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Fine Structure Mapping in Graphene: From Electronic Transitions to Atomic Orbitals

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Mapping individual molecular orbitals has been demonstrated in scanning tunneling microscopy for a couple of decades, with impressive signal to noise ratio, albeit with surface sensitivity only [1]. There is strong scientific interest to achieve a comparable feat in transmission electron microscopy: understanding chemical bonding at interfaces and defects to foster defect engineering and the development of novel materials in, *e.g.*, photocatalysis or microelectronics. While atomic scale elemental mapping is a well-established technique to probe the chemical distributions of dopants and evidence segregations in a wide range of materials, highlighting the variations of fine structures, or energy-loss near edge structures (ELNES), brings relevant information on the chemical bonding of atoms locally. Reconstructing an image by filtering specific fine structures is equivalent to mapping electronic transitions, which in a first approximation translates into mapping the distribution of atomic orbitals.

Total electron densities around atomic sites have been reconstructed by electron diffraction-based techniques [2, 6-8]. On the contrary, real space imaging of atomic orbitals has been achieved using STEM-EELS in bulk rutile TiO_2 [3] by employing unit cell averaging and distortion corrections. In the present work, we propose to explore the capabilities of STEM-EELS to map electronic states and corresponding orbitals in a crystal presenting a discontinuity due to its inherent two-dimensional nature, graphene. The density of π^* states is expected to be localized slightly out-of-C-planes, contrary to σ^* states, which lie in-C-planes. Nevertheless, this simple picture of state localization does not account for the beam geometry nor beam propagation, which play a role on the experimental fine structure maps. Here, the graphene layers are probed in side-view, *i.e.*, the electron beam is parallel to the graphene layer, in a few-layer stack of epitaxial graphene grown on SiC [4], where graphene layers are weakly bonded between each other and display properties similar to free-standing graphene.

The interpretation of the experimental data is achieved via comparison with simulated maps obtained from inelastic channeling calculations, accounting for both the propagation of the electron beam through the specimen from a multislice approach and the inelastic scattering based on density functional theory. The strong agreement between experimental and simulated π^*, σ^*, π^*/σ^* fine structure maps is discussed and confirms that the experimental contrast is indeed a signature of the corresponding $p_z \sim \pi^*$ orbitals [5]. These results also demonstrate that the effect of electron beam channeling on the fine structure maps hinders the visualization of atomic orbitals for an experimental specimen thickness of ~25 nm. These results highlight some of the key limitations of mapping atomic orbitals in terms of signal to noise ratio, but also the effect of specimen thickness. Ultimately, the thickness-induced effect on the fine structure map only becomes insignificant for unrealistic thicknesses of around 1 nm where the signal to noise ratio becomes prohibitively

small. Data were obtained on a CCD and a direct electron detector to further improve the signal to noise ratio. These results contribute to the discussion on the prospect of mapping orbitals in the transmission electron microscope [9].

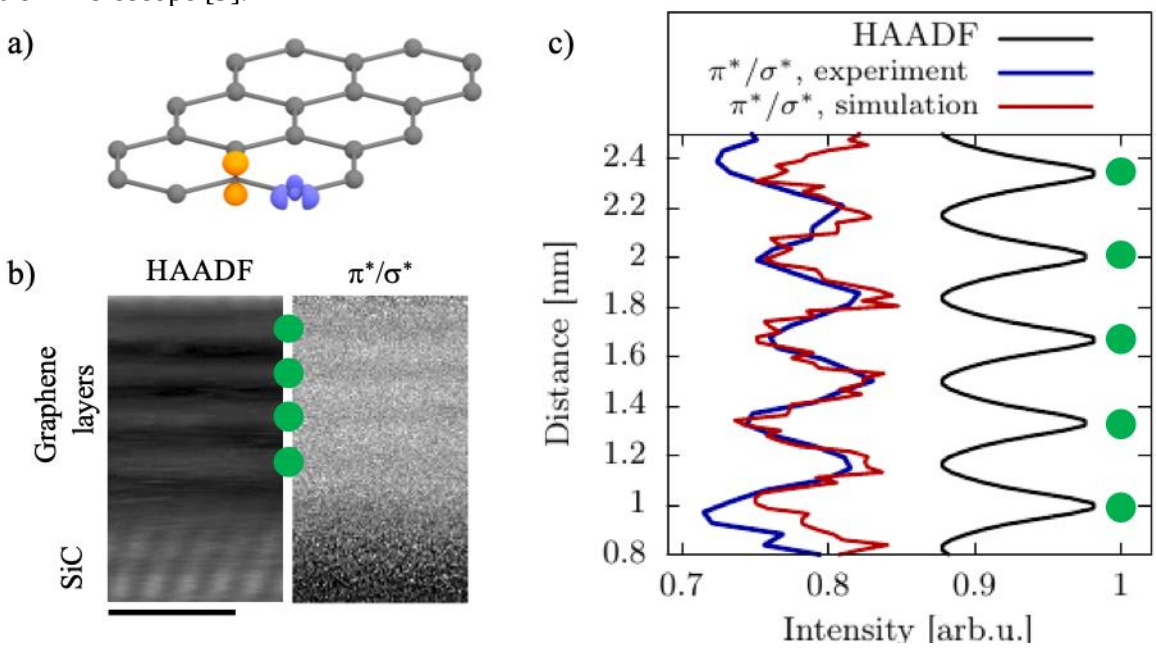

Figure 1. a) Schematic representation of the π^* (orange) and σ^* (blue) electron densities obtained from density functional theory superimposed on the structural model of a graphene layer. (b) High-resolution STEM-HAADF image of a graphene multilayer assembly grown on SiC acquired simultaneously with a spectrum image on a direct electron detector DECTRIS mounted on a Nion IRIS spectrometer. The corresponding π^*/σ^* map shows maxima between the carbon layers. Scale bar: 1 nm. (c) Experimental (CCD) and calculated (inelastic channeling) π^*/σ^* profiles extracted from π^* and σ^* STEM-EELS maps on multilayer epitaxial graphene, and corresponding calculated HAADF signal, for a specimen with 25.6 nm projected thickness. The position of the graphene layers is indicated by green circles. Probe size and shot noise corresponding to the experiments were added to the calculated π^*/σ^* profile. See reference [5] for details.

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