Ultrafast X-ray imaging by single-shot ptychography

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Hard X-ray free-electron lasers (XFEL) offer the opportunity to image ultrafast phenomena with high resolution. To capture snapshots of non-repeatable phenomena a robust single-shot imaging technique is needed. Over the years several imaging techniques have been proposed. Coherent diffractive imaging (CDI) can suffer from numerical convergence issues and most importantly requires an isolated sample, which often is impractical. In-line holography offers robust reconstruction on extended specimens, but struggles to recover quantitative values for the complex transmissivity, and the resolution is limited by the size of the on-axis focus. Ptychography offers high-resolution imaging with neither issues of quantitativeness, robustness, nor requiring a clean wavefront. However, due to its scanning nature, conventional ptychography is not compatible with single shot imaging.

Single-shot ptychography has been demonstrated in optical wavelengths, which is easier due to the readily availability of efficient lenses, beam splitters and gratings. For X-rays we propose the principle in Figure 1. The beam is first angularly split using a grating upstream of the focal point, upon free-space propagation this causes the beams to acquire some degree of spatial separation, therewith achieving the overlapping illumination of different regions of the sample. Downstream of the sample, at the detector position, the beams are completely separated and the diffracted intensities are collected in parallel using a single pixel-array detector. By extracting the separate diffraction intensities and using a phase-retrieval algorithm the complex-valued transmissivity of the specimen can be reconstructed. New algorithms will need to be developed to deal with the overlap of scattering intensities at higher angles in order to improve the resolution which otherwise is bounded by the grating period. This method would also serve as a robust single-shot technique for full wavefield characterization of nano-focused beams at Swiss-FEL.

Dynamics, for example fast domain switching, could be studied by using two-pulse sequential imaging, or by careful tuning of the arrival of different diffraction orders to the sample.

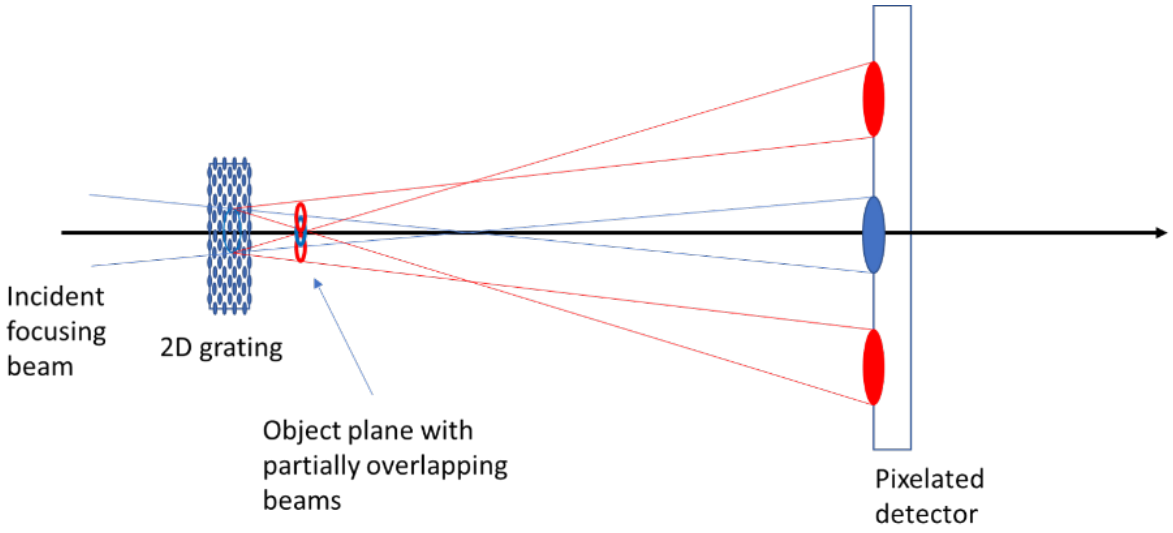

Figure 1. Schematic for X-ray single-shot ptychography. A focused beam is incident on a grating. Upon propagation the different diffraction orders acquire a spatial separation. The object is placed at a position where there is partial overlap of the beams, therewith providing the overlap constraint for ptychography. Further downstream at the detector the diffraction intensities are spatially separated and can be processed as different positions of a ptychogram.

Ultrafast 3D imaging at X-ray free-electron lasers

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The unique penetration power of X-rays allows us to study systems in their natural environment. This property has led to the development of 3D X-ray imaging techniques, such as X- ray microtomography (µCT). µCT acquires 3D information, which determines the functionality and mechanical properties of nature, by rotating a sample with respect to the X-ray source. Since its discovery, µCT has become a crucial tool for several scientific disciplines such as physics, biology, medicine, paleontology, and chemistry.

Over the last decade, µCT has become a technique capable of not only recording 3D information but also filming dynamical processes. Several breakthroughs have made this possible: i) intense X-ray sources (synchrotron light sources and X-ray free-electron lasers), ii) efficient and fast X-ray detectors, and iii) fast 3D reconstruction algorithms. Despite all of these developments, the acquisition protocols remain unchanged, i.e., the sample is only rotated faster. This fast rotation introduces forces which may alter the studied dynamics and ultimately limit the achievable temporal resolution. Furthermore, any scanning technique is not compatible with the diffraction-before- destruction imaging modality, where the sample is destroyed after being illuminated by an intense X- ray pulse.

Here, we propose an X-ray imaging technique, christened X-ray multi-projection imaging (XMPI), that avoids the sample rotation, obtaining 3D information from a single X-ray flash by splitting it into nine-angularly resolved beams which illuminate the sample simultaneously (see fig.1). This approach, when implemented at X-ray free-electron lasers, will allow the filming of natural processes with micrometer to nanometer resolution and resolve dynamics from few Hz to femtoseconds.

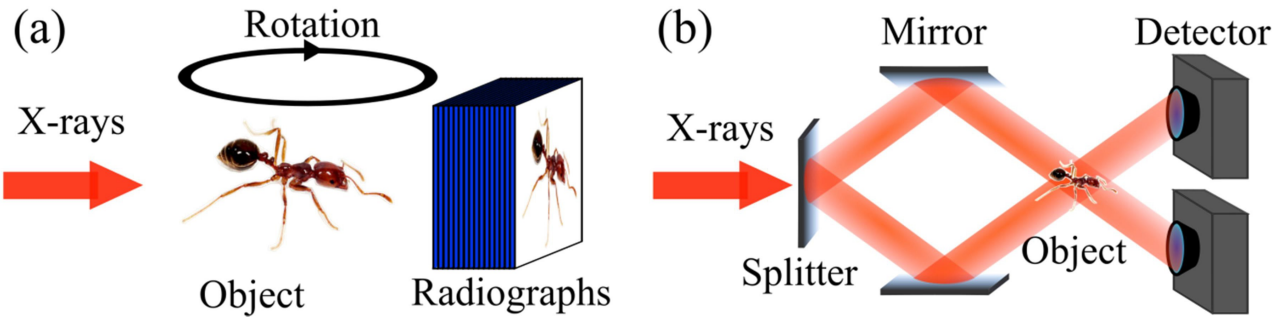

Figure 1: Comparison between conventional tomography (a) and XMPI (b). (a) Tomography rotates the sample with respect to the X-rays acquiring independent radiographs for each exposure. (b) XMPI for a single exposure records several projections simultaneously, for simplicity only two projections are shown.

XMPI, when implemented at PORTHOS, will enable: i) the study in 3D of dynamical processes with pump-and-probe approaches at temporal resolutions not possible today, ii) the acquisition of 3D information of stochastic and non-reproducible samples in diffraction-before- destruction modality, and iii) the study of ultrafast phenomena by using the optical setup for split- and-delay experiments. However, the imaging capabilities of XMPI are ultimately limited by the number of photons per pulse. Thus, enhancing this number will be crucial for widening the applicability of XMPI. XMPI can be used to address problems coming from the fourth industrial revolution, which cannot be addressed with current X-ray imaging techniques and other probes that lack the penetration power of the X-rays. Examples of future applications are i) novel materials characterization: metallic foam nucleation; ii) injection devices performance: cavitation formation; and iii) microfluidic devices characterization for efficient transport of bioparticles and drug delivery.

Time-resolved structural biology

J. Standfuss et al. (PSI)

The last decade has seen major breakthroughs in modern structural biology with over 165'000 structures of biological macromolecules deposited in the Protein Data Bank to date. Following these successes, many structural biologists now want to go beyond the "structure-is-function" paradigm towards a new frontier: time-resolved structural biology. Biological macromolecules require sequential structural rearrangements to perform their functions. To capture these dynamic movements and advance the field towards "dynamics-are-function" has been a long-standing dream of structural biologists.

X-ray free electron laser (XFELs) have proven an excellent tool to resolve structural dynamics. They provide superior data compared to pioneering experiments using Laue crystallography at synchrotrons[1]. Time-resolved serial crystallography at XFELs is furthermore the only method that allows to resolve atomistic changes in biological macromolecules down to the femtosecond regime[2-4]. Already the first user run at the Swiss X-ray Free Electron Laser (SwissFEL) provided excellent results on new phasing techniques (Nass et al., IUCrJ, *accepted*) and time-resolved crystallography in the femtosecond to millisecond range[5]. It makes sense to build on these successes when considering the opportunities given by the new Porthos beamline of SwissFEL and capitalize on (I) the shorter pulse length and (II) wider energy range to stay at the forefront of modern structural biology.

The first main difference to Aramis will be a pulse length in the order of a few femtoseconds that can be achieved without compromising beam intensity. This is relevant for one of the key promises of the XFEL technology: to outrun radiation damage by the "diffraction-before-destruction" principle[6]. The experimental evidence is clear that pulses in the order of 50-100 fs provided by Aramis are too long to avoid all radiation damage effects[7,8] and that diffraction is self-terminated much earlier[9]. Compression of the available photons into a few femtoseconds by the short pulses/high power mode of Porthos will thus not only further reduce radiation damage but also provide better data at higher resolution and from smaller crystals as more photons can contribute to the diffraction. The small size of crystals that can be measured is an important advantage for static serial femtosecond crystallography on G protein-coupled receptors and other drug targets[10]. Moreover, small crystals are particularly appealing for time-resolved experiments since the size of crystals is a critical factor determining the achievable time resolution using rapid diffusion of small molecule ligands or co-factors[11]. Today we typically use optical lasers to initiate reactions at SwissFEL, which limits the biological systems that we can study to those which can be triggered by light, i.e., either native chromophores like retinal[5] or through synthetic photoswitches (Wranik et al., *unpublished*). A future implementation of liquid application methods for time-resolved crystallography[12] or similar fixed-target devices that are already in development in the Photon Science Division would allow studying a much wider variety of biological reactions, including enzyme catalysis or the binding of small drug molecules. In its extreme, the avoidance of radiation damage in the short pulse/high power mode of Porthos may also make it worthwhile to revisit structure determination by single particle analysis that so far has been the domain of high repetition rate facilities like LCLS-II and the euXFEL.

The second opportunity for structural biology at Porthos lies in the extended energy range above the 12 keV that we typically use at Aramis. In structural biology, the X-ray energy is a critical factor for phasing by anomalous diffraction measurements. Extending the range on the upper end to 35 keV will provide the opportunity to capture the absorption edge of all elements from atomic number 20 upward in the periodic table[13]. Besides opportunities to solve the phase problem in crystallography, the identification and precise location of specific atoms can be critical to understand protein function. One example is the case when the orientation and position of small molecule ligands needs to be determined in a structure-based drug design project. Another is the mapping of metal clusters often found as catalytic sites in enzymes, like, for example, the manganese cluster that enables water splitting and oxygen evolution in photosystem II. Tracking the position of specific atoms can be particularly important in time-resolved experiments as it is not always possible to distinguish atoms with similar scattering properties. A time-resolved, anomalous difference experiment might allow following the exact translocation pathway in light-driven ion transporters that have been recently studied at SwissFEL[5],(Mouse et al., *unpublished*). Another idea would be to follow the nanochemical synthesis of polyoxometalate clusters in dedicated storage proteins[14]. Such clusters are used in the semiconductor industry because of their diverse and unique chemical and physical properties but require strict synthesis conditions, including high pressure. Time-resolved structural snapshots of how protein enzymes can catalyze such chemical reactions under more ambient conditions could lead to interesting applications in the chemical industry.

In summary both the envisaged short pulse/high power mode as well as the wider energy range of Porthos will increase the range and quality of structural biology experiments that will be possible at SwissFEL. There is no doubt that these new capabilities will be welcomed by many biologists, computational theoreticians, chemists and physicists interested in protein dynamics.

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Quantum Materials

S. Gerber, S. Johnson, B. Pedrini et al.

There are several possible avenues for new scientific directions in the study of quantum materials facilitated by the new PORTHOS branch, which depends somewhat on the choices made on the machine side.

One new direction is offered by the plan to go to shorter wavelengths at the PORTHOS branch. By extending to wavelengths a factor of two shorter than the shortest possible wavelengths at ARAMIS, some new opportunities arise. The main advantages are that transmission measurements in solids with thicknesses on the order of 10 µm becomes feasible and more *q*-range can be accessed. This allows for forward scattering geometries, which can in turn allow for pulsed magnetic fields up to and possibly even beyond 50 Tesla in combination with small angle scattering, X-ray diffraction or absorption probes. This kind of geometry is also appropriate for pump-probe experiments in cases where the pump excitation length is also $\geqslant$ 10 µm, which can be the case for THz excitation or for optical excitation of dilute impurities. Another advantage of higher energies is the ability to perform diffuse scattering experiments on solids with measurement sensitivity to many different cuts of multiple Brillouin zones with good *q*-resolution simultaneously. This is highly advantageous for experiments that extract information from correlations between structural fluctuations at different *q*-vectors, with which it is possible to approach new forms of correlation spectroscopy in nonequilibrium states.

Another key advantage of PORTHOS over existing options is the potential to apply CHIC techniques to hard X-rays. For example, bandwidth and full polarization control over the X-ray output pulses can offer a route to single-shot, pump-probe X-ray magnetic circular dichroism or time-resolved resonant diffraction studies at tender and hard x-ray edges. While some of this functionality can be achieved in principle using linear polarizations and phase plates in the hard X-ray range, there would be clear advantages, e.g. concerning flexibility and reliability, in developing such capabilities on the source side. Also, for nonlinear applications (where the polarization state can be critical) it might not be possible to implement phase plate technologies at high x-ray pulse energies. Another area of interest is the generation of timed sequences of x-ray pulses with widely different energies (up to 1 keV). This could then be used for realization of nonlinear x-ray methods such as transient grating spectroscopy, for example to measure momentum-dependent electron-phonon coupling strengths or the *q*-dependence of ultrafast demagnetization. Access to specific energies in the hard-x-ray range can potentially also exploit stimulated emission processes to achieve sensitivity to valence properties.

Finally, we point to the capabilities that would be enabled by combining CHIC techniques with self-seeding at PORTHOS. At the example of the ATHOS soft x-ray beamline it has been identified [1] that selective electron bunch degradation and transverse beam shaping in the accelerator, combined with a self-seeded photon emission scheme, yields phase-locked pulse pairs and even pulse trains. This method to generate a fixed phase relation amongst X-ray FEL pulses is also applicable in the hard X-ray regime. Trains of phase-locked pulses may permit the extension of high-resolution, frequency comb spectroscopy concepts from the optical to the X-ray regime. Phase-locked pulse pairs, on the other hand, could be used for time-domain X-ray Ramsey interferometry, e.g. for coherent control and read-out of quantum states. The schemes are based on quantum interference of two photon fields with variable time delay and fixed relative phase relation, translating into a radiation power spectrum with tunable modulation. Application can be envisaged in Fourier-transform X-ray absorption, e.g. for highly-efficient measurements electronic absorption line widths or to establish core-hole lifetimes and their impact on valence electron states. Also resonant and non-resonant elastic and inelastic scattering types of experiments would be possible by tuning the radiation power spectrum modulation (instead of scanning a monochromator), for example to establish dispersion relations of low-energy excitations. Moreover, the *q*-range accessible with hard X-rays may also allow to extract temporal and spatial modulations of, e.g. spin or charge, densities via Fourier transform in space, as well as auto-correlation measurements of speckle as with conventional split-and-delay setups. The important difference to the latter would be that the electron bunch was split in the accelerator, prior to photon generation, whereby also the phase relation of the ultrafast, Ångstrom wavelength pulses could be controlled. In principle, even tuning of the phase difference and relative amplitude of the two pulses should be possible which would opening the door towards coherent control and readout of prepared states, e.g. in photon echo type experiments.

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Time-resolved chemistry

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M. Chergui (EPFL)

Parameters
Porthos is envisioned as an undulator branch of SwissFEL[1] which covers shorter wavelengths than currently available at Aramis with shorter pulses. For the purposes of this document we have assumed a photon energy range of 12-35 keV, and a pulse duration of 5 fs (FWHM)

Introduction
Chemistry experiments at X-ray sources use a broad range of techniques, generally categorized into spectroscopy and scattering. Both of these types of techniques can be applied at higher photon energies, and several beamlines at the SLS already use such methods.

Short-wavelength spectroscopy
The SuperXAS beamline has extensive experience with spectroscopy in the photon energy range from 12-35 keV. This energy range covers the K-edges of the 4d transition metals (Mo, Ag, Pd) which provide complementary information to probing the L-edges in the tender X-ray regime available at Aramis. Methods developed for time-resolved X-ray spectroscopy measurements, both absorption and emission[2], can be extended into the photon energy range Porthos will cover with few modifications. Aspects related to sample thickness (time resolution versus efficiency of excitation with X-rays), detector efficiency, and photoexcitation efficiency will need to be addressed, but PSI has experience with some of these topics already[3].

Short-wavelength scattering
This is a field that has been explored for certain types of materials at the Material Science beamline at the SLS. In addition it is standard for pump-probe experiments at ID09 of ESRF, in particular to study photochemical reactions in the solution phase. The Aramis branch of SwissFEL is also capable of these types of techniques, but with the increase of incident photon energy methods such as Pair Distribution Function become feasible, which allow atomic resolution to be obtained from disordered or nanocrystalline materials as well as for molecular systems in the solution phase. This technique would require a large area detector with sufficiently thick sensor material to efficiently detect the scattered X-rays.

Photon parameters
Key parameters of the Porthos beamline photons will include the spectrum and photon energy stability. To perform X-ray spectroscopic measurements a monochromator will be required, meaning a narrow SASE spectrum and excellent energy stability will be crucial for these types of experiments. For the PDF measurements the full SASE spectrum can be used, but energy stability and perhaps shot-to-shot X-ray spectral diagnostics will become important. The 5 fs probe pulse duration is ideal for both using either spectroscopy and scattering methods to measure dynamics ranging from fs to ns, which is a regime not currently feasible at synchrotron light sources.

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LSF crazy ideas – Part II

C. Bostedt et al.

Nonlinear and ultra-strong field interaction phenomena

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The investigation of **X-ray nonlinear phenomena** is of paramount importance for the understanding the interaction dynamics of high-intensity femtosecond XFEL pulses with matter for fundamental and applied sciences as well as for the development of new X-ray instrumentation and theoretical modelling.

The onset of nonlinear phenomena for tender/hard X-rays is ~10^{19}-10^{20} W/cm^2 as shown in the figure reproduced from [1]. Pioneering studies of nonlinear processes allowed observation of sequential multi-photon absorption/ionization, double core-hole formation, amplified spontaneous emission and inner-shell lasing, saturation absorption, anomalous Compton scattering, highly ionized matter and plasma creation. Other predicted phenomena eg., superradiance and a number of XRL schemes have been proposed [2] and could be enabled with ultra-intense subfemtosecond XFEL pulses. In particular, the sub-femtosecond regime of X-ray nonlinear interaction effects remains to be explored [3] with development of **nonlinear spectroscopies at attosecond timescale**.

Photon-electron coincidence spectroscopy has been a longstanding idea that could not be realized so far. Such a project (MOSARIX) in the tender X-ray regime is in the course of realization [4] and could be envisaged for the hard X-ray energy range.

Ultra-strong fields could clarify the reaction dynamics in classical electrodynamics and QED, probe the structure of quantum vacuum and even reach subcritical electrical fields to produce e^+e^- pairs (see figure).

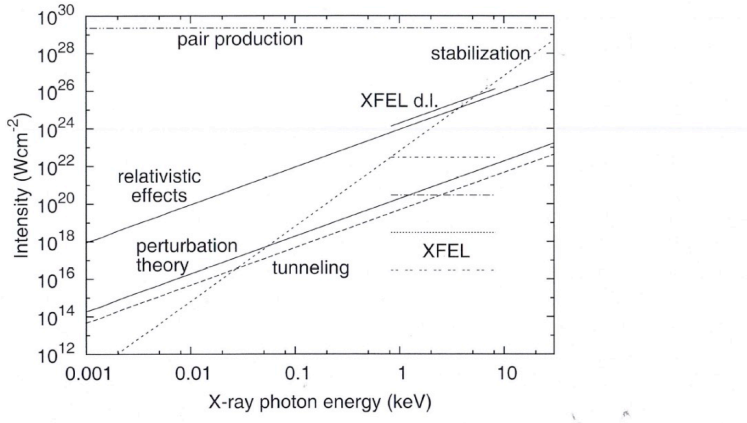

Figure 7.3 Interaction regimes as a function of x-ray intensity and energy. Shown are the intensities required for the onset of Schwinger pair production, relativistic effects, atomic stabilization, breakdown of perturbation theory, and tunneling ionization. The four horizontal lines indicate regimes that may be achieved with an x-ray free-electron laser with focal diameters of 10 and 1 μm and 100 and 10 nm for 100-fs-long pulses of 2.3-mJ energy. "XFEL d.l." indicates diffraction-limited focusing for this kind of x-ray free-electron-laser beam.

Although the community in Switzerland investigating X-ray nonlinear phenomena is still small, Switzerland should take part in this quest. The strong and established theoretical, astrophysics and particle physics communities could be interested to join the venture.

The possibility of PORTHOS to reach ultra-intense terawatt-attosecond X-ray pulses could offer unprecedented opportunities to explore a number of fundamental physics issues that have not been accessible so far and pave the way for exploring new frontiers.

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