Symmetry-Constraints for Mapping Electronic States with EELS

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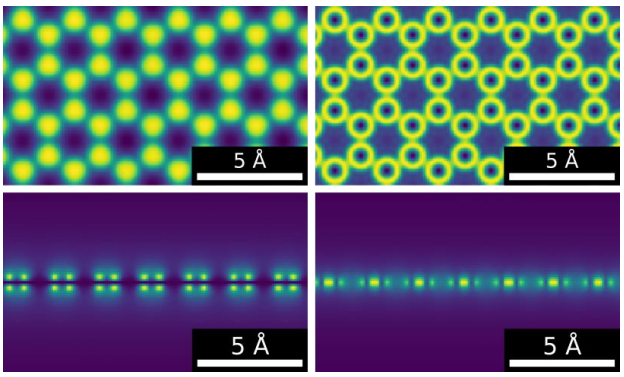
As shown recently both theoretically [1] and experimentally [2], it is possible to map individual electronic states ("orbitals") in real space using TEM and EELS. This paves the way for new insights into material properties, for the design of new, functional materials, and for gaining a deeper insight into the mechanisms of chemical bonding and catalysis. However, there are still several challenges to overcome, including the need for an improved signal-to-noise ratio, sample and instrument stability, and a better understanding of the theoretical principles that govern the formation of "orbital maps". In this work, we analyze the symmetry properties of the inelastic scattering process [3]. Based on the point group symmetries of the scattering atom and of the electron beam, we predict the general shape of energy-filtered maps, thereby unveiling under which conditions directional information about electronic states can be determined.

Our method of predicting the shapes of energy-filtered images relies solely on group theory and on the crystal's unit cell geometry, and does not require extensive numerical calculations. As such, it is very simple, fast, and universal. In particular, we use the group theoretical framework to show that directional information can only be extracted from scattering atoms with sufficiently low symmetry. For example, for dipole-allowed transitions, the scattering atom should have a rotational symmetry axis parallel to the beam's direction of propagation that is at most two-fold. This is corroborated by the figure below, which shows Graphene in two orientations for two energy losses. All maps were calculated for 300 keV purely for improved visibility and clarity - maps calculated at 80 keV and below exhibit a similar behavior. The top row shows Graphene with the *c* axis oriented parallel to the beam, whereas the bottom row shows Graphene with the *c* axis oriented perpendicular to the beam. The left column shows transitions to π* states whereas the right column shows transitions to σ* states. The top row clearly shows only disks and circles, i.e., no directional information, while the bottom row clearly shows directional information.



While these results might be considered "bad news" for studying perfect single crystals with high symmetry, it is actually "good news" for most materials of practical importance, the properties of which are usually influenced strongly by defects, surfaces and interfaces, which all break the translational symmetry of a perfect crystal. Thus, from a group theoretical point of view, such structures lend themselves perfectly to the mapping of individual electronic states in real space using TEM and EELS.

[1] Löffler et al., Ultramicroscopy 131 (2013) 39
[2] Löffler et al., Ultramicroscopy 177 (2017) 26
[3] Löffler et al., in preparation
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