chemical potential μ is then calculated from the following implicit equation

$$n_e = \int_0^\infty \rho(\epsilon) f_{FD}(\epsilon; T, \mu) . \quad (3.31)$$

For this data, I chose $T = 5$ eV and $n_e = 16$ atoms/unit cell (which is the iron electron density);

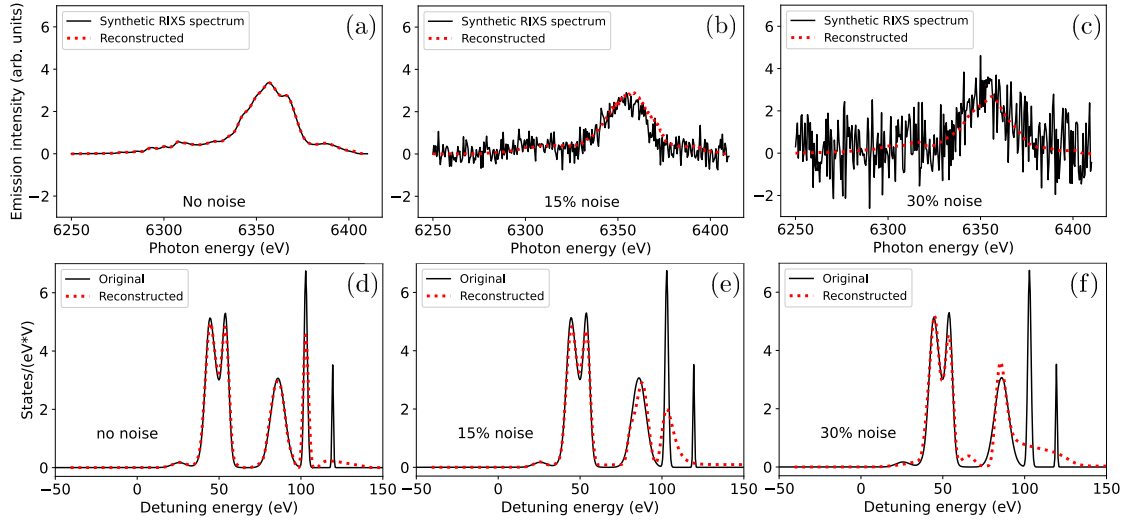


Figure 3.7: Reconstruction of a synthetic density of states from a RIXS spectrum at varying levels of noise, using a realistic SASE XFEL profile. A total of 50 single shots were used. Examples of the synthetic RIXS spectra are shown in panels (a-c), with the corresponding reconstructions in panels (d-f). The technique is robust to noise, owing to the strong inductive bias given by the model, and the stochastic nature of the SASE pulse profile Φ that allows us to oversample the DOS. The zero of the DOS energies is centred at the resonance. Note that the original ρ_{eff} corresponds to the DAS B of Fig. 3.6 modulated by the Fermi-Dirac distribution.

3. Evaluate $I_k(\omega_2)$ using Eqs. (3.14) and (3.17) with real XFEL SASE pulses as $\Phi_k(\omega_1)$.

For the physical parameters of the forward model P_{RIXS} , appearing in Eq. (3.14), I chose those specific of iron. These parameters have been taken from [215] and are shown in table 3.3.1;

4. Add Gaussian noise to the obtained spectra $I_k(\omega_2)$. The noise is distributed with a standard deviation of $\sigma = \alpha \cdot \max(I(\omega_2))$.

I chose six spiky synthetic DAS, which are both challenging to tackle for traditional deconvolution algorithms, but also representative of narrow bound states and d -band features. Examples of resultant spectra for different combinations of DAS and XFEL pulses are shown in Fig. 3.6. Note that with the noise applied, the features in the spectrum are barely recognisable. These synthetic RIXS spectra are then provided to the deconvolution scheme, alongside the corresponding SASE spectra, to extract the ρ_{eff} corresponding to a certain DAS (here T is assumed to be unknown as a more realistic case). Fig 3.7 shows the results for DAS B of Fig. 3.6 under three different levels of noise analysed, considering

that analogous behaviours are observed for all the other artificial DAS.

Parameter[units]	f	Value
$\epsilon_K[eV]$	1, 2	-7112
$\epsilon_{L,f}[eV]$	1	-723
	2	-708.5
A_f	1	50
	2	100
$\Gamma_f[eV]$	1	3
	2	2.55

Table 3.3.1: Physical parameters of iron, used for the synthetic spectra. Iron has two L-shell states, implying two possible final states $f = 1, 2$.

This approach shows good convergence of the extracted DOS for all levels of noise up to $\alpha = 30\%$. However, the accuracy of reconstruction decreases as the level of noise is raised, with the extracted ρ_{eff} starting to miss small or narrow features, especially for large detuning energies. This behaviour is expected, since the area under a DOS feature and its detuning, i.e., its distance from resonance, are the two main parameters that determine the intensity of the feature in the RIXS spectrum. Bright features closer in energy to the resonance are thus more robust to low SNR. Another common factor that deteriorates the accuracy of the reconstructions is the presence of spurious oscillations in the extracted ρ_{eff} . These oscillations are a typical byproduct of deconvolution, and are present on energy-scales smaller than the kernel’s bandwidth. Regardless, the successful extraction of features using this approach even from spectra dominated by noise, as shown in Fig. 3.7c, remains significant.

Figure 2.8 illustrates the loss function, defined as the L_2 distance between ρ_{eff} and $\tilde{\rho}_{\text{eff}}$, during the neural network training for one of the analysed syntethic DAS without noise applied. The figure also shows the evolution of $\tilde{\rho}_{\text{eff}}$ until its final comparison with the original ρ_{eff} . Convergence is achieved after approximately 6,000 epochs, with an initial steep decrease in the loss function corresponding to the reconstruction of the coarse features of ρ_{eff} . This is followed by a gradual decline, reflecting the refinement of finer details. Notably, the neural network encounters difficulty in increasing the number of inflection points, resulting in plateaus in the loss function. Similar trends are observed across all

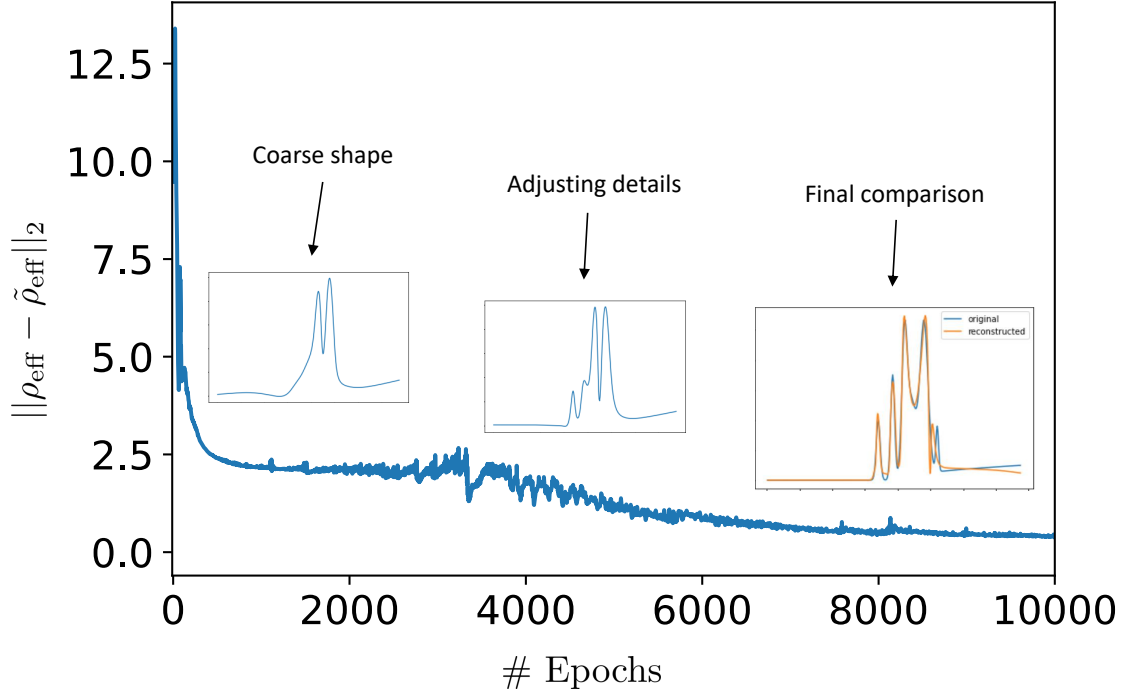


Figure 3.8: Loss function, defined as the L_2 distance between ρ_{eff} and $\tilde{\rho}_{\text{eff}}$, during the neural network training for one of the analysed synthetic DAS (distinct from that of Fig. 3.7) with no noise applied. The plot includes also the evolution of $\tilde{\rho}_{\text{eff}}$ until its final comparison with the original ρ_{eff} . Here, one epoch is completed when each Φ_k (50 in this synthetic dataset) is used for the calculation of the loss $\|\tilde{I}_k - I_k\|_2$.

the synthetic DAS analysed without noise in the spectra. When noise is introduced, the loss function exhibits greater fluctuations and eventually converges to a higher asymptotic value.

A note is in order here: in this thesis I denote as RIXS scattering processes with detuning energies up to 150 eV, following the notation adopted in [156], however, other names (e.g. high energy resolution off-resonance spectroscopy) have also been used to describe such scattering processes in the literature [240, 241]. Unlike in Ref. [156] where the incident photon energies are varied, in this work (both for experimental and synthetic data) the XFEL central energy is fixed and set at about 10s of eV below the material's absorption edge to optimise the extraction of the valence density of states.

To demonstrate the efficacy of the STEP method, in Fig. 3.9 the quality of the ρ_{eff} reconstruction is shown as a function of the number of shots in the dataset for four different approaches and two noise levels. The blue and red curves employ the paradigm described in Fig. 3.5 to reconstruct ρ_{eff} : the results using all individual experimental pairs (I_k, Φ_k)

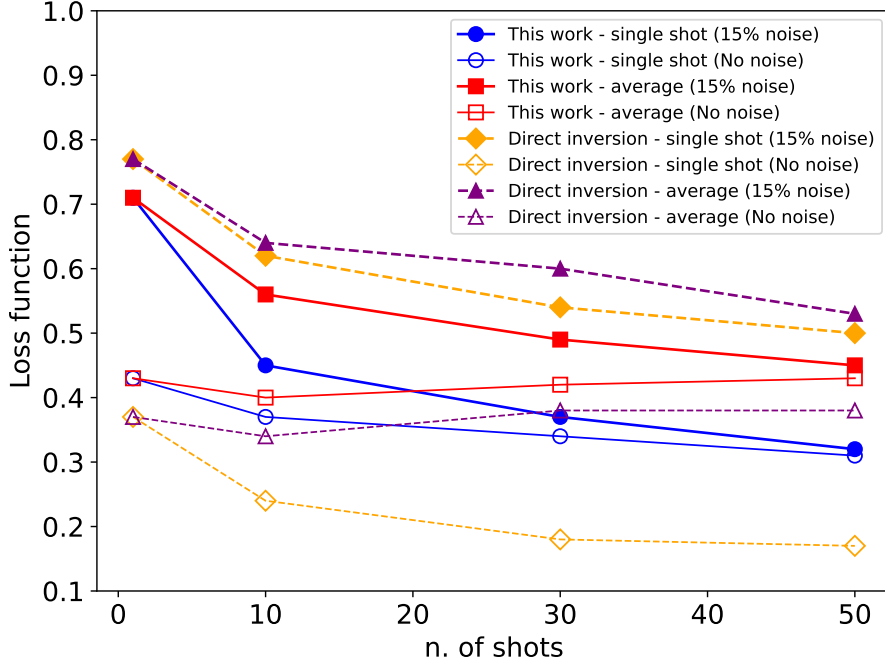


Figure 3.9: Quality of the reconstructed ρ_{eff} as a function of the number of shots N included in the inversion dataset. The DOS used is that shown in Fig. 3.7a. While the direct inversion works best for noiseless data, the quality rapidly deteriorates for real data with noise. In contrast, the STEP approach is fairly insensitive to noise. The loss function employed for this plot is a weighted L_2 distance between the reconstructed and the original DOS, with bigger weights for the energy regions where features are present. This is achieved defining the weighted L_2 norm as $1/F \sum_i |d\rho_{\text{eff}}/d\epsilon|(\epsilon_i) (\tilde{\rho}_{\text{eff}}(\epsilon_i) - \rho_{\text{eff}}(\epsilon_i))^2$, where ρ_{eff} is the original DOS and F is a normalisation factor.

are depicted with blue circles, while the results using average values ($\bar{I}, \bar{\Phi}$) are shown with red squares. Similarly to what has been done in [217, 242], Eq. (3.27) is also directly inverted via standard numerical techniques for comparison (see next section for details), both for the individual pairs (diamond markers) and for the averaged spectra (triangle markers). It is observed that while the direct inversion method achieves the best results in the absence of noise, its performance degrades rapidly as noise is added. This is due to the characteristics of P_{RIXS} , which maps very different ρ_{eff} into similar RIXS spectra, making its inversion an ill-conditioned problem. On the other hand, the STEP approach shows little variation on the quality of the reconstructed DOS with noise, and is thus more robust. In particular, it is observed that with the STEP method, the results obtained for a 15% noise level converge to those achieved without noise already for a relatively restrained $N \approx 50$. The comparison between single shot and averaged analysis indicates that

averaged calculations suffice for broad features, but that shot-by-shot analysis is required to capture finer structure, and that the averaging process leads to a loss in resolution. This can be explained considering that deconvolution is more efficient with spiky XFEL spectra, characteristic of the single shot case, rather than with relatively broad Gaussian XFEL spectra, which occur in averaged calculations⁷. Specifically, in the absence of noise, where no gain on the SNR is obtained through averaging, the use of the averaged spectra deteriorates the quality of the reconstructions as N grows.

Details of the Numerical Approach

To extract ρ_{eff} from a set of RIXS and XFEL spectra without making use of machine learning techniques, the following numerical routine is employed:

1. One first discretises the RIXS operator for each FEL spectrum Φ_k , computing the associated matrices M_k for $k = 1, 2, \dots, N$. Each M_k is constructed taking as its i -th column $P_{\text{RIXS}}[\Phi_k, \rho_i]$, where $(\rho_i)_j = \delta_{i,j}$, with $i, j = 1, 2, \dots, L$ and L the length of ρ_{eff} . Note that this discretisation is possible because P_{RIXS} is a linear operator in ρ_{eff} ;
2. One then constructs the macro-linear system of equations in ρ_{eff} by stacking the matrices M_k and the RIXS spectra I_k as

$$\begin{bmatrix} M_1 \\ M_2 \\ \vdots \\ M_N \end{bmatrix} \rho_{\text{eff}} := M \rho_{\text{eff}} = \begin{bmatrix} I_1 \\ I_2 \\ \vdots \\ I_N \end{bmatrix} := I \quad (3.32)$$

notice that the matrix M is in general not square;

3. Next, one approximates the solution of this linear system, and hence ρ_{eff} , using the conjugate gradient descent method [243];

⁷To understand this, it is better to think about the deconvolution operation in the Fourier space, where it takes the form of a division by the Fourier transform of the kernel function. A spiky kernel function has a transform with a larger support, reducing the division instabilities at high frequencies.

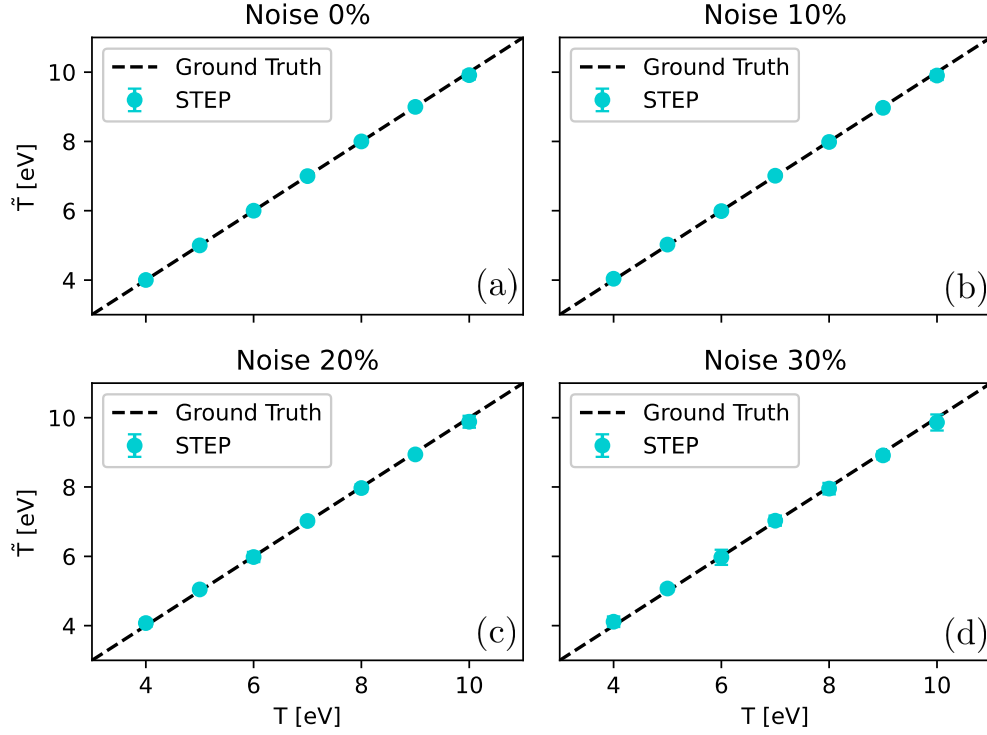


Figure 3.10: Temperatures extracted from RIXS measurements plotted against true temperatures, taken from Ref [235]. Panels (a) through (d) correspond to noise levels of 0%, 10%, 20%, and 30% respectively. Note that all values are plotted with errorbars, most of which are too small to be seen.

4. Finally, one applies a smoothing filter to ρ_{eff} to mitigate the spurious oscillation. One can show that this procedure is equivalent to perform a Tikhonov regularisation [244] with a cost function penalizing too fast oscillations in the solution.

This idea of discretizing the physical process operator and inverting the associated matrix has already been employed in the field of spectroscopic analysis [217]. An alternative approach to addressing this inversion problem is the maximum entropy method [245]. When working with the averaged spectra, one just searches for a solution of the linear system $\bar{M}\rho_{\text{eff}} = \bar{I}$, where $\bar{M}$ is constructed using the averaged FEL spectrum $\bar{\Phi}$.

3.3.4 Extracting the Temperature

As previously discussed, the STEP paradigm can also be used to extract temperature from RIXS spectra, provided the underlying DAS is known from other sources (e.g. DFT

calculations)⁸. In this scenario, the extracted B_i (refer to Eq. 3.23) becomes a scalar rather than a function, while the method itself remains unchanged. To test the extraction of T from RIXS spectra using the STEP method, the same procedure as before is followed, but incorporating the known DAS into the forward model. Consequently, the backward propagation of gradients must go through additional operations, including the division of ρ_{eff} by the DAS and the extraction of T from the Fermi-Dirac distribution. Furthermore, the chemical potential must be recalculated with Eq. 3.31 after each update of T .

This method was applied to the previously introduced set of spectra, but with seven different values of temperatures ranging from 4 to 10 eV. The results, shown in Figure 3.10, demonstrate excellent temperature predictions that remain unaffected by noise. For each noise level, the extracted temperatures and their uncertainties were calculated as the mean and standard deviation of the values obtained across all the different DAS. On average, convergence was achieved after under 2,000 epochs, depending on the initial random value of temperature. These results highlight the successful functioning of the STEP method for scalars and its robustness against noise.

3.4 Summary

This chapter revisited the theory of RIXS, tailoring it to our specific cases of interest and demonstrating how it can, in principle, provide information about the density of states and the temperature of the material being probed. The RIXS technique was also compared with other spectroscopic methods, highlighting their relative advantages and disadvantages. I then introduced a method, called STEP, which combines neural networks with physical modeling to address inverse problems where a physical quantity must be extracted from experimental measurements in which it is embedded. This method was then specified for the RIXS problem to extract the electronic structures and temperatures from the RIXS spectra. Finally, the application of this method to synthetic data was shown, testing its performances and comparing them with numerical techniques. The key finding of this study was the STEP method's improved robustness to noise compared to numerical approaches.

⁸While this assumption - especially at high pressures - is somewhat idealised (it actually represents the central challenge addressed in this thesis), reasonable approximations of the DAS are available and may be refined in the future.

Potential enhancements of this approach and ideas for other physical problems where the STEP method could be employed are given in Chapter 6.

Chapter 4: Electronic Structures of Isochorically-Heated Systems

This chapter demonstrates the application of the previously introduced method to experimental RIXS spectra collected from isochorically-heated samples of Fe, FeO, Fe₂O₃, and Gd. These spectra were acquired during an experiment conducted in November 2022 at the HED scientific instrument of the European XFEL facility [74], where samples were both heated and probed using the same XFEL pulse (“self scattering” experiment).

The chapter begins by reviewing the experimental setup and design, providing context for the measurements. In the second part, the experimental data alongside the extracted electronic structures and thermodynamic conditions for each material are presented. The analysis of the RIXS spectra is performed across different diagnostics and experimental operational modes to validate the robustness of the results. The analysis of gadolinium is discussed separately in the last part of the chapter, as it employs a slightly distinct flavour of RIXS. This case serves as a valuable example, generalizing the applicability of RIXS techniques in HED physics research.

4.1 Experimental Setup

Figure 4.1 presents the setup of the experiments along with detailed illustrations of the primary diagnostic tools. These include a flat crystal spectrometer, a von Hámos spectrometer, and a XRD detector¹. The latter captures diffraction profiles for each shot, allowing to cross-check the consistency of the sample’s chemical compositions and crystalline integrity. Only the shots that satisfied the consistency checks were retained. Both spectrometers are utilised to record the RIXS spectra, with their complementary characteristics deliber-

¹The XRD detector was calibrated using CeO₂ and LaB₆ diffraction profiles.

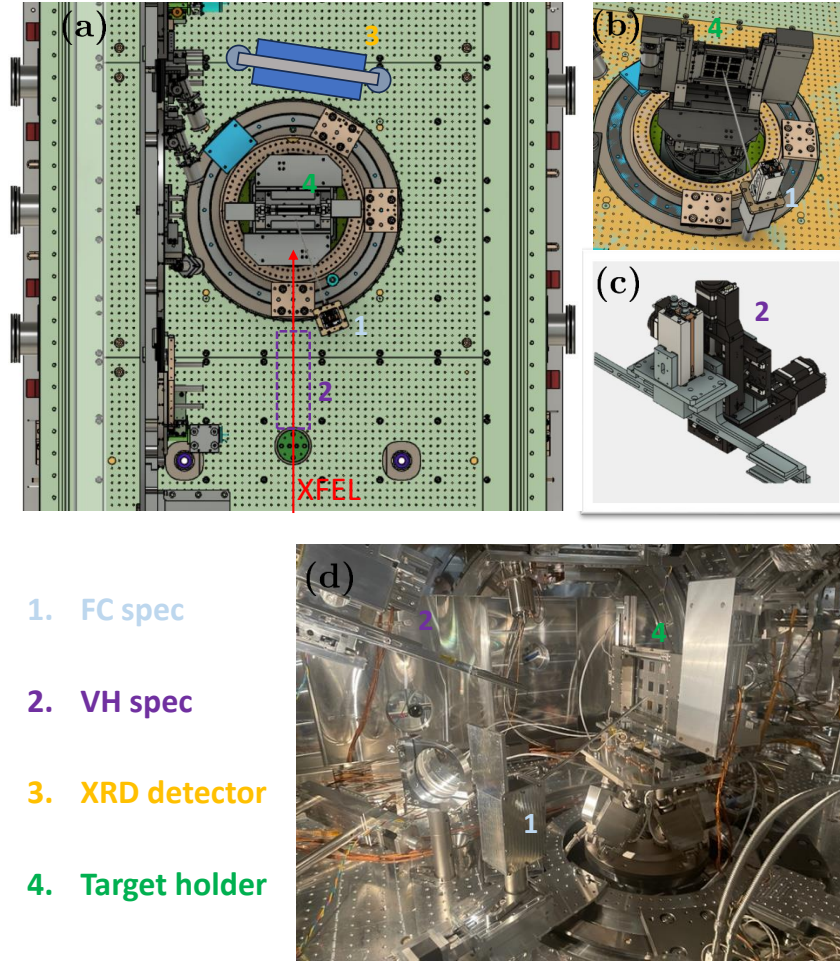


Figure 4.1: (a) A CAD model of the EuXFEL experimental setup, including a zoom around the FC spectrometer and the target holder (b), and an illustration of the VH spectrometer (c). To ensure precise positioning, a metal pin connects the front of the FC spectrometer to the target location, whereas the VH spectrometer position is adjusted using circular rails (see [74]). (d) A photograph of the experimental chamber.

ately leveraged at the expense of redundancy: the von Hámos spectrometer offers a higher single-shot SNR but lower resolution, while the flat crystal spectrometer provides superior resolution at the cost of reduced signal intensity. Both spectrometers were filtered and caged to eliminate background signals while preserving the RIXS signal, which is within the energy range of 6–7 keV. The filters, made of black kapton, had a thickness of 300 μm , which was calculated using the center for x-ray optics (CRXO) software [246].

The flat crystal spectrometer utilised a Ge (422) reflecting plane (operating in first-order reflection) paired with a ePix100 camera [247], whereas the von Hámos one employed a cylindrically bent HAPG crystal with an 80 mm RoC and a 40 μm thickness coupled to

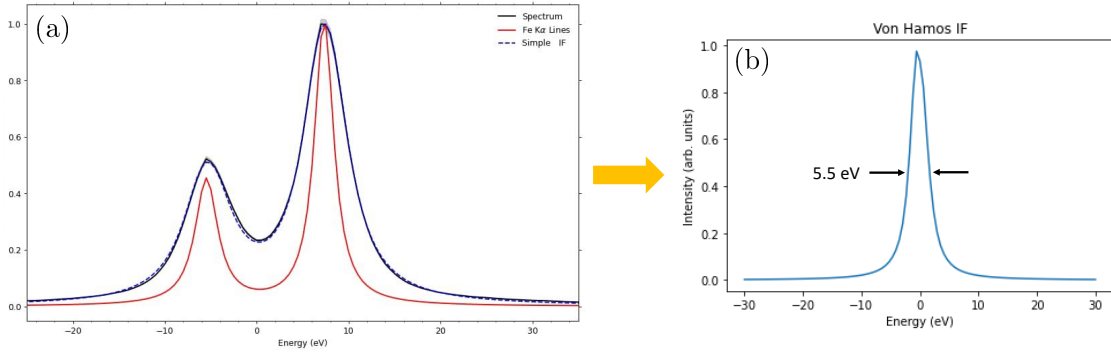


Figure 4.2: (a) The Fe $K\alpha$ emission lines (red curve) are convolved with a kernel function to produce a fit (dotted blue line) of the von Hámós experimental spectrum (black solid line). (b) The extracted kernel function, representing the von Hámós instrument function. The energy axis centres are arbitrarily chosen, as they are not relevant for these calculations. Working on calibration shots, and hence above the absorption edge, increases the SNR in the experimental spectrum facilitating the fitting. The plot in panel (a) are provided courtesy of Dr. Thomas Gawne, who also performed the fitting.

a Jungfrau detector [187, 248]. Both cameras digitise signals with 14-bit resolution, with the Jungfrau including two additional bits to encode the gain level. Analysis of spectra for single calibration shots shows that the von Hámós spectrometer detects roughly 6 times more photons per image than the flat crystal one, albeit with a lower resolution—estimated at about 5.5 eV for the VH spectrometer and 2.3 eV for the FC spectrometer. The resolution of each instrument, comprising the crystal rocking curve, pixel size effects and source broadening, can be assessed by comparing the intrinsic widths of the Fe $K\alpha$ lines (see Table 3.3.1) to their observed widths in the measured spectra, which for calibration shots (where the FEL photon energy is above the absorption edge) is not affected by the bandwidth of the source spectrum. A method for determining the spectrometer resolutions involves identifying the kernel function that, when convolved with the intrinsic Fe $K\alpha$ line profile, reproduces the experimental spectrum. These kernel functions represent the instrument functions of the spectrometers, and their widths provide estimates for the resolutions. Figure 4.2 illustrates the calculated instrument function for the VH spectrometer, along with the corresponding fit. Energy calibration for the two instruments was performed using the methods outlined in Chapter 2, with the Fe $K\alpha$ and Tb $L\alpha$ lines (6238 eV and 6273 eV) serving as reference lines. The detected energy ranges are (5773–6492) eV for the von Hámós spectrometer and (6110–6458) eV for the flat crystal spectrometer.

The XFEL was operated both in SASE and seeded mode at a central photon energy of

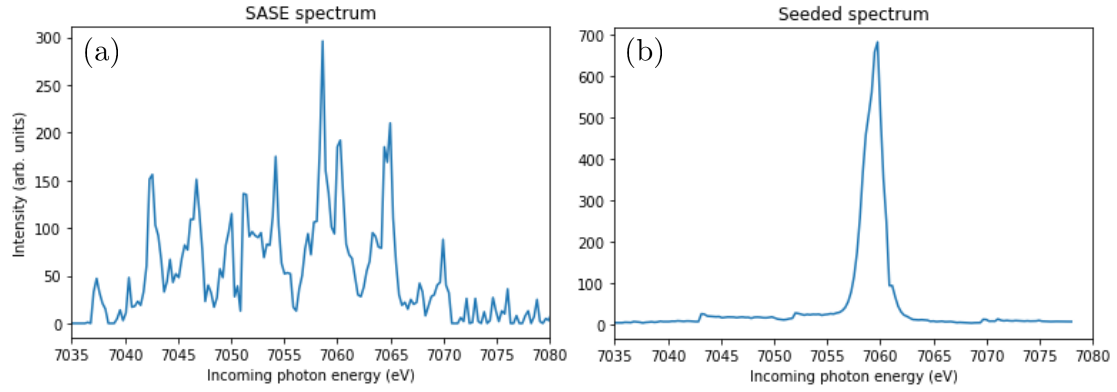


Figure 4.3: Example of measured XFEL spectra for SASE (a) and seeded (b) mode.

approximately 7060 eV (only changed for some analysis on gadolinium, see Section 4.2.4). This energy lies just below the Fe K-edge (refer to Table 3.3.1) and the Gd L_3 -edge (7243 eV), ensuring that RIXS is the dominant scattering process. Furthermore, for the iron compounds, the incoming photon energies are sufficiently close to the $K\beta$ (1s-3p) transition energy (7058 eV), enabling the probing of ionisation in the 3p states (M-shell). During the experiment, the iron 3p states can be depopulated due to the heating of the electrons via the intense x-ray irradiation. This suggests that measuring the M-shell RIXS signal, which is proportional to the number of vacancies in the shell, can provide an accurate estimate for the sample's temperature. An example of XFEL spectra for both modes is presented in Figure 4.3, showing a spectral bandwidth of approximately 20 eV for the SASE mode and a few eV for the seeded mode. In order to apply the STEP method, it is essential to measure the source spectrum on a shot-to-shot basis and correlate it with the RIXS spectra. This was achieved using the Si beamline spectrometer with a resolution of 0.3 eV [160]. Analysis revealed that, in many shots, the seeded spectrum retained a SASE background (or pedestal), making the deconvolution of the source spectrum an essential task for this case as well.

The total pulse energy in the beam ranged between 500-1000 μJ in the SASE mode, but it was constrained to be between 700-800 μJ for the analysed data in order to limit the sample thermodynamic variations. In contrast, no such restriction was needed for the seeded mode, where the pulse energy varied between 100 and 200 μJ . The pulse energy delivered to the target was measured using diodes integrated into the beamline [74]. With an average laser pulse duration of 40 fs and x-rays focused to spot sizes of 7–10 μm (mea-

sured using the knife-edge technique [249]), intensities of up to 10^{17} Wcm^{-2} were achieved. The focal spot size was optimised *in-situ* to maximise x-ray heating, diagnosed via the observed RIXS signal from the Fe M-shell.

The samples employed in the experiment are summarised in the following table.

Material	Dimensions [cm x cm]	Thickness [μm]	Type
Fe	2.5 x 2.5	20	Free-standing foil
FeO	2.5 x 2.5	12	Layer grown on 50 μm of plastic
Fe ₂ O ₃	2.5 x 2.5	10	Layer grown on 50 μm of plastic
Gd	2.5 x 2.5	5	Free-standing foil

Table 4.1.1: Specifics of samples used in the experiment. The iron oxides were fabricated on a plastic substrate using the physical vapour deposition (PVD) technique. This process introduces impurities into the samples, including other iron oxides of the form Fe_xO .

These target thicknesses correspond to roughly half the absorption length at the photon energies used, and they were chosen to maintain an x-ray heated bulk with a uniform temperature. Since the experiment operated at intensities above the damage threshold, samples were rastered, and data were collected at a repetition rate of 10 Hz.

4.2 Experimental Results

In the following sections, the experimental results will be presented, beginning with the extraction of the electronic structure for warm-dense Fe and Fe₂O₃ using von Hámos spectroscopic data acquired in SASE mode. This initial analysis demonstrates how vacant density of states can be reconstructed from RIXS spectra with a resolution exceeding the

bandwidth of the SASE spectrum, allowing us to discriminate between the valence structures of Fe and Fe_2O_3 . Additionally, the extracted electronic structures enable temperature measurements and provide estimates of M-shell binding energies with smaller uncertainties than those reported in previous studies [156].

I will then present the extracted density of states for Fe, obtained either from flat crystal data or using the seeded mode, and compare them with that obtained in the previous section. This comparison will check the consistency of the results and evaluate the quality of reconstruction from dataset with different characteristics, highlighting both the strengths and limitations of the STEP method when applied to experimental data.

Subsequently, I will discuss the reconstructed density of states for FeO, achieved after having deconvolved the measured instrument function from the RIXS spectra. This analysis demonstrates the capability of achieving very high resolutions, enabling a more detailed exploration of the fine structure of the DOS near the chemical potential, such as bandgap features. Finally, after a brief introduction on the scientific and technological applications of gadolinium, its RIXS data is analysed, emphasizing the differences from iron-based compounds. To assess the reliability of the experimentally extracted electronic structures, all results are compared with FT-DFT simulations, details of which are provided in the next section.

4.2.1 DFT Calculations

The electronic structure of Fe, Fe_2O_3 , FeO and Gd were calculated using finite-temperature density functional theory with a locally-modified version of the ABINIT v8.10.3 code [250, 251]. The relevant modification is the inclusion of the hybrid Kohn-Sham plane-wave-approximation scheme [104] as described by Ref. [252] to enable accurate high temperature calculations (see also Introduction). The ABINIT code is used to solve the Kohn-Sham system, which provides the KS states and eigenvalues. The DOS is given by the latter using Eq. (1.20), while the former can be used to calculate the dipole transition matrix elements from the initial electron core state (e.g. 1s for iron compounds) to the calculated valence states [253] (see also Sec. 1.3.2). The orbital-projected DOS was also calculated with standard techniques [253] to aid in identifying features in the total DOS.

The ion cores were represented using the projector-augmented wave (PAW) scheme [105,

254], with Fe, O and Gd PAW potentials generated using the *Atompaw* code [255]. For efficiency, the Fe 1s, 2s, 2p orbitals, the O 1s orbital, and the Gd orbitals up to the 5p states were treated with the frozen-core approximation. This approximation is suitable for the relatively low temperatures (< 10 eV) reached in this experiment, as these orbitals are not thermally ionised. Additionally, as mentioned in Section 3.1, at these energy resolutions one can neglect the core hole interactions, and therefore ignore any core hole in the pseudopotential for the intermediate state of the system.

Calculations were performed at electron temperatures of 300 K, 1 eV, 5 eV, and 10 eV, with the ions frozen in their ambient crystal lattice positions. This further approximation is justified by the femtosecond duration of the XFEL pulses, during which all the spectral emission of interest occurs. This timescale is substantially shorter than the electron-phonon coupling times of several picoseconds, leaving the ion unperturbed during irradiation. The electron temperature range was chosen based on approximate predictions of the sample temperatures, derived from calculations of laser deposition energy.

The Fe calculations were therefore performed in a bcc primitive unit cell containing a single atom. Simulations were carried out with 120 bands and a $30 \times 30 \times 30$ k -point grid, with a cut-off energy of 50 Ha for the PAW pseudo-wavefunctions and 150 Ha for the all-electron wavefunctions. For Fe_2O_3 , the calculations were performed in its α -phase [256], with a unit cell containing 30 atoms. Simulations were performed with 1440 bands and a $6 \times 6 \times 1$ k -point grid (the latter direction being the long direction of the unit cell), with a cut-off energy of 20 Ha for the PAW pseudo-wavefunctions and 100 Ha for the all-electron wavefunctions. The FeO calculations were performed in its B1 phase, with a unit cell containing 12 atoms. The simulations employed 700 bands and a $12 \times 12 \times 12$ k -point grid with a cutoff energy of 40 Ha for the PAW pseudo-wavefunctions, and 140 Ha for the all-electron wavefunctions. Finally, the Gd calculations were carried out in its hexagonal close-packed α -structure, with a unit cell containing 6 atoms, 1800 bands and a $12 \times 12 \times 12$ k -point grid, with a cut-off energy of 60 Ha for the PAW pseudo-wavefunctions and 180 Ha for the all-electron wavefunctions.

For the exchange-correlation functional, the PBE form of the generalised gradient approximation was used for the Fe, O and Gd atoms. To recover the band gaps in Fe_2O_3 and FeO, the corrective approach of a Hubbard potential (DFT+ U) was applied, with U values

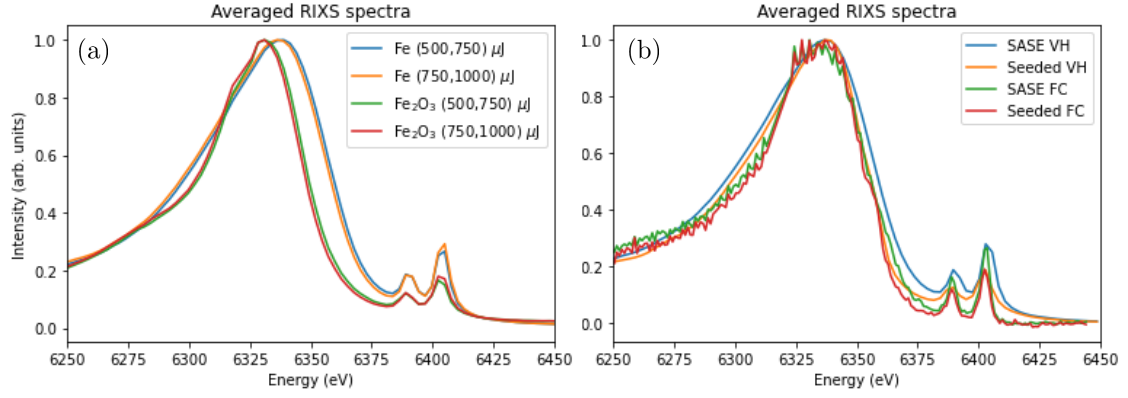


Figure 4.4: (a) Normalised and averaged RIXS spectra for Fe and Fe_2O_3 at two different energy ranges on target, measured using the von Hámos spectrometer and the FEL laser in SASE mode. Each spectrum averages approximately 3,000 shots. (b) Normalised and averaged RIXS spectra for Fe recorded using the various combinations of spectrometers (flat crystal and von Hámos) and XFEL modes (SASE and seeded). In this case, each spectrum is averaged over approximately 6,000 shots per condition.

of 4.0 eV and 4.5 eV for the iron d orbitals in Fe_2O_3 and FeO, respectively. These values yielded band gaps of approximately 2.0 eV for Fe_2O_3 and 2.4 eV for FeO, in agreement with experimental results reported in [257, 258]. As small adjustments to the value of U at the analysed temperatures did not show meaningful changes to the electronic structure of Fe_2O_3 and FeO, these U values were chosen for all calculations.

4.2.2 Electronic Structures of Warm-Dense Fe and Fe_2O_3

In Figure 4.4 averaged RIXS spectra for various combinations of diagnostic instruments, targets, and photon source configurations are presented. The left panel displays RIXS spectra for Fe and Fe_2O_3 at two distinct energy ranges delivered to the target. These spectra were recorded using the von Hámos spectrometer with the FEL laser operating in SASE mode. The differences in the electronic structures of the two materials, reflected in the different RIXS spectra, are evident, as are the subtle increases in the M-shell signal (the two peaks around 6400 eV) caused by the slightly higher laser energy, which heats more the material, further depopulating the M-shell. The small magnitude of such increases suggests a weak dependence of the resulting electronic temperature on the input energy, likely due to the behaviour of the electronic heat capacity in this region of the thermodynamic plane.

The right panel shows Fe RIXS spectra obtained using different combinations of spectrometers and XFEL modes. The broadening of features due to the lower resolution of the

von Hámos spectrometer and the SASE mode is clearly visible. Conversely, the flat crystal spectrometer exhibits a noticeable reduction in signal-to-noise ratio. As discussed earlier with synthetic data and elaborated further in the next section, this low SNR significantly hampers the STEP method, leading to a greater loss of resolution in the reconstructed DOS than the one caused by a poor resolution of the RIXS spectra. Additionally, noise features in the averaged spectra propagate into the extracted DOS, as the algorithm cannot differentiate between noise and actual physical features. For these reasons, except where explicitly stated otherwise, the following analyses for electronic structure extraction focuses exclusively on data obtained with the von Hámos spectrometer and the FEL operating in SASE mode.

Examples of single-shot experimental spectra are shown in Fig. 4.5, alongside with the corresponding extracted electronic structure. It is observable that the typical level of noise for a single-shot RIXS spectrum is on the order of 25%, comparable to the cases examined for the synthetic data. The experimental reconstructions of ρ_{eff} are compared with DFT calculations (see Section 4.2.1 for more details), which allow us to identify various features in the experimental data, and to evaluate the resolution with which $\rho_{\text{eff}}(\epsilon)$ can be extracted in practice, given our experimental setup. In all comparisons with DFT data, a translational and a multiplicative parameter were used to, respectively, align and rescale the experimental reconstructions with the DFT outputs. The experimental ρ_{eff} have been reconstructed using the dynamic kernel deconvolution scheme, as described in Section 3.3.2, over approximately 6,000 RIXS shots for each material. Six independent fitting processes were conducted, for both materials, with different random seeds for the NN. The average and standard deviation of the resulting outputs have been taken, respectively, as the best estimate for ρ_{eff} and its error. The error on the experimental RIXS spectra due to noise, which is propagated through to ρ_{eff} , becomes negligible because of the large amount of experimental shots. Hence, the error is due only to the stochasticity of the NN optimisation.

Estimation of the Resolution

The experimental reconstructions in Fig. 4.5 agree well with the theoretical predictions, demonstrating the ability to extract densities of states with a fairly complex structure from

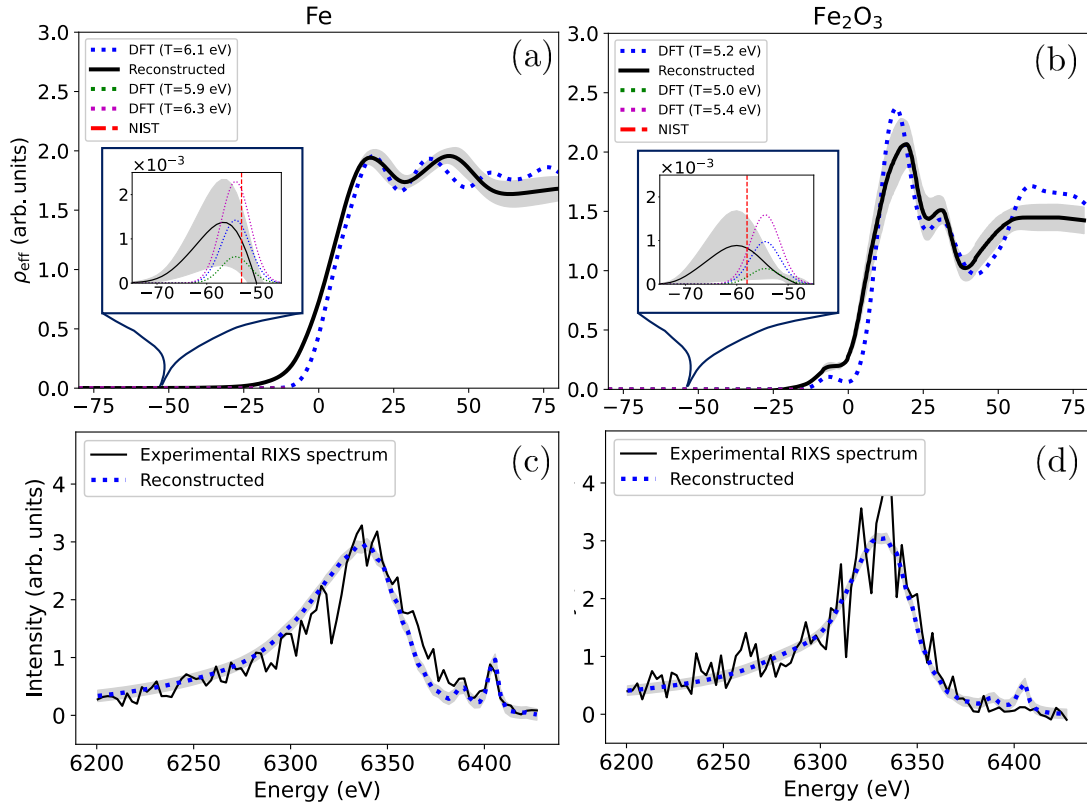


Figure 4.5: Measured accessible density of states of Fe and Fe₂O₃ (a-b), reconstructed from the RIXS measurements, along with their respective experimental spectra (c-d). The grey bands indicate the standard deviation. The measured data are compared with theoretical DFT calculations, for which a smearing width of 7 eV for Fe₂O₃ and 9 eV for Fe (see Section 1.3.2) were used. The zero of the energy axis is defined by the chemical potential obtained from DFT simulations, and this convention is maintained throughout the remainder of the thesis. The insets show the reconstruction of the M-shell vacant states, located around (-50,-60) eV. This feature is only present if the M-shell is thermally ionised by the x-ray beam, thus allowing us to estimate the temperature of the sample. The red dashed vertical line indicates a reference M-shell binding energy, taken from [259].

RIXS spectra with relatively low SNR. The resolution of the extracted ρ_{eff} was estimated with two different methods, shown in Fig. 4.6. In panel (a) the reconstructed Fe₂O₃ ρ_{eff} was fitted with a superposition of multiple Gaussians. This fitting is then used to achieve an estimate of the narrowest feature width that can be reconstructed, and therefore, of the resolution. This width is found to be 6.7 eV. Another method to evaluate the resolution is to consider the L₂ distance between the experimental ρ_{eff} and the DFT predictions, as a function of the smearing width applied to the latter. This curve is plotted in Fig. 4.6b. The minimum of this curve is found for a smearing width around 8.2 eV, yielding another estimate for the resolution of the extracted ρ_{eff} . The small discrepancy between the two

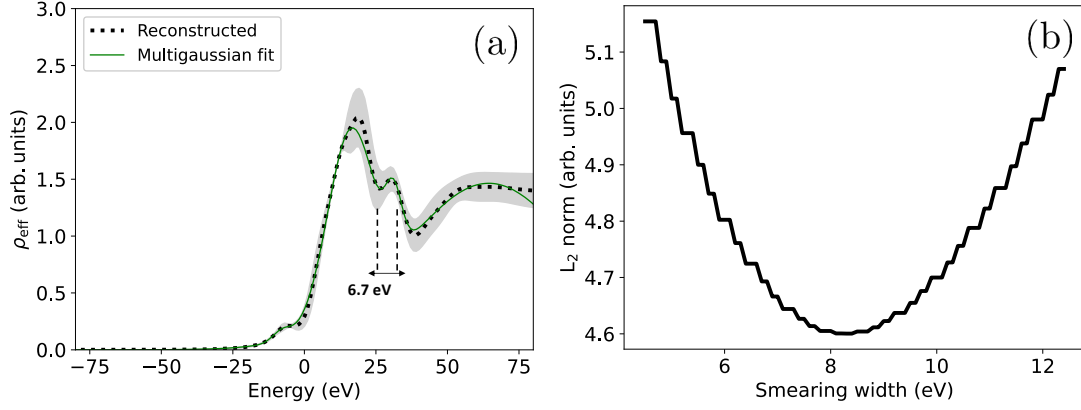


Figure 4.6: Two different approaches for the estimate of the extracted DOS resolution. In panel (a) this is carried out by fitting a superposition of multiple Gaussians to the reconstructed DOS, whereas in panel (b) the L_2 distance between the experimental reconstruction and the DFT simulations as a function of their smearing width is considered. The error intervals on the reconstructed DOS in panel (a) are identical to those of Fig. 4.5.

methods can be traced back to the different resolutions with which different parts of the DOS seem to be reconstructed (e.g. the continuum slope and the small valence band peak). This resolution is somewhat lower than the limit of 5.5 eV imposed by the spectrometer resolution in our experimental setup. This small difference is attributed primarily to the SNR of the experimental data, which was fairly low, as the data collection was done in single-shot mode. Nevertheless, the reconstructed electronic structures show resolutions up to three times higher than the spectral FWHM of the XFEL pulse (see Fig. 4.3), allowing one to distinguish the environment in which a Fe atom is embedded, via differences in the electronic structure of Fe in the insulating Fe_2O_3 or in the metallic state. Such a distinction cannot be made via RIXS with the normal spectral resolution of the SASE beam of ~ 20 eV, as it is illustrated in Fig. 4.7, where applying a smearing width of 20 eV to the DFT calculations for Fe_2O_3 would yield a ρ_{eff} similar to that of metallic Fe.

Characteristic of the Measured Electronic Structures

The comparison of the electronic structure with the orbital-projected DOS reveals that the pre-edge feature in Fe_2O_3 , located around -10 eV, contains a mixture of the $2p$ oxygen states and the $3d$ iron states, which are indistinguishable at these resolutions. The band gap between these states and the conduction ones, predicted by experimental measure-

Resolution analysis of the Fe_2O_3 reconstructed ρ_{eff}

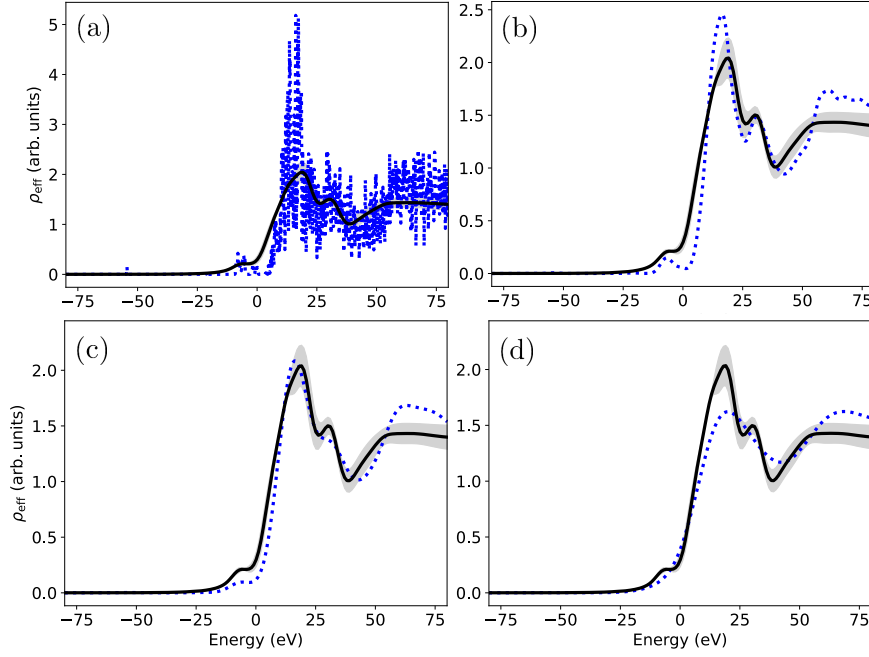


Figure 4.7: Comparison between the reconstructed ρ_{eff} for Fe_2O_3 (solid black lines) and the DFT simulations (dashed blue lines) with smearing widths of 0.2 (a), 5 (b), 10 (c), and 20 eV (d) respectively. It is observable that with a smearing of 20 eV, as it would be given by the SASE bandwidth, the characteristic features of Fe_2O_3 are no longer visible.

ments [260, 261] to have a width of approximately 2 eV, is visible in the reconstruction as a slightly convex plateau located at just below 0 eV.

In addition to the modulation in the continuum and the pre-edge feature in the Fe_2O_3 case, this method can reconstruct the M-shell for both materials, as shown in the insets of Figs. 4.5a-b. Despite the small area of these features due to the low thermal de-occupation, they are amplified in the RIXS spectra by their vicinity to the resonant energies. Thus, the reconstructed ρ_{eff} gives us a method to experimentally estimate the binding energy (BE) of the M-shell in extreme thermodynamic conditions—a quantity difficult to obtain via theoretical approaches [262, 263]. The values found from the reconstructions are (-56 ± 3) eV for Fe and (-59 ± 5) eV for Fe_2O_3 . These values and their uncertainties are determined using Monte Carlo calculations. Specifically, M arrays of the form $y(\epsilon_1), y(\epsilon_2), \dots, y(\epsilon_N)$ are generated, where each $y(\epsilon_i)$ is sampled from a Gaussian distribution with mean value $\tilde{\rho}_{\text{eff}}(\epsilon_i)$ and standard deviation equal to the uncertainty on $\tilde{\rho}_{\text{eff}}(\epsilon_i)$. Here, $\epsilon_1, \epsilon_2, \dots, \epsilon_N$ are energy points around the M-shell. Then for each of these M array the argmax is computed

and their average and standard deviation are then used as the best estimate of the M-shell binding energy and its associated uncertainty, respectively. As finite-temperature effects, such as ionisation potential depression, have a negligible impact on the BE for the temperatures reached in the experiment, these estimates were compared with the ambient M-shell binding energies documented in the NIST database [259]. The results were found to be compatible with these reference values.

Similarly to what has been done in Ref. [156], the M-shell feature can be exploited to estimate the sample temperature averaged over the beam pulse duration. However, contrary to Ref. [156], where the sample temperature is found by fitting the theoretical RIXS spectra to the experimental ones, here the DFT-computed density of accessible states ($\rho|M|^2$) can be directly fitted to the reconstructed $\tilde{\rho}_{\text{eff}}$:

$$[1 - f_{FD}(\epsilon; T)]\rho_{\text{DFT}}(\epsilon)|M_{\text{DFT}}(\epsilon)|^2 \stackrel{!}{=} \tilde{\rho}_{\text{eff}}(\epsilon) , \quad (4.1)$$

where the chemical potential must be computed self-consistently. This new procedure enables us to reduce the error bars on the temperatures estimates compared to the previous work, yielding temperatures of (6.1 ± 0.2) eV for Fe and of (5.2 ± 0.2) eV for Fe_2O_3 . These estimates justify the implicit assumption that depopulation of the M-shell is given mainly by thermal collisions (and not by photoionisation), and therefore can be described by the factor $(1 - f_{FD})$. The fitting process, based on Eq. (4.1), is performed using the curve-fitting function from Python's SciPy library [264], which also provides uncertainty estimates for the temperatures by propagating the uncertainties in $\tilde{\rho}_{\text{eff}}$. As observed in Ref. [156], these extracted temperatures provide a good estimate of the peak temperature reached in the target during the irradiation, as this dominates the photoemission. This observation is essentially due to the exponential dependence of the accessible/vacant states on the sample temperature.

Comparison with Flat Crystal and Seeded Mode Data

To validate the consistency of the results obtained in the previous section, the DOS for iron was extracted from data acquired using the flat crystal spectrometer with the XFEL in seeded mode, as well as the von Hámos spectrometer with the XFEL operating in

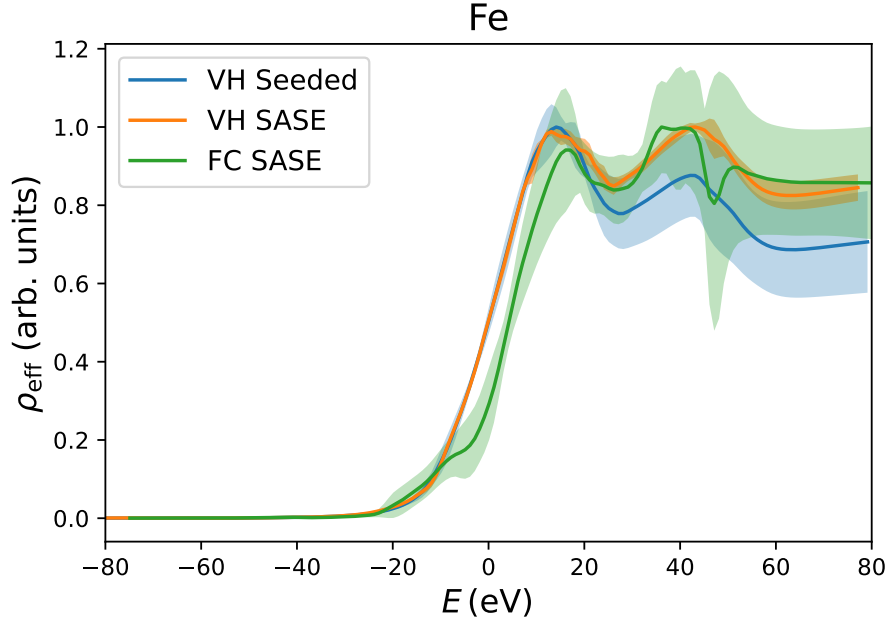


Figure 4.8: A comparison of the iron ρ_{eff} extracted from data obtained using the von Hámos spectrometer with the XFEL operating in seeded mode (orange) and SASE mode (blue), as well as from the flat crystal spectrometer with the XFEL in SASE mode (green). The shaded bands indicate the standard deviation, as seen for Fig. 4.5.

both seeded and SASE modes. The reconstructed Fe ρ_{eff} for these three experimental configurations are shown in Figure 4.8.

The extractions and their uncertainties were calculated following the same procedure described for Figure 4.5, using six independent fitting processes for each configuration. For the FC data, the ρ_{eff} was smoothed over a 2 eV energy scale, corresponding to the typical noise oscillation width in the averaged RIXS spectra of the flat crystal spectrometer (see Figure 4.4).

As observed from the uncertainty bounds, the three curves are consistent and align well with the behaviour of ρ_{eff} predicted by DFT calculations. Notably, the orange curve exhibits the smallest uncertainty bounds and is the only curve that remains within the error bounds of the other two. This observation supports our decision to use RIXS spectra recorded with the VH spectrometer and the XFEL in SASE mode for the following analysis.

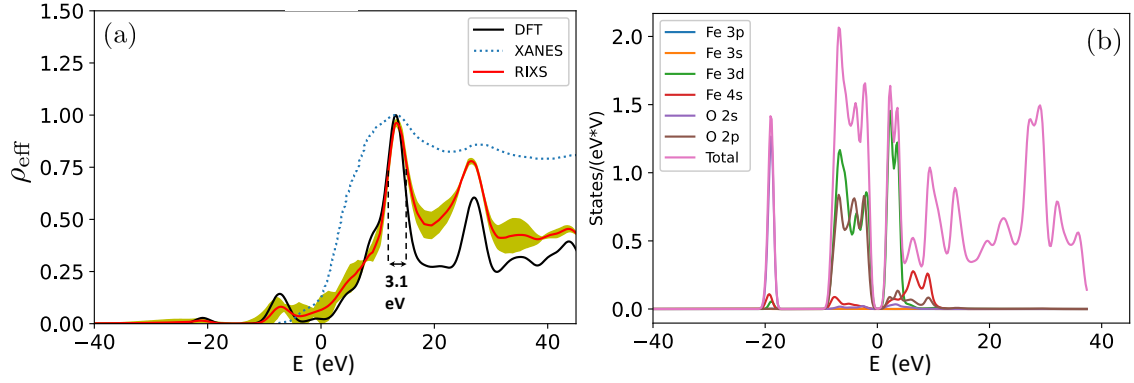


Figure 4.9: (a) Reconstructed ρ_{eff} for FeO, obtained after deconvolving the spectrometer instrument function (see Fig.4.2) from the RIXS spectra. The reconstructed data is compared with theoretical DFT calculations, for which a smearing width of 3 eV was used, and with XANES measurements reported in [148]. Uncertainty bounds are calculated and presented following the same methodology as in previous figures. (b) Orbital-projected and total DOS of FeO calculated from DFT simulations. Note that the energy range used in the calculations extends up to approximately 10 eV for the projected DOS and 40 eV for the total DOS.

4.2.3 Electronic Structure of Warm-Dense FeO with “Ultra-High” Resolution

Fig.4.9a shows the extracted ρ_{eff} for FeO, obtained by fitting approximately 6,000 RIXS spectra after deconvolving them from the measured von Hámós instrument function. Since individual RIXS single-shot spectra are too noisy for reliable deconvolution, the spectra were grouped into averaged sets of 20 shots each to improve the signal-to-noise ratio. The deconvolution was performed using Python’s built-in Richardson-Lucy algorithm on this averaged dataset, containing now about 300 spectra. Then, the reconstruction of ρ_{eff} and its uncertainties was carried out following the same procedure described for Figures 4.5-4.8 on this “deconvolved” dataset.

The extracted ρ_{eff} (red curve) is compared with DFT calculations (detailed in Sec.4.2.1) and with XANES measurements from [148]. The comparison with XANES effectively demonstrates how the RIXS-based methodology achieves a higher-resolution absorption spectrum than conventional XANES, as anticipated in the theoretical discussion (Sec. 3.2). Additionally, the comparison with the DFT-computed ρ_{eff} reveals good agreement with the experimentally-derived electronic structure, providing also estimates for both the sample temperature and the resolution of the reconstructed ρ_{eff} . These values were obtained using

the methods outlined for Fe and Fe₂O₃, yielding a temperature of 5.5 ± 0.3 eV and a resolution of approximately 3 eV - narrower than the spectrometer's instrument function (5.5 eV). This improved resolution highlights the effectiveness of deconvolving the instrument function from the RIXS spectra, surpassing the spectrometer's intrinsic resolution limits and enabling finer details in the valence bands of warm-dense FeO to be resolved.

Notably, around the chemical potential (set to 0 in Fig.4.9), the enhanced resolution reveals the characteristic bandgap of FeO, approximately 2.4 eV [258]. While this bandgap is not fully resolved, it manifests as a distinct dip near 0 eV, underscoring the ability of this approach to identify fine structural features that govern the macroscopic properties of the material, such as its conductive or insulating behaviour. Applying this methodology to compressed FeO could potentially enable a direct experimental observation of a Mott transition in compressed iron oxide, which would be a significant result. The analysis of data for compressed FeO is the focus of the next chapter.

Fig.4.9b reports the DFT-computed projected and total DOS for FeO. The orbital-projected DOS reveals that the bandgap primarily arises from the energy splitting of the iron 3d orbitals, whose delocalisation is also responsible for the closure of the bandgap under high-pressure conditions. Additionally, the plot shows that the pre-edge peak, appearing approximately 20 eV below the chemical potential, correspond to the oxygen 2p states. The clear differences between the total DOS and the theoretical ρ_{eff} , plotted in panel (a) in blue, are due to the modulations introduced by the transition matrix elements $|M|^2$ and the thermal factor.

4.2.4 Electronic Structure of Warm-Dense Gadolinium

Gadolinium is a ductile and reactive rare earth element, crystallised in a hexagonal close-packed structure at room temperature. With an atomic number of 64 and an electronic configuration of [Xe] 4f⁷ 5d¹ 6s² gadolinium presents a partially filled f-orbital that contributes to interesting behaviour in various physical and chemical environments. While gadolinium primarily exhibits an oxidation state of +3 in its compounds—utilizing its 5d and 6s electrons for bonding—the seven unpaired 4f electrons give rise to remarkable magnetic characteristics [265]. Above 20 °C, gadolinium is a strong paramagnet, a property that underpins its widespread use in magnetic applications, including magnetic resonance

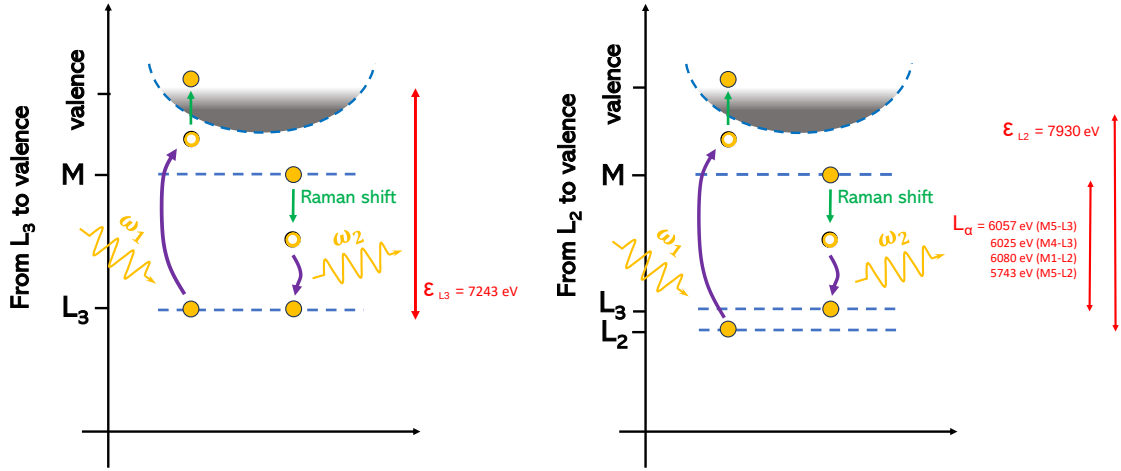


Figure 4.10: Scheme of the two RIXS channels utilised for gadolinium in the experiment, accompanied by a list of resonant energies involved in the process, as reported in [269].

imaging contrast agents [266] and magnetic refrigeration systems [267].

Beyond its magnetic properties, gadolinium is notable for its exceptionally high neutron capture cross-section [268], which suggests potential applications in nuclear technology as a neutron-capturing material, though it has not yet been utilised for this purpose. For this experiment, gadolinium was selected primarily because its absorption edges align closely with those of iron [269], providing a convenient additional benchmark for validating the RIXS-based methodology. However, the potential application of gadolinium in nuclear-related applications adds interest to studying its behaviour under extreme thermodynamic conditions, beyond the realm of fundamental material science.

RIXS in Gadolinium

For RIXS in gadolinium, two distinct channels were used in the experiment, illustrated schematically in Figure 4.10. In the first channel (left diagram), the central XFEL photon energy is tuned just below the Gd L_3 absorption edge (7243 eV) to induce a RIXS process analogous to that employed in iron compounds. The only difference lies in the electronic transitions involved: the excited electron comes from an L_3 state, and the resulting hole resides in the M-shell. For this channel, two incoming photon energies were selected: the same value used for iron (7050 eV) and 7150 eV.

The second channel is identical to the first, except that the excited electron originates

from the L_2 shell instead. Consequently, the XFEL energy was set slightly below the L_2 absorption edge (7930 eV), specifically to 7850 eV and 7900 eV. These four sets of RIXS spectra, corresponding to the different incident photon energies, can be jointly analysed within the STEP framework, effectively enhancing the performances of the deconvolution process.

Equations (3.17) and (3.23), used to model the RIXS process, are still valid but incorporate different physical parameters (e.g., A_f) specific to gadolinium, as well as modifications to account for the new electronic transitions involved in the scattering. In particular, in this case, there are four possible final states f , each corresponding to an $L\alpha$ line (see Fig.4.10). The gadolinium-specific parameters appearing in the RIXS cross-section were taken from Ref. [269].

Figure 4.11 displays the averaged RIXS spectra for the two lowest central photon energies. The plot highlights how the RIXS features, reflecting the electronic structure, shift along the Lorentzian profiles centred at the resonance lines (in purple in the plot) by an amount corresponding to the change in the incident photon energy. To align the energy window detected by the von Hámos spectrometer with the energies of the outgoing RIXS photons in gadolinium, the spectrometer's position was adjusted using a motorised stage and the calibration was repeated.

The RIXS process in gadolinium exemplifies the versatility of this scattering technique, demonstrating its applicability to various initial, intermediate, and final states, provided that specific conditions are satisfied.

Experimental Results

In Fig. 4.12a, the ρ_{eff} of gadolinium reconstructed from the RIXS spectra is shown. The calculation of ρ_{eff} and its uncertainties were performed with the same methodology used for the other materials, combining Gd RIXS spectra obtained with the different incident photon energies, totaling approximately 4,000 shots. The averaged RIXS spectrum for an incoming photon energy of 7050 eV is shown in Fig.4.12b, alongside the reconstructed spectrum corresponding to the extracted ρ_{eff} . This plot is representative of the level of fitting accuracy attained on the RIXS spectrum during the extraction process, as it is consistent with the levels achieved across the various materials and conditions.

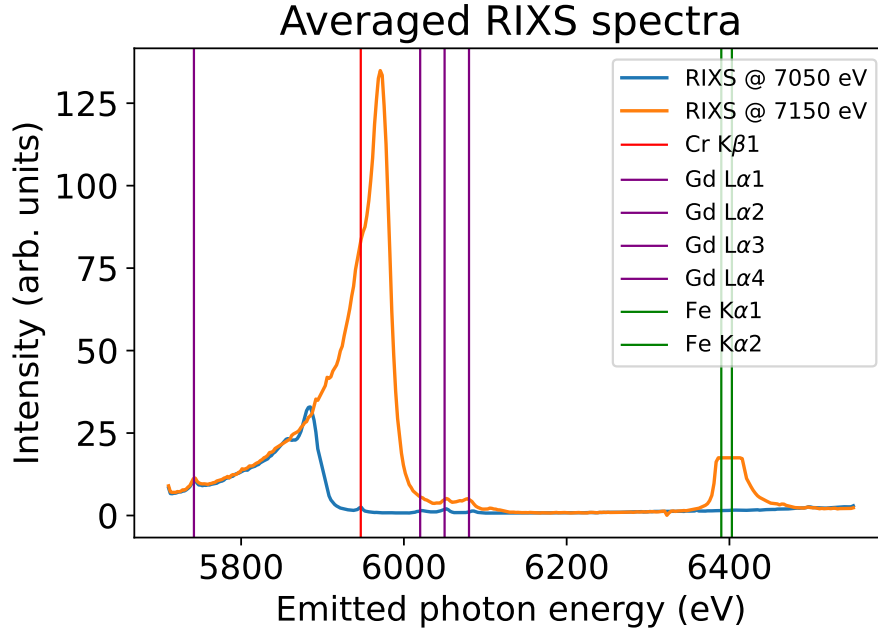


Figure 4.11: Averaged RIXS spectra of gadolinium for two central photon energies on target. The plot also shows the relevant resonant lines, including those coming from chromium and iron impurities. Chromium was used for the calibration of the VH spectrometer during the experiment. The iron $K\alpha$ lines have been cut in this plot as part of the image processing steps.

The extracted ρ_{eff} was compared to DFT calculations, demonstrating strong agreement and confirming the method’s capability to reconstruct electronic structures with complex profiles. The sample temperature and the resolution of the extracted ρ_{eff} were estimated using the same methods as for the other materials, yielding a temperature of 4.2 ± 0.6 eV and a resolution of approximately 6 eV. The slightly larger uncertainty in the temperature is attributed to the reduced separation between the bound and valence states in gadolinium compared to previous cases, which diminishes the sensitivity of the RIXS signal from these states to temperature variations. In Gd, the bound states are located around -30 eV and correspond to the $5p_{1/2}$ and $5p_{3/2}$ orbitals, as indicated by orbital-projected DOS and tabulated data [215].

4.3 Summary

This chapter presented the analysis of experimental RIXS spectra for warm-dense Fe, FeO, Fe_2O_3 , and Gd. The extracted electronic structures show good agreement with DFT cal-

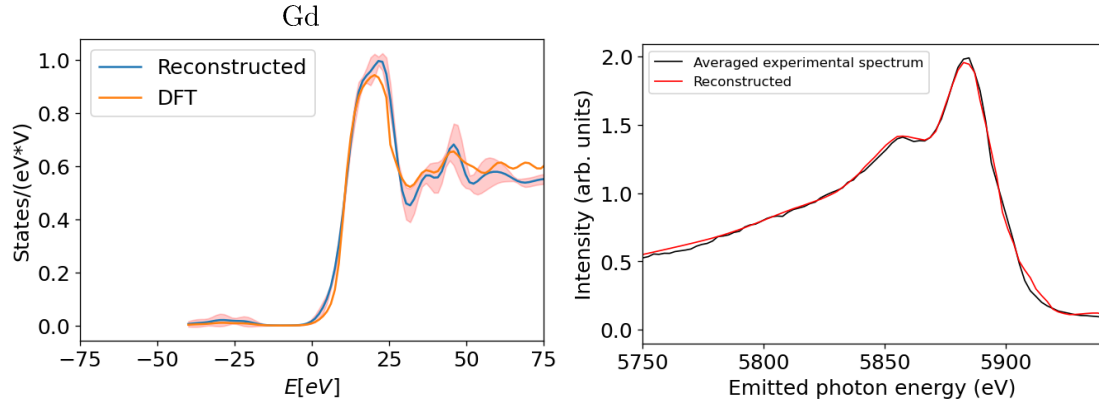


Figure 4.12: (a) ρ_{eff} for gadolinium extracted from the RIXS spectra. The reconstructed electronic structure is compared with theoretical DFT calculations, for which a smearing width of 6 eV and a temperature of 4.2 eV were used. Uncertainty bounds are calculated and presented following the same methodology as in previous figures. (b) The averaged experimental RIXS spectrum for gadolinium, shown alongside the reconstructed spectrum associated with the extracted ρ_{eff} . Only the interval of the spectrum relevant for the fitting is illustrated.

culations and reveal distinct patterns across the different materials. These distinctions are also made possible by the enhanced resolution provided by the STEP extraction scheme, which overcomes the limitations imposed by the source bandwidth. Ultimately, by deconvolving the instrument function from the RIXS spectra, resolutions of a few eV—exceeding even the spectrometer’s intrinsic resolution—were achieved. These high resolutions make it possible to detect fine features near the chemical potential, such as bandgaps, which play a crucial role in determining a material’s behaviour. Alongside the valence structure, the reconstructed DOS also include bound states, enabling relatively accurate estimations of sample temperatures and binding energies. Beyond the range of physical quantities accessible with this RIXS-based technique, its successful application to diverse materials underscores the flexibility of this method, which can exploit various electronic excitations.

Chapter 5: RIXS for Dynamically Compressed Systems

This final chapter examines the use of RIXS to study laser-compressed materials, representing a key application of this methodology. This objective exploits RIXS’s ability to capture a material’s electronic structure in just a single snapshot, highlighting its potential for time-resolved studies, particularly of irreversible physical processes like laser compression. This capability holds significant promise as a diagnostic tool during capsule implosion in inertial confinement fusion research.

On the other hand, when investigating irreversible physical processes, the number of shots that can be recorded is often limited. This constraint poses a challenge for RIXS, given its relatively low cross-section, which can introduce significant noise into the averaged RIXS spectra and, consequently, into the extracted electronic structures.

This chapter analyses the RIXS spectra of compressed FeO, recorded during an experiment conducted in July 2021 at the Matter in Extreme Conditions (MEC) instrument of the LCLS facility [159]. The analysis begins with a review of the experimental setup, with a focus on the diagnostics used to assess the pressure conditions and crystalline structure of the compressed targets. Following this, the electronic structures reconstructed from the RIXS spectra are examined, comparing results from ambient conditions to those under compression. The aim is to retrieve the experimental evidence of the bandgap closure predicted by theoretical models.

As will be shown, while the data reveal trends consistent with bandgap closure, the poor SNR, which causes a low resolution in the extracted ρ_{eff} , limits the precision of the results. Although these preliminary findings are not yet suitable for publication, they demonstrate the potential of this technique for such investigations, especially considering the ongoing

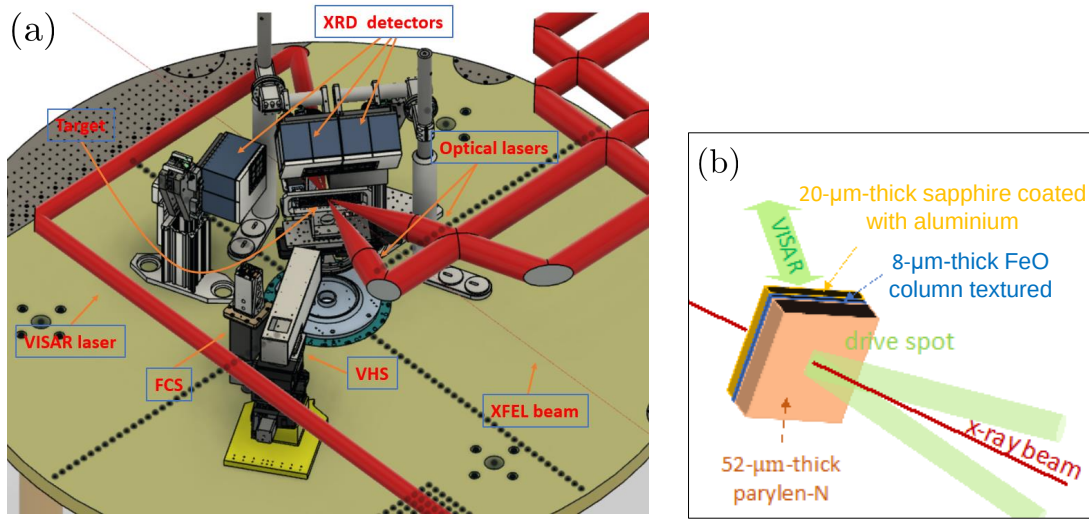


Figure 5.1: (a) A CAD model of the LCLS experimental setup, including laser beam paths and the main diagnostics. For clarity, the optics used to deflect the laser beams are not shown. The optical laser is split into two arms, further amplified, and recombined on the target at 20° and 50° angles relative to the sample normal. The target holder was specifically designed to ensure both the laser arms could illuminate the target during each shot. (b) Structure of the targets employed for the compressed shots.

technological advancements that promise to improve the SNR of RIXS spectra.

5.1 Experimental Setup

In Figure 5.1a, the experimental setup of the LCLS experiment is shown, highlighting the key beam paths, including the XFEL, the optical laser used for compression, and the VISAR laser, which is discussed in more detail in the next section. The optical laser is a Nd:glass laser system operating at 527 nm, which can be moulded to the required pulse length and shape using an electro-optical modulator, with durations ranging from 2 ns up to 200 ns [159]. For this experiment, a simple flat-top pulse shape with a duration of approximately 10 ns was employed, focused to a $250\ \mu\text{m}$ spot size using focal-length singlet lenses and incident at an angle of 35° . Synchronisation with the XFEL, achieving time precision on the order of 10 fs, is possible using the beamline instruments outlined in [270]. The laser energy was varied between 40 and 60 J to generate different pressure conditions.

For the compressed shots, the XFEL was tuned to a central energy of 7070 eV, just below the Fe absorption edge, and operated in seeded mode. To minimise heating of

the target, the XFEL beam was defocused to approximately $60\text{ }\mu\text{m}^1$ and was used solely to probe the compressed target via the RIXS mechanism. It is important to note that the XFEL at LCLS includes a third harmonic component of the fundamental photon frequency, with an intensity approximately 1% of the fundamental. These higher-energy photons, exceeding the absorption edge, induce $K\alpha$ photodecays that can obscure the RIXS signal. To mitigate this issue, the central XFEL energy must be set sufficiently below the absorption edge, effectively shifting the RIXS spectrum away from the $K\alpha$ lines and preventing spectral overlap.

The RIXS photons were detected in reflection geometry using the same diagnostic setup as in the EuXFEL experiment but with a different von Hámos spectrometer, which, along with the flat crystal spectrometer, was designed and built in Oxford. As in the EuXFEL experiment, this von Hámos spectrometer features a RoC of 80 mm and a thickness of $40\text{ }\mu\text{m}$, and it was paired with an ePix100 detector. The resolution of the spectrometers in this experiment was determined by comparing the measured widths of the $K\alpha$ lines with their tabulated values. The resolution was found to be 2.2 eV for the flat crystal spectrometer and 6.1 for the von Hámos spectrometer. For analysing the compressed data, where few shots are available, exclusively the von Hámos measurements will be used, as the flat crystal spectrometer lacks sufficient SNR for this limited dataset.

In addition, x-ray diffraction patterns were recorded in transmission geometry for each shot using four CSPAD detectors. These diffraction patterns were used to determine the crystalline structure of the compressed samples under various pressure conditions, including phase transitions and melting points along the Hugoniot curve. Correlating changes in the ionic structure with those in the density of states is crucial for understanding the interplay between electron and ion dynamics in iron oxides. A dedicated section will discuss the XRD analysis in more detail.

A schematic cross-section of the target is shown in Figure 5.1b. The targets consisted of multiple layers: a $52\text{ }\mu\text{m}$ plastic ablation layer designed to smooth irradiation non-uniformities and steepen the variable ramp compression into a shock before impinging on the target, a $8\text{ }\mu\text{m}$ FeO sample layer², and a $20\text{ }\mu\text{m}$ sapphire window layer. This final

¹Excessively decreasing the XFEL beam size can degrade measurement resolution due to source broadening.

²This chapter focuses on FeO as it represents an interesting case and serves as a proxy for Fe and Fe_2O_3 ,

layer is used for the pressure calculations, together with the VISAR system, employing the impedance matching technique. This layer was coated with aluminium to provide a reflective surface for VISAR measurements. Another aluminium flash coating (200 nm thick) was applied to the front face of all samples to minimise preheating from x-ray radiation emitted by the ablated plasma. Note that, due to the strict resonance conditions required for RIXS to occur, none of these other layers would produce RIXS photons that could affect the signal from the sample.

To perform the XRD analysis, the FeO samples were grown in a Fe (111) *fibre texture*, meaning that the polycrystallites comprising the sample are oriented with their normal closely aligned to the Fe (111) direction, though they remain randomly distributed in terms of their angular orientation around this axis. This fiber texture effectively rotates the reciprocal lattice of the FeO crystal around the Fe (111) axis, creating circumferences around this axis for each reciprocal lattice point (some of which may coincide).

As long as the x-ray beam is not aligned too closely to the fiber axis (in our experiment, a 35° angle of incidence was used), some of these circumferences intersect the *Ewald sphere* [58], resulting in bright spots along the *Debye-Scherrer* rings. During compression, as the lattice undergoes deformation, these diffraction spots generally move, shedding light on active slip systems and how the target relieves shear stress under uniaxial compression [55]. If the sample were composed of randomly oriented crystallites (as in a powder), the entire Debye-Scherrer rings would be illuminated due to diffraction interference, making it impossible to analyse the movement of individual diffraction spots. On the other hand, using a single crystal would make observing diffraction spots extremely challenging due to the unlikely intersections between the reciprocal lattice points and the Ewald sphere.

5.1.1 VISAR Diagnostic

As outlined in the Introduction, the pressure of the compressed system can be determined using Hugoniot's equations, provided the shock velocity and particle velocity behind the shock are known. These two quantities are measured using the Velocity Interferometer System for Any Reflector (VISAR), whose functioning now discussed.

The primary purpose of VISAR is to determine when the shock wave emerges from

which were also studied during this experiment.

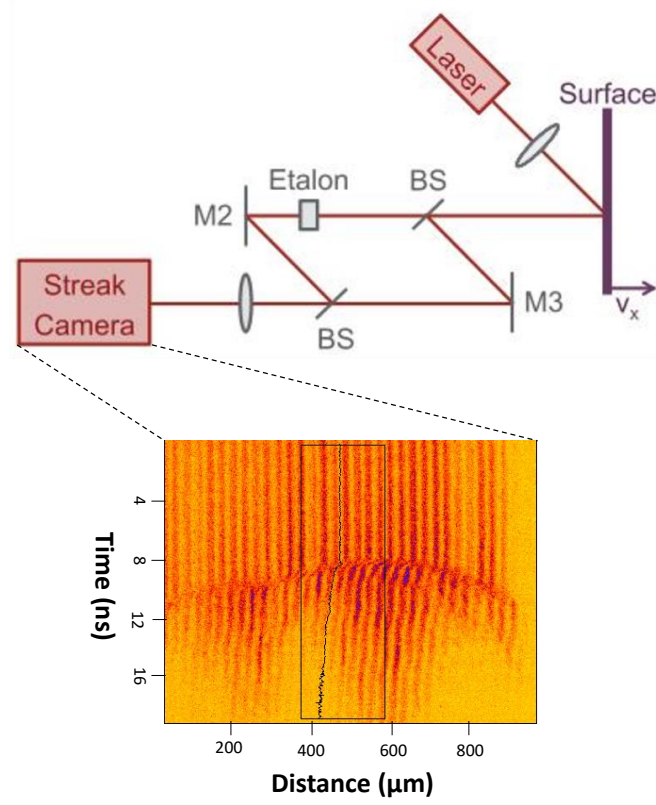


Figure 5.2: Scheme of the VISAR system with an example of a streak camera image from an experimental shot. In this image, a region of interest is displayed as a black rectangle together with the trajectory of a single fringe (solid black curve).

the rear surface of the sample and the velocity at which this interface begins to move. By measuring the time it takes for the shock to traverse the target and knowing its thickness, the shock velocity, U_S , can be calculated. At the same time, the interface velocity (also referred to as the free-surface velocity when the back of the sample is in direct contact with the vacuum) can be related to the particle velocity behind the shock. When the shock reaches the rear surface, a rarefaction wave propagates back into the target, resulting in a pressure release. By analysing this relaxation, the interface velocity, U_I , can be connected to the particle velocity, U_P , using the following relation [271]³:

$$U_I = U_P + \int_{V(p_i)}^{V(p_f)} \left(\frac{dp_s}{dV} \right)^{1/2} dV, \quad (5.1)$$

where p_i is the shock pressure, p_s is the pressure along the release path, p_f is the released pressure, and V is the sample volume. Then the others physical quantities can be found

³In many cases, the approximate relation $U_I = 2U_P$ is used.

through the Rankine-Hugoniot equations (see Eqs. 1.10). In practise, via many measurements over the years, there now exists a series of equation-of-state tables, making necessary only the measurement of U_P .

The scheme of the VISAR used in this experiment is shown in Fig. 5.2, alongside an example of an experimental VISAR image. Various implementations and versions of the VISAR system exist, each tailored to different physical contexts [45]. For this experiment, a line VISAR was employed, enabling the measurement of velocity profiles of a sample interface along one dimension (1D VISAR), so that shock planarity can be investigated.

The VISAR system operates by directing a laser beam onto a moving reflective surface. The reflected beam is then split into two paths of different optical lengths, which are recombined on a streak camera to produce an interference pattern. This configuration enables the two beams to sample the position of the reflective surface at two different time points, separated by the optical delay between the paths. The optical delay is introduced using a combination of the refractive delay from an etalon filter and, in some cases, an additional translational offset of a mirror (M2 in the figure) perpendicular to its plane. The streak camera records the central slit region of the field of view and sweeps this signal over time across the output detector. Changes in the interference pattern over time provide information about the velocity history of the central strip of the reflective surface.

When the reflective surface is stationary, the interference pattern consists of fringes parallel to the time axis (see the upper part of Fig. 5.2). This background pattern is achieved by slightly tilting one of the mirrors so that rays from the same beam travel slightly different distances before reaching the detector. The spatial frequency of this fringe pattern is determined by the mirror tilt and is typically adjusted to produce 20–30 fringes across the output image (as shown in Fig. 5.2). A shift in the fringe pattern corresponds to the motion of the reflective surface. Therefore, to determine the velocity profile, the magnitude of the fringe shift for each spatial point must be analysed, as shown in Fig. 5.2, where the trajectory of a single fringe over time is marked with a solid black line.

From this curve $U_{fr}(t)$, the interface velocity at that position can be calculated with the following transformation:

$$U_I(t) = \frac{\lambda_L}{2\tau(1 + \delta)} U_{fr}(t) = \text{VPF}_0 U_{fr}(t) , \quad (5.2)$$

where λ_L is the wavelength of the laser light reflected from the surface, τ is the temporal delay between the two arms of the interferometer, and δ is a correction factor accounting for the chromatic dispersion in the etalon. The term VPF_0 is the so-called velocity per fringe. A derivation of this formula, along with a more in-depth analysis of this measurement procedure, can be found in [272, 273].

In many experiments, including ours, a transparent window is placed to the rear surface of the sample, allowing the shock wave to propagate into the window rather than breaking out into a vacuum. As described in Section 1.2.1, such windows are often necessary to sustain pressure in the material of interest over a longer duration, preserve interfacial reflectivity, or to better characterise a reflecting shock. When observing the sample through a transparent window, a correction factor must be applied to Eq. 5.2 to account for the change in the refractive index as the laser beam passes through the window:

$$\text{VPF} = \text{VPF}_0/a , \quad (5.3)$$

where a is the constant term in the expression of the window's refractive index n , which is assumed to scale linearly with the window's density ($n = a + b\rho$). When a window is present, to establish the relationship between the measured velocities and the thermodynamic quantities, an impedance matching analysis is required (see Section 1.2.1).

From the example VISAR image in Fig. 5.2, one can determine the shock breakout time—the moment the shock reaches the back surface of the sample—by identifying the first shift in the fringe pattern. This breakout time is critical not only for calculating the shock velocity but also for determining the required delay between the XFEL and the optical laser to ensure that the XFEL probes the sample under uniform compression. Additionally, the image reveals the slight deviations in shock planarity and the region of the sample illuminated by the optical laser, which provides valuable information for aligning the optical laser with the XFEL beam.

In this experiment, pressure conditions were determined using two VISAR systems with sensitivities of 4.5241 and 1.9890 km s⁻¹ fringes⁻¹ and acquisition time windows of 10 and

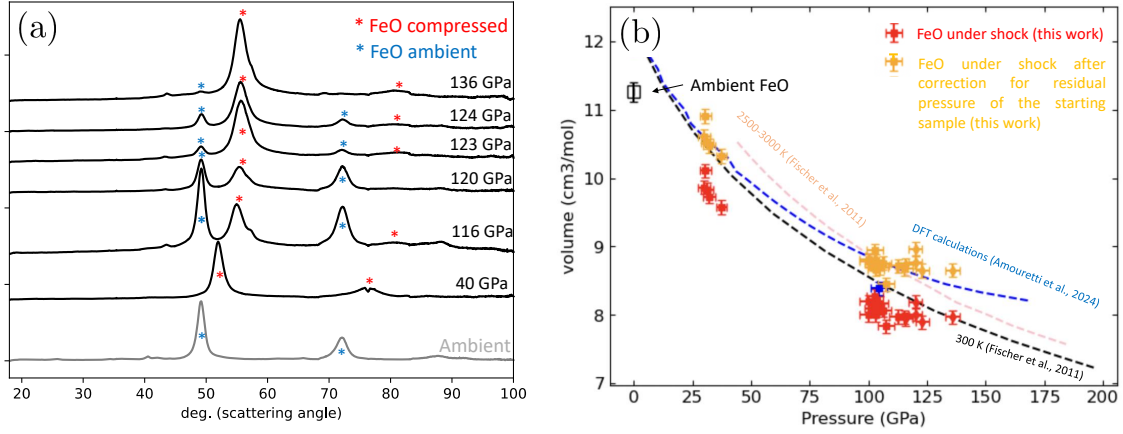


Figure 5.3: (a) XRD profiles of FeO under different pressure conditions (calculated using the VISAR system) (b) Volume measurements as a function of pressure, derived from the positions of diffraction peaks. These data are compared with various theoretical predictions of the Hugoniot curve in the $v - p$ plane [274, 275]. The plots are provided courtesy of Dr. Céline Crépinsson.

20 ns (see Fig. 5.2), respectively.

5.2 Results

The key aim of the experiment was to field XRD and RIXS diagnostics simultaneously, for the first time, to probe the changes of electronic and ionic structures of iron oxides under dynamic compression. In this section, the results of the experiment are presented, beginning with a brief discussion of the XRD analysis and the evolution of the ionic structure under pressure. The focus is then shifted onto the RIXS data obtained from compressed samples, providing insights into their electronic structure.

5.2.1 XRD Analysis

X-ray diffraction was employed to investigate possible phase transitions occurring as a function of pressure and to provide information on the ionic structure of the system. Figure 5.3a presents the XRD profiles of FeO at various pressure conditions, obtained through azimuthal integrations of 2D diffraction images recorded by the CSPAD detectors. These integrations included corrections for solid angle coverages, detector filter effects, polarisation, and self-attenuation in the sample. When such corrections were not feasible, the integration was performed using the Dioptas software, which relies on the PyFai library [276],

incorporating solid angle and polarisation corrections.

The XRD pattern recorded at ambient conditions prior to the shock is shown in grey for reference, corresponding to a rock-salt lattice structure (face-centred cubic with one iron and one oxygen atom per unit cell). Considering the orientations of the XFEL and the sample texture, this lattice exhibits two main peaks associated with the (200) and (220) planes. Upon compression, these peaks shift toward higher angles (red stars), due to the reduction of lattice parameters. Compressed samples also exhibit significant peak broadening, indicative of reduced crystallite size and increased micro-strain (lattice parameter fluctuations) under high-pressure conditions [277]. Due to timing fluctuations and challenges in synchronizing the XFEL and the optical laser, as well as potential x-ray halo irradiating unshocked material, the probed sample includes varying portions of ambient or released material. This accounts for the persistent presence of more or less intense ambient peaks (blue stars), which remain unchanged in position during compression. Minor peaks, such as the one around 43° (not labelled), are attributed to ambient and compressed Fe_3O_4 , an impurity resulting from the sample fabrication process.

Le Bail refinements [278] were performed on the XRD profiles to determine the lattice parameters and corresponding sample volume under various pressures. Figure 5.3 illustrates the results of this analysis, displaying the v - p data points with associated uncertainties. Ambient data points are shown as black crosses, while compressed data are represented by red and yellow crosses, with the latter corrected for residual pressure in the initial sample. This residual pressure arises from stresses induced during the fabrication process, which reduce the FeO unit cell volume. The corrections were quantified by comparing the ambient XRD data with those obtained from a recrystallised (stress-free) FeO crystal. The experimental v - p data points were compared with theoretical predictions [274, 275], showing good agreement.

As the rock-salt lattice was used as the underlying structure for the Le Bail refinements across all pressures, this analysis demonstrates that FeO retains its ionic structure during dynamic compression up to 136 GPa. The unit cell undergoes compression without any structural phase transitions, indicating an apparent independence between the ionic and electronic transitions, which are examined in the following section.

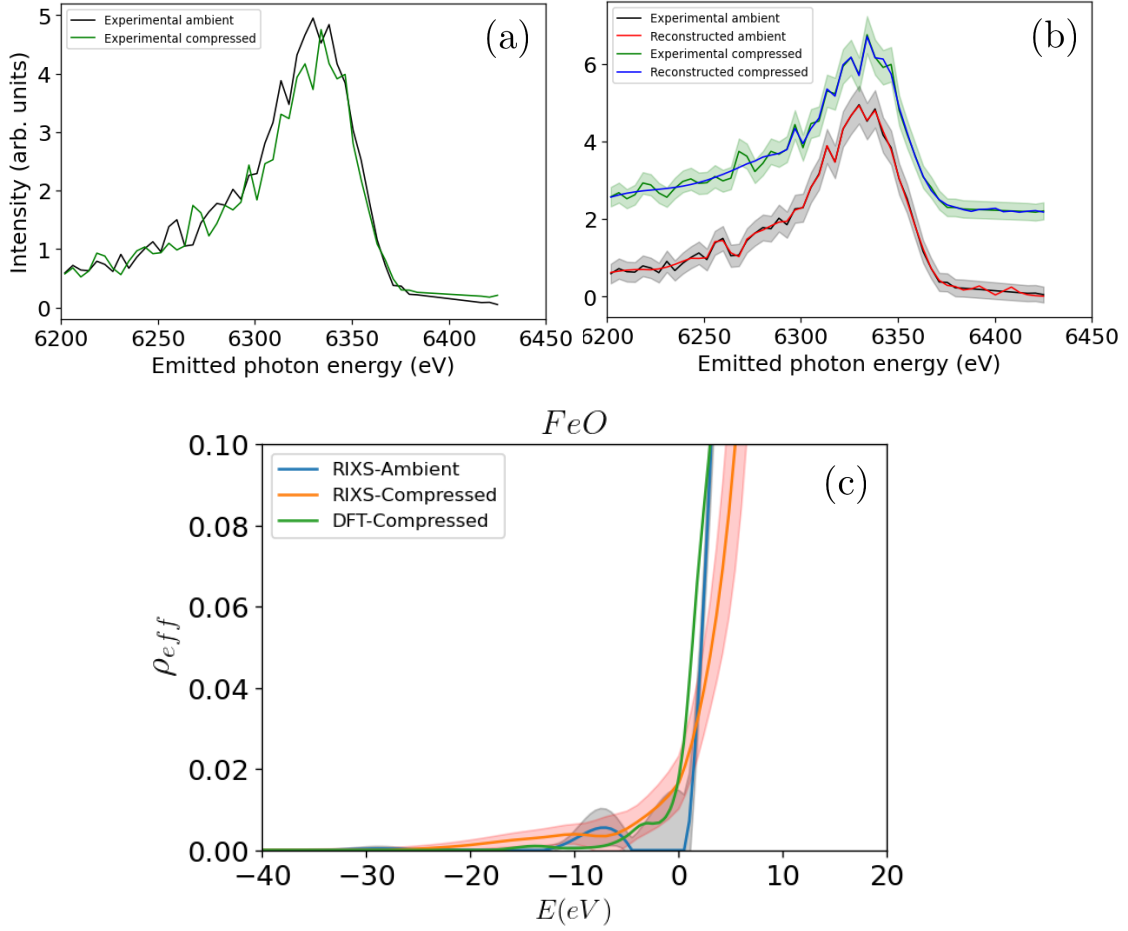


Figure 5.4: (a) Averaged RIXS spectra for compressed and ambient conditions. (b) Averaged RIXS spectra with uncertainties indicated by shaded regions, plotted alongside their corresponding STEP reconstructions. For clarity, the spectra for compressed and ambient cases are offset by 2 units. The spurious $K\alpha$ lines were removed from these averaged spectra. (c) Reconstructed ρ_{eff} for both conditions, with uncertainties, including a comparison of the compressed ρ_{eff} with DFT calculations (green solid curve).

5.2.2 Electronic Structure of Compressed FeO

Figure 5.4 shows the results of the RIXS analysis conducted on 18 shots of FeO compressed to 100 ± 5 GPa, as determined using VISAR, alongside 18 reference shots of the uncompressed target. Panel (a) displays the averaged RIXS spectra for the compressed and ambient conditions. Despite the presence of noise, systematic differences between the two curves are evident, reflecting variations in the DOS occurring upon compression. On the other hand, the noise in the averaged spectra highlights that the reconstructed electronic structures are inherently affected by this non-physical disturbances. The spurious $K\alpha$ lines, originating from the XFEL third harmonic, were fitted using the averaged spec-

tra and subsequently subtracted from each individual spectrum. In Fig. 5.4, the spectra are plotted with the $K\alpha$ lines already subtracted.

Panel (b) shows the averaged spectra with their uncertainties, alongside the corresponding reconstructions, representing the RIXS spectra associated with the extracted ρ_{eff} for both conditions. Unlike the cases analysed in Chapter 4, the uncertainties here are not negligible due to the limited number of shots. These uncertainties, computed using the methods detailed in Chapter 2, must be propagated to the ρ_{eff} extracted from these RIXS spectra. A procedure for this propagation is described in the next section. Notably, the high accuracy achieved in reconstructing the spectra, facilitated by the narrow bandwidth of the seeded beam (the mode employed for collecting these data), also results in noise-fitting, leading to spurious features in the extracted ρ_{eff} , particularly in the higher-energy bands, for which the lorentzian factor suppresses the RIXS signal. To address this issue, the reconstructed ρ_{eff} , shown in panel (c), are zoomed around the chemical potential (set to 0), as this region is both less affected by noise and critical for observing Mott transitions. At this regard, a systematic closure of the bandgap is observed: repeated fittings of the ambient and compressed RIXS spectra (eight times for each condition) consistently produced a bandgap in the ambient case and none in the compressed case. The standard deviations of these reconstructions, combined with the propagated errors from the experimental RIXS spectra, were used to estimate the uncertainty in ρ_{eff} .

The reconstructed ρ_{eff} for the compressed case was compared with DFT calculations. As in previous analyses, to achieve agreement with the experimental curve, a smearing width of 5 eV was applied to the DFT-computed ρ_{eff} , and, a translational and multiplicative parameters were used to align and rescale the experimental reconstructions. The details of the DFT calculations are the same provided in Section 4.2.1 for FeO, with the key difference being that the lattice parameters of the underlying ionic structure were modified and calculated by minimizing the system enthalpy at the measured pressure of 100 GPa. This approach is justified by XRD analysis, which indicates that FeO does not change crystalline phase up to this pressure, but only modifies its lattice.

This reconstructed bandgap closure potentially represents the first direct experimental observation of the insulator-to-metal transition in FeO under compression, as predicted by simulations and inferred from indirect measurements. However, the reconstructed bandgap

of approximately 6 eV deviates from the documented value of 2.4 eV for ambient FeO [258]. This discrepancy likely arises from noise and, ultimately, the limited resolution of our measurements, resulting in significant uncertainties in the reconstructed ρ_{eff} . These large uncertainties make the experimentally obtained bandgap value compatible with documented references when error margins are considered. The resolution limitation is inherent to our setup and stems directly from the VH spectrometer’s resolution (6.1 eV), which prevents reconstruction of features below this energy scale like the FeO bandgap. Additionally, the poor SNR of our spectra further degrades the reliability of the reconstructions and precludes effective deconvolution of the instrumental function from the RIXS spectra, which would amplify the noise, making the extracted ρ_{eff} even more unreliable.

Nonetheless, the recovery of the expected trends and the compatibility of the experimental results with DFT calculations and literature references [136], including bandgap values, show great promises for these experimental techniques. Future experiments with higher-quality data are expected to yield more conclusive and precise results.

Propagation of the Uncertainties

To compute the uncertainties on ρ_{eff} due to the errors η on the RIXS spectrum I , one should process η with the operator P_{RIXS}^{-1} . Within the STEP framework, this task can simply be obtained by applying the extraction method to the two curves $I \pm \eta = I^{\pm}$. Once the two electronic structures associated with these slightly varied RIXS spectra have been computed - including an averaging over multiple fitting process to remove dependency on the random initialisation of NN - the error bounds on ρ_{eff} is given by these two curves, denoted respectively as ρ_{eff}^{+} and ρ_{eff}^{-} . This method assumes that, at least in the region of the function space confined between I^{+} and I^{-} , the operator P_{RIXS}^{-1} is convex, meaning that for every I confined between I^{+} and I^{-} , $\rho_{\text{eff}} = P_{\text{RIXS}}^{-1}(I)$ lies entirely between ρ_{eff}^{+} and ρ_{eff}^{-} . This assumption was tested by performing extractions for various I confined within this interval. As a final step, these uncertainties were then summed in quadrature with those coming from the random optimisation process.

5.3 Summary

This chapter discussed the first experiment to simultaneously investigate the evolution of the ionic and electronic structures of dynamically compressed FeO, using x-ray diffraction and resonant inelastic x-ray scattering, respectively. After a brief overview of the experimental setup with a focus on the VISAR system, used to measure pressures within the sample, the XRD data was presented. The analysis of this data revealed that up to ≈ 140 GPa, FeO does not undergo any crystalline phase transitions, but instead experiences only lattice compression. This compression, in turn, induces changes in the electronic structure, which were explored through the RIXS spectra, analysed using the STEP method. The analysis indicated a systematic bandgap closure consistent with theoretical predictions. However, the limited resolution of the reconstructed DOS, primarily due to the small number of RIXS spectra available, makes these results not ready for publication at this stage. Despite these limitations, the preliminary findings highlight the significant potential of these experimental techniques, with future experiments expected to provide more definitive and precise results.

This experiment also served as a proof of concept for employing RIXS as a time-resolved diagnostic tool for irreversible processes in HED science. This is particularly relevant for fusion research, where processes such as capsule implosions are prominent examples. Furthermore, the combination of XRD and RIXS techniques provides a powerful approach to examining the interplay between ionic and electronic structural changes in materials under extreme conditions.

Chapter 6: Conclusions and Future Perspectives

6.1 Summary

The main effort of this thesis was to establish a method for extracting high-resolution electronic structures of materials in extreme environments, where the inherent instability and non-reproducibility of thermodynamic conditions pose significant limits to the amount of data that can be collected. This method incorporates both the experimental technique to acquire the data and the methodology for its analysis. The experimental technique is based on the resonant inelastic x-ray scattering process. As shown in Chapter 3, the spectrum of photons scattered by the material encodes rich information about its electronic structure, though in a complex manner. Extracting electronic structures from RIXS spectra involves inverting a complex and ill-conditioned operator—a challenge further compounded by the relatively low SNR of the spectra. To address this, a novel methodology was devised, combining machine learning with differentiable physical modelling. This approach, detailed in Chapter 3, enables the extraction of high-resolution DOS by deconvolving the source spectrum, which must be measured on a shot-to-shot basis and correlated with the corresponding RIXS spectra. This framework, introduced as a generalised method for extracting physical quantities embedded in experimental measurements described by complex but known physical operators, was named STEP (Surrogate Training Embedded in Physics). For the RIXS case, besides the reconstruction of DOS, this methodology also allows for the estimation of scalar quantities like the sample temperature.

The extraction of density of states and thermodynamic conditions with this method was first tested on synthetic RIXS data. These tests demonstrated good performance, particularly in terms of robustness to noise, when compared to more traditional numerical approaches. Subsequently, the RIXS-based methodology was applied to the analysis of

experimental RIXS spectra, as presented in the final two chapters. Chapter 4 detailed the analysis of RIXS spectra collected at the EuXFEL facility from isochorically-heated samples of Fe, FeO, Fe₂O₃, and Gd. This highlights the flexibility of the method, which is capable of studying a wide range of materials through different electronic excitations. The extracted electronic structures showed good agreement with DFT calculations, revealing distinct patterns across the various materials. These distinctions were made possible by the enhanced resolution achieved by the methodology, which overcomes the limitations imposed by the source bandwidth and, ultimately, the spectrometer’s instrument function, reaching resolutions down to a few eV. Such resolutions enabled the detection of fine features near the chemical potential, including bandgaps, which are critical for determining a material’s behaviour. In addition to valence structures, the reconstructed DOS also included bound states, facilitating relatively accurate estimations of sample temperatures and binding energies.

Chapter 5 presented the analysis of RIXS spectra of compressed and ambient FeO, collected at the LCLS facility during the first experiment to simultaneously study the ionic and electronic structure evolution of dynamically compressed samples using XRD and RIXS. This combination of techniques offers a powerful approach for examining the interplay between ionic and electronic changes under extreme conditions and demonstrates the potential of RIXS as a time-resolved diagnostic tool for irreversible processes in HED science. XRD analysis revealed that, consistent with theoretical predictions [136], FeO undergoes lattice compression without crystalline phase transitions up to ≈ 140 GPa. However, this compression drives changes in the electronic structure, evidenced by the extracted DOS from the RIXS, which revealed a systematic bandgap closure. While this behaviour aligns with existing literature [136], the limited resolution of the reconstructed DOS, due to the small dataset, prevents precise and conclusive results. In spite of this, future experiments, leveraging technological advancements, are expected to provide higher-quality data and more definitive insights (see also Section 6.3).

As a complementary subject, the second chapter of this thesis detailed methods for constructing spectra from camera images while enhancing their SNR and possibly their resolution. These techniques, while broadly applicable, are particularly valuable for HED science and our investigations, where low signal levels often characterise the data.

6.2 Outlook: Methods for Improving the SNR and Resolution of Camera Images

A first straightforward improvement to the routine introduced in Chapter 2 for constructing spectra from camera images is the inclusion of instrument function deconvolution, as described in Section 2.2.3. The IF can either be measured experimentally (see Section 2.2.3) or approximated using theoretical models. This deconvolution would mitigate the resolution losses due to source broadening and finite width of the crystal rocking curve, leaving only pixel-size-related effects, which can be partially addressed using the RL deconvolution, especially in regions with high photon densities.

Another enhancement, which would address pixel-size limitations, could involve incorporating centroid calculations for single-photon clusters, as described in Ref. [171], into the photon-counting algorithm. This approach would enable subpixel resolution in regions with low fill fraction λ , complementing the RL deconvolution. Detectors with small pixel sizes should be chosen to fully exploit these techniques, which could be useful also to refine the energy map calibration, as discussed in Section 2.2.1.

Within the photon-counting workflow, another avenue for improvement is the implementation of multiphoton cluster identification algorithms. These algorithms could enhance the accuracy of the analysis in regions with intermediate values of λ by expanding the set of valid cluster shapes to include those produced by multiple photons or by incorporating more advanced clustering techniques [279].

Finally, the photon counting algorithms could benefit from optimisation to improve computational efficiency. Currently, the photon counting takes approximately 8 minutes to analyse a 2048×2048 image, which is quite time-consuming, even for post-analysis. Reducing the runtime of these algorithms would significantly enhance their practical utility. One potential approach is to parallelise the analysis by distributing different regions of the image across multiple processors.

6.3 Outlook: Improvements and New Applications of the RIXS-based Methodology

A natural refinement of the method for extracting the density of states, already mentioned in Chapter 3, is incorporating the measured (or calculated) instrument function into the forward model, similar to the current treatment of the source spectrum. This improvement would enable the deconvolution of the instrument function, further improving the resolution of the reconstructed electronic structures. Additionally, another possible refinement of the forward model would be the gradual relaxation of the approximations introduced in Section 3.1, particularly concerning the influence of core-hole interactions on the intermediate state. This improvement would lead to a more accurate RIXS model, better capturing the finer energy scales of the spectra.

From a machine learning perspective, exploring alternative network architectures for representing ρ_{eff} would be valuable, especially those that can incorporate physical constraints on the DOS (e.g., positivity). This approach aligns with what is usually done in PINNs methods [225].

On the experimental side, I have already emphasised the need for higher-quality RIXS measurements under compressed conditions, which could be obtained by increasing the SNR of single shots and expanding the size of datasets. Leveraging the advanced capabilities of newer facilities—particularly improvements in XFEL pulse energy optical laser energy stability, and repetition rate—would be instrumental in achieving these goals. Our experiment was conducted at LCLS, but facilities such as the European XFEL, with its DIPOLE100X laser [280], offer significantly higher capabilities—delivering up to 100 J per pulse at a maximum repetition rate of 10 Hz, far exceeding the performance of the LCLS optical laser¹. Looking further ahead, the upcoming LCLS-II facility, expected to be operational for experiments in 2027, is anticipated to provide even greater enhancements.

In terms of scientific applications, it would be interesting to test this RIXS-based methodology on new materials relevant to high-pressure physics, such as other iron compounds, nickel, and silicates², as well as under different conditions, such as strong magnetic

¹Actually, RIXS investigations of dynamically compressed materials were already carried out recently, during a community experiment in August 2024.

²The selected materials must be compatible with our specific RIXS approach, meaning they should

fields. These studies would help characterise the modifications of electronic structures due to the chemical and physical environment.

Finally, the discussion in Section 1.3.2, along with equations (3.17) and (3.14), suggests the intriguing possibility of using RIXS measurements to probe optical conductivities. This objective would require repeated RIXS measurements for different absorption edges of the investigated material.

6.4 Outlook: Generalisation of the STEP Method to Other Physical Processes

Based on discussions with collaborators, where I had the opportunity to present the framework of the STEP method, one of the most promising prospects, in my view, is its generalisation and application to other physical processes/measurements [235]. Many researchers encounter challenges that could be effectively tackled using our approach. Here, I illustrate some example applications to x-ray diffraction analysis, though others could be made.

As described in Section 1.2.1, uniaxial compression generates a shock wave that propagates through the material and reflects off the rear surface, producing a release wave that gradually broadens over time. Consequently, at any given moment, the sample exhibits a longitudinal density profile which corresponds to a variation in lattice parameters. This density profile is therefore encoded in the observed diffraction image, and this relationship can be modelled through a differentiable forward model embedded within the STEP framework [58].

In this approach, the density profile is represented by the neural network, which is iteratively adjusted to ensure that the forward model's output aligns with the experimental XRD images. By performing these measurements at different time steps, the density evolution within the sample can be reconstructed. The resulting density profiles represent averaged values across the transverse planes. However, lattice parameters may vary significantly within these planes. Future applications aim to map the entire strain field, encompassing both longitudinal and transverse directions, as it is also encoded in the diffraction image. This approach would demonstrate the reconstruction of a two-dimensional function containing deep core states that can be excited by x-rays, thereby excluding light elements.

tion³ using the STEP method. Such a method would surpass the commonly used—but occasionally inadequate—*full-constraints model* [281], which assumes a homogeneous strain field. Additionally, another valuable two-dimensional quantity that can be extracted from diffraction images is the orientation distribution function of crystallites, $P(\theta, \phi)$, which characterises the texture of the sample.

Through these examples within the XRD field alone, I hope to have conveyed the potential of the STEP framework in addressing inverse problems—where complex physical quantities must be extracted from experimental measurements.

³Certain symmetries in the sample can be exploited.

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