Direct Quantifying Charge Transfer by 4D-STEM: A Study on Perfect and Defective Hexagonal Boron Nitride

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The charge density distribution, which fully defines the ground-state properties of a material system, can be accurately measured in single crystals using X-ray diffraction. However, there is still a lack of experimental techniques capable of measuring charge density redistribution in defective or heterogeneous crystals at the relevant atomic scale with the required precision. While this information can be effectively evaluated by modern numerical methods such as DFT, these theoretical predictions still require experimental validations. In recent years, four-dimensional scanning transmission electron microscopy (4D-STEM) has emerged as an attractive approach to achieve this goal. In principle, the technique can simultaneously provide precise structural determinations and capture details of local electric fields and charge densities. However, accurate extraction of quantitative data at the atomic scale is challenging, mainly due to probe propagation and size-related effects, which may even lead to misinterpretations of qualitative effects. Here we discuss the ultimate capabilities of 4D-STEM through a comprehensive study of pristine and defective h-BN flakes. Through a combination of experiments and first-principle simulations, we demonstrate that while precise charge quantification at individual atomic sites is hindered by probe effects, 4D-STEM can directly measure charge transfer phenomena with sensitivity down to a few tenths of an electron and a spatial resolution on the order of a few angstroms. In the last section, we will show examples of 4D-STEM in oxide films, whose thicknesses prevent any direct comparison with DFT volumetric data, but where oxygen vacancies [2] or interface reconstruction [3] can still be retrieved.

[1] L. Susana, A. Gloter, M. Tencé, A. Zobelli, *ACS Nano* **18** , 7424 (2024).
[2] Aravind Raji et al.„ *Small* **19**, 230487 (2023).
[3] Jia et al., , *Advanced Materials Interfaces* **10**, 2202165 (2023).