From electronic state to atomic orbital mapping in graphene in the transmission electron microscope

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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 (TEM): understanding chemical bonding at interfaces and defects to foster defect engineering and the development of novel materials in, e.g., photocatalysis or microelectronics. Recently, we demonstrated real space imaging of atomic orbitals in bulk rutile TiO_2 [2] using electron energy-loss spectroscopy (EELS) in TEM. Here, we explore the capabilities of STEM-EELS to map electronic states and corresponding orbitals in a crystal presenting a discontinuity due to its inherent 2D nature: graphene.

The simple picture of expected state localization ($\pi*$ states out-of-C-planes, $\sigma*$ states in-C-planes) does not account for the beam geometry nor beam propagation, which play an important role on the experimental fine structure maps. 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. The interpretation of the experimental data is achieved with simulated maps obtained from inelastic channeling calculations, accounting for both the electron beam propagation and the inelastic scattering. The strong agreement between experimental and simulated $\pi*$, $\sigma*$, $\pi*/\sigma*$ fine structure maps confirms that the experimental contrast is a signature of the corresponding $p_z \sim \pi*$ orbitals [3]. These results also demonstrate that the effect of electron beam channeling hinders the visualization of atomic orbitals, and highlight some of the key limitations to mapping orbitals in TEM [4].

References

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Figures

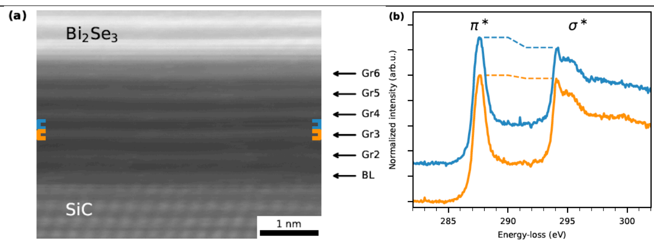

Figure 1: STEM-HAADF image (a), and C-K edges extracted from in- and out-of-C-plane (b).