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ab initio Electrostatic Potentials for 4D-STEM Ptychographic Reconstruction

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Transmission electron microscopy imaging and spectroscopy techniques provide ever-more powerful probes of the chemical structure of materials, and there is increasing interest in studying their atomic-level properties including charge transfer. Although incoherent annular dark field (ADF) imaging in scanning transmission electron microscopy (STEM) is insensitive to the valence charge distribution of the specimen, electron ptychography via convergent-beam electron diffraction maps (so-called 4D-STEM) can be used to retrieve the phase and thus achieve reconstructions of the full electrostatic potential, including any redistribution due to chemical bonds. At the same time, the increasing capabilities of instruments equipped with direct electron cameras [1,2] are making it possible to perform these measurements even in beam-sensitive materials [3] such as transition metal dichalcogenides [4] and hexagonal boron nitride (hBN) [5].

However, to interpret the results and to verify the precision of such measurements, theoretical support is required. Density functional theory (DFT) can be used to calculate the ground-state electron density and thus the electrostatic potential of model specimens, which can be used in a multislice simulation to model the scattered intensities, including any effects of valence bonding [6]. This is particularly easy in the recently developed abTEM code [7], as it is designed to directly interface with the high-performance DFT simulation package GPAW [8], which is based on a real-space implementation of the projector-augmented wave method that is ideally suited for an accurate and computationally efficient description of the full electrostatic potential. Both are open-source codes written in the Python programming language, following and reinforcing the trend towards reproducible, extendable, and interoperable software environments for materials science.

In this contribution, we report on quantitative comparisons of experimental 4D-STEM datasets acquired using aberration-corrected STEM from monolayers of insulating hBN and semiconducting tungsten disulfide (WS_2, Figure 1) with the corresponding simulated datasets, as well as that of the ptychographically reconstructed phases with the underlying *ab initio* electrostatic potentials. We study the effects of primary beam energy, beam convergence semi-angle, scanning parameters, and noise, as well as compare different reconstruction algorithms. We discuss the optimal acquisition settings for charge reconstructions and highlight what level of precision in the DFT simulation is required, thus providing perspectives for the specimen sizes that can be modeled with current tools [9].

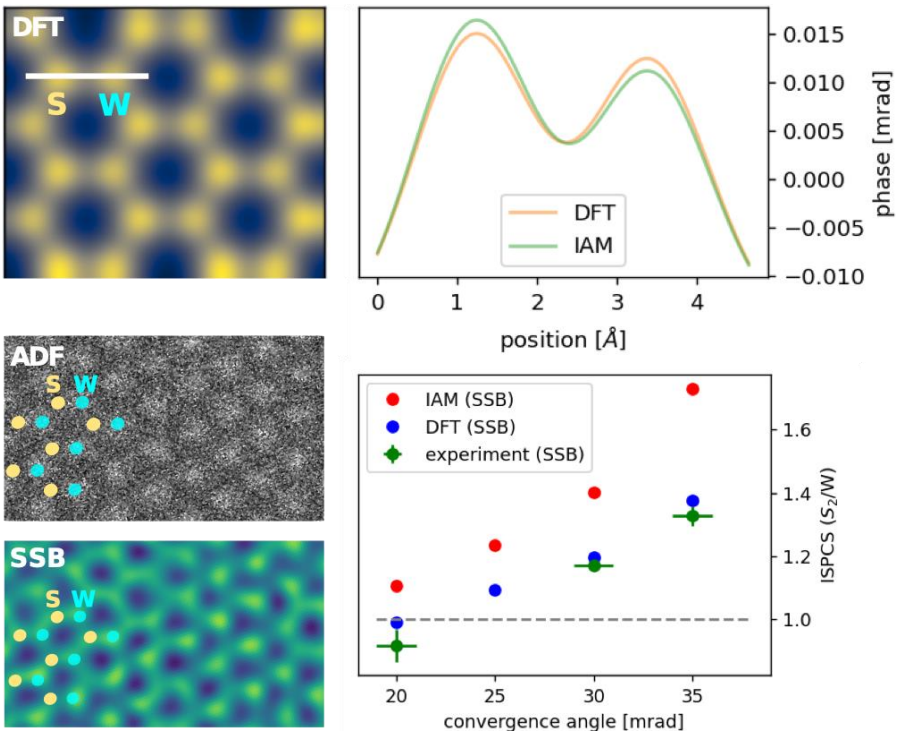

Figure 1. Comparison between experimental single-sideband (SSB) reconstructions of the phase over monolayer WS_2 with simulations based on the independent atom model (IAM) or density functional theory (DFT). The charge transfer from the W to the more electronegative S atoms screens their nuclear potentials, reducing the phase compared to independent atoms. Across a range of convergence semi-angles, DFT gives an excellent match with the experimentally reconstructed S_2/W ratio of the integrated squared phase cross section (ISPCS), where the mean of the potential was measured to be zero.

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