4D Energy-Filtered STEM: A New Approach for Mapping Orbital Transitions

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Electronic states and their interactions govern most of the physical and chemical properties of the world surrounding us, yet their direct imaging and characterization in the bulk state remains elusive. Recently, "orbital maps" in real space were reported using a combination of high-resolution scanning transmission electron microscopy (STEM) and electron energy-loss spectrometry (EELS) [1]. However, many issues remain, from a very low signal strength and signal-to-noise ratio (SNR) to tricky post-processing.

In this work, we explore the possibilities of using energy-filtered 4D-STEM with fast, pixelated detectors for the purpose of mapping inelastic transitions to individual orbitals. It has long been known that, with parallel illumination, the energy-filtered diffraction pattern carries information about the electronic states involved in the inelastic transitions [2,3]. However, parallel illumination requires perfect crystals, which precludes the application of this technique to many cases of practical importance, such as close to defects or interfaces. However, using a focused electron beam in STEM allows to probe areas on the atomic scale.

Fig. 1 shows an example of 4D energy-filtered STEM for a toy-model of a single, free-floating O atom, an electron beam focused directly onto the atom, and a single $s \rightarrow p_x$ transition (together with the scattering kernel) [4]. The outgoing wavefunction (in momentum representation) is essentially a convolution of the incident wavefunction with the scattering kernel. Several crucial aspects are immediately apparent. First, it is clearly obvious that the diffraction pattern (the intensity of the outgoing wavefunction in momentum representation) carries the same directional dependence as the scattering kernel, i.e., it shows the direction of the p_x orbital. Second, due to its phase structure, the scattering kernel acts similar to a one-dimensional edge-filter, giving rise to a peculiar, ring-like diffraction pattern in which the intensity is concentrated in two segments close to the edge of the incident beam's momentum profile. Third, the width of the ring is related to the size of the scattering kernel, which, in turn, is related to the radial profile of the electronic states involved. Thus, the energy-filtered diffraction pattern as shown in fig. 1 in principle allows the full characterization of the properties of the transition probabilities involved.

In practice, modern, fast, pixelated detectors can be used to record energy-filtered diffraction patterns such as the one in fig. 1. In the past, they have been used successfully for the calculation of the center-of-mass (i.e., first moment) of the momentum distribution required for atomic-resolution differential phase contrast [5]. However, this also means that more sophisticated calculations can be performed on the same data, such as the calculation of the covariance matrix (i.e., second moment), which yields information about the inhomogeneity and directional dependence of the signal.

The novel method presented in this work paves the way for a complete characterization of individual electronic states on the atomic scale, including their orientation, radial dependence, and relative phase structure. This will open new avenues for deepening our understanding of the underlying physics of material science on an atom-by-atom level [6].

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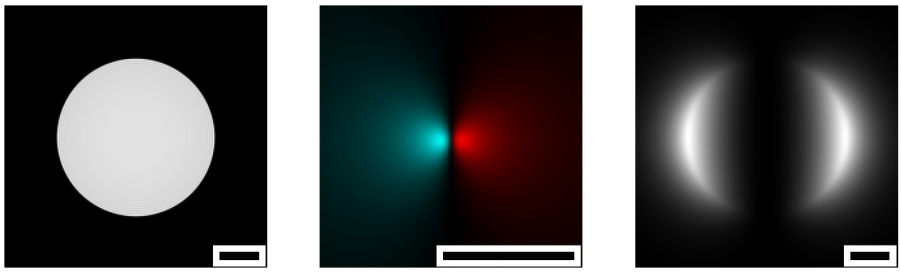

Figure 1. Intensity of the incident electron wave (left), complex scattering kernel (center) and intensity of the inelastically scattered outgoing electron wave (right) in momentum space representation (i.e., diffraction) for 300 keV acceleration voltage, 30 mrad convergence semi-angle, an electron beam focused on a single O atom, and an O-K transition $s \rightarrow p_x$. All scale bars denote 15 mrad.

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